Aspects of the Chemistry of Lead in Multiphase Soil Model Systems and the Environment

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Abstract

Synthetic model soils were used to evaluate redistribution of Pb in both the three-stage sequential extraction procedure proposed by the Commission of the European Communities Bureau of Reference (BCR, now Standards, Measurements and Testing Programme) (1993) and the commonly-applied procedure of Tessier et al. (1979). Redistribution of Pb in both schemes was found to be substantial, sufficient to render meaningless any attempts to quantify the original phase associations of Pb in cases where these are not known. In the model systems, the manganese oxide (hausmannite) and humic acid phases were found to be responsible for most of this redistribution in both schemes. Despite the fact that both schemes allow severe Pb redistribution to occur, differences are apparent in the manner in which this occurs. Whereas Tessier et al.'s procedure in all cases yielded the highest recovery of Pb at the reducing step, the three-stage BCR procedure released the most Pb at the oxidizing step, in both cases irrespective of where it originated. These differences are attributable to a combination of high temperature (96 °C) and the presence of 25% v/v acetic acid in Tessier et al.'s reducing step. These conditions were found to reduce the sorptive capacity of humic acid by more than 50%, in addition to retaining more of the Pb in solution by complexation with acetate ions.

Extensive redistribution in the three-stage BCR procedure was also observed in systems where natural soils were mixed with Pb-spiked synthetic phases. In keeping with the results relating to synthetic soil models, the organic matter and Fe/ Mn oxide fractions of the natural soils appear to dominate the redistribution of Pb during the extraction.

Two approaches were tested in terms of their ability to counteract the redistribution of Pb. Each approach was applied to the first extraction step of the BCR scheme, which underwent a range of modifications. These involved the use of 6 distinct solid sequestering materials, and 5 dissolved complexing agents. The most promising of all the approaches are those which involve the two soluble structurally-distinct complexing agents cryptand 2.2.2 (a macrobicyclic ligand) and nitrilotriacetic acid (NTA). The addition of each ligand generally improved the percentages of Pb recovered from the multi-phase model soils, with Pb originally spiked on calcite. However, the effectiveness of the cryptand and NTA at inhibiting redistribution (at concentrations of 9×10^{-3} and 1×10^{-4} M, respectively) was dependent on the percentages (by weight) of the hausmannite and humic acid in each model system. In the presence of no more than 2% hausmannite, both cryptand and NTA could satisfactorily recover about 60% of the Pb, provided that the percentages of humic acid in the systems were not higher than 10% and 5%, respectively.

The preliminary criteria for selecting a potentially useful soluble complexing agent suggested by the results of this study are that the ligand possess (a) a high stability constant for the ion involved, and (b) a semi-encapsulated metal binding site (which appears to inhibit direct surface extraction from occurring). It is desirable in the case of Pb to decrease the extraction time of the first step in the BCR scheme to minimize opportunity for redistribution.

The modified extraction solution using the cryptand successfully recovered Pb from a mixture of Pb-spiked calcite and a "clean" natural soil. However, when applied to contaminated roadside soil and dust samples (in the absence of a spiked phase), the modified extraction solution did not significantly alter the recovery pattern of Pb, relative to the conventional extraction solution. This result may reflect the natural distribution of Pb in these samples.

Four parks in the City of Hamilton were selected as monitoring sites for assessment of levels of Pb in roadside soil and street dust during the removal of leaded-petrol from the New Zealand market. Samples were collected every 2 - 3 months during November 1995 to September 1996. The mean concentrations of Pb in top 2 cm kerbside soil from all the parks reveal a slight downward trend (statistically significant in three parks) whereas those of the fine and coarse fractions of kerbside dust were oscillating.

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Note on Units

In this thesis, SI units are usually applied. However, in chapter 1: introduction and literature review, the units referred to are those originally used by the authors of the articles cited.
In the experimental, results, and discussion sections of this thesis, some commonly accepted units (i.e., prevalent in the scientific literature in the relevant fields of this study), such as M (molarity), and ppm (parts per million) are also used. When used in this work, ppm is equivalent to $\mu g\ ml^{-1}$, while ppb is to $ng\ ml^{-1}$, unless otherwise specified.

Chapter 1. Introduction and literature review

1.1. General introduction.

Lead is well known for both its toxicity and its prevalence as a contaminant in various compartments of the environment (Kabata-Pendias and Pendias, 1984; The Royal Society of New Zealand, 1986; Fergusson, 1990, 1993). In comparison with the other three most problematic toxic elements, arsenic, cadmium, and mercury, lead occurs at notably higher levels in the environment and is the one that people come into contact with most (Fergusson, 1993). The acute toxicity of lead was evidenced in the ancient period (Fergusson, 1986, 1990; Nriagu 1990a). Lead has no known essential role in living organisms; the low level exposure and accumulation of lead in the body is recognized as a human health hazard, with effects of chronic exposure including behavioural alterations, neurotoxicity, hematotoxicity and reproductive disturbances (Biddle, 1982; Miller et al., 1990; Bressler and Goldstein, 1991; Needleman et al., 1990; Goyer, 1996). A substantial group of studies implicate lead in blood as being associated with deficits in IQ, neurological disorders, and impairment of physical growth in children (Shen et al., 1996 and references therein). Levels of lead in blood are also used as a criterion of global pollution (Kalavska, 1992); lead concentrations of $\geq 10\ \mu g\ dl^{-1}$ whole blood (the level defined as indicative of childhood lead poisoning) are not uncommonly found in children residing in various communities, especially in urban areas (Africa, Nriagu et al., 1996; continental China, Shen et al., 1996). Several studies have shown children's blood lead concentrations to be related to the levels of lead in soil and dust (Charney et al., 1980; Thornton et al., 1990; USEPA, 1991 referred to in Devey and Jingda, 1995; Weitzman et al., 1993; Gulson et al., 1995; 1996).

Soil has been a common and ongoing site of contamination; in a "highly contaminated" soil, lead concentrations can be found at levels as high as a few thousand $\mu g\ g^{-1}$ (Kabata-Pendias and Pendias, 1984; The Royal Society of New Zealand, 1986; Fergusson, 1990). Evidence from several studies suggests that one of the principle sources contributing to surface soil lead is vehicular emissions from the use of leaded petrol (Gulson et al., 1981, 1996). Levels of lead in surface soils are of concern; one of the reasons being that this contaminated media is a major pathway for lead intake in children (via ingestion) (Fergusson, 1986; Tsuji and Serl, 1996). Partition of lead among soil components is of importance because only certain fractions of the metal present may participate in short-term geochemical processes and/or be bio-available.

Chemical sequential extraction is one of the few approaches widely used in obtaining information on trace metal mobility and distribution in particulate materials; therefore, the technique is considered an important tool for the assessment of environmental impacts from metal contamination (Tessier et al., 1979; Salomons and Forstner, 1980; Wadge and Hutton, 1987). However, the use of sequential extractions as an analytical tool and the interpretation of data from sequential extractions, is still a matter which attracts debate (Kheboian and Bauer, 1987; Shan and Chen, 1993; Wallmann et al., 1993). In this context, it is deemed of prime interest to improve the accuracy and reliability of the sequential extraction technique as it applies to determination of lead partitions in particulate material, such as soil. As an ultimate consequence, it may be possible to obtain a more accurate interpretation of the distribution of lead in solid samples, and a more reliable assessment and/or prediction of the environmental behaviour of the metal under a range of environmental conditions.

In this chapter is outlined an overview of lead in the environment, with a particular focus on sources and distributions of lead in environmental solid materials (in particular soils and street dusts) and impacts on the environment of the decline in lead consumption via the reduction of lead levels in petrol. Lead in the New Zealand environment is outlined in a separate section. This is followed by an overview of soil components frequently found to be associated with lead, with an emphasis on phases used in synthetic model soils developed in this study. The concept of *speciation* is introduced, and a variety of speciation techniques for solid materials are outlined, with a focus on chemical sequential extraction procedures, two of which will be investigated in this study. In a subsequent section different strategies for counteracting or inhibiting *redistribution* phenomenon are outlined. The overall aims of the thesis are presented at the end of the chapter.

1.2. Overview of lead in the environment.

1.2.1. Chemistry, occurrence, and uses.

Lead, Pb (Latin *plumbum*), is located in Group IVA of the Periodic Table, and has an atomic number of 82, atomic mass of 207.19, valence states of 2 or 4, and effective ionic radius Pb^{2+} of 1.18 Å (for 6-fold coordination) (Nriagu, 1978). Pb is a heavy metal with density of 11.342 g cm^{-3} (25 °C) (a heavy metal is often distinguished as having a density in excess of 5.0 g cm^{-3} (Wittmann, 1981) or 6 g cm^{-3} (Alloway, 1990)). According to the classification of metals based on electron-pair acceptors (Lewis acids) and electron-pair donors (Lewis bases) (Pearson, 1973), Pb is in the intermediate or border line group, but shows soft acid behaviour in that it prefers soft bases such as S. More detailed physical and chemical properties of Pb can be found in numerous publications, for example, Abel (1973), Nriagu (1978), Harrison (1987), Greenwood and Earnshaw (1989), Ewers and Schlipkoter (1990), and Fergusson (1990).

Pb occurs naturally as four stable isotopes ^{208}Pb (52%), ^{207}Pb (21.5%), ^{206}Pb (25.2%), and ^{204}Pb (1.4%); the first three isotopic species arise primarily as end products of the natural radioactive decay series, whereas ^{204}Pb is non-radiogenic in origin (Greenwood and

Earnshaw, 1989). Their relative abundance depends on the age of formation of a certain Pb ore (this is of potential usefulness as tracers in identification of Pb contamination sources--see below). One radioactive isotope, ^{210}Pb ($t_{1/2} = 22.5$ years) is formed from the decay of ^{222}Rn (Fergusson, 1986). In soils, Pb exists principally in the +2 oxidation state; the chalcophilic properties of Pb is evidence by the fact that its primary form in the natural state is galena (PbS) (Kabata-Pendias and Pendias, 1984). Forms of Pb in soils and sediments are determined by the solubility of the lead compounds, the acidity of the medium, and the oxidizing or reducing properties of the environment. Lead carbonate and lead sulfate can be found as main species occurring in oxidizing media, with the carbonate forming in alkaline conditions, and the sulfate in acidic environments. Purchase and Fergusson (1986a) illustrated variation of chemical forms of Pb with depth of river sediment; lead carbonate was largely present near the top, while lead sulfide predominated under the reducing conditions which prevailed at deeper depth (associations of Pb with solid phases are outlined in more detail in *section 1.4.*). In aquatic systems, Pb in chloride-containing forms may exist in salt water, whereas lead ion, hydroxy-species, and carbonate forms frequently dominate in fresh waters (details of the aqueous environmental chemistry of Pb can be found in the literature, for example Chow (1978), Rickard and Nriagu (1978), and Forstner and Wittmann (1981)).

Among over 200 lead minerals are known, of which the significant ones include cerussite, $PbCO_3$, anglesite, $PbSO_4$, and the heavy black mineral galena (PbS) which is of principal use for the extraction of lead (Fergusson, 1990). The extraction/ production processes of Pb are outlined in Greenwood and Earnshaw (1989), Ewers and Schlipkoter (1990), and Fergusson (1990). Pb has been mined for at least 7500 years. The Romans used Pb in water ducting and cooking vessels, as well as adding it to wine to inhibit further fermentation (details of the historical discovery and uses of Pb in ancient times can be found in several publications, including those of Nriagu (1978), and Fergusson (1986, 1990)). In modern times, the majority of Pb consumed is used for the production of Pb-acid batteries; other applications include the production of (i) organolead compounds used as an antiknock agents in petrol, (ii) lead-based pigments used as a protective coating for steel structures, for paints used on highways and for other exterior uses, (iii) lead chemicals in glassware and ceramics and as stabilizers in plastics, (iv) lead sheets, cable sheathings, solder, ammunition, and bearing alloys (Ewers and Schlipkoter, 1990). Nriagu (1990b) has reviewed history of Pb additives in gasoline, the fight to ban their use, and selected international limits on Pb in gasoline. In short, the antiknock properties of tetraethylead were discovered in 1921. Since then the organic lead compounds (tetraethyl lead and the analogous chemical tetramethyl lead) has been added to gasoline either singly or as mixtures to achieve desired octane numbers. Wu and Boyle (1997) provide a compilation of gasoline lead consumption during the period 1930 - 1990 in the US (the world's largest consumer) and some other countries. The use of lead in petrol has become controversial due mainly to increasing global scientific evidence concerning the adverse impact of environmental lead on public health and elevated concentrations of the metal in environmental compartments. In the US, the selling of unleaded gasoline began in 1975, and the consumption of leaded petrol has declined sharply since then. Pb in US petrol was reduced to 0.026 g litre^{-1} in 1989 and was banned by the end of 1995 (US public Law 84 - 159 (1990) refereed to in Orlova et al. (1995)). However, the majority of European countries began to curtail leaded fuels in around 1985 (i.e., the maximum Pb content of petrol was required to be reduced to 0.15 g litre^{-1}). The move to unleaded petrol in New Zealand is outlined in *subsection 1.3.2.*

1.2.2. Assessment of natural vs anthropogenic inputs to the environment.

Worldwide inputs of Pb and other trace elements (e.g., As, Hg, and Cd) from natural and anthropogenic sources into the ecosystem was estimated by Nriagu (1989, 1990a) and Nriagu and Pacyna (1988). Natural sources of atmospheric emissions of the trace metals included in the estimation were wind-borne soil particles, sea salt spray, volcanoes, forest fire, and vegetation/ biogenic sources. The most significant natural source of Pb to the atmosphere appears to be wind-borne soil particles; based on the median value estimated, wind-blown particulates contribute about 33% of the total amount (12 thousand tonnes) of Pb emitted per year from natural sources (the second most important source appears to be volcanoes, which contribute about 28% of the total emission). It was, however, noted that metals in wind-blown dusts often were of industrial origin, therefore, the data given probably overstated the actual natural fluxes of metals into the pre-industrial-era atmosphere. Anthropogenic sources of atmospheric trace metals included in the estimation were energy production, mining, smelting and refining, manufacturing processes, commercial uses (including agricultural uses), waste incineration, and transportation. The most important anthropogenic source of Pb appears to be transportation; based on the median value estimated, transportation contributes about 75% of the total amount (332 thousand tonnes) of Pb emitted per year from anthropogenic sources (the second most important source appears to be smelting and refining, which contribute about 14% of the total emission). The median anthropogenic emission of Pb to the atmosphere exceeds the fluxes from natural sources by about 28-fold; this was the highest ratio among the trace elements assessed. The atmosphere is also a key medium for worldwide Pb dispersal; Wu and co-workers (1997) noted that automobile exhaust Pb as well as that from other Pb sources involving high temperature processes (e.g., smelting, coal combustion, and cement production) resulted in Pb becoming attached to fine particles in the atmosphere, a significant fraction of which (order 10%) could be transported over long distances and deposited into the ocean (this could be through direct washout by rain of Pb aerosols in the atmosphere over the oceans). In contrast, coarse particles (with diameters between about 10 - 20 μm) are noted to have a substantial contribution of naturally made particles that have been created in mechanical processes such as erosion of soil and sea spray; their life times in the atmosphere are in the order of hours, and thus they are not a major contributor to the long distance transported aerosol (Foltescu and co-workers, 1994). On the global scale, Nriagu (1990a) estimated that atmospheric fallout supplied about 70% of the 138 thousand tonne annual Pb flux into aquatic ecosystems.

Other contributing sources taken into account include domestic wastewaters, electric power plants, base metal mining and smelting, manufacturing processes, and sewage discharges. Of worldwide total inputs of Pb into soil, which are estimated at 759 thousand tonnes per year, land disposal of manufactured products was estimated to account for 38%, while atmospheric fallout was responsible for 31% of the total input. Other contributing sources included in the calculation were agricultural and animal wastes, logging and wood wastes, urban refuse, municipal sewage and organic waste, solid wastes from metal fabrication, coal ashes, and fertilizers and peat (mine tailings and slags at the smelter sites were excluded). The extent of Pb dispersal, as noted by Nriagu (1990a), seemed to be such that there is unlikely to be anywhere on earth free from contamination by this heavy metal. Fergusson (1992) remarked that its persistence in the surroundings as well as its accessibility determined the significance of the toxicity of Pb to humans.

1.2.3. Distributions of Pb in the environment and relative contributions from possible sources (with the emphasis on petrol).

Pb naturally occurs at very low concentration, and is ranked at only about 36th place in order of natural abundance of elements in the earth's crust (Ewers and Schlipkoter, 1990). Patterson (1980) (referred to in Fergusson, 1992) estimated "natural/ pre-industrialized" and "background/ remote" concentrations of Pb in various environmental materials, including soil (5 and 12 - 20 $\mu g\ g^{-1}$), rock (12 and 12 - 40 $\mu g\ g^{-1}$), ocean sediment (4 and 10 - 12 $\mu g\ g^{-1}$), air (40 and 6 - 100 pg m^{-3}), ocean water (0.5 and 1 - 5 ng g^{-1}), fresh water (20 and 5 - 50 ng litre^{-1}), snow (1 and 1 - 2 pg g^{-1}), and vegetation (0.002 and 0.005 $\mu g\ g^{-1}$), and biological materials, e.g., blood (0.2 and 0.8 - 5 $\mu g\ dl^{-1}$) (Other work in the area of natural Pb levels carried out by Patterson includes Ng and Patterson (1981, 1982)). However, as outlined above, in the last several decades great amounts of Pb have been extracted, concentrated, and used by man, and re-emitted into the environment. As a consequence, now Pb concentrations are locally and regionally much higher than they used to be (for example, Kuala Lumpur, Malaysia, Ramlan and Badri, 1989; Moscow, Russia, Orlova et al., 1995; Cape Town, Africa, Von Schirnding and Fuggle, 1996). A variety of analytical techniques have been used in the determination of Pb in different types of samples, for example, soil (extracted, ASV, Fernando and Plambeck, 1992; soil slurry, GFAAS, Hinds and Jackson, 1990; Hinds et al., 1991), ice/ snow (laser-excited atomic fluorescence spectrometry, Bolshov et al., 1992), blood (ASV, Noble, 1993; electron-capture negative chemical ionization GC-MS, Baird et al., 1996; electrothermal atomization laser-excited atomic fluorescence spectrometry, Wagner et al., 1996; ICP-MS, GFAAS, Zhang et al., 1997), (digested) food (ICP-MS, GFAAS, Zhang et al., 1997). One of the methods frequently used to identify source(s) of Pb contamination is measurement of the isotopic Pb composition. Isotopic Pb analysis has been widely applied as tracer in various materials (airborne, Chow and Earl, 1970; Monna et al., 1997; soil, Gulson et al., 1981;

Walraven et al., 1997; soil and house dust, Gulson et al., 1995; soil and herbage, Bacon et al., 1996; blood, Gulson et al., 1996; roof dust and lake sediment, Chiaradia et al., 1997). This technique is based on the notable difference of the stable isotope ratios (e.g., ^{206}Pb/ ^{207}Pb) between Pb from gasoline additives and from other sources such as industry or waste incineration; thus the profile of the isotope ratios should reflect the contribution of Pb from these possible source(s) (Moor et al., 1996). This method can be coupled with thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS). Other approaches employed for the determination of sources of Pb (and other heavy metal) contamination include instrumental methods, such as electron microprobe analysis (Linton et al., 1980 (SEM/ EDAX); Davis et al., 1993), calculations based on multi-elemental analyses, such as statistical factor analysis (Hopke et al., 1980; Davies, 1997), trajectory modelling (Steinnes, 1987), and enrichment factors (Fergusson and Simmonds, 1983).

Pb in snow/ ice. In early studies of Patterson and co-workers on Pb contamination in Greenland and Antarctic ice strata, using the isotope dilution technique, it was found that Pb concentrations increased from < 0.001 μg Pb kg^{-1} ice at 800 BC to > 0.200 μg Pb kg^{-1} ice at about 1969 in north pole ice sheets, with the sharpest rise occurring after 1940 (Murozumi et al., 1969). The levels of lead in south polar ice sheets were generally found to be below those in the north polar sheets. The increase of Pb with time in north polar snows was attributed mainly to lead smelteries before 1940 and to burned lead alkyls after 1940. This was based on several factors, such as the agreement between the increase of Pb found in snow strata and the historic increase of industrial Pb production and atmospheric emissions, and the quantitative estimation that natural sources, such as silicate dusts and sea salts could not account for the high Pb concentrations found (Ng and Patterson, 1981). The difference between the concentrations of Pb in the north vs the south ice sheet was ascribed to geological/ meteorological factors which hinder the migration of aerosol pollutants from the Northern Hemisphere to the Atlantic (Murozumi et al., 1969). Nriagu (1990b) remarked that the findings by Patterson and co-workers that the Northern Hemisphere had become severely contaminated with Pb was one of a number of influential reports which drew attention to the fact that the automobile tailpipe was the main source of environmental Pb pollution, and raised concerns about the risks of long-term exposure to the large quantities of Pb being discharged into the environment.

Pb in air. Concentrations of Pb in ambient air have been noted to be widely variable (Fergusson, 1986), depending on several factors, such as types of activities in the study areas and their surroundings (e.g., residential, industrial, or commercial), traffic density, topography, meteorology, content of Pb in petrol and petrol consumption, and modes of driving (Ter Haar et al. (1972), referred to in Fergusson and Simmonds (1983), had established that lead emissions from cars increase significantly during the accelerating phase). According to a compilation by Nriagu and co-workers (1996) of the levels of airborne Pb in the urban areas of Asia, Africa, and South America, measured during the period of 1986 - 1995, the Pb levels in Tokyo, Japan, were found to be in a low range of 0.05 - 0.1 μg m^{-3}, while the concentrations found in Mexico City, Mexico, were in a high range of 3 - 14 μg m^{-3} (USEPA' s guideline (1986), referred to in Nriagu et al. (1996), for ambient air is < 1.5 μg m^{-3}). Fergusson (1986), however, summarized that typical urban air lead levels reported over a long period of time lie in the range 0.5 - 2 μg m^{-3}. High concentrations or fluxes of Pb in ambient air in cities were found to level off as one progresses into the suburbs or rural areas (Fergusson and Stewart, 1992). Automotive emission has also been noted as a major contributor to Pb in sea/ coastal atmospheres (Black Sea aerosol, Anwari et al., 1992; the west coast of Sweden, Foltescu et al., 1994). Foltescu and co-workers (1994) measured airborne particle concentrations and deposition fluxes of several metals, including Pb, (and S and Cl) on a Swedish coast, with an aim of establishing sources of these. The sampling site was located close to open sea, with no disturbing sources of anthropogenic particulate pollution in the immediate vicinity. The airborne particle samples were segregated into fine (< 2.5 μm) and coarse particles (2.5 - 1 μm). The mean concentrations of Pb in fine and coarse fractions were found to be 7.6 and 2.5 ng m^{-3}, respectively. Based on correlation analysis, the authors found that the Br/ Pb ratio in fine particles approached 0.39, the "ethyl ratio" found in fresh car exhaust. The authors, therefore, saw the evidence as indicating that traffic was the dominant source of the fine particle Br and Pb. They also remarked that the positive correlations found between most of the metals in fine particles indicated long distance transport from industrial source regions in Europe. Regarding chemical forms of aerosol Pb, it has been reported that they depend on the chemical processes involved (Harrison, 1986). (In Fergusson (1992) is listed principal forms of Pb in aerosol originating from various sources, such as automobile exhaust, mining activities, and fertilizer production). Pb from automobiles is exhausted mainly as particulates composed primarily of reactive lead halides and ammonium lead halides, generated by the ingredients added to petrol to prevent a build-up of Pb in the engine. Pierrard (1969) and Ter Haar and Bayard (1971) both found that much of the PbBrCl (the principle component) emitted as auto-exhaust was converted into $PbCO_3$ and $(PbO)_2PbCO_3$ within 18 h, possibly as a result of photolytic reactions with atmospheric CO_2 and moisture. Ter Haar and Bayard (1971) suggested that species such as lead oxide and lead carbonate, or a mixture of these would be good choices for experimental studies of the health effects of atmospheric Pb. Biggins and Harrison (1979) proposed that $PbSO_4.(NH_4)_2SO_4$, a dominant compound found in ambient air, could be a result of the reaction between $(NH_4)_2SO_4$ existing in the atmosphere and PbBrCl.

Pb in soil. The concentrations of Pb in world soils vary considerably, as can be seen in a compilation by Fergusson (1990); a range of means of 123 to 8600 $\mu g\ g^{-1}$ was reported for contaminated soils (levels of more than 100 ppm was regarded to indicate contamination). The author noted that it was not possible to find a surface soil free of some lead contamination. This notion is further supported by several recent reports of elevated Pb levels found in soils from different studied areas, for example, farmlands treated with sewage sludge (Spain, Cabrera et al., 1994), day-care centers (Moscow, Orlova et al., 1995), parks and playgrounds (Newcastle, Devey and Jingda, 1995), urban, forest, and mountainous areas (Hong Kong, Chen et al., 1997). A variety of sources including Pb-based paints, alkyl-lead petrol, smelter, mining, and sludge fertilizers can act to produce highly contaminated soils. Walraven and co-workers (1997) investigated contamination sources of Pb and other metals in surface soils in a town in the Netherlands. It was found that the polluted soil contained as much as 5000 ppm Pb. The authors found that the Pb isotopic compositions of the polluted soil samples (e.g., $^{206}Pb/\ ^{207}Pb$ = 1.11 - 1.18) differed strongly from that of the unpolluted soil (e.g., $^{206}Pb/\ ^{207}Pb$ = 1.18 - 1.20), and noted that this difference confirmed anthropogenic sources of the Pb contamination. Based on the analysis of lead isotopic ratios of soil samples and the possible lead sources and statistical analysis of the chemical data set, the authors concluded that Pb enrichment was caused by three major sources, namely (i) dumped building materials, such as Pb sheets, glazed roof tiles, and paint ($^{206}Pb/\ ^{207}Pb$ = 1.11 - 1.18), (ii) coal ashes ($^{206}Pb/\ ^{207}Pb$ = 1.173 - 1.175), and (iii) alkyl-leaded petrol ($^{206}Pb/\ ^{207}Pb$ = "± 1.111").

High Pb concentrations often found in roadside soils (away from industrial and mineralized areas) are closely related to traffic density, implicating petrol Pb. An indicator of the contribution from petrol Pb is the commonly observed exponential decrease in Pb levels with distance from roads (the drastic decrease is often observed within a short distance, e.g., < 10 m, from the road edge) (Fergusson et al., 1980; Garcia-Miragaya et al., 1981; Byrd et al., 1983; Yassoglou et al., 1987; Howard and Sova, 1993; Piron-Frenet et al., 1994; Othman et al., 1997). In addition, Pb which accumulates this way typically localizes on surface soils and sharply decreases with depth (this confirms atmospheric deposition of Pb, and also suggests little threat to ground water). Pb isotope studies have also been used to assess the petrol Pb contribution to surface soil Pb (Gulson et al., 1981; Tiller et al., 1987). In a study of Tiller and co-workers (1987) on the dispersal of automotive Pb from metropolitan Adelaide, South Australia, into adjacent rural areas, Pb isotopic measurements were found to show that all surface soil horizons up to at least 50 km east of the city contained some Pb with the isotopic composition of lead tetraethyl used in South Australia. Additional factors influencing levels of Pb found in roadside soils include meteorological parameters (e.g., wind and rain) and area topography (e.g., up and down hill) (Piron-Frenet et al., 1994; Othman et al., 1997). In a monitoring of Pb levels in surface roadside soil (up to 5 cm) over a year long period by Piron-Frenet and co-workers (1994), soil samples

were collected from both sides of the road at distances of 10 m and 500 m. The Pb levels were found to correlate with traffic data and meteorological parameters (i.e., wind and rain). The data show two distinct relationships between traffic and Pb levels in soil at the two distances. Pb levels were found to vary between 10 and 30 ppm when traffic density was < 8000 vehicles/ day; however, these values increased by a factor of between 1.6 and 5.3 when the traffic density was > 10 000 vehicles/ day, even at a distance of 500 m.
The authors found that Pb levels decreased when there was heavy precipitation; this low retention of Pb was attributed to the very low organic content in the soils investigated. It was suggested that Pb was probably adsorbed on colloid particles which could easily percolate under the action of rain.

Although it is generally agreed that PbBrCl in emitted auto-exhaust is rapidly transformed to other compounds, the fate of Pb deposited on roadside soils has been noted to be less clear (Olson and Skogerboe, 1975; Zimdahl and Skogerboe, 1977). Several researchers have investigated geochemical associations of Pb in roadside surface soil, using chemical extraction (Harrison et al., 1981; Garcia-Miragaya et al., 1981; Yassoglou et al., 1987; Ramlan and Badri, 1989; Howard and Sova 1993; Nowak, 1995) (see geochemical association of Pb and chemical sequential extraction procedures in *sections 1.4.* and *1.6.*, respectively). These studies have shown that the bulk of anthropogenic Pb in roadside soils is generally immobilized by fixation reactions involving carbonate and oxide minerals or organic matter. Harrison and co-workers (1981) applied a sequential extraction onto samples of roadside soil (containing 256 to 5949 μg total Pb g^{-1}), and street dust. In the case of the roadside soil, it was found that Pb, Cd, and Zn were predominantly associated with carbonates and Fe-Mn oxides, whereas Cu was largely in the organic phase. The authors suggested that environmental mobility and bioavailability of these metals probably declined in the following order: Cd > Pb ≈ Zn > Cu. The authors also sequentially extracted an uncontaminated soil spiked with crystalline $PbSO_4$ and found that the majority of Pb was recovered in "ion-exchangeable" fraction using $MgCl_2$ as extraction solution (this step is prior to "carbonate" and "Fe-Mn" fractions in the extraction scheme used). The major difference between the Pb recovery patterns from the contaminated soil vs the spiked soil was interpreted as being because $PbSO_4$ was probably not a significant form of Pb in the roadside soils examined; however, this is inconsistent with a conclusion of Olson and Skogerboe (1975) that this Pb species was the principal constituent in the roadside top soils sampled from three different geographical areas in their study. Harrison and co-workers (1981) further speculated that although $PbSO_4$ might be a product of the deposition of derived Pb, it was probably rapidly converted by weathering processes to other, non crystalline forms of the metal. Garcia-Miragaya and co-workers (1981) investigated roadside top soil, containing total Pb in the range of about 1700 to 7000 μg g^{-1}, sampled from a city in Venezuela.
The majority of Pb was found to associate with the organic fraction. The authors noted that the very low amount of exchangeable Pb extracted suggested that Pb originally emitted in

halide forms (which were highly soluble in water) underwent insolubilization reactions in the soil system.

The risk of Pb movement from contaminated soils to plants is believed to be low (McBride 1994). Alegria and co-workers (1991) found a negative correlation between the extractable Pb content of soils and edible parts of vegetable; this indicated that the Pb content of their soils was not the main factor that influenced the Pb content of the vegetable. Kim and Fergusson (1994) attributed Pb found in leaves of a deciduous tree investigated to deposited Pb aerosol produced from leaded petrol (each sampling sites was within 5 m from a road). Othman and co-workers (1997) found that the levels of Pb in plants collected at different distances from a road declined at longer distances. Concentrations of Pb in tree leaves were found to depend not only on traffic density, but on the characteristics of the leaves, such as surface area, and age. In addition, the authors found that Pb concentration in most of the analyzed vegetable samples was high, and normal washing did not decrease it to an acceptable level. It is interesting to note here that Satake and co-workers (1996) have used the accumulation of Pb in tree trunk bark pockets as indicator of historical aerial pollution from leaded petrol in Japan. Ho and Tai (1988) have suggested roadside grass and Markert and Weckert (1994) have used moss for monitoring possible air pollution contributed from the use of leaded petrol.

McBride (1994) remarked that the health concern with respect to lead-polluted soils arised mostly from the contamination of plants by soil particles, and ingestion of soil by humans and grazing animals. Principal pathways for Pb intake in children are outlined in a subsequent discussion.

Pb in dust. Among all of the types of dusts found in the urban environment, street dust has been noted as being one of those most highly enriched in toxic trace elements (Hopke et al., 1980); beside Pb, the elements frequently reported for their high concentrations are Cr, Mn, Ni, and Zn (Hopke et al., 1980; Ogunsola et al., 1994). The inhomogeneity and widely varying composition of street dusts have been frequently noted (Fergusson and Ryan, 1984). However, the major component of street dust has been reported to be soil materials (76%) (Hopke et al., 1980); other sources reported include iron materials, tyre wear, and de-icing salts. Street dust is readily sampled and has been frequently used as an environmental media for monitoring Pb contamination. Pb in kerbside dust can reflect more immediate input of the metal from its source(s) because it is derived from recent accumulation (i.e., storm run-off and street cleaning can frequently effectively remove dust from the kerbside) (Ho, 1990). The concentration of Pb in street dust has been found to be widely variable. Factors often reported for their effect on levels of Pb in street dust include traffic density, type of nearby industry, (as just mentioned) seasons/ weather conditions (in particular rain, drought, and wind), nature of the road surface, particle size and density, and sampling methods (Fergusson and Simmons, 1983; Davies et al., 1987; Fergusson, 1987). Some authors have noted the need for a standardized sampling protocol for dusts (Fergusson, 1986;

Gulson et al., 1995); the reason for this being that the finest particles (i.e., clay size) may not be sampled by some methods used (Fergusson, 1987). In a summary by Fergusson and Kim (1991) of Pb levels in street dust in various locations in different parts of the world, the corresponding means (or medians) were found to cover a wide range from 7.5 to 5800 $\mu g\ g^{-1}$ (for hills around Jeddah, Egypt, to areas near printing works, England, respectively). High Pb concentrations of a few thousand $\mu g\ g^{-1}$ can often be found in street dusts near smelters, and along major roads; Pb as high as about 300 000 $\mu g\ g^{-1}$ was found in street dust in the vicinity of a battery factory. Although Pb in street dust can originate from a multitude of sources, it is widely agreed that the principal source of Pb in this media is auto emissions. Fergusson (1986) remarked that Rabinowitz and co-workers (1976) had reported that the isotope ratio $^{208}Pb/\ ^{206}Pb$ of 2.015 found in street dust close to a freeway was similar to the ratio (2.020) in the petrol used in the area. Linton and co-workers (1980) used a microanalytical approach to identify possible sources of two types of Pb-containing outdoor dust samples: (i) kerbside, and (ii) next to a building having Pb-painted trim and situated at some distance from a street, collected from a non-industrial community. The samples were fractionated according to particle size, nonmagnetic/ magnetic properties, and density. Each separated dust fraction was analyzed for elemental composition, and morphology and composition of individual particles (using scanning electron microscopy/ energy dispersive X-ray spectrometry (SEM/ EDS)); X-ray powder diffraction patterns (XRPD) were also recorded. The authors based criteria for determining the sources of Pb on similarity of the morphology and composition of individual particles with those of authentic automobile exhaust particles and paint chips, and observation (or lack of observation) of associated tracer elements in individual particles, e.g., Br and Cl for automotive origin, Al, Ca, Si, and Ti for non-automotive origin. This, in conjunction with Pb mass distribution among different range of particle sizes led to the conclusion that automotive exhaust particles were the main contributors of Pb to roadway dusts and that they also contribute substantially to building dust samples.

Several species of Pb have been detected in street dust (see a compilation by Fergusson and Kim, 1991). $PbSO_4$ was reported by Biggins and Harrison (1980), using XRD, to be the most frequently observed crystalline compound of Pb in the street dust samples investigated. The authors, based on artificial weathering of $PbSO_4.(NH_4)_2SO_4$, were convinced that $PbSO_4$ was probably a product of water leaching of $PbSO_4.(NH_4)_2SO_4$ deposited from the atmosphere. It was, however, found that only a few percent at most of total Pb in the samples examined was present as crystalline compounds amenable to XRD analysis. The authors speculated that the Pb added to street dust from automotive emissions was being converted to other noncrystalline forms, and therefore suggested that alternative approaches to speciation, e.g., chemical speciation, and other solid-state instrumental methods, must be sought. In a study of Al-Chalabi and Hawker (1996), street dust samples (both total and sized fractionated) were subjected to a sequential extraction process. Most of the Pb was found to be associated with the carbonate fraction; this is generally consistent with the findings of Harrison and co-workers (1981), Fergusson and Ryan (1984), and Evans and co-workers (1992), using the same extraction procedure. With respect to street dust particle size, the concentrations of Pb were found to increase with a decrease in particle size (Biggins and Harrison (1980), however, remarked that in many cases the larger mass of Pb was found to be associated with the larger grain sizes in the dust, because of the greater mass of the larger size fractions). The relationship between exchangeable cations (especially Ca) and exchangeable Pb was found to be inverse; the authors attributed this to the operation of an ion exchange process by which Pb replaced cations from the exchange sites of mineral surfaces. The selective exchange of Pb for Ca was attributed to their similar ionic characteristics. It was therefore speculated that Ca might play an important role in the Pb adsorption behaviour.

High concentrations of Pb (and other toxic trace elements) can also be found in house dust; as with street dust, the concentration of Pb in house dust varies considerably, e.g., with mean or median values from a few hundred to a few thousand $\mu g\ g^{-1}$ (shown in a summary of Fergusson and Kim (1991) from different countries and range of sites). In comparison with street dust, house dust has an additional factor that some of it is internally generated. However, aerosol particulates, soil, and street dust particles have been noted to significantly contribute to house dust (Fergusson and Kim, 1991). Therefore, it is to be expected that where leaded-petrol is in use, a significant proportion of inside dust Pb originates from it. Pb in indoor dusts collected from buildings of different types (e.g., office vs house) and ages may originate from different sources (Feng and Barratt, 1994).

Pb in sediment. Pb found in urban runoff and street sediment shows a relationship with concentrations of the metal in road dust/ dirt (Hamilton et al., 1984; Dempsey et al., 1993; Stone and Marsalek, 1996). Pb and other toxic heavy metals associated with fine fractions of urban street dust particulate material can be easily removed from street surfaces by stormwater runoff and transported to receiving water and sediments (for coarser fractions, the probability of transport through the entire drainage system is smaller). In an investigation of Stone and Marsalek (1996) on trace metal composition in a street sediment in a city in Canada, with a range of land uses (e.g., light to heavy traffic density), the samples were sized fractionated, and subjected to a series of chemical extractants. Total Pb contents were found to be in the range of 33 - 261 ppm, with a mean content of 90.5 ppm. The authors compared total metal contents found with those in a previous summary of metal content in urban/ residential road sediments, which reported bulk concentrations of Pb in the range of 128 - 8300 mg kg^{-1}. Stone and Marsalek (1996) attributed the lower Pb levels found in their study to the use of non-leaded gasoline in Canada. Increased Pb concentrations were generally found to associate with the < 63 μm size fraction (silt and clay), the smallest of all fractions investigated in this study; however the load of Pb in this fraction was found to account for < 10% of the total load (the authors remarked that this < 63 μm size fraction served as a substrate for the metabolism of benthic invertebrates). Pb was also found to predominate in the bioavailable form (defined as that which was dilute acid extractable); whereas the results from chemical sequential extraction showed that the Pb association was in the order Fe/ Mn oxides > organic > carbonate > residual. The authors also suggested that metal loading in the street sediment could be effectively controlled by common measures including street cleaning, runoff detention and extended runoff detention. A collection of studies on urban water quality and street/ river sediments in association with highway pollution can be found in a special issue of The Science of the Total Environment 146/ 147 (1994).

Pb in food. As previously mentioned, Pb may contaminate food through various pathways. A range of Pb contents is found in a variety of common foodstuffs (Hapke, 1991; Tsoumbaris and Tsoukali-Papadopoulou, 1994; Zhang et al., 1996; Roses et al., 1997). Plant foodstuffs are noted to generally contain more Pb than foodstuffs of animal origin. However, high concentrations of Pb are frequently found in animal liver (e.g., as high as ~ 500 ppb), while low Pb concentrations are reported for milk (e.g., < 30 ppb). In a survey of the Pb content of rice collected from various areas in the world by Zhang and co-workers (1996), it was found that among the samples collected from 10 areas in Asia, the highest and the lowest geometric means were for Indonesia (38 ng g^{-1}) and Australia (2 ng g^{-1}), respectively. Among 7 regions outside Asia, the means were highest for Spain (58 ng g^{-1}) and the lowest for the US (3 ng g^{-1}). The authors found marked differences in the Pb contents in rice between both countries (e.g., in continental China, Pb content as high as 152 ng g^{-1} and below 20 ng g^{-1} were found) and regions in the world. Based on a comparison between their results and previous published reports, the authors concluded that in the last 10 - 15 years, no substantial changes in the Pb contents in rice had occurred when considered globally (i.e., although Pb content of rice in some areas of the world had increased, in other regions the Pb levels decreased). Some traditional food may contain high levels of Pb. Shen and co-workers (1996) found that one hundred percent of tested Chinese preserved egg (which is made from egg with some additives containing PbO) had Pb concentrations above allowable levels for food in that country (i.e., > 3 μg g^{-1}). Canned food can also be found to contain high concentrations of Pb. Orlova and co-workers (1995) found Pb concentrations in Russian canned foods as high as 1240 μg kg^{-1} (evaporated milk). The authors noted that most Russian food cans were made with Pb-soldered seams.

Pb in humans. Young children (e.g., age seven and under) are generally considered to be the age group of most concern with regard to environmental exposure to Pb. Exposure factors include the proximity of children to contaminated soils and dusts, because of their normal hand-to-mouthing behaviour (or in extremely cases, pica, the abnormal intake of soil, paint chips, etc.), children's tendency to play on the ground, their higher gastrointestinal absorption of Pb, their greater sensitivity to adverse effects of Pb, and their higher likelihood of having nutritional deficiencies that promote Pb absorption (Tsuji and Serl, 1996).

Possible pathways of lead intake by children from different environmental media are illustrated in *Appendix 1.1*.

For both adults and children, food is regarded as the most significant source of daily Pb intake (Fergusson, 1986, 1990). For young children, the second most significant source of Pb intake (about 30% of the estimated total of 150 $\mu g\ day^{-1}$) has been estimated to be contaminated dust and soil via fingers; whereas uptake via water, air, and dust/ soil on food are estimated to be relatively minor sources. In a 10 year study of Thornton and co-workers (1994) on Pb contamination of UK dust and soils and its implications for childhood exposure, it was concluded that for 2 year old children in the UK urban environment, approximately 50% of Pb intake was from dust ingested as a result of hand-to-mouth activity. Previous literature suggesting the importance of the "dust-hand-mouth" route includes the works of Sayre and co-workers (1974), Sayre (1981), and Duggan (1983). Duggan and Williams (1977) provided a summary of some previous literature regarding the derivation/ estimation of Pb intake and uptake values. Fine dust particles, which are typically found to contain higher concentrations of Pb than the coarser ones, have been generally regarded as being more readily retained on hands and clothing, and therefore more likely to be ingested. In the summary of Fergusson (1986), the total daily uptake of Pb by young children was estimated to be about 3 times more than that of adults.

Evans and co-workers (1992) have noted that an assessment of the hazard associated with the Pb levels measured in the soil and dust samples might be made in terms of the potential bioavailability of the materials ingested and in terms of potential contributions to the blood lead burden of young children. Hemphill and co-workers (1991) and Ruby and co-workers (1992, 1993) both studied bioavailability of Pb from mining sites. It was found that dissolution kinetics of the ingested Pb-bearing solid in the gastrointestinal (GI) tract influenced Pb bioavailability (i.e., the amount absorbed or taken up physiologically).
The dissolution kinetics were found to be affected by both the Pb mineralogy and the particle size distribution, and were under the limitation of the pH of the GI tract and the residence time of material in the stomach. The authors remarked that the complexity of the Pb-bearing mine-waste mineral (e.g., multi-phase and Pb-phase encapsulation within inert matrices) resulted in it being dissolved slowly and incompletely in the GI tract, therefore exhibiting low bioavailability. This has been reported in previous animal studies, which indicated that Pb from mine waste was much less bioavailable than Pb from other sources (e.g., in the urban environment). Evans and co-workers (1992) noted it seemed likely that soil or dust samples which contained high amounts of Pb in the exchangeable and carbonate fractions posed a greater risk than those samples with less amounts. In addition, Gulson and co-workers (1995), based on a literature survey, have remarked on the importance of particle size, in that coarse PbS is essentially insoluble under simulated GI tract conditions, whereas < 60 μm galena dissolves readily. The authors further noted that the most meaningful particle size fraction of soil to analyze from a toxicological perspective was the < 150 μm (and preferably

the < 100 μm fraction); however, there was no consensus noted for most suitable particle size in dust analysis.

Levels of Pb in various biological specimens have been used as an indicator of Pb exposure in different groups of populations and likely toxic effects; these specimens include blood (the most commonly used index) (random population, Wales, Elwood and Toothill., 1986; children, Australia, Maynard et al., 1993; children, Greece, Maravelias et al., 1994; patient, Nigeria, Omokhodion, 1994; children, Australia, Donovan et al., 1996; women, Mexico City, Farias et al., 1996; Hernandez-Avila et al., 1996; adults, Taiwan, Liou et al., 1996; children, China, Shen et al., 1996; apprentices of a technical-professional school, Portugal, Teresa et al., 1997), teeth (young adults, US, Needleman et al., 1990; general population, Spain, Gil et al., 1994), bone (Hernandez-Avila et al., 1996), and hair (adults, Austria and Italy, Wolfsperger et al., 1994; Teresa et al., 1997) (Schuhmacher et al. (1996) noted that hair concentrated more Pb per unit weight than any other tissue or body fluid). Shen and co-workers (1996) remarked that ideally, neither children nor adults should have had any Pb in their bodies, since it provided no physiological benefit, and that no level of Pb in blood was considered "safe" and "normal". Gonneratne and Olkowski (1992), Aaseth and co-workers (1995), and Burns and Currie (1995) provide details of treatments for Pb toxicity, e.g., chelation therapy. According to a summary by Fergusson (1986), a blood Pb level of 10 - 15 μg dl^{-1} might be considered as typical of contemporary urban levels. Gulson and co-workers (1996), in their survey of blood Pb in children residing in a Pb mining community, used Pb levels of ~ 0.29 μmol $litre^{-1}$ (6 μg dl^{-1}) as representative of "background" levels; this concentration of Pb was estimated from adult females who were generally mothers of the children. The authors found that 60% of the children had blood leads ≥ 0.72 μmol $litre^{-1}$ (15 μg dl^{-1}). Based on isotopic measurement, the authors concluded that even though the orebody Pb was the major contributor to blood Pb in this community, of the children whose blood Pb was ≥ 15 μg dl^{-1}, 34% had ~ 50% or more of their blood Pb derived from sources such as paint and petrol or both. Fergusson (1986) concluded from various studies that the estimated petrol Pb contribution to blood Pb ranged from very little to 46%, and that a value of at least 33% petrol Pb in blood seemed to be reasonable, or about 6 μg dl^{-1} for "average" city dwellers.

Wixson and Davies (1994) summarized recommendations of the Society for Environmental Geochemistry and Health for an establishment of guidelines for acceptable levels of Pb in soil for public health goals, especially for protecting children (i.e., SEGH model). This model was based on blood Pb and the soil/ dust Pb relationship. The derivation of the soil/ dust standard is accomplished by the use of a blood Pb target concentration, a geometric standard deviation of the blood Pb distribution, the baseline concentration of blood Pb from multiple sources, the degree of protection required for the population at risk, and the slope of the relationship of blood Pb to Pb in soil/ dust. The authors also demonstrated how the model might be implemented. It appears that the model has been modified and put to use by the Rhode Island Department of Health (Vanderslice et al., 1994). Tsuji and Serl (1996) introduced an EPA mathematical Pb model proposed to estimate blood Pb levels in young children based on environmental exposures to Pb from various sources including soil, and also to predict percent risk of exceeding a specific blood Pb level (i.e., 10 $\mu g\ dl^{-1}$). The authors used environmental (primarily soil) and blood Pb data from a residential community near a smelter to illustrate recent uses of the model in assessing cleanup of Pb in soil.

1.2.4. Impact of reduction of Pb in petrol on Pb levels in the environment.

Results of a numbers of studies have suggested that reduction of Pb in petrol results in decreases in the levels of Pb found in several environmental compartments in various parts of the world. Examples include; top soil (Louisiana, USA, Byrd et al., 1983), ambient air (USEPA, 1986 referred to in Nriagu 1990b; London, Jensen and Laxen, 1987; Sheets et al., 1997), kerbside dust (Hong Kong, Ho, 1990), snow (Greenland, Boutron et al., 1991), sediment (Santa Barbara Basin, USA, Schmdt and Reimer, 1991; lake sediment, Switzerland, Moor et al., 1996; Von Gunten et al., 1997), ocean water (Atlantic, Wu and Boyle, 1997), and biological samples (edible vegetation, Spain, Bosque et al., 1990; blood and hair, Spain, Schuhmacher et al., 1996). In general, the authors compare the changes in Pb levels in the medium investigated with timing of Pb consumption/ emission. Byrd and co-workers (1983) determined Pb levels in the top 5 mm of soil sampled in 1973, 1974, and 1979 along a highway in the US. The concentrations of Pb were found to increase from 1973 to 1974 but found to significantly decrease from 1973 to 1979 (with mean Pb reduction of about 70%). This was attributed to the mandatory use of unleaded gasoline introduced in the US in 1975. Jensen and Laxen (1987) measured concentrations of particulate-bound Pb in air, using low-volume air sampling at 13 sites in or near London, during the phase down of the Pb content of U.K. petrol from 0.4 to 0.15 g $litre^{-1}$ in 1985. Three types of sites were used as monitors: sites at the sides of busy roads, playgrounds of schools, and background sites (i.e., as far away as possible from busy roads). A sampling site in a road tunnel was also set up in order to monitor exhaust emissions as closely as possible with the minimum effect from other sources or from the weather. The results from this site in the tunnel suggested that the levels of Pb in exhaust emissions started falling near the end of Nov 1985, and reached a new, lower value by the beginning of Jan 1986; this observation agreed well with the information of fuel production. Results for the other sites were found to be compatible with this timing but showed more scatter, as well as an annual cycle with higher levels in the winter months. The Pb concentrations before the phase-down were found to be similar to those found in previous surveys in London; levels alongside busy roads were between 1 and 2 $\mu g\ m^{-3}$ and background concentrations were in the range 0.22 to 0.47 $\mu g\ m^{-3}$. The mean Pb-in-air values measured after the phase-down were found to be smaller with the observed reduction ranging from 34% at background sites to 55% at roadside sites, while 60 to 65% was expected from the reduction changes in the lead content of petrol. The authors speculated that there were two sources contributing to the observed Pb levels at a given site: one was the current UK petrol emissions while the other was a residual component, unaffected by those emissions and therefore constant during any phase-down. It was calculated that a residual component of lead in air was around 0.09 $\mu g\ m^{-3}$. The authors noted that although the residual component was not very large, since the phase down it could make a major contribution to lead-in-air levels at background sites. Source(s) of this residual component were speculated to be airborne lead transported from other European countries, a contribution from UK industrial sources, and/ or possible re-suspension of lead containing dusts. Other factors that might account for the less-than-expected decrease in lead-in-air levels included possible differences in the sampling periods in the two years in the emission rates, temperature (in 1986 the temperatures were lower than in 1985, and this would lead to increased use of chokes on car engines and therefore greater fuel consumption), and traffic flows (which might have increased, then in turn increased the total lead emissions; however, it was noted that the average annual increase in London over recent years had only been around 1%). Ho (1990) determined the effect of Pb reduction in petrol on the roadside environment of Hong Kong. It was noted that before 1981, Pb in petrol in Hong Kong averaged about 0.84 g $litre^{-1}$; after 1981 the level was reduced in a stepwise manner, and by early 1987, it was at 0.25 g $litre^{-1}$. The potential effect of the Pb reduction was assessed by comparing the Pb content in kerbside dust samples (< 0.71 mm fraction) taken in Nov 1977 - Jan 1978 and in Jan 1987 from 37 sites which covered a wide range of traffic densities. The sampling was undertaken during the dry season (Nov to Feb) in both surveys in order to minimize the effect of possible temporal changes. The mean Pb levels for the 1977 - 1978 and 1987 samples were found to be 3280 and 1080 $\mu g\ g^{-1}$, respectively and their difference was noted to be highly significant. It was also found that samples collected in 1987 showed a reduction relative to the 1977 - 1978 samples which was very consistent for all the sites, regardless of their traffic density (low, medium, and high), with the mean % Pb reduction ranging from 56 to 62%. Boutron and co-workers (1991) measured Pb concentrations (pg g^{-1}) in Greenland ice and snow from 1967 to 1989, and in combination with previous results of Murozumi and co-workers (1969) and Ng and Patterson (1981), illustrated changes from 5500 BP to 1989 of the Pb levels. Boutron and co-workers (1991) noted that although these data were obtained at widely dispersed locations, it seemed reasonable to put them together as the concentrations of major impurities such as Na, Al and sulfates were similar at these sites. The resulting relationship between the Pb concentrations vs age of Greenland snow or ice (year) revealed that after a great increase (~ 200-fold) from several thousand years ago to the mid 1960s, the Pb levels had decreased rapidly, by a factor of ~ 7.5, during the past twenty years. This was attributed to limitation the use of Pb additives in petrol from about 1970 in the US and other countries. Other possible sources, e.g., natural contributions from rock and soil dust in snow, and sea-salt spray were found to be negligible (the determination was based on, e.g., the ratio of Pb/ Al found in the samples to that in rock or soil). In a study of the effect on lake sediment of the reduction of petrol Pb introduced in 1985 in Switzerland, Moor and co-workers (1996) constructed profiles of Pb concentrations and stable Pb isotope ratios (^{206}Pb/ ^{207}Pb) for sediment cores taken from Lake Zug. Natural background Pb concentrations in pre-industrial sediments were found to be 16 μg g^{-1} at a depth of 15 cm (determined from a core that covers about 200 yr in the upper most 15 cm) with background ^{206}Pb/ ^{207}Pb ratios of 1.20. The authors found that the concentrations of Pb reached a maximum of 110 μg g^{-1} in a depth corresponding to ca. 1970, the time of highest Pb emissions, and leveled off in the most recent sediment layer. It was found that the ^{206}Pb/^{207}Pb ratio was at its minimum value of 1.13 in the depth profiles corresponding to about the year 1980 (when the traffic emissions were still the largest source of Pb) and increased to 1.16 since ca. 1990. The sharp increase in the ^{206}Pb/ ^{207}Pb ratio toward a more natural ratio in the top sediment layer was interpreted as a result of the phasing in of unleaded gasoline, since the ^{206}Pb/ ^{207}Pb ratio of Pb used for gasoline additive in Europe ranged from 1.04 to 1.10, while the ratio of natural background Pb in central Europe was about 1.20. Wu and Boyle (1997) presented data on Pb concentrations in surface and subsurface seawater sampled from Sargasso Sea near Bermuda, western North Atlantic Ocean, spanning from 1979 to 1996. Pb concentrations were found to markedly decline from the level of about 160 pmol kg^{-1} in 1979 to about 70 pmol kg^{-1} in 1990. This was attributed to the phasing out of leaded gasoline. In years after 1990 the decline was found to have slowed; concentrations during the 1990s had decreased only from ~ 70 pmol kg^{-1} in 1990 to ~ 40 - 60 pmol kg^{-1} in 1995 and 1996. The authors remarked that because US gasoline Pb emissions in 1991 already had dropped to less than 5% of peak utilization, it appeared that future reduction in the consumption of leaded gasoline in the US or Europe would not result in greatly lowered Pb concentrations in the Sargasso Sea. They suggested that after 1990, Pb in the surface Sargasso Sea was supplied by emissions from sources other than leaded gasoline. It was speculated that the present levels of Pb were determined by remote transport of high-temperature industrial emissions from the US, and that barring major changes in Pb emission controls, surface water levels were likely to remain at this level indefinitely. The authors suggested that this hypothesis could be tested by examining industrial Pb emissions and their atmospheric dispersal, and that stable Pb isotope ratio measurements might also be helpful in this regard. Schuhmacher and co-workers (1996) investigated the possible impact of a recent reduction of Pb in Spanish gasoline (from 0.4 to 0.15 g $litre^{-1}$) on the blood and hair lead levels in the population (non-occupationally lead-exposed) in a province. A total of 250 adult participants between 16 - 65 years of age and 252 children were included in the study. During the period 1990 - 1995, on average, blood Pb levels in adults were found to substantially decline from 12.0 μg dl^{-1} to 6.3 μg dl^{-1}; and the hair Pb concentrations in children were also found to decrease considerably from 8.8 μg g^{-1} to 4.1 μg g^{-1}. These decreases were noted for all the subgroups (sex, age, and place of residence) examined, and were mainly attributed to the reduced exposure to products of leaded gasoline. The authors remarked that the limitation in the use of Pb in Spanish gasoline had already induced a resulting decrease in atmospheric Pb concentrations of the province, as well as a remarkable reduction in the lead levels of edible vegetables, and a marked decrease in the dietary lead intake of the population.

1.3. Lead in the New Zealand environment.

1.3.1. Sources, distributions, and concentrations.

In New Zealand the most significant sources of anthropogenic lead have been lead-based paint on old (pre-1965) housing, leaded petrol, and soldered cans (The Royal Society of New Zealand, 1986; Hay and de Mora, 1993; Graham and Narsey, 1995). Graham and Narsey (1995) noted that the use of Pb in paints had been tightly controlled since 1983 (Jansen (1993) addressed potential hazard posed by houses with Pb-pigmented paint in NZ and a removal of the paint from timber). Graham and Narsey (1995) further remarked that the use of Pb solder in food containers was almost completely eliminated in 1981 with the introduction of welded seam technology for metal cans, however some imported canned foods might still be a significant source. On the other hand, Pb in petrol, as noted by the authors, had been maintained as a major contributor of Pb found in the environment in this country, although the quantities used were being progressively reduced since mid-1986 (the move to unleaded-petrol is outlined in the following subsection). Graham (1993) remarked that to some extent sources of lead in NZ, i.e., petrol, paint, and industrial sources had been somewhat under control; however, two areas of increasing concern were expected to be the disposal of solid wastes contaminated by lead and the level of lead in sediments.

Levels of Pb in the environment in New Zealand have been extensively studied, as evidenced in a report of The Royal Society of New Zealand (1986), and in a conference proceeding by Hay and de Mora (1993). Significant numbers of previous studies appear to have been conducted in the Christchurch and Auckland areas.

Elevated levels of Pb in soil and/ or dust have been reported for samples taken from major roadways in Auckland (soil, Ward et al., 1977a), Christchurch (dust, Day 1977; Fergusson and Simmonds, 1983; Fergusson and Ryan, 1984; Fergusson et al., 1986; dust and soil, Fergusson et al., 1980; Fergusson and Kim, 1991 (a review report)), and Wellington (soil and vegetation, Collins, 1984). Pb levels in roadside dust in urban areas in Christchurch collected during the period between 1980-1986 were found to be in the range of 200 - 13 000 μg g^{-1}. This was markedly higher than the levels of 10 - 50 μg g^{-1} noted for dust collected from rural roads (The Royal Society of New Zealand, 1986). The elevated Pb values were almost exclusively attributed to Pb from petrol. In Fergusson and Kim (1991) is illustrated variations in the concentration of Pb in street dust sampled at a very busy intersection over the period from 1975 to 1989. The concentrations of Pb appeared to be influenced by several factors, such as traffic density, weather conditions (e.g., rain, flooding and drought), and the installation of traffic lights (start/ stop/ acceleration of vehicle engines). For roadside soil, Fergusson and co-workers (1980) found mean concentrations of 860 and 300 $\mu g\ g^{-1}$ in the top 2 cm of soils collected at distances of 3.5 and 7.5 m from a busy road; whereas Collins (1984) found mean Pb concentrations of 262 and 178 $\mu g\ g^{-1}$ in the top 4 cm of soils collected from a pasture at distances of 4.2 and 10 m from a road carrying 23 000 vehicles per day. Ward and co-workers (1977a) assessed Pb in surface soil (0 - 5 cm) collected from a major thoroughfare near an Auckland battery factory and smelter. In general, the levels of Pb in soil in the factory and smelter areas were found to be notably higher than those in samples from the thoroughfare; some surface soils adjacent to the smelter contained more than 10% Pb. Elevated concentrations of Pb in vegetation samples were generally found; the levels of 1000 - 3000 $\mu g\ g^{-1}$ were not uncommon in unwashed vegetation within 150 m of the industrial site. Ward and co-workers (1977b, 1979) and Fergusson and co-workers (1980) both reported high Pb concentrations in vegetation, in particular the leaves, sampled along roadsides. Levels of Pb in tree rings have also been investigated (Fergusson et al., 1980; Stewart et al., 1991). Levels of Pb in house dust were widely studied in Christchurch area (Fergusson and Schroeder, 1985; Fergusson et al., 1986; Fergusson and Kim, 1991 (a review)). Fergusson and Schroeder (1985) reported the mean concentration of Pb in newer (post-1950) areas of the city to be 460 $\mu g\ g^{-1}$, whereas in older (pre-1950) areas it was 830 $\mu g\ g^{-1}$. These levels were noted to relate to the type of building material (brick or wood) and type of paint used (non-lead or lead paint). For the newer areas of the city, it was estimated that ~ 90% of the lead was derived from petrol additives (via street dust and aerosol), whereas in the older areas, ~ 50% of the lead was estimated to come from petrol lead and 45% from paint lead. The authors also reported mean Pb levels of 1160 and 138 $\mu g\ g^{-1}$ for samples of street dust and soils from front gardens, respectively. Fergusson and co-workers (1986) analyzed elemental compositions of house dust, street dust and soil. The authors remarked that the elements Hf, Th, Sc, Sm, Ce, La, Mn, Na, K, V, Al, and Fe might be considered to be soil-based, and contributed about 45 - 50% to house dust and 87% to street dust. The elements which were found to be enriched (> 3 times) in the dusts relative to the levels found in local soils, were Br, Cu, Cl, Pb, Zn, Cr, Ca, As and Sb in house dust, and Zn, Cr, Cu, and Pb in street dust.

Atmospheric Pb has been widely discussed, in particular in relation to the use of Pb in petrol (Day, 1977; Simmond et al., 1983; de Mora and Campbell, 1985 (tetraalkyl volatile Pb) referred to in The Royal Society of New Zealand, 1986; Fergusson and Stewart, 1992; Graham, 1993; McLaren and Herd 1993; Taylor, 1993; Kim and Fergusson, 1994; Graham and Narsey, 1995). Day (1977) calculated that for Christchurch, Pb from petrol contributed 99% of the total atmospheric burden, and suggested that roughly the same figure should have been applied for the rest of the country. Particulate Pb has been monitored at a number of different sites (e.g., residential and congested inner city) around the country, for example Auckland, Hamilton, and Christchurch, in a variety of regional and national programmes (The Royal Society of New Zealand, 1986; Graham and Narsey, 1995). A preliminary short-term study was carried out in 1995, on behalf of the Ministry of Health, to assess the levels of Pb and benzene in ambient air in some urban areas (Graham and Narsey, 1995). At the sites in Auckland and Christchurch where the measurement of Pb was carried out, it was found that all of the mean Pb levels (0.11 - 0.24 $\mu g\ m^{-3}$, 24-h average) were well below the air quality guideline of 0.5 - 1.0 $\mu g\ m^{-3}$ (3-month average). Further short-term measurements of Pb in air were not recommended, provided that existing long-term monitoring programmes are maintained. Graham and Narsey (1995) noted that prior to 1986, Pb levels in most urban areas were typically in the range of 0.1 to 1.0 $\mu g\ m^{-3}$ (3-month averages) and in areas of high traffic densities or significant congestion the levels were generally higher than this, with some results in excess of 2 to 3 $\mu g\ m^{-3}$. The authors further noted that all the long-term Pb results indicated a continuation of the downward trend observed over the last 9 years and that the Pb levels recorded at all currently operating sites were generally below the lower limit of 0.5 $\mu g\ m^{-3}$.

Several studies have reported Pb levels in sediments (river sediment, Christchurch, Purchase and Fergusson, 1986a; Manukau Harbour, Auckland, de Mora and Demeke, 1990; Porirua Harbour, Wellington, Glasby et al., 1990; Avon-Heathcote Estuary and surrounding areas, Deely, 1993; Deely and Fergusson, 1994). de Mora and Demeke (1990) investigated core surficial sediment samples to seek post-depositional variations in Pb behaviour and the local effect of the nearby NZ Steel Works with respect to Pb. It was found that the total concentration of Pb varied in the range 3.5 - 98 mg kg^{-1}. The authors noted that although background Pb concentrations were difficult to define, it was apparent that the discharges from the northern effluent outfall at the NZ Steel Works had approximately doubled sedimentary Pb concentrations in the immediate vicinity. Glasby and co-workers (1990) analyzed the < 20 μm fractions of 72 sediment samples taken from two inlets of Porirua Harbour, and found elevated concentrations of Pb and Zn (mean 93 and 259 ppm, respectively) in the sediment samples from Porirua Inlet. However, the authors found no evidence of elevated Pb contents in the sediments adjacent to State Highway No.1 which is situated in the vicinity of the harbour. Deely (1993) reviewed material relating to contents of Pb and other heavy metals in the clay fraction (< 4 μm) of suspended sediment, surface sediment, core sediment, and soils, associated with the Avon-Heathcote Estuary. The author noted that the metal concentrations were increasing towards the surface in depth profiles of this zone, and that this pattern combined with the increasingly eutrophic state of the estuary suggested more serious heavy metal contamination in the future. Deely (1993) noted that for Heathcote river, Purchase and Fergusson (1986a) found baseline values of most metals were reached within 20 - 30 cm of the surface. In the Woolston area very high levels of Pb (e.g., 55 000 mg kg^{-1}) were found in zones adjacent to former industrial effluent discharge points, such as a Pb-acid battery factory. Elevated levels of Pb in the estuary were regarded as being associated with the very high Pb contents in Christchurch street dust, i.e., the dust was carried into the drain and estuary with stormwater; the initial contamination of the street dust with Pb was attributed to petrol combustion (Fergusson and Ryan, 1984). Heavy metal studies of total surface sediment in the Avon-Heathcote Estuary showed Pb to be the most significantly enriched metal followed in order by Zn, Cr, and Cu (Purchase and Fergusson, 1986a).

Levels of Pb in blood have been investigated by several groups of researchers (Reeves et al., 1982; Hinton et al., 1984, 1986, 1993; Silva et al., 1993; Walmsley et al., 1993).
Hinton and co-workers (1984) investigated blood Pb levels in relation to industrial exposure for various occupations in the Christchurch area during the period from 1974 to 1983. Examples of types of industry studied include electroplating, paint removal, and battery handling. It was found that the mean red cell Pb concentration for 50% of employees was within the regional usual range for those not occupationally exposed. In 77% of the workers the mean red cell Pb was found to be less than 4.1 μmol litre^{-1}. However, the remaining 23% of workers had blood Pb values above this level, which the authors noted might give signs of Pb intoxication if maintained for a long time. Based on the magnitude of the mean and percentage of raised levels, the authors identified occupations with no or low risk, and those with medium and high risk. The occupations with high risk (red cell Pb mean > 4.1 μmol litre^{-1}) included painters spraying glass and metal and smelter/ furnacemen.
In another survey by Hinton and co-workers (1986) on blood Pb levels in a population which had no relevant exposure to Pb other than that from the general environment, in Christchurch and areas immediately surrounding it, it was found that during the period between 1978 - 1985 the Pb levels (in whole blood, μmol litre^{-1}) had fallen in adult males and females (> 17 years) overall by 42% , and in school and pre-school children (> 9 months) by 44%, and 46%, respectively. The authors attributed this blood Pb reduction to changes in dietary intakes and a clean up of Pb in domestic and industrial environments (during that decade the Pb content in petrol and petrol sales were noted to remain unchanged). It was noted in the Ministry of Commerce Discussion Paper (1994) that no definitive relationship between ambient Pb and blood Pb levels had yet been established in NZ. Gooneratne (1996) remarked that the average blood Pb level in NZ was ~ 7 μg dl^{-1} (well below the current figure for safe level of Pb for children of 10 μg dl^{-1}).

Levels of Pb have also been studied in various other media, such as snow and rainfall (Stevenson, 1980), teeth (Purchase and Fergusson, 1986b; Fergusson et al., 1989), urban stormwater (Williamson, 1985, 1986), sludge from a leaded petrol tank (Jones and Bingham, 1993), and food (Stevenson 1993).

1.3.2. The move to unleaded petrol.

The move to control lead in petrol in New Zealand was commenced in 1986 (Ministry of Commerce, 1994; Graham and Narsey, 1995). The steps taken involved the phasing-in of unleaded 91 octane gasoline and the reduction of lead in 96 octane petrol from the level of around 0.84 g litre^{-1} (one of the highest lead levels in the world) to about half this value. Similar schedules for controlling lead in petrol were reported in several European countries (Nriagu, 1990b). The consumption of unleaded petrol in New Zealand grew rapidly since its introduction in 1986 to the level of about 40 % of the total consumption in 1994 (Ministry of Commerce, 1994). During 1993 - 1994, the Government actively discussed many aspects concerning the move to the use of unleaded petrol (Ministry of Commerce, 1994). A main reason for wishing to remove lead from petrol was the public health concern, especially with respect to young children who are regarded as a higher-risk group. Another main benefit mentioned was that the availability of high octane unleaded petrol would allow the use of new vehicle engines and emissions control technology; specifically, catalytic converters (which are rendered ineffective by leaded petrol), and as a consequence improvements in air quality.

In 1995, the unleaded 91 petrol was reported to account for about 50% of all sales (Graham and Narsey, 1995). This market share of unleaded petrol was still lower than the share of 70% targeted (Biggar, 1995). To reach this target by 1995 or within the subsequent five years, it was decided that a high octane unleaded petrol be introduced to take the place of the high octane leaded one, and the country entered a lead-free petrol market (Graham and Narsey, 1995; Biggar, 1995; Ministry of Energy, 1995). The new 1995 Petroleum Products Specifications Regulations made it illegal to add lead to petrol either imported into or refined in New Zealand, with a commencement date of the first of January 1996 (New Zealand Government, 1996). As from this deadline New Zealand's main source of petrol (the Marsden Point oil refinery) was not able to use lead in the refining process; nor could refined petrol containing lead be imported. By the end of September 1996, leaded petrol was no longer sold in New Zealand (however, the maximum allowable Pb concentration in each regular and premium grade petrols is still specified as 0.013 g litre^{-1}).

The city of Hamilton, New Zealand, receives its main petrol supplies from Auckland and Tauranga (Mount Maunganui) (Patel, 1996). The Ministry of Commerce routinely monitor levels of lead in petrol from these supplies. Based on their figures, for the period 1993 to middle of 1996, and from these two supplies, levels of lead prior to December 1995 were in the range of 0.2 - 0.3 g litre^{-1}, but gradually decreased to less than 0.2 g litre^{-1} in early 1996 (probably due to the dilution of old stocks with newly supplied unleaded petrol) and less than 0.01 g litre^{-1} by late March. It was estimated by some distributors in Hamilton (e.g., BP and Caltex Oil), that by the end of July 1996, the petrol available in Hamilton would have all been unleaded (Cull, 1996; Richards, 1996).

It is interesting to note here that an increase in the proportion of aromatics in petrol (to raise the octane rating in place of lead) raised an issue of health risk which might be associated with a potential increase in emissions of benzene, a known carcinogenic compound (Ministry of Commerce, 1994; Graham and Narsey, 1995; Biggar, 1995). Based on a preliminary short-term study carried out in 1995 to assess the levels of lead and benzene in ambient air, Graham and Narsey (1995) suggested a further monitoring program for benzene in the main centres of urban areas. Gooneratne (1996) remarked that environmental measurements of benzene concentration were poor predictors of individual exposure to benzene because most people spend 80% of their time indoors. The most important indoor source of benzene is said to be tobacco smoke (cigarettes can contain benzene at up to 30 μg per cigarette). The author further speculated that replacing leaded petrol was not going to increase benzene emissions to a level where they would have an impact on health. The possible environmental impact of increased benzene levels is, however, a matter which attracts widespread debate.

1.4. Associations of Pb and other heavy metals with soil components.

Detailed knowledge of the interactions of trace metals at solid-solution interfaces is essential for understanding the behaviour or cycling of metals in soil and sediment environments, and modeling their movements for environmental impact assessment. A variety of approaches have been applied in order to elucidate modes and mechanisms of metal retention at the interface, and to investigate metal distribution. These include the following macroscopic techniques: (i) chemical extraction, with either a single reagent or a sequence of reagent(s) (outlined in *sections 1.5.* and *1.6.*), (ii) equilibrium-based sorption experiments, which are often accompanied by derivation of adsorption isotherms based on empirical or fundamental equations (e.g., Freundlich, and Langmuir, etc.), surface complexation models (which incorporate factors such as electrostatic influences of surface charges and surface potential, and where interface reactions are described between dissolved solutes and surface functional groups), and (iii) kinetic studies. Microscopic techniques which have been applied to the problem include the use of atomic and molecular surface resolution techniques for probing local bonding environments (e.g., X-ray photoelectron spectroscopy (XPS), and X-ray absorption (XAS)) (Scheidegger and Sparks, 1996). Factors frequently investigated in terms of their possible influence on the distribution of metals between solid and solution include pH and ionic strength of the media, characteristics of the metal ions investigated, the presence of other cations or ligands/ anions, and kinetic effects. Solid-aqueous systems containing a single well-defined solid phase with single or multi metal sorbate(s) are regularly used in the investigations of solid-solution interface phenomenon, especially in assessing factors influencing metal retentions. However, multi-phase synthetic systems and/ or natural soil and sediment samples can be found in the literature, most often in the evaluation of the validity of surface complexation models proposed to describe these more complicated systems (Lee et al., 1996; Sutheimer and Cabaniss, 1997; Wang et al., 1997). Scheidegger and Sparks (1996) remarked that understanding of the interface reactions for soil science applications was still considered to be at its rudimentary level, and that relevant research along this line would be a common theme in soil and environmental science for decades to come.

Lead is reported to be one of the least mobile heavy metals in soils (Kabata-Pendias and Pendias, 1984; Fergusson, 1990), especially under reducing or non-acid conditions. This idea is supported by the relatively low concentrations of Pb found in natural soil solutions (Kabata-Pendias and Pendias, 1984). Solid phases found in soil and marine environments commonly reported for their high concentrations of Pb and other heavy metals appear to be the oxides of Fe, Mn and Al, organic matters, clay minerals, and carbonates (Kabata-Pendias and Pendias, 1984; Fergusson, 1990). If subjected to environmental changes (such as decrease in pH due to acid rain), these major "sinks" of heavy metal contaminants are capable of replenishing the contaminants into the interface solution, and as a consequence, enhancing their availability to biological communities. The surface functional groups found on the major metal scavenging phases include the inorganic hydroxyl group, organic groups (e.g., carboxyl, carbonyl, etc.), and the siloxane ditrigonal cavity (on tetrahedral silicate sheet structure of clay minerals, see *subsection 1.4.4.*). These functional groups are principal types commonly found in the soil particle size fraction of < 2 μm (the clay fraction) of most soils; in other words, the solid phases that exhibit surface reactivity in soils are found primarily in this fraction (Sposito, 1984). In this review section, the solid phases used to construct model soils for this study are examined. These include an Fe oxyhydroxide (goethite, α-FeOOH), a Mn oxide (hausmannite, Mn_3O_4), humic substances (humic acid), a clay mineral (halloysite, $Al_2Si_2O_5(OH)_4.2H_2O$ and $Al_2Si_2O_5(OH)_4$), and a calcium carbonate (calcite, $CaCO_3$). The distribution of these solid phases in the environment, as well as their abilities to scavenge Pb (and other heavy metals, such as Cu, and Cd) are outlined, along with their structures and surface characteristics which have a bearing on their scavenging ability for metals, and possible modes/ mechanisms of metal retention. Some factors commonly investigated for their influence on metal retention are also outlined. In a separate subsection is outlined the influence of multicomponent solids on metal distribution. Some remarks on the use of model soils in this study are also made.

It would be useful to note here some terminologies commonly used in relevant literature; the following definitions are as proposed by several experts, such as Sposito (1984, 1986a, 1989), and Stumm (1992). *Sorption* is a general term used to describe a surface localization process when the retention mechanism of metal occurring at the mineral/ solution interface is not known. The term sorption incorporates potentially significant metal-scavenging processes in aquatic, marine, and ground-water environments, such as adsorption, surface precipitation, coprecipitation and diffusion into the crystal. However, as remarked by Scheidegger and Sparks (1996), some researchers have been using the terms adsorption and sorption interchangeably even though in most cases the possibility of the other processes was not thoroughly excluded. *Adsorption* commonly implies two-dimensional-interfacial accumulation of sorbate as a surface complex, without development of a three-dimensional molecular arrangement, namely the surface precipitation, coprecipitation, and diffusion (Sposito (1986a) selectively reviewed some experimental approaches for their potential capabilities in distinguishing adsorption from surface precipitation). In the adsorption process the forces involved can range from weak, physical, van der Waals forces (e.g., partitioning) and electrostatic outer-sphere complexes (e.g., ion exchange) to chemical interactions (Scheidegger and Sparks, 1996). Chemical interactions can incorporate inner-sphere complexation which involves a ligand exchange mechanism, covalent bonding, hydrophobic bonding, hydrogen bonding, hydrogen bridges, and steric or orientation effects (Scheidegger and Sparks, 1996). Inner-sphere and outer-sphere complexations are often used as the molecular basis of the term, specific- and non-specific adsorptions, respectively (Sposito, 1989). Inner-sphere complexes can be either mono- or bi-dentate. As the amount of a metal cation (or anion) sorbed on a surface (surface coverage) increases to a higher surface coverage, a *surface precipitation* can occur (in *Appendix 1.2.* is illustrated models for outer-and inner-sphere surface complexes and precipitation). Davis et al. (1987) remarked that for surface precipitation to occur, the aqueous solution must be supersaturated with respect to the equilibrium solubility of a solid phase which contains the solute of interest. In systems which are undersaturated, either adsorption or absorption may be a major reaction which controls the aqueous concentration of the solute. The term surface precipitation, as used by Sposito (1989), could also include the formation of an ordered solid solution as the growing solid phase. When the precipitation derived from chemical species of both the aqueous solution and dissolution of the mineral, it is referred to as a *coprecipitation*. *Diffusion* is used to mean to the movement of molecules or ions through crystalline solid, however since such process is extremely slow at 25 °C, the term diffusion is recommended by McBride (1994) to refer to the transfer through micropores, faults, or interfaces of the solid. Sposito (1986a) referred to absorption as the diffusion of an aqueous solute into a solid phase. It should be noted here that distinguishing between particles with trace elements distributed in the particle bulk from those with trace elements adsorbed to the surface is of importance from an environmental availability point of view (Fulghum et al., 1988). Although either adsorption or coprecipitation can remove trace metals from solution and changes in the chemical environment may reverse either process, the adsorbed metals are likely to be more readily released by such changes. In other words, adsorption and desorption equilibria/ processes in which elements are involved (rather than solid solubility) control the pathways/ movement of the elements (Tessier et al., 1985). It should also be recognized that upon adsorption on a solid, dissolved species of the elements can be oxidized or reduced (Hering and Stumm, 1990); such surface reactions can change their reactivity and toxicity.

1.4.1. Iron (oxyhyr) oxides.

Iron is the fourth most abundant element of the earth's crust (5.1 mass %) and is very reactive in that it can form stable compounds in both the divalent and trivalent states (Schwertmann and Fitzpatrick, 1992). Iron minerals, especially oxyhydroxides and oxides, are ubiquitous in almost all earth surface environments, for example in soils, sediments, weathering zones, lakes, rivers and oceans (Chao and Theobald, 1976; Schwertmann and Taylor, 1989; Schwertmann and Fitzpatrick, 1992). The Fe (oxyhydr)oxides are frequently present as very small crystals (5 - 100 nm in size) and therefore exhibit large and reactive surface areas (Borggaard, 1982). Partial substitution of Fe of the (oxyhydr)oxide structures by other cations has been observed; among the replacing cations, Al dominates in surface environments possibly because of its greatest abundance (Schwertmann and Taylor, 1989).

The importance of Fe (oxyhydr)oxides in retaining Pb and other heavy metals present in soils and sediments has been widely recognized (Jenne, 1968; Chao and Theobald, 1976; McKenzie, 1980; Swallow et al., 1980; Luoma and Bryan, 1981; Lion et al., 1982; Tessier et al., 1984; Anderson and Christensen, 1988; Feijtel et al 1988; Schwertmann and Taylor, 1989; Tessier et al., 1989; Smith and Jenne, 1991; Schwertmann and Fitzpatrick, 1992; Petersen et al., 1993; Warren and Zimmerman, 1994; Delaflor et al., 1995; Xing et al., 1995; Bellanca et al., 1996). Luoma and Bryan (1981) assessed forms of Pb, Cd, Cu, Zn, and Ag in 19 oxidized estuarine sediments, using a series of chemical extractants. The authors found strong correlations between the extractable Fe phase (i.e., operationally-defined Fe oxide fraction) and all of the metals investigated. Petersen and co-workers (1993) assessed adsorption of Cd on a coating of FeOOH on a clay mineral (kaolinite). They found that 0.1 mmol of Fe oxide coated on the clay (1 g) could adsorb up to 95% of the added metal (1 μmol litre^{-1}). In a study of Xing and co-workers (1995) on the role of amorphous Fe oxides in controlling metal retentions in two soil samples, it was found that the quantities of Cu, Zn, Co, Ni, and Cr retained in soils subjected to a treatment for removal of amorphous Fe oxides were dramatically decreased compared to amounts retained in the soils without the treatment. Fe (oxyhydr)oxides have also been widely noted for their association with anions, e.g., phosphate (Parfitt and Russell, 1977; Goldberg and Sposito, 1984a; Goldberg, 1985), and organic matters, particularly humic acids (Chao and Theobald, 1976; Parfitt et al., 1977; Tipping, 1981; Schwertmann and Taylor, 1989; Schwertmann and Fitzpatrick, 1992).

Among various Fe (III) (oxyhydr)oxides, the yellow-brown coloured goethite (α-FeOOH) is one of the most stable crystalline forms found under aerobic surface conditions; it is widespread in soils and sediments either as the sole Fe oxide or in association with one or more of the other forms, such as haematite, and maghemite (Allen and Hajek, 1989; Schwertmann and Taylor, 1989; Schwertmann and Fitzpatrick, 1992). Goethite, either synthetic or natural, varies considerably in crystal morphology; it can be found in, for example, acicular (needle like), or fibrous, or starlike forms. Goethite is the polymorph to which most other iron (oxyhydr)oxide phases eventually revert to upon aging (Murray, 1979). The basic structural unit for goethite is an octahedron, in which the Fe atom is surrounded by three O and three OH ions (Stucki et al., 1988; Schwertmann and Taylor, 1989; Schwertmann and Fitzpatrick, 1992) (a model structure of goethite is illustrated in *Appendix 1.3.*). The O and OH ions form hexagonally closed packed planes (termed α-phases). Double chains of Fe-O-OH octahedra unit cells extend along the crystallographic z-axis. Adjacent double rows within a layer are separated by a double row of empty octahedral sites, i.e., half of the octahedral interstices are filled with Fe^{3+}. Occupied and unoccupied octahedral sites alternate in successive layers to give such the structure which are joined to other double chains by sharing corners. The octahedra are bound to neighbouring double chains by Fe-O-Fe and H bonds. Three types of surface OH group can be distinguished on the basis of stereochemical reasoning, and are illustrated in *Appendix 1.3.*, along with a possible Lewis acid site.

The surface structure of goethite (and other Fe (oxyhydr)oxides) exposed to water is commonly denoted as $\equiv$FeOH, a simple hydroxyl with zero net charge (Schwertmann and Taylor, 1988). The surface charge and potential of the minerals depend mainly on pH and ionic strength of the solution (this referred to as variable charge surface). Goethite has been reported to have pH of the point of zero charge (PZC, i.e., the pH at which the net variable charge on the surface is zero) in the range of 7.1 to 9.48, as determined in electrolytes, such as NaCl (Yoon et al., 1979; McKenzie, 1981; Balistrieri and Murray, 1982; Rodda et al., 1993). Variation in the PZC can be found in different batches of synthetic goethite; this might be due to surface contamination occurring during the synthesis (Barrow, 1987) (it should be noted here that synthetic goethite has been commonly used in surface complexation studies). Unlike the situation for most layer silicates (i.e., clay minerals, outlined in *subsection 1.4.3.*), the surface charge of the Fe oxides is considered to have little contribution from permanent charge induced by possible natural isomorphous substitution of Fe for another metal.

Several attempts have been made to measure the quantity of protons released during the adsorption reaction of metals on goethite and to correlate this to a mechanism of the surface complexation, using techniques such as potentiometric titration (Hayes and Leckie, 1986, 1987; Gunneriusson et al., 1994), or batch equilibration (Kooner, 1993). Such calculations are based on the relationship between the apparent equilibrium binding constant (K_p, of a simple adsorption equation: $\alpha SOH + Me^{2+} \Leftrightarrow (SO)_{\alpha}\text{-}Me + \alpha H^{+}$) and the ratio of metal concentration in the solid phase to that in the solution at equilibrium (K_d). It is assumed that $\log K_d = \log K_p[SOH]^{\alpha} + \alpha\ pH$, where α (the number of protons released per mole of metal ion adsorbed) can be calculated from a straight-line plot of $\log K_d$ vs pH. Common electrolytes used in such macroscopic solution studies include $NaNO_3$ or KNO_3. A range in the number of protons released when one mole of Pb binds to goethite surface has been reported, e.g., 2.0 ± 0.5 and 1.8 ± 0.2 (using two different measurement methods, and in different electrolytes, Forbes et al., 1976), 1 (Hayes and Leckie, 1986), 1.25 (Muller and Sigg, 1992), 0.97 ± 0.07 (Kooner, 1993), and 1.7 and 1.5 (in $NaNO_3$ and in NaCl mediums, respectively, both at pH = 7.5, Gunneriusson et al., 1994). Kooner (1993) found that Cu^{2+} or Zn^{2+}(with similar ionic radius of about 72 pm) released more protons than Pb^{2+} (ionic radius of about 120 pm) per mole during adsorption reaction with goethite. Based on this observation, Kooner (1993) speculated that the adsorption mechanisms of Cu, and Zn were different. This was consistent with the suggestion of Padmanabham (1983a, b), based on comparative studies of adsorption-desorption behaviours of Pb, Cu, Zn, and Co at the goethite-solution interfaces, that the goethite surface had two types of adsorption sites: one of low binding energy and the other of high binding energy, corresponding with the "readily desorbed" and "less readily desorbed" fractions of Cu, Zn, and Co, respectively, but only the "readily desorbed" fraction of Pb (Padmanabham had observed that whereas desorption of specifically adsorbed Cu, Zn, or Co showed considerable hysteresis, that of Pb did not). Kooner (1993) proposed that Cu and Zn might have participated in two-step reaction mechanisms: (i) $SOH + Me^{2+} \Leftrightarrow SO\text{-}\ Me^{+} + H^{+}$, and then (ii) $SOH + SO\text{-}\ Me^{+} \Leftrightarrow (SO)_2\text{-}\ Me + H^{+}$ (which created more than one type of binding site), whereas, Pb (with a larger ionic radius) might not have become involved in the second reaction because of steric hindrance; or in other words, the sites that took part in bidentate bindings in Cu and Zn did not participate in complex formation during Pb adsorption. Kooner (1993) noted that the first adsorption reaction proposed for Pb (releasing one proton per mole metal ion adsorbed) was also that proposed by Hayes and Leckie (1987). It could be noted here a finding of Benjamin and Leckie (1981a,b) that the adsorption of Pb, Cd, Zn, and Cu onto amorphous Fe oxyhydroxide was generally inconsistent with a homogeneous surface single site model (i.e., all sites having equal binding energy), except at very low adsorption density. The authors therefore proposed heterogeneity of binding sites, i.e., the oxide surfaces comprised multisites, of which the binding energy between a given metal and the surface might vary by an order of magnitude or more from one site to another (this resulted in the averaged stability constants involving several different site types being measured). Development of the surface complexation approach to modeling sorption on Fe oxides is discussed in a number of publications, for example, that of Dzombak and Morel (1990).

Hayes and Leckie (1986, 1987) and Gunneriusson and co-workers (1994) attempted to distinguish dominant metal-goethite surface complexes. Hayes and Leckie (1986, 1987) investigated individual sorption of Pb and Cu, in varying concentrations of $NaNO_3$ electrolyte, by comparing each experimental data set with corresponding calculated results, obtained from a modified triple layer model with assumed analogs of inner- and outer-sphere surface complexes of the metals. The authors found that the experimental data of the metals agreed well with the corresponding inner-sphere model analogues (i.e., in this case, bonding occurred at an adsorbing plane closer than that of the background electrolyte), and considered that this implied that the divalent cations bound to goethite as inner-sphere complexes. Gunneriusson and co-workers (1994) investigated Pb(II) adsorption in a pH range of 2.7 to 8.5; the constant capacitance model was used to evaluate the experimental data. The authors postulated that at pH values between 4 - 5, between 5 - 7, and ≥ 7, the dominant complexes were $\equiv FeOHPb^{2+}$, $\equiv FeOPb^{+}$, $\equiv FeOPbOH$, respectively (i.e., the adsorption at pH between 4 - 5, occurred by reactions in which Pb(II) ions did not displace H^+ from the surface sites, whereas at higher pH, the reactions involved substitution of H^+ from the surface sites). The authors also postulated formation of a polynuclear surface Pb(II) species in the presence of an excess of Pb(II) ions to surface binding sites.

Several researchers have used certain surface-sensitive spectroscopic techniques to identify the formation of metal bonds at the goethite-water interface (Roe et al., 1991; Charlet and Manceau, 1993; Spadini, et al., 1994; Bargar et al., 1997). Roe and co-workers (1991) compared XAS spectra of reference compounds (i.e., structurally well-characterized Pb (II) compounds) with those of Pb-partitioned goethite samples, obtained from sorption experiments using three different total concentrations of Pb. The authors proposed that at low coverage, Pb formed monomeric, inner-sphere surface complexes, whereas, at high coverage, Pb predominantly formed surface polymers. Bargar and co-workers (1997a), also using XAS, concluded that Pb(II) adsorbed predominantly to edges of FeO_6 octahedra as mononuclear bidentate complexes on synthetic goethite and haematite (α-Fe_2O_3), in the pH range of 6 and 8 with sorption densities of 2 - 10 μmoles m^{-2}. Mononuclear bidentate Pb(II) complexes were also observed on aluminum oxides (Bargar et al., 1997b). Bargar and coworkers (1997a) suggested that the edge lengths of surface AlO_6 or FeO_6 octahedra partially determined the reactivities and densities of available surface sites.

Sorption of Pb or other heavy metals onto goethite was found to be low at low pH, but as the pH increased a steep rise in the metal sorption occurred within a narrow range of pH, in some cases approaching completion at pH of about 7 (Forbes et al., 1976; Barrow et al., 1981; McKenzie, 1980; Padmanabham, 1983b; Djafer et al., 1989; Kooner, 1993). McKenzie (1980) investigated individual sorption of Pb, Cu, Zn, Co, Ni, and Mn onto three synthetic Fe oxides, including goethite. At a given metal and goethite concentration the positions of the adsorption edge (i.e. the pH at which the reaction begins to rapidly increase) of the metals, except for Pb and Cu, were found to increase as the first hydrolysis constant increased; the corresponding sequence of the reaction appeared to be Cu > Pb > Zn > Co > Ni > Mn (pK_1 Pb, 7.71; Cu, 8; Zn, 8.96; Co 9.65; Ni, 9.86; and Mn, 10.59). An interpretation of this observation was that relative to unhydrolyzed ions, hydrolyzed species, i.e., MOH^+ were preferentially sorbed on the goethite. The order of the adsorption edges of these metal ions and the interpretation appeared to be consistent with those reported in many studies on similar systems. As a consequence, K_1 of divalent cations, as a representative of the ability of the ions to form hydroxyl species, is regularly used as a relative measure of the cation affinity for goethite and other oxide surfaces. However, in a study of Barrow and co-workers (1981) with an application of a model on experimental data obtained from adsorption of Pb, Cu, or Zn onto goethite, it was found that the slope of the Pb adsorption curve (Pb adsorbed vs pH) was too low to be explained by adsorption of $PbOH^+$, although the adsorption occurred at about the pH that would be expected from its pK_1. The authors, therefore, speculated that Pb^{2+} was an adsorbing species and that increase in adsorption with pH was (at least partially) due to the decreased charge on the surface and thus decreased repulsion.

In general, ionic strength does not appear to have a significant influence on the adsorption of Pb onto goethite. Swallow and co-workers (1980) found that varying the concentrations of $NaClO_4$ solutions (e.g., 0.005 M, 0.05 M and 0.5 M) did not significantly influence the adsorption of Pb and Cu on an amorphous Fe oxide. Balistrieri and Murray (1982) found that the adsorption of Pb, Cu, Cd, or Zn on goethite from 0.53 M NaCl and 0.1 M $NaNO_3$ was the same even though the ionic strength was different in the two systems. The authors speculated that the insignificant effect of the changing ionic strengths might be due to the adsorption processes resulting in no net change in charge and, therefore, not being susceptible to changes in surface charge caused by ionic strength variations. Hayes and Leckie (1986, 1987) found that varying ionic strength from 0.01 to 1.0 M of $NaNO_3$ did not have a significant effect on the position of the Pb adsorption edge. These observations were in good agreement with those of Kooner (1993), who used the same electrolyte in the same concentration range, but in whose systems the initial concentration of Pb used was about 100 times lower. It was suggested that the insignificant effect of $NaNO_3$ could be because Pb did not significantly complex with NO_3, and Na and NO_3 did not strongly interact with the goethite surface. In contrast, Barrow and co-workers (1981) did report an ionic strength effect. They found that the adsorption of Pb onto goethite was more enhanced in 0.075 M NaCl media than in 0.0075 M NaCl media. However, in this case, it might be that the electrolyte used contained a complexing ligand (Cl^-), so it is difficult to distinguish the direct effects of this with those of ionic strength; for instance, it might be that formation of the species $PbCl^+$ enhances adsorption on the mineral.

Major ions present in the environment differ in their effects on the adsorption of metals on goethite. Balistrieri and Murray (1982) investigated individual adsorption of Pb, Cu, Zn, or Cd on goethite from 0.1 M $NaNO_3$ solution (an inert electrolyte) and from synthetic solution containing major seawater ions (Na, Mg, Ca, K, Cl, and SO_4) at their natural concentrations. The authors compared the resulting adsorption curves of the metals obtained from the $NaNO_3$ solution, the synthetic seawater, and various solutions containing combinations of the major ions. It was found that Cl^- did not influence the adsorption behaviours of the metals, whereas Mg^{2+} could inhibit and SO_4^{2-} could enhance adsorptions. Their effects, as determined from the triple-layer model of Davis et al. (1978) with the equilibrium constants estimated in the previous work (Balistrieri and Murray, 1981), were attributed to a combination of changing the electrostatic conditions at the oxide-solution interface and decreasing available binding sites on goethite. Balistrieri and Murray (1982) remarked that their Pb and Cu results were in contrast with those of Swallow and co-workers (1980) investigating sorptions of the metals onto an amorphous $Fe(OH)_3$. In the earlier work, Pb sorption was found to decrease in the presence of reactive Cl^- ligand (in relation to the indifferent electrolyte $NaClO_4$ used); this was presumably due to competing complexation in solution. In addition, Cu sorption was not affected by changing the background electrolyte from $NaClO_4$ to synthetic seawater. Balistrieri and Murray (1982), however, speculated that the notable difference of the metal sorption behaviours for the two forms of Fe oxides observed might, in part, be due to the concentrations of the oxides used and the pH range of the metal's adsorption edge.

The high surface areas of Fe (oxyhydr) oxides appear to play an important role in metal retention. Oxides of higher surface areas are found to sorb Pb more than those with lesser surface areas, e.g., magnetite (85 $m^2\ g^{-1}$) > goethite (75 $m^2\ g^{-1}$) > haematite (20 $m^2\ g^{-1}$) (McKenzie, 1980). Borggard (1982) remarked that the surface areas of the oxides increased as their crystallinity decreased; the amorphous/ microcrystalline oxides might be more prone to continue to react with adsorbates (Barrow, 1987). Delaflor and co-workers (1995) noted that among Fe oxides with different degrees of crystallization investigated, Cu had a general tendency to associate with the amorphous and microcrystalline oxides. In a study by Kooner (1993) of the effect of the surface area of goethite on adsorption behaviour of Pb, the author found that at a constant Pb concentration the metal adsorption edge shifted to a lower pH with the increase in the surface area (this is conceivable since, at constant pH, with an increase in surface area more goethite was available in the suspension to remove Pb). The shift in adsorption edge was, however, also found to be dependent on the initial Pb concentration. Change in the adsorption edge per unit surface area per litre was more notable at the low Pb concentration used (2.0 ppm) than at the high Pb concentration (5.0 ppm). It could be noted here that in this study variation of goethite surface area could be seen as changes in amount of adsorbent or the ratios of adsorbent to adsorbate. Kooner (1993) further found that at constant pH and initial Pb concentration, the magnitude of distribution coefficient (K_d) was not significantly affected by the changes in the goethite surface area (K_d was defined as the ratio of Pb concentration in the solid phase to that in the solution at equilibrium). However, at each of the two initial Pb concentrations investigated, the calculated amounts of lead adsorbed per gram of goethite showed a systematic decrease with the increase in goethite surface area. At pH values around 7 the decrease was directly proportional to the surface area (i.e., by doubling the surface area, the amount (moles) of Pb adsorbed per gram of goethite decreased by half and so on). Based on a further comparison between the K_d of Pb with those of Zn and Cu, Kooner (1993) found that in the pH range 4 - 7 the curves for Pb and Cu were nearly superimposed and the plot of Zn was situated at a higher pH range. The author interpreted this by suggesting that under similar conditions, more zinc was available in solution than Pb or Cu, and that in comparison with Cu or Pb, a higher pH was required to remove the same percentage of Zn from the solution via adsorption onto the goethite surface.

In an investigation of Balistrieri and Murray (1982) on competition of some heavy metals for surface sites on goethite, the authors found no marked difference between adsorption curves (% metal sorbed vs pH) of individual Pb, Cu, Zn, and Cd and those of the corresponding metal in the presence of other metals. This implied that there was little or no competition for surface ligands between Pb, Cu, Zn, or Cd in synthetic seawater systems investigated.

Relatively few studies on adsorption kinetics of metals and goethite have been reported (Hayes and Leckie, 1986; Bruemmer et al., 1988). Breummer and co-workers (1988) remarked that most adsorption studies on Fe oxides had their emphasis on the initial adsorption reactions of trace metals and were carried out at relatively short reaction times of a few hours or even less; however, several authors had found that the adsorption of metals on Fe oxide surfaces could continue to increase even after long reaction times of several weeks. In their, Breummer and co-workers investigated the influence of reaction time (2 h to 42 days) and other parameters, such as temperature and pH, on the adsorption of Ni, Zn, and Cd onto goethite, with particular attention to diffusion of the metals into the oxide particles. The authors found that at constant temperature and initial metal concentration, an increase in reaction time commonly resulted in a shift of the adsorption curves (% adsorption vs pH) of the metals to lower pH. The effect of increasing reaction time was consistent with that of increasing temperature (Rodda et al., 1993). Breummer and co-workers (1988) found that at 20°C and 5.0 μmol M^{2+} g^{-1} goethite, the slopes for the relationships between pH_{50} (a pH at which 50% adsorption occurred) and time were found to be steep in the initial stage of the adsorption, and flattened off after about 7 days for Cd and 21 days for Ni and Zn; these curves, as noted by the authors, also showed that after 42 days of reaction time none of the metals had completely reached adsorption equilibrium. The authors remarked that this indicated that the kinetics of heavy metal adsorption by goethite could be characterized by low reaction rates, and thus long reaction times might be needed to achieve equilibrium. However, a different combination of temperature and initial concentration of the metal could alter the reaction time required to attain the equilibrium. At 35 °C and 0.5 μmol M^{2+} per gram goethite, the pH_{50} values of Zn and Cd were equal for each metal at 7 and 21 day reaction time; this meant, as noted by the authors, that under these conditions, Zn and Cd could reach the equilibrium by 7 days. In order to establish a common basis for the comparison of the reaction kinetics of the three metals following the initial adsorption, the amounts of metal adsorbed were plotted against the square root of the reaction times, at the pH values where 5%, 10% and 50% adsorption of Ni, Zn, and Cd was observed (with other conditions being a 2 h reaction time, an initial concentration of 5.0 μmol M^{2+} g^{-1} goethite and a constant temperature of 20°C). The resulting three sets of adsorption curves for the three metals were found to comprise an initially rapid adsorption reaction lasting a few hours, followed by a much slower reaction which showed a linear relationship with the $\sqrt{t}$, and lastly a plateau region. Based on this observation, the authors proposed that the reactions of the metals with goethite involved (i) adsorption processes on the surface of the oxide particles which probably dominate during the first period of up to 24 h, (ii) a slow solid-state diffusion of the metal ions from the surface to the interior of the oxide particles, and (iii) equilibrium conditions being attained between metals adsorbed on the external and internal binding sites. The authors further determined the pH-dependent relative diffusion rates (RDR) of Ni, Zn, and Cd from the slopes (amount of metal adsorbed $h^{-1/2}$) of the regression lines calculated from linear parts of the adsorption curves. The resulting RDR values were plotted against pH. It was found that with increasing pH, RDR values increase to maximum values at pH 5.7 for Zn, 6.3 for Ni, and 6.4 for Cd. The authors noted that when pH was further increased, relative diffusion rates strongly decreased despite the more favourable boundary conditions from increased metal hydrolysis, and increased negative surface charge. At 20°C and initial concentrations of 0.5 and 5.0 μmol M^{2+} g^{-1} goethite, the maximum diffusion rates of the metals were found to increase with increasing metal concentrations and were also found to be related to the ionic radii, in that the smaller the metal, the higher the diffusion rate (i.e., Ni (69 pm) > Zn (74 pm) > Cd (97 pm)).

The effect of temperature on the adsorption of heavy metals onto Fe oxides has also been receiving relatively little attention (Bruemmer et al., 1988; Johnson, 1990; Srivastava and Srivastava, 1990; Rodda et al., 1993). In an investigation of the effect of temperature (10 to 70°C) and pH on the adsorption of Pb(II), Cu(II), and Zn(II) onto synthetic goethite, Rodda and co-workers (1993) analyzed the data according to the model for the adsorption of hydrolyzable metal ions developed by James and Healy (1972) and interpreted the results in terms of the variations with temperature of cation hydrolysis and the surface charge of the mineral. They found that an increase in temperature shifted the PZC of the goethite (determined from potentiometric titration data) and the adsorption edges of each metal to lower pH. In addition, at a given pH, the extent of the adsorption of each cation was found to increase with temperature. These observations of temperature-dependent adsorption are consistent with those of Bruemmer et al. (1988) for Ni, Cd, and Zn in the temperature range of 5 - 35°C and of Johnson (1990) for Cd in the same temperature range tested by Rodda and co-workers (1993). Moreover, Rodda and co-workers (1993) found that the shift of the adsorption edges with the temperature for each cation correlated with the appearance in solution of the (calculated) first hydrolysis product (MOH^{+}) in that the shift in cation hydrolysis with temperature was in the same direction as, and of similar magnitude to, the shift in the adsorption edges. The pH at which the maximum concentration of MOH^+ occurred was also found to correspond to a point on the adsorption isotherm curves representing between 50 and 70% adsorption. The authors indicated that this finding was in agreement with the view previously mentioned that the first hydrolysis product was the most significant adsorbing species for divalent cations. Rodda and co-workers remarked that the results from this study in combination with those of Bruemmer et al. (1988) and Johnson (1990) showed that the sequence of temperature dependence for adsorption onto goethite was $Ni > Zn > Cd > Cu \approx Pb$. The authors also noted that the change in the adsorption of Cd(II) onto goethite with increasing temperature found by Johnson (1990) was double that reported by Bruemmer et al. (1988); it was speculated that the differences were a reflection of the differences between goethite samples employed.

1.4.2. Manganese oxides.

Manganese is a widely distributed element in surficial environments, frequently occurring as the Mn oxyhydroxide and oxide minerals (Chao and Theobald, 1976; McKenzie, 1989; Dixon and Skinner, 1992; Post, 1992). These minerals occur as coatings on other soil particles, as deposits in cracks and veins, and often in aggregates with Fe oxides (McKenzie, 1989). Many Mn (oxyhydr)oxides are commonly found as poorly crystalline mixtures of small grain size and have large surface areas; they tend to be dark brown to black in colour (Post, 1992). Mn has several oxidation states, however, only Mn^{2+}, Mn^{3+}, and Mn^{4+} are found in nature. Most of Mn (oxyhydr)oxides found in the surface environments are compounds of Mn^{4+} with some Mn^{3+}, with a few containing only Mn^{2+}(Dixon and Skinner, 1992). Mn (oxyhydr)oxides in which the valence of the metal is less than 4 are known as the lower oxides (McKenzie, 1989). Only two of these are important in soils, namely, manganite (γ-MnOOH) and hausmannite (Mn_3O_4). Hausmannite is formulated as $Mn^{2+} (Mn^{3+})_2O_4$, and has a spinel-like structure, with Mn^{2+} in the tetrahedral and Mn^{3+} in the octahedral sites (Post, 1992) (a crystal structure of hausmannite and an ideal spinel structure are illustrated in *Appendix 1.4.*). Distortions of the Mn^{3+} octahedra lower the symmetry of hausmannite to tetragonal, as opposed to cubic for ideal spinel structures. It could be noted here that although birnessite and vernadite, two Mn dioxides ("higher oxides") with layer structures, are the prevalent forms identified in soils (McKenzie, 1989), hausmannite is used in this study because its synthetic form appears to be adequately stable (Kim, 1994). In addition, since information directly concerning the sorption/ desorption of Pb or other heavy metals on hausmannite are found to be relatively scarce, much of the material outlined below is based on what can be deduced from MnO_2. It is, however, possible that the adsorption behaviour of hausmannite would show general similarities to the behaviour of other manganese oxides.

The high concentrations of heavy metals found naturally in Mn (oxyhydr)oxides have been widely reported to be disproportionate to the absolute abundance of the minerals in soils (Taylor and McKenzie, 1966; Jenne, 1968; Loganathan and Burau, 1973; Gadde and Laitinen, 1974; Childs, 1975; Chao and Theobald, 1976; McKenzie, 1972, 1978, 1980, 1981; McBride, 1994; Mench et al., 1994; Salim et al., 1996). Taylor and McKenzie (1966) and Childs (1975) compared concentrations of several heavy metals in whole soils and in Mn nodules extracted from the soils, and found that the concentrations of the metals in the Mn extracts were significantly higher than those present in the whole soils. McKenzie (1978) found that the addition of Mn oxides to contaminated soils could reduce the uptakes of Pb, Co, and to a lesser extent Ni, by plants. The author also remarked that the result suggested that soil with higher concentrations of Mn dioxide would be the most suitable for the disposal of wastes rich in the metals. In agreement with this work, Mench and co-workers (1994) found that among several chemical compounds (e.g., CaO or $CaCO_3$, hydrous Fe oxides, and hydrous Mn oxides) added separately into contaminated soils, the hydrous Mn oxides could reduce the amount of Pb and Cd recovered in soluble fractions (e.g., water or dilute acid extracts) the most; this was reflected in decreasing concentrations of metals being taken up in the plants investigated.

Many studies have strongly suggested that Mn (oxyhydr)oxides, as a group, are better scavengers for heavy metals, such as Pb, Cu, and Co, than Fe (oxyhydr)oxides (Jenne, 1968; McLaren and Crawford, 1973; Gadde and Latinen, 1974; McKenzie, 1980, 1981); this is despite the fact that Mn is less common than Fe both in the Earth's crust (0.9 g kg^{-1}), and in average soils. Fe is the element that Mn most resembles chemically and biochemically (Chao and Theobald, 1976; Dixon and Skinner, 1992); in both cases the naturally prevalent forms possess the reactive hydroxyl surface functional group. The greater chemical reactivity of the Mn (oxyhydr)oxides might be due to, at least in part, their complex mineralogical structures (i.e., non-stoichiometric oxides, with Mn in mixed valence states in the same oxide), and their wide range of PZC values (Ponnamperuma et al., 1969; Chao and Theobald, 1976; McKenzie, 1980, 1981, 1989). In an investigation by Gadde and Laitinen (1974) of the effect of pH (2 - 8) on the percentage adsorption of Pb on individual oxides of Mn, Fe, and Al, it was found that in the pH range below 7, the hydrous Mn oxide was the most effective in removing Pb from the solution; at a low pH of 2, about 70% of Pb was found to be retained on the Mn oxide. In a study by McKenzie (1980) of individual adsorption of Pb, Co, Cu, Mn, Ni, and Zn on various oxides of Mn and Fe, in a pH range of 2 - 8, the resulting adsorption curves (pH vs concentrations of metal sorbed), and the adsorption isotherms showed that all of the metal ions were more strongly adsorbed on the Mn oxides than on the Fe oxides; in the case of Pb, the adsorption by the Mn oxides was found to be up to 40 times greater than that by the Fe oxides. In addition, Pb was adsorbed more strongly than any of the other ions studied by all of the oxides, except goethite.
The authors also found that it was difficult to remove the adsorbed Pb from the Mn oxides, i.e., a very high proportion of Pb adsorbed was not extractable by 2.5% acetic acid, whereas,

most of Pb originally sorbed on goethite could be extracted by the acid. This was consistent with a finding by Guy and co-workers (1978) that none of the Pb originally retained on MnO_2 was recovered in NH_4Cl solution (pH 5), and not all of the Pb was removed from the oxide even at pH 1 (HNO_3), whereas majority or all of the Pb originally retained on a clay mineral bentonite, and on a humic acid, were recovered by the extractants. In an investigation by McKenzie (1981) of surface charges of four Mn oxides and a goethite, in relation to pH, it was found that all of the Mn oxides studied were negatively charged throughout the range of pH studied (2 to 11), whereas, the goethite was positively charged in the pH range of below around 7.5. It is, therefore, possible that Mn oxides develop a very high negative surface charge in the wide range of pH values of interest in soils. Manceau and co-workers (1992) investigated the reasons for the differences in adsorption behaviour among oxides by applying XAS techniques on several case studies, including Pb sorption onto a Mn and an Fe oxide. The authors suggested that the difference in the affinity of Pb for the different oxides was associated with a difference in sorption mechanisms. At similar surface coverage, a polymerization of Pb(II) was observed to occur on the Mn oxide, but not on the Fe oxide. The authors remarked that this polymerization could be due to the reductive dissolution of the Mn oxide by H_2O which, based on thermodynamic computations, might have occurred at pH 3 and would have been a local source of hydroxyl ions. Due to the high charge of Pb polymers, their affinity for the Mn oxide surface would be correspondingly larger than the one of monomers.

McKenzie (1980) proposed that Pb adsorption onto Mn oxides could be accounted for by three possible mechanisms, namely, (i) strong specific adsorption, (ii) a special affinity for oxides of Mn as found for Co (McKenzie, 1970) with the possibility of oxidation of the Pb, and (iii) the formation of some specific Pb-Mn mineral such as coronadite. The author assessed the relative importance of the proposed mechanisms in the adsorption of Pb by comparing the adsorption result of Pb with that of other metals investigated. In the adsorptions of Co or Mn onto Mn oxides, a colour change from brown to black was observed in the oxides after the metal adsorption; this was not evident with Pb or the other ions assessed. The author speculated that there was a special affinity between Co or Mn with the Mn oxides (several studies have discussed this special feature, e.g., Posselt et al. (1968) and McKenzie (1970)). For Pb, according to a study of Gadde and Laitinen (1974), some oxidation of Pb^{2+} by MnO_2 to Pb^{4+} could occur. However, in the possible oxidation reactions proposed by Gadde and Laitinen (1974), estimates of the numbers of protons or Mn^{2+} ions supposed to appear in solution (i.e., 2 protons, and 1 mole of Mn^{2+}, per each mole of Pb^{2+}) were not in agreement with the observations of McKenzie (1980). McKenzie (1980) found that the moles of H^+ released per mole of Pb^{2+} adsorbed on the Mn oxides investigated varied but were generally close to 1, and the concurrent release of Mn^{2+} from the oxides was found to be very small (i.e., less than 0.05% of the amount of the metal ion adsorbed).

Therefore, the author concluded that oxidation of the Pb could not have occurred to any extent. In addition, the author found no evidence of XRD spacing belonging to coronadite or any other Pb-Mn mineral during the investigations. Based on all these observations and the rapid fixation of Pb by Mn dioxides in soils observed in his previous work (McKenzie, 1978), McKenzie (1980) concluded that the fixation of Pb by Mn oxides was due to specific adsorption over a wide range of pH. The author also remarked that some Mn oxides with layer structures and small particle size adsorbed more Pb than others; this was attributed to a penetration of Pb into the interlayer regions, as evident by XRD results which showed that the adsorption of Pb induced a distortion in the layer structures of the Mn oxides.

It should be noted here that McKenzie (1980) also found that there was considerable adsorption of Pb by birnessite at the PZC (pH 1.8). Since the pH at the PZC was far below the first hydrolysis constant (pK_1 for Pb $\approx$ 8), the concentration of the unhydrolyzed ion in the solution would significantly exceed that of the first hydrolysis product. The author, therefore, considered that the most likely adsorbed form was the Pb^{2+} ion.

Gadde and Laitinen (1974) investigated competition between Pb with other ions, namely, Cd, Zn, Tl, Ca, Mg, or K for a Mn oxide. The results, obtained at pH 6, showed that Pb was adsorbed much more strongly than any other metal ion studied. For example, in the case of a system containing equal amounts of Pb and Cd, almost all of the Pb added was found to adsorb onto the oxide, whereas only about 16% and 18% (depending on which metal was adsorbed first) of the Cd added was found to be retained on the oxide; in the absence of Pb, about 82% adsorption of Cd was observed. Except in the case of Cd, there was little variation in adsorptions of the other competing ions whether Pb adsorption occurred first or after the adsorption of the other ion. The authors then suggested that the adsorption processes were reversible and that an adsorbed metal ion could be replaced by other competing metal ions.

In a kinetic investigation of McKenzie (1972) on the individual sorption of Co, Ni, Zn, and Cu, by various lower oxides of manganese, the author found a rapid sorption of all elements during the first day, followed by a period of slow sorption in certain cases. In the case of sorption of Co onto a synthetic α Mn_2O_3, the Co sorption curve (metal uptake per solid vs time) was observed to be consistent with the plot of Mn released from the mineral into the solution during the same period of time for 42 days (i.e., moles of Mn released were approximately equivalent to moles of Co sorbed). In addition, in a separate Co sample where solutions were periodically renewed for 6 months (i.e., "saturated" sample) Co adsorption was found to increase about four fold compared with the amount of Co retained on the oxide sample with a 42 day equilibration time. Based on these observations and the lack of evidence for the existence of precipitated Co hydroxide, the author interpreted that the rapid sorption of Co by the α Mn_2O_3 was due to a fast replacement of the Co for exchangeable Mn, and that the slow reaction reflected a gradual replacement for lattice Mn.

1.4.3. Humic substances.

Organic matter found in soils and sediments is usually subdivided into non-humic and humic structures (Schnitzer, 1977, 1978; Schnitzer and Khan, 1972; Stevenson, 1994; Sposito, 1984; Vernet, 1991; Schulten and Schnitzer, 1995). Non-humic substances include those with still recognizable chemical characteristics (e.g., carbohydrates, proteins, peptides, amino acids, fats, waxes, and low molecular weight organic acids). Most of these compounds are attacked relatively readily by microorganisms and have usually only a short life-span in soils and sediments. In contrast, humic substances (hereafter "HSs") do not exhibit specific physical and chemical characteristics (e.g., exact elementary composition, definite IR spectrum, melting and boiling points, refractive index, etc.). HSs are generally used as a collective term referring to the major component of soil organic matter which are amorphous, dark-colored, and refractory decomposition products of living, mostly plant materials. The formation of HSs is hypothesized to occur via the microbially-mediated degradation of plant biopolymers (e.g., lignin) to small molecules, and/ or condensation-polymerization reactions (in *Appendix 1.5.* is illustrated commonly proposed structural precursors of HSs in soils). Different opinions pertaining to the macromolecular structures of HSs exist, however, so far the materials are generally characterized as partly aromatic, polyelectrolyte-like materials (i.e., charged polymers), comprising of C, H, N, and O, with molecular weights in the range of several hundred to several million, and possessing a variety of functional groups, namely: carboxyl, phenolic, and alcoholic hydroxyl, quinone and ketonic carbonyl, amino, and sulfhydryl. The abundance of these different functional groups varies depending on the origin of the HSs (e.g., soil vs stream water) and the methods of measurement. HSs are currently commonly classified based on the solubility in alkali and acid, into three categories: (i) humic acid (hereafter "HA"), which is soluble in dilute alkali but is coagulated when the alkali extract is acidified; (ii) fulvic acid (hereafter "FA"), which remains in solution when the alkaline extract is acidified, that is, it is soluble in both dilute alkali and dilute acid; and (iii) humin, which cannot be extracted from soils by dilute base or acid. The three humic fractions are structurally similar, but differ in properties such as molecular weight and functional group content, with FA having a lower molecular weight, containing more O but less C and N, and having a higher content of oxygen-containing functional groups (e.g., CO_2H, OH, C=O) per unit weight than the other two humic fractions (Schnitzer, 1977; Vernet, 1991). The principal reason for the chemical differences is probably the difference in source material, with possible additional diversification imposed by environmental factors (Vernet, 1991). More detailed descriptions of the methods of extraction and purification of HSs, which are normally multi-step methods, can be found in several publications, such as those of Schnitzer and Khan (1972), Stevenson (1994), and Tan (1996).

Several researchers have attempted to establish representative model(s) of core structural molecules of soil organic matter, specifically for HAs (Schulten and Schnitzer, 1995; Schulten, 1995, 1996; Schulten and Schnitzer, 1997), as such models could provide important fundamental knowledge for understanding and predicting the composition, dynamics, and reactivity of natural and anthropogenic organics in soil and water systems (Schulten and Schnitzer, 1995). Many structural features of HAs have been proposed based on various characterization approaches involving both nondegradative (e.g., spectroscopic techniques) and degradative methods (e.g., oxidative or reductive treatments, hydrolysis, thermal and biological degradation) (Schnitzer, 1977; Stevenson, 1994; Gobbles and Puttmann, 1997). Degradation of HAs has been found to yield phenols, or a series of phenol-carboxylic acids and aliphatic substances. However, Tan (1993) has noted that depending on the severeness or mildness of the reactions applied, any given breakdown product could be obtained and a transformation from its initial degradative form could occur during the residence time of the reaction mixture. It seems that so far none of the existing relevant concepts/ theories and model structures for HAs, such as lignin-protein (Flaig et al., 1975), and phenol-dimer (Stevenson, 1994) has found wide acceptance, as a consequence the search for a consistent and more definite representative model continues. In a study by Schulten and Schnitzer (1995), utilizing a combination of approaches that included an instrumental analytical method (i.e., pyrolysis-mass spectrometry), chemical and biological techniques, and computations to assist in developing a model structure for HAs, the authors concluded that the structure of HAs consisted of many major classes of compounds, such as benzene, n-alkyl benzenes, alkyl naphthalenes, and alkyl phenanthrenes, with the presence in the structure of voids of various dimensions, which could trap and bind other components, such as carbohydrates, proteinaceous materials, lipids, and inorganics (e.g., clay minerals, and hydrous oxides). The proposed HAs structure also possessed prevalent free hydroxyl groups, which could complex with metal ions, and form hydrogen bonds. The authors further remarked that with minimizing the total energy, the volumes of the humic structures and their voids with or without trapped material decreased and finally approached a globular end form. In an investigation of molecular structure of extracted terrestrial HA, Widayati and Tan (1997) applied atomic force microscopy (AFM, a technique which can provide real molecular and atomic images of organic substances) onto monolayer thin films of the HA deposited on mica strips. The authors observed the presence of benzene rings in the HA, and with the use of IR, the side chains attached to these ring structures were identified to be carboxyl and carbonyl groups. Widayati and Tan (1997) noted that the AFM image did not support the hypothetical structure of HA proposed by Stevenson (1994), which composed of four building blocks, a dimer, a phenol-amino acid complex, a hydroxyquinone, and a C_4 - C_3 structural unit of lignin. In contrast, the AFM micrographs showed a continuous arrangement of phenols next to each other into polymers to which the side chains were attached; this, as remarked by the authors, was the first direct evidence at a molecular level of resolution supporting the theoretical models of HA molecules that consisted of benzene rings with various sizes of alkyl chains. Celi and co-workers (1997) compared quantitative measurement of carboxyl groups in soil HAs using three methods based on different principles, i.e., the chemical Ca-acetate method (a widely used method which based on ion-exchange of H of COOH for Ca of Ca-acetate), FTIR, and liquid-state ^{13}C NMR. The authors found good correlations between the three methods, and as a consequence they suggested the methods as choices for determining numbers of COOH groups in HAs.

HSs have been noted as one of the most powerful metal-binding agents among natural organic substances; they are found to associate with metals of environmental (e.g., Pb, Cu, Cd, and Zn (Lo et al., 1992)), and economic interests (e.g., Au, Pt, Pd, V and U (Wood, 1996)). A large number of publications have suggested that aspects of the chemistry or behaviours of heavy metals in soils, sediments, and natural waters, are related, in one way or another, to the complex formation with HSs or other organic matter (Stevenson, 1976a; Balistrieri et al., 1981; Hart, 1982; Elliott et al., 1986; Lo et al., 1992; Ducaroir and Lamy, 1995; Schnitzer, 1995; Kedziorek and Bourg , 1996; Gao et al., 1997; Sutheimer and Cabaniss, 1997). Balistrieri and co-workers (1981) studied adsorption properties of trace metals on sinking particulate matter in a deep ocean. They found that the metal-particulate matter interactions closely resembled the interactions between metals and organic compounds, and suggested that the adsorption properties of marine particulate matter were controlled by organic coatings. Elliott and co-workers (1986) studied the adsorption sequence of Cd, Cu, Pb, and Zn for mineral soils and soils containing appreciable amounts of organic matter. For mineral soils, the sequence was found to be Pb > Cu > Zn > Cd, however, for organic soils the sequence between Zn and Cd was switched. This suggested that organic matter increased Cd retention preferentially over that of Zn. In addition, extraction of soil organic matter notably reduced adsorption of all four metals. In a study by Sutheimer and Cabaniss (1997) of Al binding to HSs using commercially prepared river and field lake samples, the authors remarked that organic complexation of Al was not limited to acidic waters but appeared to be important even at the alkaline pH values typical of marine systems. Based on this and other evidence from the literature, the authors therefore hypothesized that Al in seawater was substantially complexed by organic matter. HSs have also been noted for their ability to interact with major elements found in the environment (e.g., alkaline earths (commonly Ca and Mg), Saar and Weber, 1982), anions (Parfitt et al., 1995), and oxide minerals (of e.g., Al, Si, and Fe) including clays (Greenland, 1971; Schnitzer and Khan, 1972; Inoue and Wada, 1971a,b; Hatton and Pickering, 1980; Davis, 1982; Odes, 1989; Inoue et al., 1990; Schulthess and Huang, 1991; Gu et al., 1994; Zhou et al., 1994; Schnitzer, 1995). It should be noted here that the association of organic matters with minerals is considered fundamentally important in soil chemistry and has profound physical, chemical, and biological effects on soil quality (in *Appendix 1.6.* is illustrated an association model of organic matters and clays). Several types of modes/ mechanisms have been proposed for the interactions between humic materials and minerals (Greenland, 1971; Inoue and Wada, 1971a,b; Schnitzer and Khan, 1972; Inoue et al., 1990; Stevenson, 1994); examples of these include polyvalent cation bridges in which the cations (e.g., Fe^{3+}, and Mn^{3+}) with high solvation energies present on mineral surfaces act as a bridge between charged sites on clays and on HSs functional groups, adsorption on interlamellar spaces of the clay structure, ligand exchange reactions involving displacements of OH groups on oxide surfaces or in the coordination shells of structural Al on the edges of clay structures, by COO^- ions, and H-bondings between polar groups of the organic molecules and adsorbed water molecules or oxygens of the clay silicate surface.

Binding of metal ion(s) by HSs may involve several processes, such as ion exchange (Bunzl et al., 1976; Gamble et al., 1983) and chelation (Stevenson, 1994); however it is generally recognized that the binding would occur first at those sites that form the strongest complexes (e.g., formation of coordinated linkages, and ring structures), and as the stronger sites become saturated, binding at the weaker sites become increasingly important (Stevenson, 1994). Xia and co-workers (1997), based on XAS data, concluded that in their soil HSs, Pb^{2+} and Cu^{2+} formed inner-sphere complexes with the HSs; the binding environments of the metals were found to compose of oxygen and carbon atoms, with C atoms in the second atomic shell of the binding sites. Many investigators have suggested that carboxylic and phenolic groups are responsible for the majority of metal binding on HSs, and that predominant bidentate binding sites for metal and proton on HSs might be similar to simple organic compounds, such as *o*-phthalic, salicylic acids, and catechol (Schnitzer and Khan, 1972; Gamble et al., 1980, 1983; Gamble, 1986; Schnitzer, 1995). However, binding sites involving other atoms/ groups may be of importance, e.g., Cheshire and co-workers (1994) observed that the Cu-organic matter complexation involved nitrogen ligands as well as oxygen. Wood (1996) noted that even if carboxylic and phenolic were the main groups responsible for metal binding, the structure of humic substances was so complex that it was unlikely that any two binding sites would be exactly identical in a given sample. Sposito (1984) remarked that the polyfunctional character of HSs could produce a wide range of stereochemical and charge distribution characteristics. Therefore, the properties of surface functional groups on HSs were not well-defined, but instead could only be characterized by ranges of values; this distinguished the organic surface functional groups from functional groups bound to small organic molecules. Moreover, as mentioned earlier, HSs are polyelectrolytic, i.e., they could be considered as macromolecules with many ligand sites per molecule (Davis and Leckie, 1978; Cleven and van Leeuwen, 1984; Buffle, 1984; Sposito, 1986b). Cleven and van Leewen (1984) compared the binding of Ba^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} to natural HA with the characteristic binding of the cations to model polyelectrolytes (i.e., polyacrylic and polymethacrylic acids). The authors found the strong analogy between the two systems and this suggested the interactions between HA and the cations was controlled by electrostatic effects, resulting from the field around the polyions. Other characteristics of HSs include hydrophilic and structural lability, i.e., they have capacity to be associated intermolecularly and to change molecular conformation in response to changes in, e.g., pH, ionic strength, and extent of metal ion complexation. Examples of studies showing dependence of metal sorption on these parameters are outlined below.

Changes in pH can induce changes in the extent of ionization of carboxylic groups. At low pH values HSs may be in a tightly coiled conformation where metal binding sites are not readily available, whereas at higher pH values they may be in dispersed or more open forms (McBride, 1994). It should be noted here that the properties of HSs mentioned are also possessed by other biopolymers, such as proteins and polysaccharides, however, in geopolymer HSs these properties reflect the behaviour of a heterogeneous mixture of polymeric molecules instead of the behaviour of a structurally well-defined, single macromolecule (Sposito, 1986b). All these characteristics suggest a complexity of possible associations of metals with HSs, and that the interaction of metals ions with humic substances should be difficult (if not impossible) to described in strict mathematical terms.

Numerous methodologies have been developed for studying metal-humate interactions; the most common method used appears to be potentiometric titration, usually with the use of ion-selective electrodes (Van Dijk, 1971; Stevenson, 1976b; Buffle et al., 1977; Takamatsu and Yoshida, 1978; Gamble et al., 1980; Saar and Weber, 1980; Turner et al., 1986; Lund et al., 1990; Seki and Suzuki, 1995; Bryan et al., 1997). Other techniques include fluorescence spectroscopy (Senesi, 1990; Glaus et al., 1995), polarographic methods (Greter et al., 1979; Lund et al., 1990), gel filtration, ion exchange, UV-visible spectroscopy, and others (general reviews can be found in several publications, such as those of Pitluck et al. (1987), and Stevenson (1994)). Studies of trace metal-HSs complexation have been primarily focused on determination of stability constants and composition (stoichiometry) of the complexes, as well as parameters describing binding capacities (MacCarthy and Perdue, 1991), information which is of use in estimating the fate or extent of potential hazard associated with each metal. Stevenson (1976b) determined stability constants for the complexes between Cu^{2+}, Pb^{2+}, and Cd^{2+} and three terrestrial HAs from diverse sources, at various ionic strengths (I). The authors found that complexes of Cu^{2+} and Pb^{2+} were considerably more stable than those of Cd^{2+}. The calculated average stability constants values (as log K) for the three HAs in the absence of supporting electrolyte were found to be 8.9 for Cu^{2+}, 8.7 for Pb^{2+}, and 6.9 for Cd^{2+}. The authors also noted that stability constants obtained at very low I were more likely to represent conditions existing in the soil solution and in natural waters than those at high I. In a study by Takamatsu and Yoshida (1978), using fourteen soil HAs, the order of calculated stability constants for Cu^{2+}, Pb^{2+}, and Cd^{2+} were found to be consistent with those of Stevenson (1976b), and the constants were found to increase with increasing pH. The authors also noted that the overall stability constants of HAs with low contents of very weakly acidic functional groups showed relatively small values compared with other types having a higher content of such functional groups; no relation between the nitrogen contents of HAs and stability constants was observed. Lund and co-workers (1990) studied complexation properties of aquatic humic material (water sample and FA) and Cu or Cd, at pH 5.0 - 6.7, by measuring free metal ion concentration using differential pulse polarography. The authors also noted that the formation of the metal-humic complexes was found to be complete within 3 min. The complexation capacity and stability constants were calculated using five different procedures, taking into account both inert and labile metal complexes (the author defined the complexation capacity as total molar concentrations of ligand site, expressed as mmol g^{-1} total organic carbon); the results were found to be influenced to some extent by the choice of calculation procedure. Vernet (1991) summarized some previous studies to arrive at the following stability sequence for some metals with HAs (Mg < Ca < Cd = Mn < Co < Zn = Ni < Cu) and noted its similarity to the Irving-Williams order of stabilities of chelates formed by metal ions with ligands (Irving and Williams, 1949). In general, stability constants of Pb and Cu for HAs extracted from various sources were reported to be higher than those of the other heavy metals, such as Cd, Ni, and Zn; the stability constants of the metals for HAs appeared to be substantially higher than those for FAs. The sequence of stability constants were reported to be affected by both pH (see also a work by Kerndorff and Schnitzer (1980) outlined in the remainder of this subsection) and I. The effect of the former could be due to an influence on the charge of HSs (as mentioned earlier) and also the state of hydrolysis of the metal ions; the effect of the latter could be associated with the degree of possible competition between the different ions in solution to complex with HSs.

A large number of thermodynamic models have been proposed for describing quantitatively the nature of metal-humate binding (Sposito, 1986b). However, Sposito (1986b) noted that as an alternative less demanding in its need for input data, a conceptual equation containing a simplified symbol such as SH_n could be used (where S and H represent the humic moiety and a mole of proton associated with functional groups), with the objective of describing the average sorption behaviour of the metal. Wood (1996) remarked that most of sorption models for metal-humic materials could be categorized into (i) discrete, (ii) continuous, and (iii) analogue-based models. The first type includes those in which an assumption is made that metal-humate binding can be represented by one or more binding sites of different, but constant strength (examples of studies applying discrete models include those of Turner et al., (1986), Fish et al. (1986), Hering and Morel (1988), and Gobran and Tipping, 1993, and Dzombak et al. (1986) the last of whom critically examined the theory underlying discrete and continuous multiligand models). The second category incorporates those assuming that a spectrum of sites exist which range from very strong to very weak without any sharp dividing line among them (e.g., that of Perdue and Lyte (1983)) (A comparison of discrete and continuous models is provided by Turner et al. (1986)). The last group comprises those based on the equating of binding sites on the HSs with simple organic analogue moieties (examples of studies applying this type of model include those of Mountney and Williams (1992), and Bryan et al. (1997)). All three categories of models have been employed both with and without provision for the electrostatic effects associated with the build-up of charge on a polyelectrolyte as a function of increasing pH, and changes in surface potential owing to variations in ionic strength. Perdue and Lyte (1983) examined some discrete and continuous models, and suggested that the latter ones were more appropriate for application on HSs. The authors proposed a continuous ligand distribution model with an assumption that ligand (binding site) concentrations were normally distributed with respect to their log K values; a particular "class" of ligands could be characterized by a given mean log K value and the standard deviation of log K values about that mean. The authors concluded (based on, for example, a comparison of the outcome from the Gaussian model vs experimental and published sets of data) that the proposed continuous model successfully described binding of protons and Cu(II) by HSs. Mountney and Williams (1992) used a computer program to generate a humate model, and in combination with a geochemical speciation program, simulated interactions between the HSs and metal ions. The generated model initially comprised a random collection of thirteen simple organic compounds, with known stability constants values for the complexes of the metal of interest with each of the 13 organic analogues. Outputs from the modeling program included parameters such as concentrations of the component ligands, etc. Other restrictions noted were the omissions of N and S during the random generations of the organic analogues, as well as the effects of electrostatic binding, and the conformational change within the molecule. After an initial investigation of Co(II)-HA and Cu(II)-FA interactions, the authors found that only a small number of the overall 13 ligands played a major role in the complexation. The approach was then modified to identify the ligands which were statistically significant within each particular system. Subsequent speciation modeling with these significant ligands resulted in a reasonable agreement between experimental and modelled data. The systems studied also included U-and Ni-HA interactions. Observations from the plots between total metal concentrations and metal concentrations in the organic phases, suggested that in the upper range of the total metal concentration values the simulated data was underestimated. The authors speculated that this might be due to proportionately more cationic complexation occurring at higher metal loadings (after the majority of covalent sites were saturated). Other thermodynamic models recently proposed include those of Benedetti et al. (1995, 1996), and Kinniburgh et al. (1996).

Many studies have investigated kinetics of metal-HSs using a variety of approaches, and in several studies the metal sorption process has been reported to be very rapid at the initial stage (Bunzl et al., 1976; Rate et al., 1992a,b; Jin et al., 1996; Yu et al., 1996). Rate and co-workers (1992a,b) investigated the kinetics of Cu(II)-humate dissociation reactions under conditions of varying pH, metal : humic acid ratio, ionic strength, pre-dissociation equilibration time, and temperature. Two types of HAs were used, and the reaction rates were measured by inducing Cu^{2+}-HA dissociation with a competing metallochromic ligand and following the formation of the Cu^{2+}-ligand complex spectrophotometrically. The authors applied a model for heterogeneous systems, based on a log-normal distribution of first-order dissociation rate constants, to analyze the resulting kinetic data. The authors found that the rate of Cu^{2+}-HA complex dissociation decreased with increasing pH or pre-dissociation time, and increased with increasing Cu^{2+}: HA ratio or ionic strength, or temperature. The authors discussed the application of the model in relation to other possible methods of kinetic data analysis, such as a discrete multicomponent model. The application of the log-normal kinetic model was found to provide a good agreement between the observed and predicted dissociation, comparable with that achieved via use of the discrete model (which contained twice the number of adjustable parameters as the log-normal model). The authors also found that the application of the log-normal model on published data of Ni(II)-fulvic acid dissociation resulted in a very good agreement between observed and predicted kinetics. Jin and co-workers (1996) investigated kinetics of single and multiple metal ion sorption processes on two HAs samples from different sources and a peat sample. In most cases, the sorption was found to occur within a few minutes, but it did not reach equilibrium within the experimental time periods (1480 min). For single metal adsorption on a HA sample, the extent of the reaction (amount adsorbed vs time) was found to be Cr(III) > Pb(II) > Cu(II) > Ag(I) > Cd(II) = Co(II) = Li(I). The extent of the reaction in the case of multiple metal adsorption on each of the two HAs samples was found to be similar in that Cr (III) >> Pb(II) > Cu(II) = Ag(I) = Cd(II) = Co(II) = Li(I). However, compared with the single system, when competition was present, all metals showed a decrease in the amount adsorbed. Cr showed the least reduction in the percentage sorbed and some other metals were not adsorbed at all. For a peat sample, the extent of multiple metal sorption was found to be Cr (III) > Pb(II) > Cu(II) > Ag(I) > Co(II) = Cd(II) = Li(I), with some other differences from the results of the multiple metal sorption of the HAs samples, e.g., Cr and the ratio of Cr/ Pb sorbed were found to be much lower. The authors speculated that those metals having a lower adsorption affinity than Cr(III) were initially sorbed, but during equilibration, Cr(III) desorbed these ions, resulting in minimal ultimate adsorption of the other five metals, with Pb(II) being the least affected. The authors noted that Cr(III) had a highly competitive nature but requires a longer time period to reach equilibrium, and based on their previous experience, although Cr(III) was strongly bound by river sediment, its sorption reaction could take more than 7 days to reach equilibrium. The authors further evaluated the applicability of the non-linear Langmuir-Hinshelwood kinetic model to metal-humic substances systems. In general, the model could describe some sorption kinetics; it revealed that among the seven metals, Cr(III) had the largest k_1 (first-order reaction rate constant of the model, min^{-1}), and in the multiple ion systems, the k_1 of all ions except Cr(III) were at least an order of magnitude smaller than they were in single ion cases. Moreover, in the presence of Cr(III) maximum reaction rates of most ions were greatly decreased. The authors noted that although not fully successful, the results of the model were more logical than those obtained with traditional kinetic models, e.g., strict zero-order or first-order kinetics, and that structural dynamics of macromolecules might play crucial roles in linking microscopic to macroscopic properties. In a related study, Yu et al. (1996), using a concept of lumping (i.e., summation or average of a group of parameters to describe the overall trend in a complex system), concluded that during the initial sorption period, metals with high sorption affinities such as Cr(III) and Pb(II) determined the rate constants and reaction order of the mixture (of the seven metals) investigated, and that the mixture behaved like a first-order reaction. However, at longer periods of time, those metals with lesser affinities such as Cd(II), Ag(I), and Li(I) became the major contributors to the lumped parameter values.

The influence of pH on the interactions of metals and HSs has been reported in many studies (Kerndorff and Schnitzer, 1980; Ladonin and Margolina, 1997). In an investigation by Kerndorff and Schnitzer (1980) of the effect of pH on the interaction of HA in a solution containing equimolar concentrations of 11 different metals ions, the authors found different orders of sorptions of the metals at different pH values. For examples, at pH 2.4, the order of sorption (% metal sorbed) was Hg > Fe > Pb > Cu = Al > Ni> Cr = Zn = Cd = Co = Mn, whereas, at pH 5.8, the order was Hg = Fe = Pb = Al = Cr = Cu > > Zn > Ni > Co > Mn. In all the pH ranges tested, Hg(II) and Fe(III) were always sorbed most readily by the HA, while Co and Mn were sorbed least readily. The authors also remarked that there was no correlation found between the difference in the sorption sequence observed with any of the simple ionic or atomic parameters. Ladonin and Margolina (1997) studied retention of Pb, Cu, Cd, and Zn by two different types of HAs, using initial solution in the pH range of 3 to 7. Their resulting sorption curves were found to exhibit wave-like characteristics. In this study, the authors indirectly measured the amount of metal sorbed on HAs by analyzing the concentrations of free ions in solution, which was separated from the coagulated HA at the end of the 24 h reaction time by use of a filter membrane; free ions were isolated from the soluble metal-humic complex by use of a cation-exchange resin. The authors attributed the characteristics of the sorption curves observed to the consecutive activation of acidic functional groups of different strength, as a result of ionization caused by the pH increase.

Competition between metal ions for HSs is a subject which has been widely studied (Bunzl et al., 1976; Kerndorff and Schnitzer, 1980; Gamble et al., 1983; Hering and Morel, 1988; Randle and Hartmann, 1995; Mota et al., 1996; Ladonin and Margolina, 1997). Hering and Morel (1988) titrated solutions of HAs with Ca or Cu. The titration results of each individual metal were found to be consistent with the results from a discrete ligand site model for metal-humate binding. In systems with 0.3 and 0.6 mg litre^{-1} HAs, the titration results of Cu in the presence of 10^{-2} M Ca were similar to results obtained with Ca absent. In contrast to the HA systems, the presence of 10^{-2} M Ca was found to have a notable effect on Cu complexation by nitrilotriacetic acid (NTA). The authors speculated that the lack of competition between Ca and Cu for binding to HAs (even with a large excess of Ca over Cu) could be because Ca and Cu were bound selectively at different sites or the mechanisms of binding were completely different for the two ions. In a study of Mota and co-workers (1996) on competition between Al^{3+} and Pb^{2+} for complexation with humic matter, the humic samples were titrated with Pb in 0.01 M KNO_3 (pH 4.5), both in the presence and in the absence of Al. Analysis was by use of anodic stripping voltammetry; in the presence of Al, the titration of humic matter with Pb began 1 h after the Al addition. The authors found that at any constant humic matter concentration the concentration of free Pb increased with increasing Al^{3+} concentrations. This was attributed to competition of Al with Pb for the humic matter complexing sites. The competition was also found to increase with decreasing ligand concentrations. For the concentration ranges used, the authors concluded that an electrostatic effect of Al^{3+} (which affected the charged complexing sites of the molecule) contributed to the competition of Al with Pb observed; the effect could be expressed by an exponential factor which was a function of Al and humic matter concentrations. Ladonin and Margolina (1997) found that in the systems containing equal concentrations of Pb, Cu, and Zn and varying concentrations of HAs from 0 to 3.5 mg ml^{-1}, the resulting characteristics of sorption curves (metal sorbed vs conc. of HA) of each metal were different; the authors considered this result to be a reflection of different mechanisms of the interactions of the HAs with the metal ions simultaneously present. At concentrations of HAs lower than 0.05 mg ml^{-1}, sorption of both Pb and Cu increased, while that of Zn decreased. This implied that among the three metals, Zn was the weakest competitor for the reaction positions (this implication was consistent with the previously mentioned order of the affinity of metals for HSs). With increasing concentrations of the HAs, sorption of the metals generally increased and leveled off at a maximum. This reflected that at higher concentrations of HAs the number of reaction sites became more than sufficient for any free metal in solution. In all concentrations of the HAs investigated, Pb was found to be the most sorbed metal among the three (i.e., Pb > Cu > Zn). The authors noted that the differences in sorbing capcity of HAs with respect to these elements was partially determined by the chemical nature of the cations in that the electronic configurations of Pb and Cu tend to favour formation of covalent bonds (specific adsorption); whereas bonds formed by the closed-shell cations Zn^{2+} and Cd^{2+} would tend to be more electrostatic in nature.

Ladonin and Margolina (1997) also investigated the effect of ionic strength (Ca^{2+}) on individual sorptions of Pb, Cu, Cd, and Zn onto HAs, at the initial solution pH of 6. In the range of Ca^{2+} concentrations tested (0 to 1 M), the concentrations of Pb and Cu retained on the HAs were found to be greater than those of Cd and Zn. In addition, the resulting sorption curves of Pb and Cu were found to be independent of the concentration of Ca^{2+} (i.e., the sorption curves did not have a pronounced maximum or minimum and were practically parallel to the abscissa). It was speculated that this could be due to specific adsorption of the metals onto the humic acids. It should be noted here that the outcomes obtained in this study could be seen as results from the effect of the presence of major elements on the sorption behaviours of the metals on the HAs. For Cd and Zn, an increase in Ca^{2+} concentration from 0.01 to 0.05 M appeared to decrease the amount of the metals sorbed, however, a further increase in the concentration of Ca^{2+} appeared to enhance the metal sorptions, which then reached the maximum and exhibited the plateau-like curves at around the 0.5 M Ca^{2+}. The authors, therefore, speculated that Cd and Zn were associated with the humic acids through both non-specific and specific adsorptions. The early part of the curves (at low concentrations of Ca^{2+} of ≤ 0.05 M) reflected the process when Ca^{2+} occupied nonspecific exchange positions, hence the adsorption of Zn and Cd were suppressed by the increase in

Ca^{2+} concentrations. However, a further increase in Ca^{2+} concentrations could induce conformational changes in the molecules of the humic acids. This provided additional specific sites for adsorption for Zn and Cd that could not be suppressed by Ca^{2+}, and as a result, the adsorptions of the metals were reinforced. The sorption of the metal ions studied were found to be approximately equal at high Ca^{2+} concentrations of > 0.5 M. This observation suggested that an increase in the ionic strength of the solution made the sorption of different ions independent of their affinities for HAs. The authors concluded that ionic strength of the solutions appeared to have more affect on metals with low stability constants for HSs more than those with high stability constants.

There are relatively small numbers of studies directly related to the effect of temperature on the stability of HSs (or their possible structural unit analogues) in aqueous solutions (Kawamura and Kaplan, 1987; Boles et al., 1988), or on metal-humate complexes. These studies generally suggest that HSs are destroyed very quickly at high temperature and that under such conditions it is unlikely that HSs could persist unchanged, and, therefore, that HSs were less likely to play a major role in metal transport at elevated temperatures of near or above 100 °C. Since it was commonly agreed that carboxyl functional groups were important for metal retention on HSs, and when HSs were subjected to high heat, decarboxylation was likely to occur, it was possible that metal binding characteristics of the HSs would significantly changed as temperature increased above ambient conditions. Nevertheless, it was also considered possible that the breakdown products of HSs could still play a role in metal transport or deposition at high temperature.

1.4.4. Clay minerals.

Clay is used as a rock term and also as a particle-size term in the mechanical analysis of sedimentary rocks, soils, etc (Grim, 1968). In general, the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water (by plasticity is meant the property of the moistened material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed). Clays generally are essentially composed of extremely small crystalline particles of one or more members of the clay group of minerals. Clay minerals are primarily hydrous aluminosilicates (i.e., they contain mainly Al, Si, and O). However, Mg and Fe are often found substituted for Al to varying degrees, and alkali and alkaline earth elements can also be essential constituents (Grim, 1968; Newman and Brown, 1987). These substitutions cause wide diversity in chemical composition within the broad general class of phyllosilicates (or layer silicates) to which the clay minerals belong. As a particle size term, the clay fraction is that size fraction composed of particles of < 2 µm, and this fraction of most soils is dominated by phyllosilicate minerals (Schulze, 1989).

All phyllosilicates comprise sheets of SiO_4 tetrahedra (SiO_4 is the fundamental unit of all silicate structures found in soils) in close association with sheets of AlO_6 octahedra (i.e, a metal cation and six anions) (Sposito, 1984; Schulze, 1989). The plane of oxygen atoms bounding a tetrahedral silica sheet in a layer silicate is called a siloxane surface.

The functional group associated with the siloxane surface is the ditrigonal cavity formed by six corner-sharing silica tetrahedra. This has a diameter of about 0.26 nm, and as a unit the cavity functions as soft Lewis-base (in *Appendix 1.7.* is shown a ditrigonal cavity).

The reactivity of the ditrigonal cavity depends on the nature of the electronic charge distribution in the phyllosilicate structure. For example, isomorphic substitution of Al^{3+} by Fe^{2+} or Mg^{2+} in octahedral sheet or Si^{4+} by Al^{3+} in tetrahedral sheet enhances Lewis-base character of the ditrigonal cavity. The cavity can hold hydrated (outer-sphere) or dehydrated (inner-sphere)-cation complexes (Sposito, 1984). The sites for cation sorption on the surface layers are described as areas with reduced steric effects (e.g., near cavities, where the cations exert a neutralizing electric charge over the negatively charged region). In addition to the ditrigonal cavity, two types of surface hydroxyl groups, i.e., aluminol and silanol, can be found at the edges of the octahedral and the tetrahedral sheets, respectively (illustrated in *Appendix 1.7.*) (Sposito, 1984). Either kind of the hydroxyl group can possibly form outer-(e.g., exchangeable) and inner-sphere complexes with metal cations.

The phyllosilicates in soil clays can be classified into three layer types, distinguished by the number of tetrahedral and octahedral sheets combined, and five groups, differentiated by the kinds of isomorphic cation substitutions that occur (the classifications and structural details of phyllosilicates could be found in many publications, such as Bailey, 1980a,b; Sposito, 1984; Allen and Hajek, 1989; Schulze, 1989; McBride, 1994). Three layer type phyllosilicates include 1 : 1, 2 : 1 layers, and 2 : 1 layer with hydroxide interlayer. The 1 : 1 layer structure consists of a unit made up of one octahedral and one tetrahedral sheet stacked one above the other, with the apical O^{2-} ions of the tetrahedral sheets being shared with (and part of) the octahedral sheet (Allen and Hajek, 1989) (in *Appendix 1.7.* is illustrated a structure of 1 : 1 type). There are three planes of anions. One plane consists of the basal O^{2-} ions of the tetrahedral sheet, the second consists of O^{2-} ions common to both the tetrahedral and octahedral sheets plus OH^- belonging to the octahedral sheet, and the third consists only of OH^- belonging to the octahedral sheet. In soil clays, this 1 : 1 layer structure is referred to as kaolinite group, with Al^{3+} in the octahedral sites and Si^{4+} in tetrahedral sites. The octahedral sheet has two thirds of its cation sites occupied (this is referred to as a dioctahedral phyllosilicate). In this group, there is normally no significant isomorphic substitution for Si(IV) or Al(III), as is common with soil clay minerals. Two major representatives of this 1 : 1 layer structure are kaolinite (the most common member and a prevalent mineral in soils) and halloysite. The hydrated form of halloysite (10-Å, usually has a formula of $Al_2Si_2O_5(OH)_4.2H_2O$, with the adjacent 1 : 1 structure separated by a layer of H_2O molecules (in *Appendix 1.7.* is illustrated a structural model of halloysite). The dehydrated form (7-Å,

meta-halloysite) has the same formula as kaolinite. Halloysite and kaolinite differ primarily in morphology, i.e., halloysite is often found in tubular or spheroidal forms, whereas kaolinite is typically platy. Halloysite is usually found in soil formed from volcanic deposits, particularly volcanic ash and glass (Allen and Hajek, 1989; Nizeyimana, 1997), and forms early in the weathering process but it is generally less stable than kaolinite and gives way to kaolinite with time (Allen and Hajek, 1989) (however, Singh (1996) and Singh and Mackinnon (1996) have demonstrated experimentally that the transformation of kaolinite to halloysite was possible). Common impurities present with halloysite include quartz (SiO_2) and gibbsite ($Al(OH)_3$) (Norrish, 1995). The 2 : 1 layer type of clay has two tetrahedral sheets sandwiching each octahedral sheet. The three clay groups with this structure are mica (illitic), vermiculite, and smectite (montmorillonite). The 2 : 1 layer type with hydroxide interlayer is represented by dioctahedral chlorite. In general, Al in the 2 : 1 layer types is significantly substituted by Fe and Mg; this results in having higher layer charges than those of the 1 : 1 layer types (the layer charge is defined as the number of moles of net electron charge per unit cell that is produced by isomorphic substitutions) (Sposito, 1984).
In addition, the cation exchange capacity (CEC) of the 2:1 layer clay types is typically higher than that of the 1 : 1 layer types (e.g., montmorillonite CEC = 80 - 120 $cmol_c\ kg^{-1}$ vs kaolinite CEC = 3 - 10 $cmol_c\ kg^{-1}$). CEC is often used as a measure of the surface charge of clay minerals. The sources of the CEC values are generally described as having a pH-dependent charge component which is due to ionization of the hydroxyl groups on the crystal edges, and a permanent charge component due to isomorphic substitution or vacancies of coordinated cations in the crystal structure (Sposito, 1984; Schlthess and Huang, 1990; McBride, 1989, 1994). CEC values are commonly expressed in mmol or centimole of charge per kg of the solid.

It is worthy of note that clays and clay minerals show great potentials for both environmental applications (e.g., land waste disposal, Yong et al., 1990, Lo et al., 1996; solid waste/ waste water treatment, Alther, 1995, Lothenbach et al., 1997) and industrial applications (e.g., Murray, 1991, 1995; sorbent in industrial air separation, Cheng and Yang, 1995; electrochemical analysis, Walcarius, 1996; catalyst, Brown and Rhodes, 1997). Today one of the most common environmental applications for clay minerals involves waste disposal barriers for landfills and hazardous waste sites; the clay most commonly used in this respect is Na-montmorillonite (Murray, 1995). Several types of clay liners have been available for use with different types of wastes, including geosynthetic clay liners which comprise a permeable synthetic textile product with a clay layer sandwiched between textile sheets (Murray, 1995). The general properties of clay minerals, such as fine particle size, large surface area, charged surfaces, good sorptive properties for several ions and compounds (e.g., metals, Srivastava et al., 1989; Khan et al., 1995; Xing et al., 1995; Suraj et al., 1996; radioactive nuclides, Jeong et al., 1996, Olguin et al., 1996; organic liquids, Raussel-Colom and Serratosa, 1987), and their common occurrence have made them important both industrially and environmentally at present, and, as noted by Murray (1995), they will become more important in the future as new uses are found.

Sorption behaviours of metals on clay minerals generally support the concept of heterogeneity of surface sites on the minerals (Farrah et al., 1980; Srivastava et al., 1989). Farrah et al. (1980) investigated individual adsorption at 25 °C and pH 5 of Pb, Cu, Zn, Mg, and Ca ions by Na^+-form kaolinite, illite, and montmorillonite. The sorption data were described in terms of Langmuir-type isotherms. The derived capacity (mmol kg^{-1}) values for each clay mineral were found dependent on the cation used, and in each case the range was too broad to be attributed solely to experimental error. This suggested that the adsorption mechanism was not a simple, stoichiometric ion exchange process, and that not all sites were accessible to each cation or that several types of active site present, with only some cations having a high affinity for one particular type of site. The authors remarked that while the radii of the hydrated ion could be a contributing factor where penetration into interlamellar spacings was involved or where site density was high, there was no clear-cut patterns. In a study by Srivastava and co-workers (1989) on individual sorption of Pb and Cd by kaolinite and montmorillonite, the sorption data in the entire metal concentration range studied was found neither represented by the Langmuir nor Freudlich models in the case of the kaolinite, whereas in the case of montmorillonite the data agreed well with the Langmuir model for both the metal ions. The values of adsorbate required for complete monolayer formation calculated from the Langmuir plots for both metals on montmorillonite were found higher than the maximum adsorption observed. The authors remarked that some factors could be responsible for this observation, e.g., the orientation of the adsorbate molecules on the surface of the adsorbent and its heterogeneous nature, and inaccessibility of some adsorption sites.

The cation exchange process is frequently referred to as being an important reaction for metal retention on clay minerals (Hem, 1976; Abd-Elfattah and Wada, 1981; McBride, 1994; Schulthess and Huang, 1990). Hem (1976) developed a model to test a possible significance of the cation exchange process and to predict the equilibrium distributions of Pb between dissolved and adsorbed forms, using synthetic halloysite as a substrate. (In this model, however, some factors which might affect the metal distributions, such as specific or irreversible adsorption, and organic complexing or biological assimilation, were not included.) The clay mineral was measured for CEC (in this study, the unit used was moles of unit negative charge per litre of aqueous clay suspension), while the selectivity of the substrate for Pb over other species present (e.g., Na, Ca) was calculated. The results formed the basis of an equation for determination of Pb in the adsorbed form. An equation for the dissolved species of Pb was based on a number of complexing equilibria using relevant thermodynamic data selected from literature. Both equations were related as their summation equated to total Pb input into the system. Total concentrations of Pb applicable in this model (e.g., between 10^{-6} and 10^{-7} M) were in the range expected in natural or polluted waters. From a plot of dissolved concentrations of Pb at equilibrium as a function of pH (4 to 9) and

CEC (10^{-3} to 10^{-5} M), at a total Pb concentration of 10^{-6} M, trial calculations for CEC = 10^{-3} M revealed that 90% or more of the total Pb was removed from solution by cation exchange adsorption between pH about 6 and 9. This result suggested that cation exchange sorption could be a major factor in the behaviour of Pb in surface and underground water systems. However, the author remarked that certain factors prevented the immediate application of this model to actual natural systems. For instance, it was unknown how similar the selectivity calculated for the halloysite would be to those of the natural sediments. The author, nevertheless, concluded that the resulting model demonstrated a general concept of cation exchange processes in multi-ion systems that even when a metal cation was added to the system at concentrations many orders of magnitude less than those of the dominant cations, if a large amount of mineral surface was available, the cation exchange adsorption process could very effectively decrease the dissolved concentration of the minor element. This effect could take place even when the surface was not particularly selective toward the minor element. In addition, the author noted that in natural systems the total area of mineral surface to which a given volume of water was exposed, and hence, the effective CEC, could be very large due to movement of the water through the system. It is interesting to note here a finding of Maes and Cremers (1975) from their study on cation-exchange hysteresis in a clay mineral. They found that the extent of irreversible adsorption of the cations investigated in the clay depended upon the composition of the solid phase and the pH. At low and intermediate occupancy of the divalent cation, the adsorption was perfectly reversible up to a pH value of about 6. At very high occupancies, approaching saturation, a significant portion of the adsorbed divalent cations became "irreversibly" fixed, but could be desorbed by lowering pH significantly.

Hydroxyl functional groups of clay minerals are suggested to be major sites for exchange reactions with metal ions (Ferris and Jepson, 1975). McBride (1994) indicated that the silanol group was the most likely edge site to adsorb cations at typical soil pH values (< 7). Schulthess and Huang (1990) speculated that Al and Si components of clays might be independently contributing to metal adsorption mechanism, and in the absence of a permanent (pH-independent) charge, the clays should behave as mixtures of their component oxides. In an attempt to elucidate the role of the type of metal-sorption sites, Schulthess and Huang (1990) investigated the similarities of adsorption behaviours of metals between oxides and clays by comparing the pH values of the adsorption edges of Si and Al oxides with those of three clay minerals of different structures, namely, natural kaolinite (layers of adjacent clay sheets held by H-bonding, i.e., not a swelling clay), montmorillonite (the inner peripheral space able to swell with adequate hydration), and mordenite (a synthetic zeolite, with three-dimensional frameworks). In this study, the abrupt changes in adsorption behaviour as the pH was varied were interpreted as being due to the action of pH-dependent sites. The authors found that in the case of Ni sorption on kaolinite, the sorption curve (% Ni removal vs pH) required an additive contribution of both Si and Al sites. Kaolinite removal of Ni by Si sites occurred at an adsorption edge over the pH range 3 to 5, whereas a more dramatic removal by

Al sites occurred at the adsorption edge over the pH range 6 to 7. The Si and Al sites were identified by matching the increase in adsorption by the clay with the increase in adsorption by the individual Al and Si oxides. Based on the observation that the relative amounts of Ni adsorbed by the Al sites on the kaolinite were much greater than amounts adsorbed by the Si sites, and the fact that the structural formula for kaolinite indicates a Si/ Al ratio of 1 : 1, the authors concluded that the Al sites have a stronger affinity for Ni adsorption than Si sites. Adsorption behaviour of Ni observed for montmorillonite was found to be similar to those of the Si and Al oxide surfaces, but with an additional adsorption edge observed at a low pH range of 2 to 3. This additional part was attributed to adsorption on the Si sites on the interlayer structure of the clay. The notable adsorption edge of Ni by the zeolite mordenite was also found to occur at a low pH range of 2.5 to 4.5, and included a slight kink at pH 3.4; this kink was attributed to the increased Ni-binding stability inside the channels of the zeolite structure. The authors concluded that the adsorptions of the cations investigated by these clay minerals could be grouped into Si-related and Al-related sites, and that the adsorption edge could function as an indicator of the type of reaction site involved in the uptake of the metal cation. It also appeared that the cation sorption was strongly influenced by several factors, such as, the Si/ Al surface site ratio and steric effects of interlayers or channels. The authors also remarked that presumed pH-independent cation-adsorption behaviour below pH 6 by 2 : 1 clay minerals was probably due to pH-dependent adsorption on amorphous Si oxide sites that could induce ion-exchange reactions at much lower pH values than previously assumed. In work along the same lines as that of Schulthess and Huang (1990), Spark and co-workers (1995) attempted to determine the preferred surface type for metal adsorption on kaolinite, by comparing individual adsorption of Cu, Zn, Co, and Cd on alumina, silica, and kaolinite, over a wide pH range of 3 to 11. The authors found that for Zn, Co, and Cd, the adsorptions on kaolinite apparently occurred in two stages (i.e., there was a slight kink on the adsorption curves). In the first stage all four metals began to adsorb at the same pH of about 4.5; a phenomenon which, as noted by the authors, was not commonly observed for adsorption on other oxide and oxyhydroxide substrates (this presumably implied that variable-charge surface hydroxyl groups did not participate in the initial sorptions of the four metals on kaolinite). The onset of this initial adsorption of the four metals was also found to correspond with the pH at which Al(III) species (dissolved from kaolinite at the low pH) was nearly completely resorbed (precipitated) onto the surface; this implied that the initial adsorption was not coprecipitation or cosorption of the metals with $Al(OH)_3$ because at this stage only small fractions of the metals were adsorbed at a time when Al(III) resorption was effectively near completion. Based mainly on these observations, the authors speculated that the initial adsorption of Zn, Co, or Cd, occurred on permanent negatively charged siloxanol face planes. At higher pH values, the adsorption curves for Zn, Co, and Cd were found to be generally similar in shape to those for adsorption on alumina; the authors regarded this as suggesting that variable charge sites of kaolinite which play a major role in adsorption occur both on alumina face and aluminol edges of the mineral.

In order to elucidate the role of the type of metal ions in the adsorption reaction, Schulthess and Huang (1990) studied the individual removal of Ni, Zn, Cd, and Pb by montmorillonite as a function of pH. It was found that the removal curves of Ni, Cd, and Zn by the clay were generally quite similar, but slightly different from the curve of Pb. It was speculated that the differences observed between the metals were due to the different ability of each metal to compete with protons for surface sites; an idea which was in agreement with one of Spark and co-workers (1995) on the sorption characteristics at the initial stage of Cu, Zn, Co, and Cd immobilization on kaolinite. Schulthess and Huang (1990) noted that the amount of metal removed at pH 2 to 3 (the suggested interlayer Si sites) was higher for metal ions with smaller hydrated radii (the hydration radii are 0.401 nm for Pb, 0.404 nm for Ni, 0.426 nm for Cd, and 0.430 nm for Zn). In addition, the strong removal of each of the metals by montmorillonite was found to be consistent with the pH condition where a small fraction (usually < 3%) of the corresponding metal hydroxide species form in the aqueous phase. Aqueous Pb, which speciates to PbOH at much lower pH values than the other three metals investigated, was found to be completely adsorbed at a much lower pH value (i.e., around 6) than the other metal cations. Therefore, the aqueous hydrolysis species (e.g., above pH 5.9 for PbOH) were postulated to be the metal species adsorbed by Si sites on montmorillonite.

Spark and co-workers (1995) also investigated effect of substrate concentration, and the nature and concentration of the supporting electrolyte (i.e., 10^{-3} to 10^{-1} M KNO_3 or NaCl) in sorption of Cu, Zn, Co, and Cd on kaolinite. Based on adsorption curves (% metal adsorbed vs pH) of all cases investigated, the authors found that the adsorption edges shifted to lower pH values as the substrate concentrations increased. With increasing electrolyte concentration, adsorption of all metals studied was found to decrease. The effect of the electrolyte concentrations was especially significant for the initial adsorption processes (apparently observed in Zn, Co, and Cd sorptions) in that once the electrolyte concentration was increased to 10^{-1} M, the initial adsorptions were effectively suppressed. KNO_3 was found to reduce adsorptions of all metals to a greater extent than NaCl; this was particularly apparent when an intermediate concentration of the supporting electrolytes was used.
In order to determine whether this effect was due to the cation or the anion of the supporting electrolyte, the authors compared the results for adsorption of Zn(II) in the presence of 10^{-2} M KNO_3 and NaCl with adsorption in 10^{-2} M KCl and $NaNO_3$ solutions. They found that Zn(II) was adsorbed on kaolinite to about the same extent in NaCl and $NaNO_3$ and that there was a similar correspondence for KCl and KNO_3 solutions. This suggested that the cations in the KNO_3 and NaCl background electrolytes were the principal source of the reduction in metal ion adsorptions observed. Based on these observations, it was suggested that K^+ competed more effectively with the adsorbing metal ions than Na^+, at the intermediate electrolyte concentration, for sites on the permanent negatively charged kaolinite faces.
The much smaller effect of electrolytes on metal adsorption at higher pH suggested that the

competition of K^+ and Na^+ with the metals was less effective in the case of aluminol sites. The authors also noted that the large supporting electrolyte concentrations could cause face-to-face flocculation as the charge on the faces was screened by electrolyte ions, and this could possibly contribute to the reduction in metal adsorption.

The pH dependent character of metal sorption on clay minerals has some similarities to that observed in (oxyhydr)oxide minerals (e.g., correlation between MOH^+ formation and pH at the adsorption edge) (Kishk and Hassan, 1973; Hildebrand and Blum, 1974; Guy et al., 1975; Farrah and Pickering, 1977, Farrah et al., 1980; Srivastava et al., 1989; Schulthess and Huang , 1990; Spark et al., 1995). In a study of sorption of Cu onto different clay minerals, Kishk and Hassan (1973) found that in all cases Cu sorptions increased with increasing the equilibrium pH. The authors attributed smaller adsorption values observed at low pH to the competition effect of protons and the release of octahedral Mg, Fe, and Al from the 2 : 1 clay minerals in acid solution. The higher sorption of Cu at higher pH values was attributed to the absence of competitive protons, and the increase in the pH-dependent negative charge in some cases (e.g., kaolinite).

Farrah and Pickering (1977) assessed possible effects of ligands on Pb and Cu sorption by clay minerals. The ligands studied included those having strong affinity for the metal ions, such as glycine, and nitrilotriacetic acid (NTA), etc. The resulting sorption curves were presented as plots of the amount of metal removed from the systems, in the presence or absence of ligands, vs pH (3 to 11). In this study, the authors considered that the amount of metal removed could be attributed to adsorption and/ or precipitation. With the use of glycine : Pb in the ratio of 6 : 1, the resulting sorption curve of Pb for kaolinite was found to be similar to that of the corresponding system in the absence the ligand, i.e., the amount of metal ion adsorbed by the clay increased gradually as the pH was increased from 3 to 6; at higher pH values the residual metal ion was precipitated as sparingly soluble hydroxy species. This indicated that this ratio of ligand to Pb concentration was not sufficient for effective masking to occur. However, a similar excess of glycine in Cd solution resulted in precipitation of the metal being deferred until the pH was approximately two units higher than that observed in the ligand-free system; in other words, formation of the Cd-glycinate species resulted in extension of cationic adsorption into the alkaline region. Since the stability constants of Cd- and Pb-glycinate complexes were similar in magnitude, the authors, therefore, attributed the different behaviours of the metals to the differences in solubility product values. In the case of NTA, a slight excess of the ligand in solutions of Cd or Pb (i.e., 6 : 5) significantly reduced these metal's sorptions by the clays investigated to near zero over a limited range of pH only; the authors attributed this to high stability of the metal ion-NTA complexes (log K_1: 10 for Cd; 11.5 for Pb). However, below pH 7, the clays appeared to successfully compete against NTA for the metal ions; the authors noted that the effective complexing power of the ligand was reduced by protonation as the pH was decreased. At high pH, the high stability of the metal-NTA complexes was considered not sufficient to prevent some precipitate formation. The authors remarked that using a larger excess of NTA or a more reactive ligand (e.g., EDTA) could broaden the pH region in which minimal loss of metal ion from solution occurred. This study showed that stability of the metal-ligand complex, the relative concentrations of the metal and the ligand, as well as the solution pH, were all important parameters affecting the masking ability of the ligand in the system studied.

1.4.5. Calcium carbonates.

Calcite ($CaCO_3$) is the most abundant carbonate in soils, shallow ground water aquifers, and marine sediments (Doner and Lynn, 1989), and is known as a significant factor affecting the pH of these systems (Jenne, 1968; Zachara et al., 1993). There are relatively small numbers of studies on sorption of trace metals on calcite or carbonate minerals (compared with other minerals such as Fe/ Mn oxides) however, the studies which have been undertaken suggest the importance of these minerals as a sorbing phase (as long as environmental conditions guarantee their stability) for metals, such as Pb, Cu, and Cd (McBride, 1980; Davis et al., 1987; Fuller and Davis, 1987; Elkhatib et al., 1991; Zachara et al., 1991; Garcia-Delgado et al., 1996; Salim et al., 1996). In a study of Fuller and Davis (1987) on Cd^{2+} sorption by a calcareous aquifer sand and the sand components, it was found that clean grains of primary minerals, e.g., quartz and aluminosilicates, sorbed much less Cd^{2+} than grains which had surface patches of secondary minerals, e.g., carbonates, Fe and Mn oxides. Calcite grains were found to sorb the greatest amount of Cd^{2+} on a weight-normalized basis despite the greater abundance of quartz. In an investigation by Elkhatib and co-workers (1991) of Pb sorption by three soils that differed in texture and $CaCO_3$, it was found that Pb sorption conformed to both Freundlich and Langmuir isotherms, and that the quantity of Pb sorbed by the soils followed the trend $CaCO_3$-rich > clay > sandy. It was possible that the greater amount of Pb sorbed by the $CaCO_3$-rich soil was attributable to greater quantity of $CaCO_3$ present; however, in this study, no attempt was made to determine contribution from soil components to the sorption of Pb by the three soils studied.

Description of calcite is usually in terms of hexagonal rhombohedral unit cell, with Ca in sixfold coordination with one O from each of six CO_3^{2-} groups (Doner and Lynn, 1989) (in *Appendix 1.8.* is shown a calcite model). The surface of calcite is noted for an ability to develop charge in response to a surface excess of the potential determining ions, Ca^{2+} and CO_3^{2-} (Zachara et al., 1993). Morse (1986) summarized that the PZC of calcite could range from 8 to 9.5 and noted that this meant that in most natural solutions, if no other ions were to interact with the calcite surface, the surface would have a slightly positive or close-to-neutral charge. Zachara and co-workers (1993) noted that some researchers had speculated that HCO_3^-, OH^-, $CaOH^+$, and $CaHCO_3^+$ exist as surface species on calcite. However, Thompson and Pownall (1989), using a streaming potential methods, suggested that Ca^{2+} and CO_3^{2-} species were the major calcite surface ions. This is consistent with the finding of Stipp and co-workers (1991, 1994), using XPS and low energy electron diffraction (LEED) and atomic force microscopy (AFM) to directly observe surface structure of pure calcite crystals exposed to water. They found spectral evidence for *S*. CaOH and *S*.CO_3H (where *S*. represented a calcite surface site) on the hydrated calcite surface. These hydration species were also found to be consistent with surface species postulated from a surface complexation model proposed by Van Cappellen and co-workers (1993) upon exposure of a fresh $MeCO_3$ mineral surface to water (Me = Ca, Mn, Fe, etc.).

Sorption of metal ions on calcite may involve more than one type of reaction. One possibility is exchange of metal ions with Ca in exposed structural lattice sites, and another is complexation to carbonate groups bound in a disordered hydrated surface layer. In a study by Sturchio and co-workers (1997), using a combination of synchrotron X-ray standing wave (XSW) and X-ray reflectivity techniques to investigate Pb adsorption at the calcite-water interface, it was found that majority of Pb adsorbed on calcite occupied the Ca sites in the calcite surface layer, despite the large ionic radius of Pb (120 pm) relative to Ca (99 pm). The authors explained this phenomenon in terms of thermodynamic driving force, taking into consideration the balance between the lattice Coulomb energies, the oversize repulsive energy, the hydration energy and additional energies of comparable importance. A different conclusion was reached in a study by Kozar and co-workers (1992) of single and simultaneous adsorptions of Pb^{2+} and Cd^{2+} in systems comprising a commercial calcite in calcareous river water of various salinities, where it was found that the adsorption isotherms for simultaneous adsorptions of the metal ions at a salinity unit tested were negligibly different from the isotherms for the adsorptions of single ions. The authors speculated that lead and cadmium ions were adsorbed at different surface sites of the calcite, and since Pb was known to have strong affinity for the CO_3^{2-} ligand (Bilinski and Schindler, 1982) and the ionic radius of Pb^{2+} was greater than that of Ca^{2+}, the adsorption of Pb was suggested to occur via the CO_3^{2-}surface group. In contrast, Cd^{2+} has low affinity for CO_3^{2-} ions but has almost identical ionic radius to that of Ca^{2+}, and the authors, therefore, suggested that Cd^{2+} exchanged with Ca^{2+} at the calcite surface. It could be noted here that for Pb, discrimination between coprecipitated and adsorbed Pb on calcite was reported to be possible by examining two types of prepared particle using surface analysis techniques, such as XPS and secondary ion mass spectrometry (SIMS) (Fulghum et al., 1988; Wouters et al., 1988). In a kinetic study of Cd adsorption, McBride (1980) found that the quantity of Cd removal from solution onto pure calcite depended upon the calcite particle size (with high surface area favouring more immobilization); this suggested that adsorption was the predominant process involved in the Cd^{2+} retention. However, Davis and co-workers (1987) remarked that the observation of McBride (1980) might have involved the formation of solid solution in a surface film.

Davis and co-workers (1987), based on the results from their study on the kinetics of the Cd^{2+} sorption process at the calcite surface, proposed that the process comprised an adsorption reaction of Cd^{2+} to CO_3^{2-} at easily accessible sites on the hydrated $CaCO_3$ layer, followed by diffusion of the Cd^{2+} into the overlying layer of the crystalline calcite, and a recrystalization as an ordered solid-solution mixture of Cd-Ca carbonate on the upper most layer of the crystal. It was found that the adsorption reaction was fast and the diffusion process appeared to reach completion within 24 hours, but the recrystalization proceeded at a slow and nearly constant rate for at least 7 days. The rate of desorption of Cd^{2+} from the hydrated layer was also found to be slow. Stipp and co-workers (1992), applying near-surface sensitive techniques (XPS, LEED), and Auger electron spectroscopy (AES) to investigate interface processes of Cd^{2+} uptake by pure calcite crystals exposed to aqueous solutions containing various concentrations of the metal ions, also found that the main processes involved were adsorption and solid-state diffusion into the crystal, which resulted in the formation of a solid-solution. In an investigation by Zachara and co-workers (1991) of sorptions of seven divalent metals (Ba, Sr, Cd, Mn, Zn, Co and Ni) on calcite, the sorption was found to follow the sequence $Cd > Zn \geq Mn > Co > Ni >> Ba = Sr$. The metals varied in their sorption reversibility, a factor which was found to correlate with the single-ion hydration energies of the metal sorbates. The strongly hydrated metals (Zn, Co, and Ni) were most desorbable. The authors found that the resulting sorptions compared well with the use of a sorption model that included aqueous speciation and Me^{2+} - Ca^{2+} exchange on cation-specific surface sites. Exchange constants for the surface complexes were not uniformly correlated with any single property of the metal ions, but found to correlate, in part, with the ionic radius of the metal sorbates, and the solubility products of $MeCO_3$ (s) solids. The sorption of Cd, Mn, Co, and Ni could be described by a single exchange constant over a wide range of pH values, Ca concentrations, and surface concentrations, while the sorption of Zn exhibited non-linear behaviour and required exchange constants that varied with surface coverage. The data for Cd and Mn were found to suggest that the metals dehydrated soon after their adsorption to calcite and formed a phase that behaved like a surface precipitate (this was found to be consistent in trend with the model of Davis et al., 1987). In contrast, Zachara and co-workers (1991) noted that Zn, Co, and Ni appeared to form surface complexes that remain hydrated until the ions were incorporated into the structure by recrystallization. In a study by Zachara and co-workers (1988) of Zn adsorption on calcite, it was speculated that the process occurred via exchange of Zn^{2+} and $ZnOH^+$ with surface-bound Ca^{2+}. The identification of $ZnOH^+$ as a sorbing species reduced the likelihood of strict lattice replacement because the ionic size of $ZnOH^+$ exceeded that of Ca^{2+}. However, the authors noted that the less than one-to-one Zn^{2+} to Ca^{2+} exchange stoichiometry at certain Zn concentrations suggested binding to sites that were not fully occupied with Ca^{2+}, as might be expected in an adsorbed layer with hydrated anionic sites.

1.4.6. Influence of multicomponent solids on metal distributions.

As outlined above, a large number of studies have revealed that mineral oxides, organic matter, and carbonates can significantly influence the distribution of metals. Most of these studies, however, dealt with retention on relatively well-defined or simplified solid systems. By contrast, in nature, multicomponent solids commonly occur as a result of the interactions of components with each other. Examples of these reactions include dissolution, adsorption, surface precipitation, and colloidal adhesion/ aggregation. The bulk and surface properties (e.g., surface charge, Tipping and Cooke, 1982) of the heterogeneous solids are thus modified, and as a consequence their adsorptive characteristics for metal ions may well be different from those of the original pure components. Many researchers have attempted to model distributions of trace metal ions and anions among multicomponent solids, e.g., deep-ocean particulate matter (Balistrieri et al., 1981), and noncalcareous soils (Goldberg and Sposito, 1984b). Anderson and Benjamin (1990b,c) remarked that what these models generally had in common was the simplifying assumption referred to as an "adsorptive additivity" (noninteracting solids) proposed by Honeyman (1984). According to this concept, adsorptive properties of mixtures could be predicted from a weighted average of the adsorptive properties of the mineral components, that is an addition of a second adsorbent to a system should increase the total amount of metal adsorbed, given other things being equal. However, several studies using binary solid systems have reported that when a second adsorbent is present in the system, the metal sorption results could range from enhanced sorption to diminished sorption to no effect (Hatton and Pickering, 1980; Anderson and Benjamin, 1990a; Siegel et al., 1992). Responses are found to depend on the specific adsorbents and adsorbates under investigation and solution pH, and follow no apparent pattern. Palmer and co-workers (1981), Altmann (1984), and Honeyman (1984) remarked, as summarized by Siegel and co-workers (1992), that in general the adsorptive additivity concept was found to be invalid for the oxide-silicate and oxide-organic systems investigated and that the adsorption constants obtained in single-solute/ single-sorbent systems could not be used in multi-solute/ multi-site systems. Anderson and Benjamin (1990b,c) suggested that a modified adsorptive additivity concept was appropriate for modeling a few specific systems.

Several multicomponent systems have been investigated in relation to their potential effects on metal distributions; for example, Fe/ Mn/ Al (oxyhydr)oxides and organic compounds (Davis and Leckie, 1978; Davis, 1984; Kedziorek and Bourg, 1996), Fe (oxyhydr)oxides and clay minerals (Siegel et al., 1992), clay minerals and humic materials (Hatton and Pickering, 1980; Baham and Sposito, 1994; Schnitzer, 1995; Kedziorek and Bourg, 1996), and oxides of Al, Fe, and Si (Anderson and Benjamin, 1990a,b,c).

Hatton and Pickering (1980) studied the effect of pH (range from 3 to 10) on the individual retention of Cu, Pb, Zn, and Cd by mixtures of a humic acid (commercials or soil extracts) and a clay (kaolinite, illite or montmorillonite). The equilibrium metal concentration values obtained from the binary phase systems were plotted as a function of solution pH, and compared with those predicted from the summation of the effects observed using similar amounts of each adsorbent individually. The authors found that the amount of Cu, Pb, Zn, and Cd retained by mixed suspensions varied markedly with pH, the nature of the clay, and the chemical nature of the organic components. For example, the adsorption values of the metals obtained from the mixtures of a commercial humic acid and illite in acidic ($pH < 6$) media were found to agree well with those predicted. However, in almost all of the acidic mixtures of humic acid and montmorillonite investigated, the sorption values of Cu and Zn were found to be significantly less than those predicted by combining clay and humic acid effects, but greater than those observed using humic acid only. The authors attributed this to varying degrees of adsorbent interaction in that the stereochemistry of the Cu and Zn humate complexes allowed bridging between the two adsorbents, either through the formation of the Cu^{2+} or Zn^{2+} forms of montmorillonite promoting adsorption of humic acids, or through cationic Cu or Zn humate complexes competing for clay surface sites. The authors noted that in general, in acidic media humic acids had a tendency to dominate the adsorption process, however, in alkaline media there was competition between the ability of humic acids to form soluble metal humates and the tendency of the clays to strongly retain the sparingly soluble metal hydroxy species formed at $pH > 6$, and in most systems studied retention by the solid phase predominated. Anderson and Benjamin (1990a) investigated the bulk and surface characteristics of binary oxide suspensions of Al, Fe, and Si and assessed how they differed from their component parts. Batch adsorption experiments were performed for Ag, Cd, PO_4, SeO_3, and Zn, and the resulting adsorption behaviours obtained from individual phase systems were compared with those from binary phase systems. The binary systems of the oxide suspensions involved (i) $Al(OH)_3$ and $Fe(OH)_3$, and (ii) SiO_2 with either $Al(OH)_3$ or $Fe(OH)_3$. The oxide suspensions of Al and Fe were prepared by either coprecipitation or mixing the individual solid suspensions, whereas the suspensions with SiO_2 were prepared in a different manner, i.e., sequential precipitation or mixing aged Al or Fe suspensions with a suspension of SiO_2. The authors found that the adsorption curves (fractional removal vs pH) of Cd, Zn, and Ag obtained from single solid systems were typical for metal cation adsorption onto oxide surfaces (i.e., the adsorption increased as pH increased).

The adsorption results of the metals from Al-Fe binary oxide suspensions revealed a slight enhancement in Zn removal in both the coprecipitated and mixed binary systems compared to the systems with $Al(OH)_3$ or $Fe(OH)_3$ only. In contrast, the removal of Cd from the solutions of both Al-Fe binary systems were found to be higher than that of the individual $Al(OH)_3$ system, but less than that of the individual $Fe(OH)_3$ suspension (the results for Ag were found to parallel those of Cd). The differences between the behaviours of Cd and Zn was further investigated in the series of coprecipitated Al-Fe binary systems which contained a constant concentration of Fe but varying Al concentrations. The authors found that with increasing Al, Zn removal increased, but the removal of Cd was always inhibited compared to a system with no Al at all. In an attempt to identify the underlying cause of the different responses of Cd and Zn, the authors compared physical and chemical properties of the solids in the binary suspensions with those in the individual solid systems. The properties determined included particle size distribution, point of zero charge (PZC), specific surface areas, and electron-binding energies and stoichiometry of the top few molecular layers of the solids (using XPS). The authors found that the particle size distributions in both Al-Fe binary systems (mixed and coprecipitated) were different from those in the pure $Al(OH)_3$ and $Fe(OH)_3$ suspensions, and that the majority of the particle sizes of greater than 10 μm in a pure $Fe(OH)_3$ suspension vanished when $Al(OH)_3$ was added into the systems.

The measured specific surface areas in the Al-Fe binary suspensions were found more than double the expected values. The authors remarked that the results of the particle size distribution patterns and the specific surface areas suggested that small amounts of $Al(OH)_3$ dissolved, migrated to the surface of $Fe(OH)_3$ agglomerates, and caused them to disaggregate. The results from XPS analyses were in support of the hypothesis that Al was enriched at the surface of particles in the Al-Fe binary suspensions, representing about 70 - 80% of the surface metal atoms. The PZC determination revealed that the PZC of the particles in the binary systems approximated that of pure $Al(OH)_3$ particles, indicating that $Al(OH)_3$ strongly dominated the particles' acid/ base reactions with solution. The authors remarked that the most likely process consistent with these findings involved partial dissolution of $Al(OH)_3$ particles and adsorption or reprecipitation on the surface of the $Fe(OH)_3$. This was also found to be in agreement with the observation that at the solid concentrations studied, Cd and Ag bound less to $Al(OH)_3$ than to $Fe(OH)_3$, while Zn had approximately equal removal onto the two surfaces. Therefore, the replacement of an Fe surface by an Al surface might weaken the Cd-surface and Ag-surface bonds, while not affecting Zn sorption very much. The postulated surface coating and site replacement were also found to be consistent with the observations that the removals of the metals investigated in the coprecipitated Al-Fe binary systems, rather than those in the mixed suspension, were closer to the removals of the metals in the individual $Al(OH)_3$ suspension (i.e., the process of surface coating and site replacement was expected to be more complete when the Al and Fe were coprecipitated than when the preformed solids were mixed). In the case of SiO_2 binary suspensions, the adsorptions of all the metals studied in the binary systems were nearly the same as if the SiO_2 was not present, regardless of whether the other adsorbent was precipitated in the presence or absence of SiO_2. The authors found that in contrast with the Al-Fe systems, for the SiO_2 suspensions the shape of the particle size distribution for the mixed Fe-Si and Al-Si systems revealed that the larger particles (which in these systems were apparently the SiO_2) remained in the suspensions, but the smaller and intermediate-size particles (the $Al(OH)_3$ and $Fe(OH)_3$) were lost. The specific surface areas of the binary systems with SiO_2 were found to be similar to the expected values from the noninteracting particles. The XPS indicated that Al was enriched at the surface in the Si-Al system, while Si was surface enriched in the Si-Fe system. The PZC of both binary systems with SiO_2 were found to be similar to those of individual $Al(OH)_3$ or $Fe(OH)_3$. The authors, therefore, deduced that for the binary systems with SiO_2, the $Al(OH)_3$ and $Fe(OH)_3$ particles disappeared as distinct entities and became associated with the larger SiO_2, and that whatever this association was, the $Al(OH)_3$ or $Fe(OH)_3$ at the SiO_2 surface had essentially the same cation adsorbent properties as when they were alone in suspension. In addition, the SiO_2 surface was substantially shielded from interactions with the solution in the mixed systems. The authors remarked that the results from their study indicated that particle interactions could affect trace element distribution and transport processes by influencing adsorbent surface characteristics and adsorbent particle size, and that the experiments involving $Al(OH)_3$ implied that, as a result of processes such as dissolution and sorption, aluminum oxides could mask the presence of other solid surfaces and play a dominant role in aquatic environments. In a continuation of this work, Anderson and Benjamin (1990b) attempted to adapt the available constant-capacitance surface complexation model to quantitatively describe the previous sorption results (adsorptive non-additivity) and the changes in the physical characteristics of the solids. The model was modified in various ways to test a few of the possible scenarios, such as that the dissolved Al competed with other adsorbates for $Fe(OH)_3$ surface binding sites, and $Al(OH)_3$ on the mixed solid blocked and replaced $Fe(OH)_3$ sites with new binding sites. Some computer programs were used to select surface complexation constants for the adsorbates in the single-oxide suspensions, and these constants were used in all subsequent modeling. With some assumptions for each model calculation, the authors concluded that in general the model results of the latter scenario were in better agreement with the experimental results than those of the former simulation. The relative roles of several factors that might affect adsorption behaviour in a system were coating form, including the relative affinity of the adsorbate for the mineral that forms the coating versus the mineral being coated, their relative surface site densities, and the fractional dissolution of the coating mineral. The net effects of these factors was that adsorption of Zn, which had a fairly strong intrinsic preference for Al sites, increased slightly when Al was added, but sorption of Cd, which had a weaker intrinsic preference, decreased significantly. Anderson and Benjamin (1990c) remarked that a similar modeling effort for binary systems of SiO_2 and $Al(OH)_3$ or $Fe(OH)_3$ suggested a process involving partial SiO_2 dissolution. The model results, in agreement with experimental results, indicated that the presence of soluble Si interferes with the adsorption of anionic adsorbates (e.g., Se_2O_3, PO_4) but has little effect on cationic adsorbates. Siegel and co-workers (1992) arrived at a more traditional conclusion in their study on Pb adsorption in multi-phase systems containing synthetic goethite and a clay mineral (Ca-montmorillonite), with an inert matrix (quartz sand). The experiments were carried out over a pH range of approximately 3.5 - 7.5, with two initial concentrations of Pb but systematically varying concentrations of the oxide and silicate over quite a wide range. The authors compared adsorption behaviour of Pb in the individual phase systems with that in the mixtures. The results were that at a constant concentration of goethite, and low concentrations of clay, the adsorption curves of Pb in the mixtures were similar to that of the individual oxide system (i.e., goethite dominated the adsorptive behaviour of the mixtures). At the highest clay concentration investigated, the adsorptive response of the mixture increased and this seemed to be in response to the clay. The conclusion was therefore made that the adsorptive behaviour of the mixture depended on the relative concentrations of the individual components and the metal-binding strengths of the two types of sites (clay was considered to possess fixed-charge sites, and amphoteric Si-OH and Al-OH sites, whereas the oxide provided amphoteric Fe-OH sites), and that this reflected the competition between the two minerals. The authors further compared the experimental adsorption results to the modeling results (the calculations of the relevant parameters, such as surface complexation constants for adsorption of Pb on the individual phases, were based on literature figures), and found that they were reasonably similar at all the ratios of minerals : Pb, and the range of pH studied. Based on these findings, the authors were convinced that it would be possible to model and predict the adsorption of metals by complex mixtures of multiple minerals by understanding the adsorption of metals in simpler systems. Kedziorek and Bourg (1996) investigated solubilization (remobilization) of Pb, Ni, and Cd from spiked kaolinite, Fe oxide, and humic acid vs dual-component model solids, as a function of pH. For individual kaolinite or Fe oxide, the solubilization of heavy metals was found to decrease with increasing pH; in the case of Fe oxide, none of the metals was found to solubilize when the systems had reached a pH of about 6. In contrast, for individual humic acid, the solubility of heavy metals increased rapidly above pH 3; this was found to be consistent with the dissolution pattern of the humic acid (% remobilized organic carbon vs pH). In dual-component, humic acid and amorphous Fe oxide systems, at low pH it was found that the solubilization of heavy metals was greater than predicted on the basis of purely additive dissolution behaviour, and this was particularly notable in highly acidic medium of pH < 2.5. The authors noted that at this pH range the humic acid was strongly linked to the surface of the Fe oxide, and part of the metal load was solubilized because protons competed with heavy metals for binding to humic acid functional groups. At a higher pH range of ≥ 5, it was found that the predicted values were higher than the observed ones; this was attributed to the domination of sorption by the oxide over the humic acid under these conditions.

Davis and Leckie (1978) investigated changes in Cu uptake that result when Fe oxide surfaces were modified by adsorbed organic compounds, such as glutamic acid, salicylic acid and picolinic acid. They considered that these complexing ligands were useful models because their chemical structures and functional groups (e.g., phenolic and carboxylic) were similar to those of naturally-occurring humic substances. The authors compared adsorption curves obtained from the systems containing (i) Cu and Fe oxide in the absence of a ligand, (ii) Fe oxide, with varying concentrations of a ligand, and (iii) Cu, Fe oxide, and a ligand. The total concentrations of Cu, the oxide, and the ionic strength of the solutions were kept consistent among these systems. In the absence of ligand, the percentage adsorption of Cu onto Fe oxides increased with increasing pH, and reached a plateau at pH of about 6.5. Most of the complexing ligands at their concentrations tested were found significantly adsorbed onto Fe oxide in the pH range from the lowest tested, 4, to about 6.5. The authors found that the effects on the adsorption of Cu onto the oxides varied widely among the complexing compounds. In the cases where ligands enhanced the Cu adsorption, the authors speculated that it might be because the metal-ligand complexes could adsorb onto the oxide surface, and/ or the metal could be complexed by the adsorbed ligands, i.e., functional groups of the adsorbed ligand might serve as "new adsorption sites" for Cu at the surface (which might be more reactive than an isolated oxide surface site), or might simply stabilized adjacent surface sites. In the cases where the ligands had a minor effect on or decreased the Cu adsorption, the authors speculated that the major coordinating functional groups of the adsorbed complexing ligand might be involved in surface bonding with the Fe oxide, and as a consequence, the adsorbed compound could not function as a complexing site for the Cu. This implied the importance of the orientation of an adsorbed ligand in determining the overall effect on Cu uptake by the oxide. However, the authors remarked that the magnitude of the effect of complexing ligands on metal uptake also depended on the relative intensities of metal binding by the complexing ligands and the oxide surface. Results from this study were said to suggest that the distribution of trace metals in natural aqueous systems might be controlled by surface binding on colloidal particles coated with humic compounds rather than reactions with simple oxide surface sites, and complexation of metal ions at the surfaces of natural particulate matter might resemble complexation with dissolved humic compounds.

1.4.7. Use of synthetic model soils.

The solid phases used in this study are regarded as only approximate representatives of their naturally occurring analogues in soils and sediments. For instance, they are relatively pure and have not been subjected to environmental modifications brought about by weathering. However, each solid phase used in this study not only represents a major Pb-adsorbing phase commonly found in soils/ sediments, but also corresponds to the chemical classes targeted by each stage of a sequential extraction procedure of Tessier et al. (1979) investigated in this study.

Synthetic models are of a much lower complexity than natural soils and sediments, and are certainly not expected to provide information about the expected behaviour of all systems. In view of the complexity of the natural systems, the advantage of the use of manageable synthetic models in this study is that they allow us enough control over the systems to enable us to focus on particular processes of interest, in the hope of gaining better understanding the factors effecting the performance of sequential extractions (see *section 1.6.* below) at a fundamental level.

Difficulties in extrapolating the results from laboratory synthetic models to natural soil systems are recognized. However, mixing natural samples with a spiked phase serves to bridge the gap, and allows us to move a step closer to the real situation.

1.5. Speciation.

1.5.1. General overview.

The term *speciation* has been used to encompass the identification and quantification of forms in which an element occurs in a given matrix. This could involve species of metals, metalloids and organometallic compounds (Lund, 1990; Das et al., 1995). According to several investigators, such as Kersten and Forstner (1994), Ritchie and Sposito (1994), and Ure and Davidson (1994), in current use, the term speciation can be applied from any one of the following three perspectives; (i) a functional process, such as plant nutrient uptake (e.g., "available" and "unavailable" forms); toxicity (e.g., "biologically active" form); and mobility (e.g., "readily leacheable" and "slowly leacheable"); (ii) the operational process of detection and quantitation used (e.g., acid/ water soluble fractions, and certain particle size fragments), and (iii) specific molecular forms of the compounds or elements (e.g., types of bonding between an element and other matrix components). Tack and Verloo (1995) remarked that the term *fractionation* is frequently used intermittently with speciation but emphasizes the concept of subdividing a "total content" (also, the analytical preparations for separating metal species are referred to as "fractionation").

It has been widely recognized that the knowledge of specific chemical forms of elements, rather than their total levels, is essential for developing understandings of their behaviour and fate in the environment (Bernhard et al., 1984). Elements in different forms will generally exhibit different chemical activities; this influences the corresponding characteristics of mobility, biological availability, toxicity, and distribution. Although the total content/ concentration of an element determines its pool size, Tessier and Campbell (1987) remarked that this measurement provided little indication of potential interactions of the element with the abiotic or biotic components present in the environment. From an environmental impact point of view, speciation does not necessarily produce the whole picture, however, the total amount is not in itself sufficient information to assess the impact of the element on contaminated soils and sediments. Howard (1988) noted that the activity of trace element in aquatic systems might also be influenced by physical factors, such as the disturbance of sediment layers by natural turbulence or by mechanical dredging; these physical disturbances can expose new sediment-water interfaces for exchange of the element. In a review by Millward (1995), based on field observations, controlled laboratory experiments, and biogeochemical models, is discussed some principal processes influencing the speciation of trace metals in estuaries.

Speciation analysis is regarded as being more challenging than determination of total elemental contents (Pickering, 1994); this is attributed to difficulties associated with isolating the compound(s) of interest from complex matrices. In addition, most of the speciation techniques available disturb (to some extent) the equilibria existing between the various chemical species present in the system under investigation, and suitable standard reference materials are often not available. For trace elements, Lund (1990) emphasized that the analytical difficulties were not only related to the choice of relevant techniques for measuring the individual species, but also to the fact that the concentration of the elements is often so low that even the total concentration is extremely difficult to determine; a further fractionation was then rarely possible, unless preconcentration techniques that would not disturb the species distribution were available. Das and co-workers (1995) remarked that much of the published work had dealt with the determination of trace metal species in natural waters and now it was possible to determine ng g^{-1} quantities in aqueous systems, but not in solid matrices. A range of speciation strategies including instrumental techniques are applied for determination of chemical speciation of metals in solid and liquid phases; these fall into categories such as electroanalysis, spectroscopy, chromatography, and physico-chemical fractionation (Pickering, 1994; Tack and Verloo, 1995) (an outline of techniques for the speciation of metals in solid matrices is provided in the following subsection). Greenway (1994) noted that, in general, it was necessary to use at least two analytical techniques; the first is used to separate the species, which may then be identified in the separation process or may be identified and quantified by the second analytical technique. In recent years, the coupling of different separation and preconcentration techniques with various instruments, in which the separation and elemental detection processes occurs on-line, are increasingly established. The coupled or hybrid techniques are noted for being less time consuming and for their potential to minimize the losses of analytes.

The increasing availability of coupled speciation methods led Das and co-workers (1995) (in a paper on metal speciation in solid matrices) to conclude that speciation studies are expected to be more widely applied in the near future. In addition, the approaches which have been used to date in studying speciation, namely (i) the identification of unknown species by rigorous methods, and (ii) the identification of compounds in experimental samples by comparison with standard compounds, will both be required in the future; in this respect, there is a need both for stable certified materials and fast accurate speciation methods.

1.5.2. Speciation of metals associated with solid phases.

For solid samples, techniques that have been used to determine speciations of trace elements include both direct instrumental methods, and indirect and non-instrumental methods. Methods in the former category include scanning electron microscopy/ energy dispersive microanalysis (SEM/ EDX), certain X-ray techniques (X-ray diffraction, photoelectron spectroscopy, and particle-induced X-ray emission spectrometry (PIXE)), and vibrational spectroscopy (Glidewell and Goodman, 1994). Methods in the latter category include calculations based on conditional equilibrium constants, chemical single and sequential extraction procedures, and ion exchange resins. Techniques used for metal speciation in solid matrices are discussed in several publications, such as those of Kersten and Forstner (1989) (sediment), Ure (1990) (soil), and Das and co-workers (1995) (soil and sediment, and including other matrices, such as solid biological and food materials). Tack and Verloo (1995) remarked that the development of solid phase speciation techniques is still in an early stage, where method development should primarily be aimed at increasing selectivity and specificity; this can be contrasted with the current situation for speciation analysis in solution, where the main analytical challenge is to improve sensitivity.

Instrumental methods are generally of limited application to solid speciation determination because of their insensitivity to the low concentrations of metals which are generally found in the environment, as well as the frequently non-stoichiometric nature of such species and structural and chemical complexity of host matrices (Kersten and Forstner, 1989). Desimoni and co-workers (1992) applied X-ray photoelectron spectroscopy (XPS) to environmental specimens of airborne particulate matter, industrial dust and volcanic rock. The authors noted that although the technique seemed to be useful in giving direct information on the chemical nature of surface atoms, there were some fairly significant problems associated with the use of the technique, e.g., surface charging, and the huge number of possible constituents (therefore requiring the analysis of a series of proper standards, and as a result, being costly and time-consuming). In recent years, an X-ray absorption spectroscopic (XAS) method has been investigated for its capability in providing information about the local environment around a sorbed element (some examples of the use of XAS to investigate metal sorption on Fe and Mn oxides have been outlined in *section 1.4.*). Brown, Jr. and co-workers (1989) applied a synchrotron-based Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) system in their study of metal complexes sorbed at oxide/ water interfaces (cobalt on γ-Al_2O_3 and TiO_2, lead on γ-Al_2O_3, and selenium oxo-anions on α-FeOOH). The authors derived average bond distances, numbers, and identities of first- and second-neighbours surrounding the sorbed atoms in these samples. From this information they were able to deduce, for example, that Co^{2+} (at pH 6.8) formed inner-sphere complexes on γ-Al_2O_3 and TiO_2 and formed multi-nuclear complexes on γ-Al_2O_3, but smaller polymers or monomeric complexes on TiO_2; Pb^{2+} (at pH 6.0) probably formed dimeric or a combination of monomeric and small multi-nuclear complexes; and selenate was sorbed as an outer-sphere complex (at pH 3.5), whereas selenite was sorbed as an inner-sphere, bi-dentate complex (at pH 5.6) on α-FeOOH. Manceau and co-workers (1996) examined the potential of EXAFS to speciate and quantify the forms of Pb in contaminated soils sampled from nearby three different sorts of industrial activities, namely, an alkylead production plant (for gasoline antiknocks), a lead battery reclamation facility and a Pb-Zn smelter. The authors concluded that in soil contaminated by alkyllead compounds, Pb was in the divalent form and complexed to salicylate and catechol-type functional groups of humic substances. In the vicinity of the battery reclamation area, Pb was reported to be predominantly in sulfate and silicate-bound forms. The authors concluded that Pb near the smelter was in divalent forms and coordinated to O and OH ligands; however, they also noted that the metal was present in several chemical forms, which prevented the species from being identified individually. It was thought that the multiplicity of Pb species in soils contaminated by smelting activities was due to the long-term nature of the atmospheric emissions and to the variety of Pb-containing phases simultaneously, and successively, emitted to the atmosphere. The authors suggested that the technique could probably be applied to a variety of matrices including sediments, solid and liquid wastes, and fly ash particles. In assessing remediation strategies for a Superfund site, Hesterberg and co-workers (1997) used EXAFS to determine whether Pb and Zn sulfides were dominant mineral phases in contaminated aquifer solid samples. It was found that Pb sulfide, PbO, $PbCO_3$, $PbSO_4$, and ZnO were not dominant metal species.

Calculations based on conditional equilibrium constants have been noted as having little practical application to molecular speciations of trace elements in solid systems because of the wide variability and usually incomplete availability of such "constants" for many natural systems. Kersten and Forstner (1989) noted that thermodynamic models gave suggestions as to the expected trace element species distributions, but might yield results far removed from the real solid speciation because of the important role of kinetically controlled processes in biogeochemistry. The modeling of the behaviour of sediment-bound metals is regarded as being far less advanced than is the modeling of dissolved species (Tessier and Campbell, 1987). Nevertheless, in some studies, thermodynamic calculations have been applied for determination of partitioning of metal between different geochemical phases in sediment systems (Oakley et al., 1981; sulfide-bearing sediment, Wallmann et al., 1993). Oakley and co-workers (1981) proposed the use of a simple theoretical equilibrium adsorption model which uses conditional equilibrium constants (K_{AD}) determined from linear portions ($K_{AD} = [MeS]/([Me_T]\ \{S_T\})$) of adsorption isotherms (i.e., when $\lambda\{S_T\} >> [MeS]$, where λ is the number of moles of surface sites per unit mass of adsorbent, $\{S_T\}$ is the total concentration of the solid phase in g litre^{-1}, [MeS] is the concentration of metal-solid complex in mol litre^{-1}, and $[Me_T]$ is the total soluble trace-metal concentration for metal Me in mol litre^{-1}. That is, the adsorption of the trace metal must have only a negligible effect on the total concentration of available surface sites). The fraction of metal adsorbed on a particular solid phase was proposed to be: $[MeS\ (k)]/\ [Me_{ST}] = K_{AD}(k)\ \{S_T(k)\}/\ (1+ \Sigma^k\ K_{AD}(k)\ \{S_T(k)\})$, where $[Me_{ST}]$ is the total concentration of metal in the system, both soluble and adsorbed, and k is numbers of competing solid surfaces. As a test of the usefulness of the model, the authors examined the adsorption and the partitionings of Cu and Cd on artificial solid phases, namely, a bentonite clay, $Fe(OH)_3$, MnO_2, and humic acid. Values of K_{AD} for each metal investigated and for each of the four solid phases were determined from laboratory adsorption experiments in seawater media. All of the isotherms exhibited a linear portion in which the assumptions were valid; the equilibrium soluble-metal concentrations within the linear range were found to be well above those typically measured in estuaries and coastal waters (i.e., valid for concentrations of Cu and Cd likely to be encountered in the natural environment). Cu was found to exhibit a much higher affinity than Cd for all solid phases. The K_{AD} for Cu-humic acid was found to be high relative to the other three phases; whereas, the K_{AD} for Cd-humic acid was found to be low relative to the other three phases. The hydrous manganese oxides showed the highest K_{AD} values for both Cu and Cd. The authors remarked that based on the K_{AD} values estimated, and the fact that the true solution concentration of the solid phases in a typical sediment were within the high mg litre^{-1} to g litre^{-1} range, the term $(1+ \Sigma^k K_{AD}(k) \{S_T(k)\})$ in the second equation shown above could be reduced to $\Sigma^k K_{AD}(k) \{S_T(k)\}$. The concentrations of solid phases in a sediment based on a weight basis (in %) were estimated from those cited in the literature; the authors noted that although these values might not be representative of all geographical areas, they gave an approximation of the orders of magnitude of concentrations that it would be reasonable to utilize in their study. Distributions of Cu and Cd for various concentrations of hydrous oxides, clay, and humic acids (within the ranges cited) were plotted (i.e., % metal in geochemical phases vs % clay in sediment, whereas other components were fixed). It was found that except for cases where the humic acid concentration was high, clay was the dominant sink for both Cu and Cd. The authors, however, noted that much more research needed to be done to enable this model to be applied to natural systems.

As an alternative, at present the least complicated and widely used set of techniques to identify trace element partitionings between various solid phases are those which involve chemical extractions. The principle of the extractions is generally based on the supposed selectivity of the extractants toward the specific physicochemical forms. Chemical extractions yield distributions which are operationally defined, and as a consequence the results given by the procedures are interpreted as being reflective of chemical reactivity and species distribution patterns rather than true molecular species. The extractions can be carried out either by undertaking a series of separate analyses using different aliquots of the solid samples, or utilizing a sequence of selective extractants on a single sample of the solid. Quevauviller and co-workers (1994) noted that the use of single and sequential extraction procedures had increased over the previous 10 years.

Single reagent leaching extraction is most often used to assess the "bioavailable" fraction of elements in various solid samples, including soils (e.g., those amended with sewage sludge) and sediments; the results are frequently correlated with plant uptake or toxicity and nutritional deficiency effects (Lindsay and Norvell, 1978; Hani and Gupta, 1985) ("available" forms of metal cations are usually referred to as"easily exchangeable" and "organically-bound" ions). Tack and Verloo (1993) suggested that the appropriate leaching test simulating natural field conditions could be used in assessing possible environmental effects occurring in dredged sediment material upon dewatering and consolidation, since changes in the material might result in significant modifications in leaching behaviour without influencing the chemical fractionation to an important extent. A range of single extractants have been widely used for routine monitoring of soils for the available metal concentrations (summarized in the reviews by Lake and co-workers (1984), and Alloway and Jackson (1991)); the frequently used reagents appear to be dilute solutions of $NaNO_3$, $CaCl_2$, EDTA, and DTPA (diethylenetriaminepentaacetic acid). In recent years, the Commission of the European Communities has been attempting to harmonize single (and sequential) extraction procedures. Single extractants investigated for their potential use in heavy metal speciation included solutions with different concentrations of EDTA, acetic acid, and ammonium acetate (Ure, 1996). EDTA was chosen as the most suitable overall, it being noted that this reagent could be regarded as extracting the metals in all the non-silicate-bound soil phases, and results from its use are likely to reflect the metal availability in both the short-term and relatively long-term. Acetic acid has similar qualities but its effectiveness is limited in highly calcareous soils (probably due to neutralization). Ammonium acetate, which is capable of extracting the readily exchangeable species, was regarded as an appropriate reagent for use on neutral alkaline soils and is also suited to agricultural needs where the compound is used as a component in fertilizer. Certified reference soils listing the portions of each metal extractable by EDTA and by acetic acid are commercially available. A collection of recent studies highlighting the use of single extraction procedures in soil research and corresponding research trends can be found in a workshop report edited by Quevauviller (1996).

The use of a sequence of chemical reagents to distinguish between different physico-chemical states of metals is outlined in the following section. It could, however, be noted here that sequential extraction procedures are regarded as providing more information than single leaching tests, and have some advantages over them. The use of sequential extraction schemes are thought to give more detailed information on the origin, mode of occurrence, biological and physicochemical availability, potential mobilization, and transport of trace metals. As summarized by Das and co-workers (1995), the sequential extraction procedure tends to more readily identify the sediment component(s) responsible for retaining the majority of the elements; therefore, it is considered an essential tool in establishing element partitioning. The extraction is also comparable to various natural and anthropogenic procedures in that it simulates changes in environmental conditions; therefore it is an important means in estimating potential remobilization of metals under such environmental changes. In addition, the results can be checked for internal consistency (i.e., total sum of all fraction should be more or less 100%).

In recent years, several investigators have proposed ion exchangers (in the different forms, e.g., bead or membrane) as an alternate approach for speciation of metal in solid samples, such as soils, sediments, and sludges (in *subsection 1.7.1.* is outlined features of some ion exchangers and their potential application in this present study). Recovery of metal of interest by ion exchangers in equilibration with an aqueous suspension of solid sample are frequently compared with that obtained by single chemical extraction, using a dilute mineral acid (e.g., HCl, electrolyte solution (e.g., $CaCl_2$), or a chelating agent (e.g., EDTA, or DTPA); the results are often discussed in relation to the potential in determining bioavailability of the metal. In several studies a strong correlation has been identified between the amount of metal extracted by chelating materials and the amount taken up by plants (Hamilton and Westermann, 1991; Jing and Logan, 1991; Lee and Zheng, 1993). Beveridge and co-workers (1989a) remarked that the transfer to the exchanger materials might simulate natural processes (e.g., uptake by roots) more closely than direct chemical attack. Introduction of different exchanger materials such as strong-/ weak-acids, or chelating forms (to yield a different system pH and/ or cation affinity) has been proposed for allowing a subdivision of total metal content to several categories (Slavek et al., 1990; Liang and Schoenau, 1996). In an assessment of labile metal content of sediments by Slavek and co-workers (1990), the sediment suspensions were mixed overnight with sulfonated-/ carboxylated-cation exchanger resins (H^+ and Na^+ forms), or chelating resins possessing either iminodiacetate or aminophosphonate (Na^+ form); the cations transferred from the sediment were subsequently back-extracted from the resins into EDTA solution. The EDTA extracts were analyzed for several metals; the corresponding results were designated as low-pH labile (RSO_3H), weak-acid labile (RCOOH), exchangeable and readily desorbed at sediment-suspension pH (RSO_3Na), weak-base labile (RCOONa), high-pH labile (chelating resins), non-labile soluble forms (i.e., aqueous fractions of metals that left in contact with the sediment residue), and detrital/ non-soluble metal content (i.e., total metal content minus labile and non-labile soluble fractions). The authors claimed that the ion-exchange technique was more selective than direct reagent attack since it allowed distinction between "labile" cations and non-labile species. However, some obvious disadvantages have also been noted, namely the fractionation proposed could be more time-consuming than the direct chemical extraction, and matrix attack could be greater than with salt solutions.

1.6. Chemical sequential extraction.

In this subsection, general characteristics and applications of sequential extraction (hereafter "SE") methods are outlined, with an emphasis on a widely discussed possible disadvantage of the procedures; namely, redistribution/ readsorption of elements during the extraction. A variety of previous investigations on the redistribution problem are outlined, along with the few attempts previously made to counteract it.

1.6.1. General features of sequential extraction procedures.

Sequential extraction procedures for solid samples involve the stepwise application of a series of chemical extractants of different types, of successively increasing chemical strength (Kersten and Forstner, 1994). Variations in the composition of the extraction solutions and the order of addition have been devised to address specific situations, however, most of the schemes consist of up to five extraction reagents (summarized in *Appendix 1.9.*). To date, the most widely applied SE scheme appears to be that of Tessier et al. (1979), originally developed for sediment samples. In general, SE protocols are based on the primary concept that by using appropriate extractants, the different forms of a given element that are retained among distinct sediment (and soil) compartments (e.g., as carbonate, as complex with organic material, etc.) can be selectively extracted (Tessier et al., 1979). As the reagents become increasingly aggressive, elements which are weakly bound or associated with readily soluble phases are progressively separated from those which are associated with chemically inert phases (Howard, 1988). The extraction conditions included in SE methods generally simulate various natural environmental conditions (e.g., presence of reducing or oxidizing conditions), however, extraction conditions are more intense than their environmental counterparts, compressing the process into a relatively short period of time. Solid phases commonly referred to in SE protocols are those prevalent in geochemical samples and are considered to differ widely in chemical activity and mode of association with the elements. Geochemical phase associations and/or retention modes of elements typically included in SE schemes appear to be (1) at ion-exchange sites on the surface of particles, (2) bound to carbonates, (3) bound to Fe/ Mn oxides and oxyhydroxides, (4) bound to organic matter and sulfides, and (5) incorporated as part of inert mineral lattice (Tessier et al., 1979; Robinson, 1984/ 1985; Salomons and Forstner, 1984; Pickering, 1986; Hirner, 1992; Ure et al., 1993; Yong et al., 1993). The "exchangeable" ions are frequently determined using a 0.05 to 1 M solution of KCl, $MgCl_2$, $BaCl_2$, or ammonium acetate (these reagents are commonly used in the measurement of cation exchange capacity (CEC) of soil and sediment samples) (Salomons and Forstner, 1980; Scokart et al., 1987). Extraction by $MgCl_2$ may reflect conditions in soils contaminated with de-icing salt as well as transformations that might occur on mixing with sea water (Kersten and Forstner, 1994). However, ammonium acetate (1 M, pH 7) is perhaps a preferred reagent as its relatively high concentration and the metal complexing power of acetate may prevent readsorption or precipitation of released metal ions (Ure, 1996). Acetic acid and/ or sodium acetate (acidified to pH ~ 5) are widely used for assessing metals associated with carbonates, whereas hydroxylamine hydrochloride is a commonly used reducing reagent for metals retained on reducible oxides (Shuman, 1982). Extractants for "organically and sulfide-bound" ions include hydrogen peroxide (Tessier et al., 1979), potassium pyrophosphate (Miller et al., 1986), and sodium hypochlorite (Shuman, 1983); the most widely used treatment seems to be the oxidation of organic matter with 30% H_2O_2 acidified to pH 3, followed by an addition of ammonium acetate (Ure, 1996). Strong acids, such as HF or its mixture with nitric and hydrochloric acids, are generally used to dissolve silicates or minerals that have not been attacked by the milder reagents in SE protocols.

1.6.2. Applications of sequential extraction protocols in environmental related studies.

Sequential extraction protocols have been widely applied on various solid environmental samples containing a broad range of metal concentrations. The methods have been extensively used for examining metal partitionings in three main research areas, namely, physico-chemical/ mineralogical studies in geochemistry, evaluation of potential mobilization of metals due to environmental changes in environmental chemistry, and correlation studies of metal contents in extracts with those in biological markers. These fields of study are interrelated, with an underlying assumption that mobility and biological availability of elements are associated with the solubility of their geochemical forms under different environmental conditions, and this decreases in the order of extraction (Hickey and Kittrick, 1984; Ma and Rao, 1997). The potential uses of SE methods are perhaps increased as a result of promising developments in coupling them with instrumental techniques capable of simultaneous multi-element analysis, such as ICP spectrometry (Scokart et al., 1987; Van Loon and Barefoot, 1992; Li et al., 1995; Tack and Verloo, 1995). Such multi-element methods considerably increase the speed of elemental analysis, allowing more information to be obtained from a given extract, along with a more comprehensive picture of the environment.

Sequential extraction methods have been used to investigate both the phase-associations of trace metals present at low levels in native or relatively slightly contaminated soils (McLaren and Crawford, 1973; Arunachalam et al., 1996; Chlopecka, 1996; Chlopecka et al., 1996) and sediments (Tessier et al., 1979), and those of metals present at high concentrations in contaminated systems, which include soils (roadside soils, Yassoglou et al., 1987; Nowak, 1995; sewage sludged-amended soils, Sposito et al., 1982, 1983; Lake et al., 1984; LeClaire et al., 1984; Sims and Kline, 1992), dust (urban road dust, Biggins and Harrison 1979; Harrison et al, 1981; herbal dust, Kwapulinski et al., 1992), sediments (Salomons and Forstner, 1980; harbours, Hickey and Kittrick, 1984; lakes, Feijtel et al., 1988; street sediment, Stone and Masalek, 1996), municipal solid waste (Prudent et al., 1996), sewage sludge (Lake et al., 1984), combustion waste (Kersten and Forstner, 1994; ashes from incinerated sludge, Fraser and Lum, 1983, and municipal solid waste, Kirby and Rimstidt, 1993; fly ash from coal combustion and refuse incineration, Wadge and Hutton, 1987), and landfill liner (Salim et al., 1996). In some cases, the SE methods were used in monitoring behaviour of elements previously spiked onto natural samples (Yong et al., 1993; Salim et al., 1996).

In geochemistry-related studies, sequential extraction protocols have generally been used in estimating the relative importance of various geochemical phases in binding elements investigated (Hickey and Kittrick, 1984; Feijtel et al., 1988; Baruah et al., 1996; Chlopecka et al., 1996; Guo et al., 1997). Several sediment studies have involved additional assessments on biogeochemical processess/ mechanisms potentially dominating in the depositions (Tessier et al., 1979; Lion et al., 1982; Tessier et al., 1989; White et al., 1989;

White and Gubala, 1990). Tessier and co-workers (1989) investigated partitionings of Zn in a variety of oxic lake sediments, as well as the metal concentrations in the associated porewaters and the overlying waters. The data were found to fit well to a simple surface complexation model involving iron oxyhydroxides as the sorption substrate. This and the finding that concentrations of dissolved Zn in the overlying waters were highly undersaturated with respect to $Zn(OH)_2$ (s) and $ZnCO_3$ (s), and in general with respect to $ZnSiO_3$ (s), led to a suggestion that relationships between dissolved and particulate Zn were better described by sorption reactions than by solubility control by a pure phase. The empirical model was also used in predicting the gross partitioning of Zn between the water column and the oxic sediments in lakes when pH or Zn concentrations in the water were changed. In an investigation by White and co-workers (1989) on the influence of biogeochemical processes on the geochemical record of Fe and S in the sediments of an acidic lake, the authors concluded that microbial activities played a dominant role in the depositions of Fe and S, rather than historical changes in sediment accumulation rates. However, in a later relevant study by White and Gubala (1990) on accumulation patterns of metals (Al, Fe, Mn, Pb, and Zn) in acidic lake sediments, "labile" forms and total contents of the metals were quantified and used in enhancing interpretation of the historical changes of chemical stratigraphy of the lake cores. The authors observed the temporal increases in the inputs of "labile" fractions of Pb and found that these were in agreement with known atmospheric emission history from fossil fuel combustion into the region. Increases in concentrations of "labile" Al were also noted and these were consistent with acidification of the lakes, recognized in recent years.

Comparing sequential extraction data of elements present at different study sites has shown potential uses in differentiating contamination sources (Nair et al., 1991; Li et al., 1995). Li and co-workers (1995) found a significant difference in the partitioning patterns of Pb between the soils taken from smelting areas and those from mining areas; the most notable difference was a much higher exchangeable fraction of Pb at the former sites. The major contamination sources of Pb in soils at the smelting areas were emission of particulates and dumping of slag, which contained anglesite ($PbSO_4$) and Pb-oxides (PbO and Pb_3O_4). In contrast, in the old mining areas, the majority of Pb in soils was in the forms of cerussite ($PbCO_3$), galena (PbS) and pyromorphite ($Pb_5(PO_4)_3Cl$), which have very low solubility in the $MgCl_2$ solution used for determining the exchangeable fraction in this study. It could be noted here that SE data of elements investigated obtained from "non-polluted" and "polluted" regions are frequently different (sediments, Hung et al., (1993); mangrove soils (native vs receiving wastewater), Tam and Wong, 1996). Hung and co-workers (1993) investigated species of Cu and Zn in sediments collected from ocean and coastal areas. High Cu and Zn levels were generally found in the exchangeable and acid soluble fractions of the coastal sediments as compared to the ocean sediments; the authors suggested that the higher metal contents in these two fractions might indicate a problem arising from pollutants discharged from households and industries.

Sequential extraction methods have been used to assist in examining factors influencing metal retention in soils and sediments (differences in the loading levels of contamination, Chlopecka et al. , 1996, Tam and Wong, 1996; inherent chemical properties of the matrix, Yong et al., 1993). In an attempt to design specific physicochemical treatments for binding heavy metals to immobile fractions for landfill applications, Yong and co-workers (1993) assessed the relationships between pH and metal retention capacities of various clay soils used in landfill liner systems. The results from determinations of metal distributions in the soils, previously prepared by mixing with spiked-leachate solutions at various initial pH values, indicated that the retention of the heavy metals in any phase depended on the soil solution pH, soil constituents involved and the identity of the metal. The authors also noted that the findings supported the conclusion of the significance of soil buffering capacity with regard to heavy-metal retention. It is interesting to note here an approach proposed by Salim and co-workers (1996) for investigating metal retention in landfill liners. In this study, a series of SE data obtained from clay-rich lake sediments previously spiked with various concentrations of heavy metals were used to construct sorption-isotherms for the individual geochemical forms. The authors noted that the combined approach had advantage in determining the sorption capacity of individual phases while they were together in a natural system. They suggested that the approach might prove useful for predicting the attenuation capabilities of soils and sediments and for regulating the land disposal of untreated heavy metal-bearing wastes. In addition, the SE data indicated that the geochemical partitioning of the metals was different from that at background levels and in some cases, changed significantly as loading levels increased.

Information of chemical associations of metals obtained from sequential extraction methods has been extensively used to deduce potential mobilizations/ fates of the metals due to environmental changes; this offers help as a decision-making tool in making a more realistic estimation of trace element impact (Arunachalam et al., 1996; Prudent et al., 1996). Many studies concerning metal mobilizations involve monitoring possible transfer of metals from one phase to another present in the systems, as a result of physical (Forstner et al., 1991; Tack and Verloo, 1993) or chemical (Amrhein et al., 1992; Howard and Sova, 1993; Li and Shuman, 1996) treatments. Considering a possible use in assessing an environmentally acceptable treatment strategy for contaminated dredged sediments prior to disposal, Tack and Verloo (1993) investigated chemical changes induced in a dredged sediment by thermal oxidation at increasing temperature. In their work, a dredged material was subjected to thermal treatment at temperatures ranging from 120 ° to 450 °C, followed by a single leaching using ammonium acetate-EDTA solution in parallel with an SE procedure. They found that the consolidation of the material at $\leq$ 350 °C increased leaching of Cd, Cu, Pb, Zn, and Mn, but did not significantly change the metal fractionation patterns, except for Cu. The authors attributed the changes in leaching behaviours to shifts in the binding energy distributions of the solid fractions (rather than changes in chemical forms) as a result of the thermal treatment. Howard and Sova (1993) used SE as a tool for testing a hypothesis that chlorides derived from deicing salt were responsible for Pb translocation in particular roadside soils. The authors found that Pb was mainly in the carbonate and Fe-oxide forms in heavily polluted top-soils near a highway, whereas organic forms predominated farther away. This together with the elevated Pb levels in subsurface horizons and the presence of a water-soluble Pb component, suggested that a partial dissolution of soil organic matter due to the presence of excess NaCl derived from highway deicing salts was a major cause of the Pb migration observed. Li and Shuman (1996) used EDTA as a model compound to investigate the effect of organic amendments often added to soils on distributions of Zn, Cd, and Ni. They found that for most of the soils pre-mixed with EDTA, the metal concentrations in the "exchangeable" fraction consistently increased with increasing EDTA amounts, while the metal concentrations in the organic fractions decreased with an increase in EDTA amounts. The authors therefore concluded that the added EDTA enhanced the solubility of metals in these soils.

Assessment of biological significance of elements in geochemical samples has frequently depended upon sequential extraction methods. Relationships between chemical forms of metals in a variety of geochemical samples systems and concentrations of the metals in biota have been examined in several studies (sediments vs organisms, Diks and Allen, 1983, Tessier et al., 1984; Bourgoin et al., 1991; plants vs amended-soils vs sewage sludges, LeClaire et al., 1984, Singh and Narwal, 1984, Sims and Kline, 1991). In an investigation on correlation of Cu distribution in a pre-equilibrated, Cu-amended freshwater-sediment systems to bioavailability, Diks and Allen (1983) assessed the amounts of copper within various fractions of the surficial sediments, in the corresponding water column, and accumulated in benthic worm (the organism was considered exposed to the metal in solution as well as that within the sediment or particulate matter). Among several variables included in regression analyses (using Cu concentrations in the worms as the independent variable), the most significant correlation found was between copper concentrations in the manganese oxide/ easily reducible phase and those in the organism. The authors attributed this finding to dissolution of the oxide coatings due to the particular redox potential and pH conditions present in the worm's gut (Cu was then available for the uptake by the organism). Bourgoin and co-workers (1991) assessed factors influencing Pb availability to a filter-feeding marine mussel collected near a Pb smelter. They found the highest correlation between tissue Pb concentrations and the metal fractions "bound to carbonates/ specifically sorbed" in the sediment. However, the authors found that normalizing each extracted metal fraction with respect to total S present in the sediment increased the correlations between the normalized values and the tissue Pb concentrations. The normalized Pb concentrations in the metal fraction "bound to organic matter & sulfides" (F4) appeared to have the highest correlation with the metal concentration in the mussel. The authors believed that normalizing the Pb levels in the F4 fraction assisted in correcting for the large amount of Pb extracted from the sulfide phase, which might have been caused by insufficient selectivity of the reagents used in the SE procedure used. LeClaire and co-workers (1984) and Sims and Kline (1991) utilizing the same SE, found that Zn extracted from a sewage sludge-amended soil by KNO_3 and H_2O (in sequence) showed a significant correlation with the metal in plants; this fraction was considered to be a labile and bioavailable fraction in the soil. LeClaire and co-workers also proposed relationships between sequentially-extracted Zn fractions and Zn bioavailability. Zn extracted by NaOH, EDTA, and nitric acid were assumed to be labile, quasilabile (both of which were bioavailable), and non-labile, respectively. In addition, Sims and Kline noted that for some metals regression models involving the plant metal concentrations, soil pH and the metal concentrations in each soil fraction were consistently more useful than total soil metal content in predicting metal concentrations in plants.

In summary, the applications of sequential extraction procedures are very extensive and the partitioning data obtained can be put to a wide range of uses. From the point of view of environmental impact assessment, metals recovered in "non-residual" fractions are of more concern than those present in "residual" fractions. Heavy metals in "exchangeable" and other "non-residual" forms are considered by many investigators to be more susceptible to remobilization due to changes of the chemical environment, and thus are likely to be biologically available (Diks and Allen, 1983; Ma and Rao, 1997). The "exchangeable" fraction is generally taken to imply presence of metals held by a cation exchange process, which is a relatively unstable chemical association; therefore, this fraction is normally considered as being suggestive of anthropogenic origin of the metals (Salomons and Forstner, 1980; Ma and Rao, 1997), and is commonly singled out for close monitoring when assessing pollution trends. The "non-residual/ labile" metal fractions are found to increase with increasing pollutant inputs (e.g., heavy metals in soils amended with sewage sludge, Sposito et al., 1982). Metals found in the "residual" fraction are considered to be those in inert lattice positions in the mineral substances of natural rock debris (Forstner, 1981), and as such not expected to be soluble under normal environmental conditions (Tessier et al., 1979), or released in the short to medium term on a geological time scale. Therefore, the metals in the "residual" phase are generally considered as neither available for biological uptake nor a potential source of contamination to ground waters, at least in the short term (Wadge and Hutton, 1987), and are commonly interpreted as having come about as a result of natural (lithogeneous) rather than anthropogenic sources (Tack and Verloo, 1993).

1.6.3. Problems associated with sequential extraction procedures.

Despite the current large number of applications of SE methods and their increasing use as tool in monitoring of pollution trends and assessing environmental risk, such methods still require further improvement. Apart from their apparent disadvantage as time-consuming techniques, SE schemes, because of their operationally defined nature, are greatly influenced by experimental factors. Factors investigated in this respect include pretreatment of samples, ratio of the volume of the extractant per weight of solid, and types and sequences of extraction reagents. In this subsection, the sensitivity of the SE data to these parameters will be outlined with an emphasis on the fact that applications of different SE procedures on the same sample could result in different patterns of metal partitionings, and as a consequence, different conclusions might be made. The two most discussed problems associated with the use of SE schemes, namely, the non-selectivity of extraction reagents toward specific solid compartments and the possibility of readsorption/ redistribution of liberated elements on to the remaining solid phase(s) during the extraction process, are described in *subsections 1.6.4.* and *1.6.5.*, respectively. Of the two, the redistribution problem is less trivial, as it has a greater potential to significantly affect the accuracy of the interpretation of the SE partitioning results.

The importance of sample pretreatment has been emphasized by several investigators, especially with relation to sample preservation between collection and analysis of anoxic samples (Rapin et al., 1986; Tessier and Campbell, 1987; Kersten and Forstner, 1989; Wallmann et al., 1993). Rapin and co-workers (1986) investigated possible effects of sample preservation techniques on metal partitionings of oxic and anoxic contaminated sediment samples, as determined using the extraction method of Tessier et al.(1979). The preservation techniques assessed included wet storage at 4 °C, freezing, freeze-drying, air and oven-dryings. The partitioning patterns of the metals obtained after treating the sediments samples were in many cases different from those of control sediment samples analyzed within 24 h after collection. Of the methods assessed, oven-drying and freeze-drying were found to have significant effects on the patterns of metal partitionings. The authors remarked that the pretreatments investigated could favour the formation of new mineral solid phases, accelerate the crystallization of solids (e.g., Fe-Mn oxides), and promote Fe, Mn, and S oxidation (especially in the case of air-drying). Freezing or short-term wet storage (1 - 2 °C) were suggested as acceptable preservation techniques. Among the metals investigated, Cu, Fe, and Zn appeared to particularly sensitive to sample pretreatment. In addition, the investigators observed notable differences between metal partitioning patterns obtained from two sets of duplicate anoxic samples, one set in which atmospheric oxygen exposure during the extraction was prevented (a control set) and another set which was extracted without such precautions being taken; however, such differences were not found in oxic sediments. As a result, the authors concluded that it was generally not possible to predict the consequences of exposure to oxygen during extraction, and stressed that maintaining oxygen-free conditions during the course of sediment extractions was of crucial importance.

Ratios of solid mass to extraction solution volume can cause a shift in metal recovery patterns (Rauret et al., 1989a,b; Howard and Sova, 1993). In their investigation of partitionings of Cu, Cr, Pb, and Ni in heavily-polluted river sediment samples using the Tessier et al.'s extraction scheme (1979), Rauret and co-workers (1989a) found that the majority of the metals were recovered from the residual phase; this was attributed to incomplete solubilizations in previous fractions of the scheme. The authors modified the SE by using successive applications of each reagent at the second to the fourth extraction steps. The first extraction step was not modified because the metals recovered at this step were found negligible in relation to the total amount recovered. Concurrent with the modification of the reagents, other parameters, i.e., pH, extracted Fe and Mn, and redox potential were controlled at extraction steps 2, 3, and 4, respectively. Application of this modified extraction scheme resulted in more of the metals being recovered in the early steps of the extraction; moreover, a significant reduction of the metal recoveries at the residual step was observed. However, in most cases, the total recoveries of the metals from the conventional and the modified Tessier schemes were found reasonably similar. Noting the tedious and time-consuming task of repeated successive extraction, Rauret and co-workers (1989b), in subsequent work, further investigated the effect of increasing the ratio of volumes of the three extractants per weight of each river sediment sample (containing a high and low amounts of pollutant). The investigators concluded from their preliminary tests that the "volume" variable, rather than the extraction time, played a more important role in metal solubilization. They found that in almost all of the cases (except for Cr in the heavily polluted sample), the partitioning patterns of the metals obtained from the use of the conventional and the optimized volume/ weight ratio schemes were apparently different. In all cases of the metals in the less polluted sample and in the cases of Pb and Ni in the heavily polluted sample, increasing the volume of acetic acid-acetate buffer reagent from the conventional 8 ml to 50 ml (per g sample) significantly increased the recoveries of the metals in this step. However, an optimized (50 ml g^{-1}) ratio of hydroxylamine hydrochloride and hydrogen peroxide reagents did not significantly increase the recovery of the metals in each sample. Comparison of the performances of the three extraction methods on the heavily polluted sample revealed that metal recoveries from the residual fractions decreased in the following order: the conventional Tessier et al.'s scheme, the optimized volume/ weight ratio method, and the repeated successive extraction procedures, respectively.

A difference in the sequence of reagents can also alter the partitioning results. Miller and co-workers (1986) assessed the partitionings of Cu and Mn in top-soil samples, using a 9-step extraction. The ordering of reagents for (1) adsorbed metals (Pb-displaceable vs acid soluble fractions), and (2) structural metal forms (manganese oxide vs organic fractions) were investigated; the reagents involved were (1) $Pb(NO_3)_2$ vs acetic acid; and (2) hydroxylamine hydrochloride vs potassium pyrophosphate ($K_4P_2O_7$), respectively. In all cases, the order of the extraction (using either Pb or acetic acid first) was found important in that the reagent used first in the sequence extracted the majority of the Cu present (the sum of the two fractions were found similar). In the case of the extraction sequence for manganese oxide and organic fractions for Cu and Mn, amounts of extractable Cu and Mn in $NH_2OH.HCl$ solution were substantially higher when this reagent was used first in the extraction scheme than when the pyrophosphate was used first.

Robinson (1984/ 1985) applied three different sequential extractions (a modified Tessier et al.(1979), Filipek and Owen (1978), and Robinson (1982)) on composite samples prepared to simulate hydrous coatings of Mn- and Fe-oxide on stream alluvium. The composite samples contained goethite, quartz, Mn-oxides ore, and humic material.

Applications of each extraction scheme resulted in a different partitioning pattern for each of the metals (Fe, Mn, and Zn). The very low recovery of Zn found in the organic fraction of the Tessier et al.'s scheme would have suggested the insignificance of this fraction for Zn in the samples. In contrast, the significant amount of Zn recovered in the organic fraction of the Filipek's scheme would suggest that this partitioning fraction was very important for Zn. In addition, by comparing the initial amount of Mn, Fe, and Zn assessed in each component of the composite sample and the total amount of the metals in the sample, to the amount of the individual metal recovered in each fraction of the extraction schemes, the authors concluded that in general, all the three procedures were quite efficient in extracting Mn and Zn but differ in their efficiency for Fe. The sum of Fe recovered in each fraction of the Tessier et al.'s scheme was found to be only about 1% (by weight) of the total amount of the metal in the composite sample. However, about 90% of the total amount of Fe in the sample was recovered in hydrazine hydrochloride solution at the reducing step of the Robinson's scheme.

Contaminated sediment samples containing different levels of heavy metals were used by Lopez-Sanchez and co-workers (1993) to compare the efficiency of two sequential extraction schemes; namely, a modified Tessier et al.'s procedure and the three-step protocol (BCR) (1993). They found that the partitioning patterns of Cd, Cr, Cu, Ni, Pb and Zn obtained from the two extraction schemes were significantly different. With the use of the Tessier et al.'s procedure, the recoveries of all the metals were distributed among the acetic acid-acetate, hydroxylamine hydrochloride, and hydrogen peroxide fractions. However, with the three step extraction scheme, except for Cd, the majority of the metals were recovered in the hydrogen peroxide fraction. The total amounts of the metals recovered from non-residual phases in the less polluted samples by the two extraction schemes were found in good agreement whereas those in the more polluted samples were different. The investigators remarked that the two procedures extract metals from the non-residual phases with different efficiency and speculated that the differences in the experimental conditions used to isolate each fraction probably contributed to the differences in the partitioning results obtained; however, the authors did not carry on testing their speculation.

It should be noted here that metal partitioning patterns obtained from the use of SE may be found to be different from those suggested by other solid speciation techniques. In the investigation by Lee and Kittirck (1984) on Cd-contaminated harbour sediment samples, the SE data obtained showed that exchangeable Cd, and carbonate and Fe-Mn-oxide-bound Cd represented the most important fractions in the sample. However, thermodynamic calculation and electron beam microprobe suggested that the majority of Cd was associated with only sulfur. The authors noted that the SE results might have been affected by improper handling of the anoxic samples by drying them prior to the extraction.

As previously outlined, sequential extraction techniques are very sensitive to several experimental parameters, and for this reason it is difficult and often inappropriate to compare the data obtained between different studies. However, since SE methods have been extensively used, in several researchers' views, there is a genuine need for a "common" or "standard" extraction method for the speciation of particulate metals (which should be a relatively simple protocol for routine practice), so that it becomes possible to establish a common database on the mode of occurrence of metals in soils and sediments (Salomons and Forstner, 1980, 1984). In recent years, a group of European experts has developed a three-stage sequential extraction, and validated it in terms of interlaboratory precision under the auspices of the Community Bureau of Reference (BCR, now Standards, Measurements and Testing Programme) (Ure et al., 1993, 1995; Quevauviller et al., 1994; Ure and Davidson, 1994). The development of this program was extensively discussed in a workshop organized by the BCR in 1992 (Rauret and Quevauviller, 1993). The three-step scheme has been used to prepare reference materials which would for the first time allow data produced by different laboratories to be directly compared in terms of precision (Quevauviller et al., 1994; Ure et al., 1995). Heavy metals investigated under this newly proposed extraction scheme included Cd, Cr, Cu, Ni, Pb, and Zn (the detail of the investigations on the agreed common sequential (and single) extraction schemes can be found in Ure et al., 1995). This project could lead to the adoption of the BCR extraction as an international standard method, for instance by ISO or CEN. Effectiveness of the BCR scheme as an analytical tool has already been assessed by several researchers (Davidson et al., 1994; Thomas et al, 1994; Whalley and Grant, 1994; Coetzee et al., 1995; Marin et al., 1997). It could be noted here that Davidson and co-workers (1994) and Thomas and co-workers (1994) reported satisfactory repeatability of the BCR procedure for the determinations of Cd, Cu, Cr, Ni, Pb, and Zn in river sediments. However, a study aiming to investigate thoroughly the different parameters which may have an influence on the results of using the method has recently been executed; in this study the procedure is also expected to be tested with different sediment and soil samples (Quevauviller, 1996). It could be noted here that while the BCR scheme is still being subjected to further investigation for its use as analytical tool, it has already been applied in environmental related-studies (Mench et al., 1994; Belazi, et al., 1995).

It is interesting to raise here a comment on a proposal for a "standard" extraction method made by Howard (1988) that one could argue that natural solid systems, such as sediments, vary so greatly in chemical composition that one can question whether it is reasonable to assume that a common extraction procedure would be suitable for all metals in all sediments. Howard further stressed that alternate methods for evaluating the accuracy of extraction procedures, e.g., a use of well-defined solid system, must be developed. Hall and co-workers (1996) expressed a concern that adaption of a "standard" extraction scheme (such as the BCR) promoted by influential organizations could result in a tendency to overlook the deficiencies and lack of suitability of the protocol concerned. It could be noted here that based on their findings of the non-specificity of a reducing agent for amorphous Fe oxyhydroxides in an SE investigated, Hall and co-workers stressed a need for thorough examination of the effectiveness of the reducing step of the BCR scheme for quantitative dissolution of Fe oxyhydroxides, species which should fall into the "reducible" category.

In the future when additional research has been performed on a variety of sediment and soil types, a number of "common" extraction schemes, each specific for a different type of sample might be developed. Particular "certified" schemes might be found most appropriate for given samples, such as sediments with high organic matter contents vs inorganic or low organic sediments, and different levels of contamination vs unpolluted soil/ sediments.

Some recent discussion has also focussed on the terminology used in labelling the extraction fractions. It appears that a link exists between the reagents chosen and the soil components most strongly attacked and many researchers have frequently referred to the geochemical host phases and the extractants interchangeably (e.g., "bound to Fe/ Mn oxides" fraction is often considered to be related to or included in "reducible" fraction). However, in order to avoid a misleading interpretation of SE data which could result from the terminology used in labelling the extraction fractions according to host phases (e.g., "bound to carbonate", "bound to Fe/ Mn oxides" fractions), some researchers suggest use of a purely operational definition for each fraction according to the reagents used (Slavek and Pickering, 1987; Kersten and Forstner, 1994; Arunnachalam, 1996), such as "salt-displaceable", "acetate extractable", "acid-reducible", "ammonium acetate extractable fraction" etc. However, in the view of at least one researcher (Howard, 1988) this approach avoids the real problem of not having an objective method to evaluate the accuracy or causes of inaccuracies in SE methods.

1.6.4. Non-selectivity of extraction reagents.

A general goal of an extraction reagent designed for the use in SE methods is to selectively attack or dissolve one particular phase or be specific in its action, so that the recovery results can be interpreted in terms of a specific original geochemical phase or retention mode (Tessier and Campbell, 1987). This requirement has been widely assessed both experimentally and theoretically (by calculations), however, it is generally recognized that to a certain extent, all SE procedures suffer from non-selectivity of the reagents. This is where a reagent designed for dissolving a specific phase (and causing liberation of elements associated with it) concurrently attacks other constituent(s) present. Non-selectivity of the extractants is regarded by Wallmann et al. (1993) as being most responsible for the operational nature of SE methods. The problem has been investigated using various natural samples and geochemical models of a range of complexities.

Selectivities of the extraction reagents used in the SE protocol proposed by Tessier et al. (1979) were investigated by several researchers, with an emphasis on the selectivity of the extractant for the sulfidic phase. During an application of the extraction protocol on anoxic lake sediment samples under an atmosphere of nitrogen, Rapin et al. (1986) observed a significant recovery of acid volatile sulfides in fraction 3, designed to solubilize the Fe/ Mn oxides component, instead of the "bound to organic/ sulfides" fraction expected. Kheboian and Bauer (1987) investigated the effectiveness of the extraction protocol using synthetic sediment models incorporating metals (Cu, Pb, Ni, and Zn) doped into known

compartments. They found that a majority of Zn originally doped on FeS (mackinawite) was recovered in fractions 2 and 3, which were designated to recover Zn "bound to carbonates" and "bound to Fe/ Mn oxides". The authors speculated that the early recovery of the metal in fraction 2 might be attributable to partial oxidation of the sulfide (since the system was exposed to air) and/ or slight adsorption of the dissolved Zn onto colloidal iron.
The significant portion of Zn extracted at step 3 was almost certainly a result of the solubilization of the FeS by 25% acetic acid used at the reducing step, since this was accompanied by the evolution of a strong odour of hydrogen sulfide. In the work of Shannon and White (1991), amorphous FeOOH, FeS, and FeS_2 were added separately to natural lake sediments and sequentially extracted using Tessier et al.'s scheme. During the extraction, an N_2 atmosphere was maintained to reduce possible oxidation of sulfides.
The selectivity of the extraction scheme for the spiked phases was assessed by determining the difference in the amount of Fe extracted from the spiked and control (unspiked) sediments. In the systems with spiked FeS, about 20% of the added Fe was recovered at the reducing step. The authors regarded that this result was in agreement with the previous observation of Rapin and his co-workers (1986), using the same extraction scheme but on the unspiked sediment samples. However, in the experiments of Rapin et al., for systems both exposed to air and maintained under an N_2 atmosphere, the majority of the acid volatile sulfides were recovered in fractions which preceded the "bound to organic/ sulfides" fraction (in the case of anaerobic handling, the majority of the sulfides were recovered in "bound to Fe/ Mn oxides" fraction), whereas in the system of Shannon and White, the majority of FeS (FeS is often a major component of AVS in sediment) was found in the fourth fraction. Shannon and White (1991) indicated that this inconsistency could be attributable to the differences in the crystalinity of the FeS extracted, i.e., the crystallized form of FeS used in their study could preserve the sulfide through the earlier extraction steps (and as a result, the reagent used was considered sufficiently selective). Wallmann et al. (1993) utilized thermodynamic equilibrium calculations to assist in an investigation of selectivity of reagents used in a modified version of Tessier et al.'s SE scheme for the metal analysis of a contaminated, anoxic, sulfide-bearing sediment sample. Thermodynamic calculations of the chemical reactions during the extractions revealed that Cd, Co, Pb and Zn sulfides were to a notable extent soluble in the acetate-exchangeable and oxalate-reducible fractions.
The calculations were generally in agreement with SE data that trace metal in sulfide minerals were not completely extracted in the "sulfide" fraction, but in all fractions to an amount depending on their solubility.

Karlsson and co-workers (1987) found that the organic matter (analyzed using a UV absorbance determination) present in a highly contaminated sediment was retrieved at the extraction steps preceding the oxidation treatment (step 4) of Tessier et al.'s SE scheme (1979). In general, the sum of about 13- 28% of the total extractable organics was recovered from the first three steps of the SE scheme, with recovery about 10% of the organics at the reduction step 3. In addition, significant amounts of Fe and Mn (known to be significant structural components of sediments) were found at the oxidizing step. The authors were convinced that this was attributable to the organics comprising a notable portion in the amorphous Fe/ Mn oxide phase, and preventing a complete dissolution of the oxides at the reducing step. As a consequence, the authors deduced that the notable recoveries of Cd, Cu, and Zn at the reducing and oxidizing steps might not be a reflection of their actual phase partitionings but the interaction of different geochemical constituents during sequential extraction of the soil samples. This aspect was also examined on soil samples by Tu et al. (1994a), using two different SE procedures modified from the scheme proposed by Tessier et al. (1979); one with two successive reduction steps, followed by an oxidation (H_2O_2) and a third reduction step, and another with an oxidation (NaOCl) step followed by three successive reduction treatments (both of the schemes contained ion exchange and acid soluble steps). They found that the partitioning patterns of both Fe and Mn obtained from both protocols were consistent in that the metals were still significantly recovered at the second and third reduction steps. The authors noted that it was more likely that some portions of Fe and Mn were progressively extracted (rather than selectively, one at a time as originally designed for in the procedure) from different geochemical phases. It should be noted here that the authors ruled out a possibility that the concentration of the reducing reagent used at the first treatment was not sufficient for a complete dissolution of the Fe/ Mn oxide phases because the amounts of the $NH_2OH.HCl$-extractable iron and manganese oxides in their samples did not exceed those originally designed for by Tessier et al. However, it appeared from the use of the first extraction protocol that when the organic fraction had been removed beforehand, more Fe was recovered in the extracts of $NH_2OH.HCl$ (the authors noted that a lower recovery of Mn was probably due to a partial dissolution of manganese oxide by the hydrogen peroxide solution). This was in agreement with the results obtained from use of the second extraction scheme in that most of Fe, Mn, and other associated metals investigated were recovered in the first extract of the reducing reagent after the removal of the organic fraction. The authors, therefore, deduced that soil organic matter was responsible for coating or occluding some portion of amorphous Fe and Mn oxides and partly impeded the dissolution of these oxides by the reducing agent. They stressed the insufficiency of the extraction procedure in distinguishing metals associated with amorphous Fe/ Mn oxides from those associated with the organic phase and the importance of taking into account the complexity of the soil constituents in interpreting SE data.

In their investigation of hydroxylamine hydrochloride extraction of Cu, Cd, and Pb in soil samples with respect to time, Bermond and Eustache (1993) examining the effects of acetic and nitric acids added to adjust the pH of the reducing reagent, noted that at a given pH, the reagent containing acetic acid extracted more metallic cations than that containing nitric acid. The authors speculated that this might due to the ligand properties of the acetate anion. In their evaluation of the effect of acidity without using acidified hydroxylamine, the authors found that the acids alone could remove substantial amounts of the metals from the substrates; therefore, they concluded that the selectivity of this reagent was due to the use of an acid.

Also investigating a reagent used at a reducing step, Hall and co-workers (1996) found that 0.25 M hydroxylamine hydrochloride in 0.25 M HCl, 60 °C (the condition intended to solubilize the amorphous Fe oxyhydroxide phase), could significantly dissolve sphalerite (ZnS) and galena (PbS) from sulfide-rich control samples (reference or in-house prepared materials). In addition, the authors found that increasing the concentration of the acid, rather than that of the $NH_2OH.HCl$, resulted in more of the metals being recovered in the solution (this was in agreement with the finding of Bermond and Eustache). Based on this observation, Hall et al. (1996) suggested that selectivity of the reducing extractant for the Fe oxide fraction could be improved by a minimization of possible dissolution of sulfides, especially for ZnS and PbS, using a lower concentration of HCl in the extraction. The authors, however, noted that the acid must be present in sufficient concentration to ensure a complete dissolution of the oxide phase. In their further investigation of the effect of the concentration of HCl, the authors leached samples of synthetic amorphous Fe oxyhydroxides which contained Zn, Pb and other metals of interest, using 0.25 M hydroxylamine hydrochloride in various concentrations of HCl ranging from zero to 0.25 M. It was found that Fe and the spiked metals were significantly recovered in the solution containing the acid up to about 0.05 M, after which the metal concentrations were at a plateau. The authors, therefore, considered that 0.05 M HCl was sufficient for a complete dissolution of the Fe oxides. In the reducing extractant containing 0.05 M HCl, it was found that only low percentages of Zn and Pb were dissolved from the sulfides. Hall and co-workers (1996) also investigated a possible dissolution of organic component in the 0.25 M $NH_2OH.HCl$ solution. They found that regardless of HCl concentrations at either 0.05 or 0.25 M, a notable amount of organic component in soil samples investigated was dissolved by the hydroxylamine reagent. It could be noted here that Campanella et al. (1995) proposed a five-step extraction procedure for separating metals bound to organic matter from those in sulfide forms. After the ammonium acetate and hydroxylamine hydrochloride steps, which are designed to remove exchangeable metal ions and those bound to carbonates, and metals present in Mn/ Fe oxide forms, respectively, Campanella and co-workers (1995) substituted nitric acid and hydrogen peroxide with a sequence of HCl, NaOH, and HNO_3. In the proposed scheme, the HCl and NaOH fractions were designed to recover metals associated with humic substances (which represent the prevailing portion of organic matter), whereas metals in the inorganic form were to be solubilized by HNO_3. The proposed extraction protocol was applied on marine and lakustrine sediment samples, with organic matter contents (expressed as loss on ignition) of about 4% and < 0.5%, respectively. The recovery patterns of Cu, Pb, Ni, Mn, and Zn obtained were compared with those from the use of a three-step traditional extraction scheme, in which metals bound to organic matter and sulfides were not separated (i.e., the HCl and, NaOH treatments were not included). They found that the amounts of solubilized metals from both types of samples using their proposed five-step procedure were generally higher than those using the three-step scheme. Based on this finding the authors deduced that the organic matter was probably not completely mineralized by only the nitric acid treatment.

Several researchers have been assessing selectivity of reagents used in a newly developed SE scheme of the EC Standards, Measurements and Testing Programme (formerly BCR) (Whalley and Grant, 1994; Coetzee et al., 1995). It should be noted here that so far the assessment of the BCR procedure has been focused more on the reagent selectivity and reproducibility of the extraction than on the redistribution problem. Whalley and Grant (1994) evaluated the geochemical phase-specificity by applying the extraction to various single synthetic substrates previously equilibrated with artificial sea water spiked with a mixed metal solution of Cu, Ni, and Zn. According to the designation of target solid phase, reagents, and assumed mechanisms for each extraction step, the authors reported good specificity for metals bound to calcium carbonate, kaolinite, feldspar, and manganese dioxide but varying quality of specificity for those bound to humic acid and quite poor specificities for those associated with amorphous iron oxide and montmorillonite. The authors deduced that the early recoveries of Ni and Zn originally retained on humic acid at steps preceding the oxidation step suggested that metal release might be determined by relative binding capacities, rather than chemical degradation of the substrate itself. Based on recovery results of all the metals, Whalley and Grant (1994) noted that it was not clear whether metals were released because the reagents had differing chemical properties, or simply because addition of each new reagent concurrently caused the pH of the system to decrease. Coetzee and co-workers (1995) evaluated BCR's extraction scheme for Zn, Cu, Cd, Cr, Ni and Pb, using various model sediments. They found that about 50% of Ni originally co-precipitated with goethite was recovered by acetic acid extraction solution, whereas the remaining metal was recovered by hydroxylamine hydrochloride solution. The authors noted that the performance of this reducing agent provided inconclusive evidence of selectivity, and speculated that recovery of Ni in the acetic acid solution could have been attributable to dissolution of a thin layer of Ni partially precipitated on goethite particles, whereas the metal recovered at the reducing step was considered to be that incorporated into the goethite structure. The authors observed poor selectivity of hydrogen peroxide for the organic phase in that about 70% of Zn originally sorbed on natural humic acid was recovered by acetic acid solution, and that elements recovered most at the oxidizing step were not necessarily associated with the organic phase. In general, the chemistry of a metal (i.e, nature of the retention mode (e.g., co-precipitated vs adsorbed) and the complexing binding strength of the metal with the substrates or anions in the solution) was emphasized as being a possibly more important parameter than the phase targeted in determining the recovery pattern of the metal.

It is interesting to note here that according to Slavek and Pickering (1987), sequential extraction schemes generally include an Fe/ Mn oxide fraction as a targeted phase but do not specifically mention the aluminium oxide phase, which can also sorb metal ions to a reasonable degree. In their work, 15 different reagents were separately assessed for their extraction efficiency in removing Cu, Pb, Cd, and Zn previously spiked in various amount on $Al(OH)_3$ and Al_2O_3. The reagents investigated included many commonly used in SE schemes for identifying ion exchangeable fractions, weakly sorbed material and metals bound to the hydrous oxides of Fe and Mn. From the observation that no single reagent appeared to be sufficiently selective to the aluminium oxide phases investigated, the authors speculated that a variety of metal retention modes might be involved, and they believed that no single reagent was sufficiently selective for this mineral fraction.

1.6.5. Readsorptions/ Redistributions of metals during sequential extraction procedures.

Redistribution/ readsorption phenomenon is a process in which elements initially liberated into solution by application of a given reagent reassociate with remaining solid phases(s) in the system, within the time-scale of the extraction. As a result, the metal distribution patterns obtained might be inaccurate. The redistribution phenomenon is one of the two main controversial problems associated with the use of SE techniques; however, possibly as a result of its complex nature, it has been received less attention than the non-selectivity problem. A variety of approaches have been used to investigate the extent of redistribution for different metals, particularly that which might occur in Tessier et al.'s scheme.
These approaches have included the use of (1) models containing artificial phases with doped metals (Guy et al., 1978; Kheboian and Bauer, 1987; Gruebel et al., 1988; Kim and Fergusson, 1991; Schriner, 1994; Coetzee et al., 1995), or natural mineral compositions (Shan and Chen, 1993; Tu et al. 1994b), (2) standard addition methods, carried out either by adding pure synthetic phases to natural samples (Ajayi and Vanloon, 1989) or by adding trace elements to some extractants used in the SE scheme (Rendell et al., 1980; Belzile et al., 1989), and (3) comparing the results of other solid speciation methods, such as thermodynamic calculations and instrumental methods, with those of SE procedures applied to the same samples (Lee and Kittrick, 1984; Tipping et al., 1985; Bermond and Sommer, 1989; Wallmann et al., 1993). The extent of redistribution of metals reported to occur during the course of the extraction ranges from "not significant" (Ajayi and Vanloon, 1989; Belzile et al., 1989; Kim and Fergusson 1991) to "substantial" (Rendell et al., 1980; Tipping et al., 1985; Kheboian and Bauer, 1987; Gruebel et al., 1988; Shan and Chen, 1993; Schriner, 1994; Coetzee et al., 1995), in many cases apparently depending on the metal involved. Although many studies reported substantial evidence for redistribution phenomena, it has also been the subject of some debate. For instance, an argument has been advanced that some systems used to investigate Tessier et al.'s procedure were inherently biased toward redistribution (Tessier and Campbell, 1988; Tessier and Campbell, 1991) and that the extent of the problem might not be serious enough to devalue results obtained from natural samples (Tessier and Campbell, 1988; Ajayi and Vanloon, 1989; Belzile et al., 1989; Kim and Fergusson, 1991; Tessier and Campbell, 1991). Part of this reasoning is that in real sediments "natural" redistribution may have already occurred to a large extent prior to extraction, so the extent of the post-extraction readsorption was unlikely to be significant (Ajayi and Vanloon, 1989; Tessier and Campbell, 1991). This is a valid enough argument, but is unfortunately also an unprovable one, given that no redistribution-free extraction has yet been devised with which to test it. A second point worth making in this regard is that, despite their original intended use (natural sediment systems) a need has been developed for the monitoring of precisely such natural redistributions as they occur at contaminated sites,

and sequential extractions are being more routinely applied to such problems. The observed trends may instead reflect redistribution occurring during extractions of the samples collected, if a possibility of metal redistribution is ignored when SE data is interpreted. As evidently shown or speculated in some studies, unlike the case for reagent selectivity, redistribution is as much a function of the metal under investigation as the nature of the extraction scheme. For some metals (e.g., Cd) redistribution is usually not significant whereas for others (e.g., Cu) it may be severe (Kim and Fergusson (1991) vs Schriner (1994). The ability of an extractant to form a soluble complex with the metals liberated, and the specific composition of each sample are also factors which have an influence on redistribution of the metals (Wallmann et al., 1993; Tu et al., 1994b). Clearly, in the interests of accurate data interpretation there is still a need to document the conditions (metals, reagents, soil/ sediment characteristics) most likely to encourage redistribution.

1.6.5. (a)The use of models containing artificial phases with doped metals.

Several researchers have remarked that it was difficult to use natural sediments/ soils to assess the efficiency of fractionation procedures. As one of the first in this group to use synthetic models containing spiked metal(s) of known original phases to evaluate the potential of metal readsorption/ redistribution, Guy and co-workers (1978) spiked three solid phases (synthetic MnO_2, commercial humic acid, treated bentonite clay) with Pb and Cu. The individually spiked phases and two compartment-mixtures containing a spiked phase were extracted using each of three solutions, namely, nitric acid at pH 1, H_2O_2, and NH_4Cl (these extractants are commonly found in SE methods). It was found that H_2O_2 could recover all of the metals originally retained on humic acid and that NH_4Cl was able to remove majority of the metals initially retained on the clay. However, in the two-phase systems comprising (1) spiked humic acid and clay or MnO_2, and (2) spiked clay and humic acid or MnO_2, the recoveries of metals by H_2O_2, and NH_4Cl, respectively, were found to be lower than expected; this was attributed to the released metals being sequestered by the other residual phase. The authors also remarked that in the case of the two-phase system containing MnO_2, another possibility could be the decomposition of H_2O_2 by the manganese oxide, which would result in the humic acid not being completely oxidized.

In their study of the applicability of sequential extraction techniques for determining partitionings of Se and As in sediment and soil, Gruebel et al. (1988) specifically investigated two commonly used steps in the SE protocols, i.e., reductive dissolution of amorphous iron oxides and the oxidation of organic material. Each solid phase used including synthetic goethite, amorphous iron oxide, natural clay (montmorillonite), and commercial anatase (titanium dioxide), were separately spiked with solutions containing a mixture of As (V) and Se (IV). The individually sorbed-amorphous iron oxide was completely dissolved in the 0.25 M $NH_2OH.HCl$/ HCl extraction, therefore all the adsorbed As and Se were released into the solution. However, in the cases of the individually sorbed-goethite and anatase, a very low amount of the sorbed oxyanions were extracted by the reducing agent. In the two-phase mixtures composed of amorphous iron oxide pre-equilibrated with As (V) and Se (IV), and goethite or anatase, it was found that almost none of the As or Se was recovered in the reductive extraction solution. Since it was found earlier that As (V) and Se (IV) could be adsorbed by goethite and anatase under the conditions of the extraction, it was apparent that As and Se released from the completely dissolved amorphous iron oxide were readsorbed onto the remaining goethite or anatase. In the case of two-phase system where the concentration of anatase was reduced by an order of magnitude, As and Se initially sorbed on the amorphous iron oxide were partially recovered by the extractant. The authors therefore noted that the concentration of surface sites available for As and Se adsorption was crucial in determining their final concentrations in the extracts. In the case of the two-phase system containing montmorillonite, all As and Se were detected in the extracts. This was attributable to the previous finding by the authors that the clay did not adsorb either As (V) or Se (IV) at the low pH of the extraction.

In their often cited investigation of the accuracy of Tessier et al.'s extraction scheme (1979), Kheboian and Bauer (1987) doped each of four metals (Pb, Zn, Cu, and Ni) independently by adsorption or co-precipitation into various solid phases, including synthetic calcite (Pb), iron hydroxides (Cu or Ni), iron sulfides (Zn), commercial humic acid (Cu and Zn), and natural clay (illite) (Ni, Cu, and Zn). Three model sediments containing different levels of the spiked metals ("polluted" and "non-polluted", with adsorbed or co-precipitated metals) were prepared by combining phases and diluting with silica or cleaned illite. The recovery patterns of Pb originally spiked on calcite in both polluted and non-polluted co-precipitated systems were found similar, in that the majority of the Pb was recovered in fraction 3 (under reducing conditions), however this was not the appropriate recovery step (fraction 2) predicted according to the SE investigated. Extraction of the individually Cu doped illite resulted in about 80% (of that introduced) being recovered in fraction 1 ("exchangeable"), however in the non-polluted co-precipitated system containing the doped illite, the majority of Cu was recovered in fraction 5 ("residual"). A significant recovery (40%) of Zn from an extraction of individually Zn doped-illite was found in fraction 2 ("bound to carbonate"), but only about 20% of the metal in the non-polluted adsorbed system was recovered in the same fraction. The authors attributed the late recoveries of the metals observed to readsorption of the released metals onto remaining phases in these systems. Worthy of note here are some interesting aspects raised by other researchers commenting on this type of approach to assessing redistribution (Kheboian and Bauer, 1988; Tessier and Campbell, 1988, 1991). The use of artificial phases has been generally criticized by some authors with regard to how representative they were of components of natural systems. For example, the coexistence of Fe oxide and Fe sulfide in the models of Kheboian and Bauer (1988) was criticized, as the two phases are not simultaneously present in natural sediments (Tessier and Campbell, 1988). As part of their response to this comment, Kheboian and Bauer (1988) indicated that the results of their study using the models were in agreement with those of

Rapin et al. (1986) using natural systems in that labile sulfides were not extracted selectively by the SE scheme. The use of spiking methods to investigate the metal redistribution problem certainly has the distinct advantage that it assisted in reasoning the changes in recovery patterns of the metal (Kheboian and Bauer, 1988). It has been noted that the purpose of models is not necessarily to duplicate natural properties but to sharpen or focus certain questions; and that the use of well-defined systems such as synthetic models can provide some useful understanding about phenomena which may occur in the systems. In fact, Kheboian and Bauer (1988) and Tessier and Campbell (1988, 1991) seemed to agree on a point that further research on redistribution potential should be investigated using both synthetic models and natural systems as the approaches were complementary and should not be considered as being incompatible; and that alternative approaches, such as a "standard addition" procedure (in which metals are added to the extracting solution during the extraction of natural sediments and the recovery of the added metals is verified), and a "pre-equilibration" method (in which all synthetic components are initially equilibrated with metals studied) could be considered as possible candidates, as they seemed to minimize some of the debated problems.

The effectiveness of Tessier et al.'s extraction scheme at fractionating Cd was investigated by Kim and Fergusson (1991) using synthetic soil models in a similar manner as Kheboian and Bauer (1987). The metal was spiked by adsorption and co-precipitation onto synthetic calcite, crystallized Fe oxide (goethite), manganese oxide (hausmannite), commercial humic acid, and natural clay (illite). Various five-phase systems were also prepared by mixing a doped phase with four other clean ones (cleaned silica sand was used as diluent). In addition, each doped phase was mixed with uncontaminated natural soil in such a ratio that the Cd contribution from the real soil constituted only a minor portion of the total metal in the systems. The recovery patterns of each individually spiked phase were compared with those of the five-phase systems containing the corresponding spiked phases; the difference in the recovery patterns would suggest a possibility of Cd redistribution. The authors found that redistribution of Cd was minimal; only about 10% of Cd originally sorbed on or co-precipitated with calcite in both five-phase synthetic and spiked "real soil" systems was recovered in fraction 3 (" bound to Fe/ Mn oxides"), compared to the zero recovery of the metal by the same reagent observed from the extraction of individually-spiked calcite.
In addition, only a small percentage of Cd initially sorbed on hausmannite in the synthetic soil model was found in fraction 4 ("bound to organic matter"), which compared favourably with none of the metal being detected in the same fraction of the individually spiked-phase system. The authors speculated that the minimal redistribution of Cd observed, in contrast to the severe redistribution of Cu, Pb and Zn reported by Kheboian and Bauer (1987) could be due to the fact that of the four metals, the Cd^{2+} ion was stable over the widest pH-Eh range.
The difference in the behaviour of metals during SE was further shown in the work of Schriner (1994) who use the same synthetic systems as those of Kim and Fergusson (1991) to investigate in the same manner the effectiveness of Tessier et al.'s SE procedure to speciate Cu. In contrast to the results for Cd, in all of the five-phase systems tested, substantial

amounts of Cu, normally released in the early fractions during the extractions of individually spiked phases, were detected in fraction 4 ("bound to organic matter"), and to a lesser extent in fraction 5 ("residual") during the extraction of five-phase systems containing the corresponding spiked phases. Schriner (1994) remarked that the preference of Cu for redistribution towards the nominal "humic acid" phase implied in his study was in agreement with the capacity of humic acid to sorb metals at low pH values and the high affinity of Cu for organic matter.

Redistribution of Pb and Cu in the newer BCR scheme were observed in model soils studied by Coetzee et al. (1995). They found that in the case of mixtures of spiked natural solid phases: humic acid, kaolin, ochre (primarily iron oxide and alumino silicate), and quartz, the majority of Pb originally on the quartz phase was recovered at the extraction step 2 (reducing conditions), whereas in the case of the individually Pb-spiked quartz, all of the Pb was recovered at extraction step 1 by the acetic acid reagent. In the similar multi-phase solid system with Cu-spiked kaolin, about 50% of the Cu was recovered in the acetic acid solution, which compared to the recovery of almost all of the metal by the same reagent observed from the extraction of the individually spiked kaolin. The authors further investigated the effect which each phase(s) might have on the redistribution of Pb observed in the four-phase system, by sequentially extracting a mixture containing kaolin, humic acid and Pb-spiked calcite. They found that the concentration of Pb recovered by acetic acid at the first step of the extraction was decreased when the amount of the humic acid was increased. It was speculated that the humic acid, which is known to have a particularly strong affinity for Cu species, was likely to have played a major role in the redistribution of Cu observed.

1.6.5 (b). The use of models containing natural mineral compositions.

According recognition to the argument that use of models containing metal-doped phases might be biased toward redistribution (Tessier and Campbell, 1988; Tessier and Campbell, 1991), Shan and Chen (1993) proposed use of a model soil containing natural minerals and humic acid. The authors indicated that the model had a distinct advantage, which was that each mineral contained other minor geochemical phases, suggesting that the major and trace elements would have already been distributed among the various phases. In addition, the humic acid used was previously separated from a particular soil, providing knowledge of its origin and chemical characteristics. Therefore, the natural minerals used (calcite, haematite, pyrolusite (an amorphous manganese oxide), illite, and montmorillonite) and the humic acid were considered to have similar properties to those of the corresponding components of real soils. In this experiment, the possibility of redistribution phenomenon in Tessier et al.'s extraction scheme was assessed by comparing the recoveries of major and trace elements at each step observed from the extractions of model soils to the calculated values obtained by summing the amounts of the elements removed in each fraction by extraction of the individual natural minerals. The authors found that in almost all the cases studied, the experimental values from the extraction of the model soil for step 1 to 3 were smaller than the corresponding calculated values. In contrast, the experimental values for most of the elements recovered in fraction 4 and 5 were greater than the corresponding calculated results. This suggested that for most elements studied, exchangeable, carbonate-bound and amorphous iron-manganese oxide-bound fractions could be transferred from the solutions to the remaining solid phases, e.g., humic acid, crystalline iron oxides, and clay minerals, during the extraction. Since humic acid possesses an ability to form relatively stable complexes with Cu, Mn, Ni, Cu, Zn, Pb, and V, it was deemed consistent with observation that the humic acid might have played an important role as the sequestering phase in this experiment. The authors, however, noted that it was difficult to quantify the extent and to explain clearly the mechanism of such redistribution/ readsorption phenomenon. The author recommended that further study was required to gain a better understanding of the redistribution/ readsorption processes.

Tu et al. (1994b) utilized the model soil comprising natural minerals proposed by Shan and Chen (1993) to selectively investigate redistributions of Cu and Pb during the extraction of the fraction designated as "carbonate-bound" in the scheme of Tessier et al. (1979), with an objective of gaining an understanding about how the redistribution of trace metals was affected by changes in soil compositions. To achieve this, the authors conducted adsorption experiments, thermodynamic calculations, and redistribution experiments. In the adsorption experiments, the HOAc/ NaOAc extraction solution spiked with either Pb or Cu, was added to various two-phase solid systems containing calcite and either pyrolusite, humic acid, haematite, montmorillonite, or illite. Before being subjected to the adsorption experiments, the solid systems were treated with $MgCl_2$ to remove any exchangeable trace metals.
The results from the adsorption experiments were used to derive adsorption isotherms for Pb and Cu with the five individual phases. Thermodynamic calculations for conditional equilibrium constants (K_A) were then performed for each pair of metals and the solid phases. Pb-pyrolusite, and Cu-humic acid were found to possess the two highest K_A values. In the redistribution experiments, the spiked extraction solution was added into a series of model soils, each containing the same amounts of calcite, haematite, and montmorillonite but varying in their amounts of pyrolusite and humic acid. Each system tested in the redistribution experiments contained the same percentages of calcite and ratios of calcite to the extractant as those used in the adsorption experiments. It was found that the amounts of Pb extractable by HOAc/ NaOAc solution decreased with increasing amounts of humic acid and pyrolusite, but pyrolusite seemed to play a more significant role in the amount of Pb extracted than the humic acid did. These observations were in agreement with the finding that Pb has its highest K_A with pyrolusite. In the case of Cu, the presence of pyrolusite in the models appeared to have a negative effect on the metal recovery, as expected based on the observed high K_A of Cu and pyrolusite. In contrast, Cu present in the extracts was found to directly correlate with the portions of humic acid in the model soils. The authors assumed that this might be due to partial dissolution of humic acid during the course of the extraction, and further speculated that the dissolved ligand could possibly enhance the stability of Cu,

as a result of a competition between sorption sites on the solid humic phase and complexation sites on the dissolved humic acid. However, for Pb, different competing mechanisms might be involved which resulted in the different behaviours of the two metals observed; three possibilities for Pb were noted: (1) the Pb-humate complexes were adsorbed onto the solid surface; (2) the dissolved humic acid was adsorbed and then complexed with Pb; or (3) Pb bound to insoluble humic material rather than soluble humics due to differences in the classes of humic material. The authors concluded that the occurrence and extent of redistribution were determined by both the soil composition and the specific nature of a given metal. In the light of their findings, the authors noted that it was important to specify these variables for natural soil systems under investigation with regard to potential redistribution processes.

1.6.5. (c) The use of standard addition methods.

Ajayi and Vanloon (1989) added pure artificial phases (calcite, goethite, humic acid) into portions of the sediments under investigations in order to provide fresh unoccupied sites for retention of any metals released during extraction. Each portion of synthetic calcite, goethite, and commercial humic acid was added to the wet sediment just before the extraction step 2, 3 and 4, respectively (the addition was 10%, i.e., 0.1 g synthetic phase per g dry sediment). In some cases, a synthetic phase was added in a series in ratios ranging from 2.5 to 20%. The spiked sediments were subjected to a modified SE scheme of Tessier et al. (1979) in parallel with a control sample, then the results were compared. The effect on element distribution patterns of spiking samples with additional synthetic phases was observed for all the sediments tested, with clearer trends revealed in the sediments containing high levels of metals. However, the distribution patterns of Cd, Cu, and Ni obtained from the sediment containing a high metal content were only slightly changed after the single 10% addition of any of the synthetic phases. For Cu, no change in the distribution pattern was observed even with the highest 20% of an additional phase; it might be that in the systems investigated, humic acid, the most favourable destination phase of all the first 4 fractions, already dominated the retention of the metal. In the cases of Cr, Pb, and Zn, similar shifts in recovery patterns resulted from additions of the synthetic phases, with the largest effect shown in the partitioning patterns of Pb. In the case of Pb, with 10% addition of goethite, a clear redistribution from fraction 2 ("bound to carbonate") to 3 ("bound to Fe/ Mn oxides") was observed; with the addition of humic acid, significant redistribution from fraction 2 to 4 ("bound to humic acid") and additional shift from fraction 3 to 4 were evidenced. In the case of Mn, each additional phase promoted shift from fraction 1 ("exchangeable"). The authors concluded that although the redistribution did occur, the extent of this was generally quite small and not as great as reported in the work of Kheboian and Bauer (1987); therefore, for most metals redistribution might not be sufficiently large to invalidate the SE method.

Another alternative approach to standard addition which has been reported involved addition of trace elements during the extraction. Rendell et al. (1980) investigated the potential for adsorption of Cu, Pb, or Cd onto river sediment in the presence of various extractants including reducing agents, strong and weak complexing agents, a weak acid, an oxidizing agent, and a cation exchanger. These reagents were regarded as representatives of the types commonly used in extractions of soil and sediment. The loss of each metal from solutions was assumed to be evidence for potential readsorption of the metal released during sediment extraction. In the cases of almost all of the extractants investigated, except for EDTA and 0.1 M HCl, the adsorption of each metal onto the natural sediment was found to be significant (control experiments, i.e., systems without added metals, were performed in parallel for all cases). In the cases of Cu in ammonium acetate and Pb in H_2O_2, the adsorptions were found to be as high as > 96%, and about 85%, respectively. The authors remarked that the results strongly suggested that the readsorption of the metals investigated and other heavy metals would occur during an actual extraction.

In the study of Belzie et al. (1989), small amounts of trace elements were added into sediment samples in order to investigate post-extraction redistribution of As, Cd, Cu, Ni, Pb, and Zn during the modified procedure of Tessier et al. (1979). The amounts of the elements added at each of the extraction steps were established from their natural concentrations in each fraction observed, from the extraction of the original sediments. This was to preserve the conditions of normal extraction, i.e., the natural concentrations were not changed greatly (but the added amounts were still easily detected). In general, the additions did not exceed 100% of the amounts of the elements present in a given fraction of the control samples, and were made at the beginning of the extraction step investigated. By comparing the recovery patterns of the elements from the spiked samples with those from the unspiked samples (the original metal concentrations at each fraction), it was found that in all cases, except for Pb, quantitative recoveries of the spiked trace elements were observed, in the appropriate fractions within the limits of experimental error. In the case of Pb, a 90% loss was found in the acetic acid/ acetate buffer fraction. The authors speculated that it was possible that as the sediment samples investigated were low in carbonate, the acetic acid/ acetate extractant could probably have leached Pb from the surface of iron oxyhydroxide (which has high affinity for Pb), and at the pH of 5 the extracted Pb could have partially readsorbed onto this substrate, especially when the Pb concentration was increased (by spiking) in the extract. The authors also observed in their additional tests that adding large amounts of trace elements into natural samples could result in significant losses to readsorption during the extraction; this was speculated to be a reason for low recovery of trace elements spiked during the extraction of natural sediments with $NH_2OH.HCl$, previously reported by Rendell et al. (1980).

The authors, therefore, concluded that the extent of the redistribution problem in the natural sediments was probably not significant, however they noted that more studies on various natural sediment types were required before accurate conclusions could be drawn.

1.6.5. (d) The use of other techniques in parallel with SE methods or partial extraction.

During their investigation of the use of an SE procedure comprising hydroxylamine hydrochloride followed by oxalic acid/ ammonium oxalate for determining the distribution of metals between oxides of manganese and iron in samples removed from the wall of a lead mine, Tipping et al. (1985) observed redistribution phenomenon of some elements occurred during the $NH_2OH.HCl$ treatment. In this study, electron microprobe microanalysis (EPMA) was used to assess the elements (in relative contents) present in the sample before and after the hydroxylamine treatment. The results from EPMA revealed that Pb in the sample was found predominantly in the Mn phase, however after the treatment, a considerable amount of Pb was detected in Fe oxide phase. The results from sequentially extracting the sample revealed that one-third of Pb was recovered in the hydroxylamine extractant and the rest was found in the subsequent extraction step which involved an oxalate reagent. It was, however, observed that the hydroxylamine reagent could solubilize nearly all the Mn in the sample (but only about 10% of Fe), whereas the oxalate extractant was able to dissolve almost all of the Fe oxide phase. Therefore, the results from the SE and EPMA methods were not consistent with respect to the original phase association of Pb (i.e., Fe oxide vs Mn oxide phases, respectively). The authors speculated that under the slightly low pH of the hydroxylamine reagent, a considerable amount of the Pb released from the original Mn oxide phase was readsorbed onto the remaining Fe oxide compartment. The authors also noted that readsorption of Pb evidenced in this work was in agreement with the finding of Rendell et al (1980) (mentioned in the preceding *subsection 1.6.5. (c)*).

Bermond and Sommer (1989) applied thermodynamics in a study of limitations of the use of SE methods to speciate heavy metals in soil samples. The authors used arbitrary conditional constants to simulate the effects from the extractions of contaminated soil samples using two extraction steps commonly included in SE procedures, i.e., a divalent cation-exchange using calcium nitrate reagent and an oxidation of an organic constituent using hydrogen peroxide. The results from the calculations and those from the chemical extractions were found in agreement in that metal (M^{2+}) released from a constituent by the oxidative destruction reaction could reassociate with another component remaining in the sample. However, the authors implied that kinetic considerations, which were not included in this study, could significantly affect the outcome of the simulation. It should be noted here that in the subsequent report by Bermond (1992), thermodynamic considerations alone were used to provide reasonable explanations in support of the redistibution of Pb observed by Kheboian and Bauer (1987) (mentioned in the previous *subsection 1.6.5. (a)*). In addition to the investigation on the selectivity of the hydroxylamine hydrochloride reagent for Fe and Mn hydroxides components of soil samples (as mentioned earlier in *subsection 1.6.4.*), Bermond and Eustache (1993) had also studied time aspects of the extraction of trace elements by the reagent with a particular attention to the possibility of readsorption of such elements. They found that although there was no evidence of kinetics being important in the cation transfer phenomena from one constituent onto the others (i.e., each metal extracted increased with time but seemed to reach equilibrium state in all cases), the use of kinetic modelling with simple assumptions showed that the transfer might be involved during the acidified hydroxylamine treatment of the samples, without being detected simply on the basis of the shape of (kinetic) time curves.

In the work by Wallmann et al. (1993), previously mentioned in *subsection 1.6.4.*, thermodynamic calculation was also used to evaluate artefacts observed during sequential extraction of an anoxic sediment. Based on their findings that some sulfide minerals were more or less prematurely extracted in acidified extractants (pH ~ 5), the authors suggested that the dissolved sulfide anions generated (especially from the solubilization of ZnS and amorphous FeS) might precipitate trace metals originally bound in non-sulfidic phases as sulfide minerals during the extraction. They speculated that this redistribution process by dissolution and precipitation, rather then insufficient reactivity of the reducing reagent, was possibly responsible for the observation of Kheboian and Bauer (1987) that Cu originally retained on the amorphous Fe oxide in the synthetic soil model, was recovered later than expected in the extraction.

1.6.6. Previous attempts to counteract the metal redistributions.

Only a few attempts to inhibit or counteract metal redistribution have been reported. Martin et al. (1987), attempted to counteract redistribution of Ca using buffered $EDTANa_2$ (0.01 M) in a few steps of an extraction procedure. However, this was unsuccessful, since the presence of EDTA made no significant difference on the recovery of Ca at the first extraction. Howard (1988) attempted to capture Zn, Ni, Cu, and Pb released from solubilized calcite, during a single step extraction using sodium acetate, onto a polydithiocarbamate (PDTC) resin held in dialysis bags immersed in the solution. In the case of Pb, the presence of goethite (an iron oxide) had a significant negative effect on the uptake of the solubilized metal by the confined resin. The author speculated that this might be limited by the kinetics of Pb permeation through the dialysis membranes and/ or thermodynamics effect of the resin, and suggested that a different method for containing the resin and/ or another complexing agent should be explored. The author noted that in the case of Ni, the PDTC was useful in preventing redistribution onto the goethite, whereas, in the cases of Cu and Zn, the resin seemed to work, however the unresolved analytical problems and possible sediment inhomogeneity which resulted in inconsistent data prevented a specific conclusion. Schriner (1994) modified the first two extraction steps of Tessier et al.'s SE procedure by adding an organic phase containing a chelating agent into the system which previously contained a synthetic model sediment with a Cu-spiked phase and the conventional aqueous extraction solution. The approach was based on the idea that if a metal released from the original phase by a conventional extractant can be simulteneously removed from aqueous solution into an organic phase, reassociation of the metals onto the remaining solid phase in the system would not be theoretically possible (discussed further in *subsection 1.7.2.*).

In this work, the transport was facilitated by a complexation of the Cu, in the conventional extraction solutions, with the pyrrolidinedithiocarbamate ligand (PDC), initially introduced into the system via MIBK in the form of a $Zn(PDC)_2$ complex. At the end of the extractions, Cu in the $Cu(PDC)_2$ complex in the MIBK phase was extracted back into an aqueous phase (and later anlayzed), by the same principle of ligand substitution but using palladium (introduced as palladium chloride solution). The author applied this approach on several model sediments containing Cu in sorbed- and co-precipitated-modes of retention on various doped phases. However, by comparing the recovery patterns of the metal obtained from the use of the modified and the conventional SE schemes on model sediments with results obtained by applying the conventional procedure to the corresponding individually-spiked phases, the author considered that the modified extraction method was most promising in counteracting Cu redistribution in the model sediment containing Cu-sorbed humic acid. In the modified scheme, Cu concentrations in the first two extractions steps were slightly higher, and those in the later reducing and oxidizing steps were slightly lower (compared with Cu recovery patterns obtained from application of the conventional procedure on the same sediments). The author considered that the difficulty in retrieving colloidal solids in the region of the solvent interface was a major cause of the low total recovery of the metal observed in some cases. Based partially on this, the author recommended that before the potential of the modified scheme was fulfilled, more research was needed on how the SE and the solvent extraction techniques could be made more compatible with each other. Howard and Shu (1996) investigated the potential usefulness of a chelating agent, nitrilotriacetic acid (NTA), in inhibiting potential readsorption of metals (Pb, Ni, and Zn) in contaminated quartz-rich sediment and soil samples (each contained less than 6% organic matter (Walkey-Black method)). The authors initially used single phase reference materials and an artificial quartz-rich sediment spiked with solutions containing Pb, Ni, Cu, and Zn to assess the effects of various concentrations of NTA on the metal adsorption and on the potential solubilization of the solid phases. An NTA concentration of about 200 mg $litre^{-1}$ was found most promising in counteracting the adsorption of the metals onto the solid materials studied; at this concentration (comparing to its absence), the NTA did not seem to significantly dissolve the goethite, pyrolusite, calcite, and peat moss (reference materials for Fe-oxide, Mn-oxide, carbonate, and organic matter, respectively). The authors added 50 and 100 mg $litre^{-1}$ NTA to all reagents used in sequential extractions of the contaminated natural samples. In general, the levels of the metals recovered at the first two extraction steps (designed to target "water-soluble" and "exchangeable" forms) were found to increase significantly with increasing NTA concentration, with a corresponding reduction being observed in the metal recoveries at later steps of the extraction procedure. The authors noted that at higher concentration of strong sorbents such as organic matter, a higher concentration of NTA might be needed to inhibit the redistribution, but this was at a risk of causing phase-dissolution. In the light of their findings, the authors suggested that the effects of NTA at higher concentrations and a wider range of sample types should be a focus for further investigation.

1.7. Strategies for counteracting redistribution problem applied in this study.

Redistribution or reassociation of metal ions (being released from their originally associated phases) onto the remaining solid phases in the system during the course of an extraction, may be inhibited or counteracted by either introducing an alternative solid "sink" for the ions to react with before they have a chance to redistribute, or by complexing the ions to form stable water-soluble complexes in solution. Sequestering material in solid form, such as a cation exchanger, is of prime interest because use of such material represents the least modification/ disturbance to the system, having a low potential to directly attack the non-target phases present. In addition, solid material tends to be easily removed from the system or separated from the soil particles. Regeneration and reuse of such material is also possible. To be potentially useful, solid sequestering material must have sufficient chemical and physical stability under the extraction conditions applied; for instance, it must be stable in acidic extraction media, with vigorous shaking, or at high temperatures. Introduction of a soluble complexing ligand into the system is also of interest since the ligand will be present in the immediate environment of the metal ions, as they are being released into the solution by conventional extractant. This approach may have an advantage in kinetic aspects over the former approach. However, soluble complexing ligands of potential use should be capable of being used in low concentrations for counteracting redistribution of the ions investigated; at such concentrations, the ligand should not directly remove the metals originally bound on the non-target solid phases. To prevent this possible direct removal of the metals, the complexing agent could be introduced into the system via a second immiscible liquid (i.e., organic) phase. For both approaches, kinetics of the metal association reaction could play an important role; therefore, a sequestering/ complexing agent under investigation should be introduced into the system simultaneously with a conventional extractant, so that as soon as the metal ion becomes available in the solution (i.e., is released from a solid phase by the extractant) the sequestering/ complexing agent is available to compete for it.

Sequestering/ complexing agents of interest are those which not only have high affinity for metal under investigation but which also preferentially discriminate against other ions (which may be prevalent in the system) in favour of the analyte. In this study, the metal of interest, Pb, has strong affinity for a few elements, namely S, N and O. Therefore, sequestering/ complexing agents possessing functional group(s) containing such elements as active/ donor sites are generally considered as potentially useful for counteracting redistribution of Pb (should it occur during sequential extraction of synthetic soils). Examples of sequestering agents to be trialed in this study include a synthetic cation exchanger with sulfonic acid functional groups, polymeric materials functionalized with chelating groups (e.g., dithiocarbamate, $-NHCS_2^-$), and macrocyclic ligands with a polyether-like structure. A full list of sequestering agents used in this study is given in *Chapter 2 section 2.2*. In some cases, the same functional groups of interest are trialed in both solid (carrier) and dissolved forms. Examples of applications of the potentially useful sequestering agents in both environmental-related areas and other fields are also outlined.

1.7.1. Solid sequestering agents approach.

Ion exchangers are solid or suitably insolubilized high molecular weight polyelectrolytes which can exchange their mobile ions for ions of the same charge from the surrounding medium (Dorfner, 1991). The resulting ion exchange is reversible and stoichiometric, with the displacement of one ionic species by another on the exchanger. The exchange mechanism generally involves mass transfer processes within the liquid phase and the ion exchanger; the former process commonly referred to as film diffusion which is the counter-movement of ions to and from the liquid surrounding the ion exchanger and the surface of the exchanger, whereas the latter is described as particle diffusion which is the countermovement of ions within the ion exchanger in response to the process occurring at the surface of the exchanger. Ion exchangers can be any material including cellulose derivatives, clay and clay minerals, non-siliceous inorganic ion exchangers, and materials based on coal and other organic natural products. However, the most widely used modern ion exchangers are organic materials based on synthetic polymers. Synthetic ion-exchangers (commonly referred to as resins), developed about 60 years ago, have shown great potential for both environmental analytical applications (e.g., treatment of raw, polluted and waste waters), and industrial applications (e.g., metal recovery in plating industries). Details of the historical development and uses of ion exchangers can be found in many publications, such as Walton and Rocklin (1990) for uses in analytical chemistry, Dorfner (1991) for a comprehensive review, Howe-Grant (1995) for uses in chemical technology, and Skogley and Dobermann (1996) for the uses in soil and environmental studies. The most important starting material generally used in synthesis of resin ion exchangers is styrene. Styrene is polymerized with itself to produce long chains; these chains are reacted with divinylbenzene (DVB) to produce cross-linkages (varying degrees of polymer chain cross-linkage can be obtained, which influence the physical and chemical properties of the resin) (Skogley and Dobermann, 1996). The matrix plays a strong role in resin properties, but the chemical properties are conveyed primarily by reactive groups (called ionogenic groups). The ionogenic groups can be cationic or anionic moieties which are incorporated into the resin during its manufacture; for cations, they include strong acid of sulfonic acid type, weak acid of the carboxylic type, and medium-strong acid of phosphorus and arsenic types. Cation exchange resins, especially the sulfonic resins, have the widest industrial application in water softening (Dorfner, 1991). The effective pH ranges of strong and weak acid cation exchangers are approximately 0 - 14, and 5 -14, respectively.

Parameters frequently used in characterizing the behaviour of ion-exchangers include exchange capacity, selectivity, and distribution ratio (e.g., the ratio of the concentration of solute in the ion exchanger to its concentration in the external solution). Exchange capacity of resins (strongly influenced by the type of ionogenic group and the degree of cross-linkage) (Skogley and Dobermann, 1996) is defined as the amount of counter-ion (the mobile exchangeable ions, e.g., H^+-form for cation resins and OH^--form for anion resins) that a resin can accumulate (Dorfner, 1991), and may be expresses in units of $cmol_c\ kg^{-1}$. It was noted that most ion-exchange resins have capacities between 50 and 500 $\mathrm{cmol_c\ kg^{-1}}$, with nominal values between 100 and 300 $\mathrm{cmol_c\ kg^{-1}}$, figures which greatly exceed the cation-exchange capacity of most bulk soils (Skogley and Dobermann, 1996). Selectivity is defined as preference of resins for one ion over another present in the same solution, and is normally characterized as the ratio of the ionic fraction of the exchanging ions in the two phases (e.g., in the exchange of Mg^{2+} and Ca^{2+}, the selectivity coefficient, $k_{Mg/Ca} = [Mg]_r\ [Ca]/\ ([Mg]\ [Ca]_r)$, where the subscript "r" designates concentrations in the ion exchanger). Due to exchange processes being governed by electrostatic coulombic force, some properties of the counter-ion which favour uptake include higher valence (especially in dilute solution), smaller size of the hydrated metal ion (i.e., distance of closest approach to functional group), greater polarizability, stronger complex formation with the fixed ion, and weaker complex formation with co-ions (mobile ionic species with a charge of the same sign as the fixed ions); i.e., if a metal ion can complex with an anionic ligand, its net positive charge is reduced and this decreases its retention by the resin). For a general purpose cation exchanger and aqueous solutions usually the following selectivity sequences (sometimes referred to as strength of binding) are valid for the most common cations: for univalent ions $Tl^+ > Ag^+ >> Cs^+ >> Rb^+ > K^+ > Na^+ > H^+ > Li^+$ and for divalent cations the order is $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > UO_2^{2+}$ (Dorfner, 1991). In terms of charge, the order of preference is $+1 < +2 < +3 < +4$. However, selectivity among cations could be practically poor, in particular, separations within the group of Ni, Cd, Cu, Co, and Zn, as revealed in a summary by Warshawsky (1976/1977) of the use of sulfonate resins with varying degrees of DVB cross linking; for instance, with 4% DVB cross linking, the relative affinities (in relation to that of Li) for Ni, Cd, Cu, Co, and Zn were found to be only very slightly different, i.e., 3.45, 3.37, 3.29, 3.23, and 3.13, respectively. Dorfner (1991) noted that although standard ion exchangers with well-known groups (e.g., sulfonic and carboxylic) were characterized by their selectivities, if the relative selectivities of ions in a mixture were close to each other, these exchangers would take up all ions, regardless of whether this was desired or not. Warshawsky (1976/1977) also demonstrated that increasing DVB cross linking in polystyrene strong acid resins led to an increase in the selectivity; this was attributed to the fact that the increase in DVB led to a decrease in the extent to which the resin would swell in solution, and consequently, to a decrease in the average pore size. The resin therefore becomes more selective for smaller cations with increasing DVB.

More recently, Beveridge and co-workers (1989b) attempted to examine the effect of soluble Ca on the determination of the labile contents of Pb, Cu, Cd, and Zn in sediments with various cation-exchangers. Based on the evaluations using synthetic mixtures of the ions (each with concentration of 2, 5, or 10 mg $\mathrm{litre^{-1}}$), and calcium-rich waste substrates, the ion uptake found to be most influenced by Ca competition was that of Zn; uptake of Pb was found to be the least affected. The authors remarked that for minimum error in the determination of the labile fraction, the level of free Ca^{2+} present in the solution should not have exceeded 300 mg $litre^{-1}$; in addition, the amount of exchanger added must provide an excess of exchange sites in relation to the amount of cations released from the sample. The authors also noted that weak cation-exchangers were particularly sensitive to the competing effect of the Ca ion.

The most common resins used in soil research are macroporous (also called macroreticular) resin beads (Skogley and Dobermann, 1996). Macroporous ion exchangers are types in which a solvent is used during production from the monomers, so that a porous matrix structure of large internal surfaces is formed in the course of polymerization (Dorfner, 1991). In its early applications, the loose resin was suspended in a given soil-water mixture with a subsequent separation by either sieving (provided that its bead size is different from the soil particles) (Sibbesen, 1978) or other separation techniques, such as density-gradient centrifugation (Thien and Myers, 1991). Separating resin beads from soil particles is quite a tedious task, and therefore, several researchers attempted to confine the loose resin beads by placing them into a cage made of rigid plastic (Beveridge et al., 1989a, b; Slavek and Pickering, 1989; Slavek et al., 1990), or a bag made of a piece of porous nylon fabric (Sibbensen, 1977), prior to the introduction into the systems investigated. In more recent studies, introduction of the ion exchange in membrane form has shown to reduce the difficulty at the separation stage (Saggar et al., 1990; Abrams and Jarrell, 1992; Kay, 1996). In this present study, the commercial cation exchange in membrane form (with sulfonate functional group) will be trialed. Ion exchange resins applied in soil science research have been commonly used as ion sinks (i.e., to determine the quantity of target ions accumulated by the resin) for assessing bioavailability of trace metals (Beveridge et al., 1989a,b; Slavek and Pickering, 1989; Slavek et al., 1990), and essential anionic moieties, such as phosphate, or sulfate (anion exchangers in membrane form were applied in the studies of Saggar and co-workers (1990), Abrams and Jarrell (1992), and Kay (1996)); the ion exchange resin technique has also been found to be of potential use in determining the total flux of N (measured as NO_3^- or NH_4^+) occurring below the root zone in soil (Schnabel, 1983).

In a further development in ion exchange resin technology, resins have been synthesized in which a variety of metal-specific reactive groups are incorporated; the reactive groups generally have properties of a specific reagent, and commonly have a few elements that can act as electron donors, namely O, N, S, P or As. These resulting resins are generally referred to as chelating/ coordinating/ selective/ specific resins (Nicol et al., 1987; Warshawsky, 1987a; Dorfner, 1991); according to Warshawsky (1987a), "coordinating" ion exchange resins are polymers carrying pendant ligands which are usually neutral, most notably macrocyclic ligands (in this study, macrocyclic ligands in dissolved forms will be used; in *subsection 1.7.2.* is outlined fundamental chemistry and the applications of the ligands). Metal ions are retained onto chelating resins from aqueous solution by a mechanism similar to that of cation-exchange resins. However, the exchange of metal cations in solution with protons on the resin does not involve dehydration of the metal ion for cation-exchange resins, but for chelating resins it does, and the metal cation is bound in the resin phase by a combination of outer-sphere ionic and inner-sphere covalent forces; as the name implies, the reaction usually results in a cyclic structure formation (Nicol et al., 1987; Warshawsky, 1987a; Dorfner, 1991). Therefore, for binding with chelating resin, the size of the ion, its charge and other physical properties are of secondary importance compared with the nature of ligands and the metal (e.g., electronic configuration). In chelate ion exchange resins, bond energies for divalent cations are commonly found to be 5 to 10 times greater than those of cation exchange resins. Chelating ion exchangers are also more specific (i.e., have greater selectivity) for certain metals than the cation-exchange resins. The introduction of these specific resins significantly increases the applications of resins in the fields of chemical analysis and hydrometallurgy (Nicol et al., 1987) (e.g., recovery of metal from strongly acidic and dilute solutions). Hydrometallurgy, as the name implies, involves the processing of an ore or concentrate by dissolution, separation (from other species that may be present in the original solution), and purification and precipitation of the desired metal by the use of aqueous solutions, where the extraction is from the aqueous phase to a liquid or a solid organic phase (Nicol et al., 1987; Warshawsky, 1981). In this study, a commercial macroreticular resin with thiol functional groups (RSH) will be investigated. Examples of the applications of resins containing the thiol group or its derivatives (e.g., dithiocarbamate, $-NHCS_2^-$) include a separation of Ag, Hg, Bi, and Au from acidic aqueous solution (Moyers and Fritz, 1976), a preliminary extraction of ^{106}Ru from acidic simulated nuclear waste effluent containing high salt concentrations (Dyer et al., 1984), a removal and determination of toxic metals (e.g., Hg, and Cd) from sea water as noted by Warshawsky (1987a), a separation of Hg from a solution containing 10 mg litre^{-1} each of Cd, Pb, Cu, and Hg, as noted by Dorfner (1991), a determination of Pb in snow, Cu in whole milk and tapwater, and Cu, Cd, and Pb in natural water, using polydithiocarbamate chelating resins (Hackett and Siggia, 1977) and the use of polyisothiourea resins for preconcentration of Au prior to pelletization and analysis using X-ray fluorescence (Blount et al., 1973), or for extraction of Pt group metal ions in the hydrometallurgical process (Warshawsky, 1987b) (Pt group metals have a wide range of applications, e.g., in petroleum refining, electrical uses, glass industry, exhaust gas converters in automobiles, and cancer therapy). The synthesis and characterization of polydithiocarbamate chelating resin and potential applications to trace metal analysis can be found in a numbers of publications, such as those of Dingman and co-workers (1974), Hacket and Siggia (1977), Horvath and Barnes (1986), and Cras and Willemse (1987). In this study, dithiocarbamate ligands in the dissolved form will be assessed; fundamental chemistry of this ligand and its applications in the dissolved form are outlined in *subsection 1.7.2*. It is interesting to also note here some applications of aminodiacetate resins, whose functional group is similar to a chelating agent, NTA (nitrilotriacetic acid), to be used in dissolved form in this present study. Aminodiacetate resins have been used for analysis of trace elements in geological solid samples (Co, Bi, and Ni, Blount et al., 1973), seawater (e.g., Cr, Cu, Cd, and Pb, Sturgeon et al., 1979), and marine molluscs (V, LaTouche et al., 1981).

Chelating or coordinating groups can be attached to materials other than synthetic polymers using suitable reaction (Warshawsky, 1987a); examples of these "support" materials include silica, alumina, cellulose, and chitosan (a natural polysaccharide obtained from fungal organisms and marine animals). Inorganically-supported chelators, such as functionalized silica, may exhibit faster kinetics than corresponding organic based ones, as the sites are on the surface of the inorganic matrices (Hudson, 1986). In this study, the following functionalized matrix will be assessed: silica gel with thiol groups ($Si(CH_2)_3SCH_2CHOHCH_2SH$), silica gel and wool with dithiocarbamate, wool containing phosphorus-containing ligands (wool-N-CH_2-$P(CH_2OH)_2$; wool-THP), and a cotton fabric with P-reactive group. The functionalized cotton fabric with a P-reactive group, commercially known as Proban, is used as flame retardant material for safety purposes (Harper and Beninate, 1988; Faroq et al., 1994; Hall et al., 1994) (the P-functional group possibly binds metals via interactions with P=O and/ or C=O, Henderson (1996)). Hercules and co-workers (1973) used glass surfaces coated with the dithiocarbamate group, in combination with electron spectroscopy (ESCA) for trace analysis (e.g., Pb, Tl, and Hg) in water (the surface was produced by treating glass fibre with an amino functional silylizing reagent and subsequently with carbon disulfide and sodium hydroxide to form the dithiocarbamate). Similarly, Leyden and Luttrel (1975) immobilized several chelating groups, including dithiocarbamate, onto silica gel; these materials were then determined for their potential as a preconcentration matrix for metal analysis (e.g., Pb, Cu, Zn), using X-ray fluorescence.

It is interesting to note here a development in ion exchange resins to meet the need for ion-selective resin for potential applications, especially in metal separation in hydrometallurgy. This involves solvent impregnation of resin. In a solvent-impregnated resins (SIR), the organic complexing agent (extractant) in liquid form (or retained in liquid state by an addition of a diluent) is physically incorporated (i.e., dispersed homogeneously) into the pores of an inert solid polymeric carrier without undergoing chemical bonding to the polymer (Warshawsky, 1981). In general, SIR resembles closely the behaviour of the extractants in solvent extraction systems, as regarding complexation and decomplexation chemistry, ion-selection patterns, ion-distribution behaviour, and kinetics. SIR were introduced to bridge the gap between liquid-liquid extraction and solid ion exchange in that they should eliminate the disadvantages inherent in solvent-extraction and ion-exchange processes, and consolidate their respective advantages (Nicol et al., 1987); they should combine the fast mass transfer rates, high distribution factors, and selectivity factors distinctive to the extractants dissolved in a liquid organic phase, with the simplicity of equipment and operation distinctive to solid-ion-exchange technology. Trialled uses of SIR, as summarized by Warshawsky (1981) and Nicol and co-workers (1987), include the use of solvent-impregnated phosphorus-containing resin in recovery of Au from very dilute cyanide solutions, and in the separation of Zn from Co sulfate solution in a cobalt electrorefining plant. Horwitz and co-workers (1994) systematically investigated the selectivity of an impregnated chromatographic resin for Pb in acidic aqueous solutions over selected elements and the effect of macro levels of several elements on the Pb retention. The resin was prepared by sorbing a solution of a derivative of a macrocyclic polyether compound, 18-crown-6, in isodecanol on an inert polymeric substrate. The resin (now commercially available) was found to retain Pb efficiently and selectively over a wide range of nitric acid concentrations. In cases where other ions, such as Sr^{2+}, were retained on the resin to varying degrees under certain conditions, the differences in the resin capacity factors for these ions were sufficient to allow the isolation of only Pb. In addition, most commonly encountered cations, such as Ca^{2+}, Fe^{3+}, Na^+, were essentially not retained by the resin. The resin was also found to effectively isolate Pb from digested geological samples, for a subsequent determination of Pb isotopes (additional applications of this resin in analytical chemistry can be found in the literature, for example, Horwitz and co-workers (1991), and Sooksamiti and co-workers (1996)).

1.7.2. Dissolved sequestering agents approach.

Various organophosphorus acids have been used as commercial extractants in solvent extraction of metals in hydrometallurgy (Flett, 1977; Nicol et al., 1987); for example, in the recovery of U from nuclear waste liquors or from solutions obtained by the leaching of low-grade ores with sulfuric acid, and in the separations of In(III) and Tl(III) from Cu or Zn plants. In this present study, a commercial phosphorus-containing extractant derived from phosphine, known as Aerophine (sodium di-isobutyl-dithiophosphinate; $R_2PS_2^-Na^+$) is to be assessed. This compound has been used as flotation reagent ("collector") for separation of galena, chalcopyrite, and precious metals from complex sulfide ores (Brinen et al., 1993) (Flotation is a mineral separation technique, which relies upon the selective conversion of water-wetted (hydrophilic) solids to non-wetted (hydrophobic) ones. This enables the latter to be separated if they are allowed to contact air bubbles in a flotation froth. If the surface of the solids to be floated does not possess the requisite hydrophobic characteristic, it must be made to acquire the required hydrophobicity by the interaction with, and adsorption of, specific chemical compounds known as collectors (Nicol et al., 1987)). Gorken and co-workers (1992) remarked that in contrast to the xanthate ($-OCS_2^-$) and dithiophosphates ($-O_2PS_2^-$) groups, the dithiophosphinates were more resistant to aqueous oxidation and formed more stable, insoluble complexes with many transition metals and lead. They are expected to be stable at elevated temperatures. The authors further noted that these characteristic properties of dithiophosphinates could partly explain the observed high collector strength, adsorption and flotation kinetics for Pb, Cu, and precious metal values, and the improved selectivity against iron sulfides and sphalerite. Jdid and co-workers (1995) investigated a selective recovery of silver from photographic bleach-fix solutions by ionic flotation using Aerophine as a collector. The authors found that for a collector concentration ranging between once and twice the silver concentration, the recovery rates reached 99% and they were not significantly affected by a pH variation from 4 to 8 and a temperature increase between 20°C and 40°C. It could be noted here a work of Brinen and co-workers (1993) who used Secondary Ion Mass Spectrometry (SIMS) to investigate the surfaces of natural galena crystals treated with a homologous series of dialkyl dithiophosphinates, obtained during mineral flotation. It was found that the technique could detect the adsorbed species and characterize the mineral surface before and after the adsorption of the organic molecules. In a continuation of this work, Brinen and Nagaraj (1994) used SIMS to examine the nature of any Pb-Aerophine complex on the surface of galena. They found evidence for the presence of a 1:1 complex of the reagent and Pb; however, no evidence had been found for the possibility of S-S bonding between PbS and diisobutyl dithiophosphinate.

In analytical chemistry for the determination of trace metals, liquid-liquid extraction methods are commonly used preparation strategies for the simultaneous separation the metals from interfering matrix components and preconcentration the metals from sample solutions (Sachsenberg et al., 1992). With respect to the analysis by AAS, extraction procedures using dithiocarbamate chelating ligands ($R_2NHCS_2^-$) have been one of the most widely used preparation techniques (Lo et al., 1982). In this study, the principle of the extraction procedure using the dithiocarbamate ligand for transporting metal(s) from aqueous sample solution to organic phase will be applied (a general comment on the adaptation of the liquid-liquid extraction process for use in the present study is further outlined below).

Dithiocarbamates, as a class of compounds, are capable of forming exceptionally strong, insoluble, and often highly coloured complexes with several elements; metal chelation occurs via the two S atoms with the establishment of a four-membered ring (in Cullen (1964) is illustrated 1:1 and 1:2 metal : ligand complexes). Normally, a high degree of strain and hence instability is associated with small chelate rings but here electron delocalization within the rings which extends into the rest of the ligand exerts a counterbalancing stabilization effect (Bell, 1977). Notable exceptions to this are the alkali and alkaline earth elements (Sachsenberg et al., 1992). For this reason, dithiocarbamate complexing agents have been of great interest in trace analytical work related to natural waters where these elements exist in high concentrations (Hackett and Siggia, 1977). A large numbers of studies on the sea water (natural or artificial, with or without spiking) matrix have been reported (Kremling and Petersen, 1974; Danielsson et al., 1978; Jan and Young, 1978; Sturgeon et al., 1979; Magnusson and Waterlund, 1981; Lo et al., 1982; Sachsenberg et al., 1992; Zhuang et al., 1994). Waters polluted with, for example, surfactants have also been studied (Cu, Ni, Fe, Co, Cd, Zn, and Pb, Pakalns, 1981). In addition, dithiocarbamate liquid extraction methods have also been applied to various types of samples; for instance, acidic solutions obtained from digestion of rocks/ ores (Co, Cd, Cu, Ni, Zn, Fe, and Pb, StJohn, 1970; Au, Ag, Cu, and Cd, Pernicka et al., 1978), wine (Pb and Cd, Anders and Hailer, 1976), EDTA extracts of soil (Cu, Pb, Cd, Ni, and Co, Pedersen et al., 1980), blood (Pb, Baird et al., 1996) and urine (Cd and Pb, Aydemir and Gucer, 1996).

Dithiocarbamate (DTC) derivatives commonly used in trace metal analysis include diethyldithiocarbamate (DDC) and pyrrolidinedithiocarbamate (PDC) (Shen et al., 1980). DTC reagents are generally only slightly dissolved in organic solvents (Brooks et al., 1967). However, metal-dithiocarbamate chelates have a relatively high solubility in organic solvents, like MIBK, 2,6-dimethyl-4-heptanone (DIBK), chloroform, etc; Sachsenberg and co-workers (1992) remarked that distribution coefficient values (K_D, defined as $[\text{complex}]_{\text{in organic phase}} / [\text{complex}]_{\text{in aqueous phase}}$) could be in the order of > 5,000. Shen and co-workers (1980) noted that the extraction constant values for metal-dithiocarbamates ($K_{M(DTC)m} = [M(DTC)_m]_{org} / ([M^{m+}]_{aq}\,[DTC^-]^{m}_{aq})$) was of importance in predicting feasibility of separating selectively a single metal or a group of metals, from an aqueous phase to an organic phase. In an early attempt along this line, Wyttenbach and Bajo (1975a) investigated the order of extraction for 14 elements. In their study, $Zn(DDC)_2$ in $CHCl_3$ was used as a reagent; successive substoichiometric increments of this reagent were used to extract mixtures of two elements (all marked with appropriate isotopes) from a 0.1 N H_2SO_4 medium. The extraction order was established by comparing the extraction curves obtained from plotting the extracted fraction of the metal vs amounts of reagent added. The order found for successive extractions was Au^{3+}, Hg^{2+}, Tl^{3+}, Ag^{+}, Cu^{2+}, Bi^{3+}, Sb^{3+}, Te^{4+}, Mo^{6+}, Se^{4+}, In^{3+}, As^{3+}, Pb^{2+}, Cd^{2+}. However, no quantitative values of extraction constants were reported in this study. Wyttenbach and Bajo (1975b) and Bajo and Wyttenbach (1977, 1979) further investigated the use of HDDC and several different metal-DDC compounds as extractive reagents to achieve selectivity; this resulted in a scheme for selective isolation of Cd^{2+} from a variety of matrices (in Wyttenbach and Bajo (1975b) is summarized the order of metal extractions at various pH values reported in the literature). Yeh and co-workers (1980) determined extraction constants for DDC complexes of Hg(II), Bi(III), Cd(II), As(III), and Fe(II) using substiochiometric extraction and radiotracers; $Zn(DDC)_2$ or TlDDC were used as extraction reagents. The extraction constants in $CHCl_3$/ dilute HCl systems reported in terms of (1/m) log $K_{M(DDC)m}$, were as follows: Hg(II) (20.3, in 0.1 N HCl), Bi(III) (13.8, in 0.22 N HCl), Cd(II) (9.45, in 0.1 N HCl), As(III) (8.14, in 0.1 N HCl), and Fe(II) (7.70, in 0.15 N HCl); the authors noted that these values were in good agreement with those in the literature. The authors noted that $K_{Cu(DDC)2}$ and $K_{Zn(DDC)2}$ used in their study (i.e.,$10^{26.8}$ and $10^{15.9}$, respectively) for evaluation of other extraction constants were those reported in the literature. Shen and co-workers (1980) determined extraction constants for DDC and PDC complexes of Pb(II), Zn(II), Tl(I), and Mn(II) using a two-step extraction method with a radiometric technique, with HDDC or HPDC as extracting agents in chloroform solution. In this study, $K^{acid}_{M(DTC)m}$ (= $[M(DTC)_m]_{org} [H^+]^m_{aq} / ([M^+_m]_{aq} [HDTC]^m_{org})$ was determined from the extraction procedure. $[H^+]$ was measured using pH meter, $[M(DTC)_m]_{org} / [M^+_m]_{aq}$ was determined from distribution ratio of the metal in two phases (which was measured by radiotracer activity), and $[HDTC]_{org}{}^m$ was determined by shaking an appropriate amount of organic phase with an excess of Cu^{2+} solution immediately after the organic phase was separated by centrifugation, subsequently the material balance for the two-step extraction method was derived. $K^{acid}_{M(DTC)m}$ was then used for the calculation of $K_{M(DTC)m}$. The authors reported both $K_{M(DTC)m}$ and $K^{acid}_{M(DTC)m}$ for both types of ligands. The extraction constants in $CHCl_3$/ water systems reported in terms of (1/m) log $K_{M(PDC)m}$, were as follows: Pb(II) (8.13), Zn(II) (6.96), Tl(I) (6.46), and Mn(II) (3.63).

Extraction of metal ions from aqueous solution by complexation with a DTC reagent is influenced by several parameters including the type of metal ion (as outlined above), the acidity, types and concentrations of the DTC, types of organic solvent, interfering ions, and reaction time. From a practical point of view, Brooks and co-workers (1989) and Murakami and Takada (1991) noted that extraction of metal chelates from a very acidic solution had significant advantages, for instance, metals could be directly extracted from a sample dissolved in acid (a condition likely to be encountered in the course of geological samples) without pH adjustment and a requirement for dilution of the sample solution was only minimum; thus the extraction would save time. However, acidity of aqueous phase has been commonly noted for its influence on both the stabilities of the DTC reagent and the metal-dithiocarbamate complex after extraction into an organic solvent. DTC reagents are reported to be unstable in highly acidic solution. The decomposition can proceed through formation of HDTC and is characterized by a loss of CS_2 and a formation of amine derivatives (Dellien and Persson, 1979). Anders and Hailer (1976) noted that for ammoniumpyrrolidine dithiocarbamate (APDC), at pH values < 4, formation of the free acid occurred, which then decomposed with a half life of 40 min at pH 3 and of 26 min at pH 2. The authors further remarked that in practical work this decomposition is highly unwanted since it not only lowers the effective APDC concentration to levels unknown but also yields a flake-like material which may block the entrance of the capillary suction tube of the AAS instrument. However, PDC is also remarked on for its relative stability in acidic solution (Murakami and Takada, 1991). Dellien and Persson (1979) noted that PDC was often reported as a preferred reagent to DDC when extractions are performed in acidic solution; the authors, however, also noted that there were a few studies, such as those of Tweeten and Knoeck (1976), and Hannaker and Hughes (1977), showing the usefulness of DDC for metal extraction in the pH range 2 - 4. In order to allow for the decomposition of the reagent at low pH, an addition of an excess amount of chelating agent is not uncommonly suggested (Takada, 1982). As an alternative to the introduction of ligand into the system via aqueous (acidic) solution, Wyttenbach and Bajo (1975a) suggested the addition of a ligand via an organic phase, namely, $Zn(DDC)_2$ in $CHCl_3$. The authors remarked that this reagent was preferred to an aqueous solution of NaDDC because HDDC, which was formed upon acidification, has a half-life of decomposition of only 7 s in solutions of pH < 2. It was, however, noted that when the reagent was shaken with acid aqueous solutions, it would be partially protonated (approximately 50% at pH 1 and 95% at pH 0) and thus reacted as an organic solution of HDDC. The reagent stability against acid decomposition under these conditions was found to be great enough to allow extraction times up to 15 min. Bajo and Wyttenbach (1979) subsequently found that that when solutions of $Cd(DDC)_2$, $Zn(DDC)_2$, or HDDC as reagents in $CHCl_3$ were used to extract acid aqueous solutions, they deteriorated as a function of pH and time; however, this deterioration was much less rapid than the destruction of a solution of NaDDC. Although the importance of acidity on the stability of pure dithiocarbamic acid in aqueous solution has been widely reported, it appears that the time stability of the metal complexes after extraction into an organic solvent is generally considered more important. Several reports have commented on the limited time stability of PDC-complexes in MIBK (Brooks et al., 1967; Kinrade and Van Loon, 1974; Dellien and Persson, 1979; Takada, 1982). In a study of Takada (1982) on the effect of acidity of the aqueous phase on the kinetic stability of a Cu(II)-PDC extract in MIBK, it was found that the complex was formed under a wide range of acidities (0.01 to 6 M HCl); however the half-life of the Cu(II)-PDC extract decreased as aqueous acidity increased (note: (i) the rate of decomposition was monitored by taking samples at various time intervals and measuring the absorbance of the copper chelate, (ii) the timing was started when the pH of Cu-PDC solution was adjusted (which was followed by shaking with MIBK for 5 min), and (iii) the MIBK extract was separated rapidly from the aqueous phase without washing). At an acidity of more than 7 M HCl, the chelate readily decomposed during the extraction period of a few minutes; however, at an acidity of ≤ 0.1 M, the copper chelate in MIBK was stable for more than 4 h. Takada (1982) also found that at very low pH, if the extract was separated quickly from the aqueous phase and washed with water, there was no measurable decrease in absorbance after 1 h; the authors attributed this to the removal of free acid in the MIBK phase by the washwater. Similar observations of the stability of the MIBK extract if separated from the aqueous phase was reported by Dellien and Persson (1979), who investigated the effect of hydrogen-ion concentration on the extraction of Co, Ni, Cd, and Pb, using APDC/ MIBK. Dellien and Persson (1979) noted that kinetically labile complexes would decompose when the concentration of free ligand had decreased below the level necessary for the formation of the extractable (i.e., neutral) complex (the decomposition products of the ligand may also react with the metal ions to form precipitates) and that the decomposition could be accelerated not only when the acidity of the aqueous phase was increased but also when the contact area between the two phases was large (produced by the geometry of the system or by shaking). The authors found that the time stability of the extracted complexes in MIBK increased in the order Cd < Pb < Ni < Co (assessed at pH 1). In addition, the results of individual extractions of Pb, Cd, Cu, and Ni at different pH values ranging from 0.2 to 6, with 1 min shaking time with MIBK, revealed that Pb and Ni were extracted equally well over this pH-range, while Co and Cd required pH > 1. The authors deduced that this showed that an "optimum" value for the extraction of any of these metal ions did not exist, in the sense that there was not a particular pH value that gave better extraction than other values slightly different from it. The authors, thus, remarked that there was no need for precise pH control anywhere in the range 1 - 6 for the metals investigated. In a study of Brooks and co-workers (1989) on complexation in strongly acidic media, approximating the actual conditions likely to be encountered in the course of silicate rock analysis, the authors found that stable complexes of 24 metals with APDC were formed in strongly acidic (0.5 - 6 M) solutions and could be extracted into MIBK; Pd (K_d = 8000), Sb (K_d = 10 000) and Bi (K_d = 3500) were found to be particularly easily extracted. Murakami and Takada (1991) investigated the limit of acidity for the extraction of Cu with the APDC/ DIBK system from concentrated HCl (0.01 - 8 M) and (0.01 - 5 M) nitric acid media. It was found that with the use of 8×10^{-2} M APDC (500-fold reagent : metal molar ratio), the complete extraction could occur at solution acidities of up to 8 M HCl or 4 M HNO_3. The authors also noted that a considerably larger amount of the reagent is needed for complete extraction of Cu chelates extracted from nitric acid solution than from HCl solution; this was attributed to possible oxidation of the reagent and the chelate by the HNO_3. Some researchers used a mixture of ligands, such as APDC + DDC (Kinrade and Van Loon, 1974; Lo et al., 1982) and APDC + oxine (8-hydroxyquinoline) (Sturgeon et al., 1979), as extracting agents. A combination of ligands was found to provide a broader working pH range and a stabilizing effect for extractions of some metals, such as Ag, and Mn. A variety of organic solvents, as mentioned earlier, have been used to extract the metal complexes formed. A number of desirable characteristics of the solvent, as noted by Kinrade and Van Loon (1974), include not only that it extracts the desired metal-chelates but also that it be immiscible with the aqueous solution, not tend to form emulsions, and in case of direct analysis of the organic extracts (see below) have good burning characteristics and enhance rather than suppress the AA sensitivity as compared to the metal in water.

The authors noted that MIBK was one of the more favoured solvents. However, Murakami and Takada (1991) noted that MIBK was less suitable for the extraction in strongly acidic media, because a considerable part of the MIBK phase was dissolved into the acidic aqueous phase, and a large amount of free acid contaminated the extract and caused decomposition of the Cu chelates. In contrast to MIBK, the authors noted that DIBK was virtually insoluble in up to 10 M HCl. It was found that the Cu chelate extracted into DIBK exhibited excellent stability. Lo and co-workers (1982) used chloroform as solvent in the determination of trace metals in seawater samples. It was noted that unlike oxygenated solvents, chloroform will not extract Cl^- and Br^- which may cause interference in AAS. The authors also remarked that chloroform had low solubility in water and had high extraction efficiency for most of the metal dithiocarbamates, suitable for the extraction of low levels of metals in a large volume of seawater (it could be noted here a comment by Sturgeon and co-workers (1979) that for complex matrices, such as seawater, competitive equilibrium reactions that bound metal ions into non-extractable forms, e.g., formation of anionic chloro-complexes, non-reversible adsorption on colloidal particles and complexation with naturally occurring ligands to yield non-labile hydrophilic complexes, could result in low metal recovery). In general, the kinetics of the extraction of the metal complexes formed is found to be fast. Wyttenbach and Bajo (1975a) investigated the extraction kinetics of single elements using a quantity of $Zn(DDC)_2$ sufficient to extract 50% of the metal present. It was found that in the majority of cases (Au, Hg, Cu, Bi, Sb, Te, Cd, and Pb), this expected extraction occurred within less than 15 s; however, Mo, Se, In, and As were extracted completely only after several min. In an extraction of Pb and Cd from wine samples, Anders and Hailer (1976) found that the extraction times needed (i.e., 25 min) were much longer than those quoted in the literature (e.g., that of Kinrade and Van Loon (1974)). The authors pointed out that the time data for the extraction in the literature originated from quite pure aqueous solutions, but the sample solution investigated here was highly complex. They attributed the long extraction time to various possibilities, such as the idea that amino acids in the wine might be strong Lewis acids by virtue of their N and S containing groups and might therefore interfere with the complexation of APDC. Lo and co-workers (1982) found that about 20 min of shaking is sufficient to quantitatively extract all of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn at concentrations of 20 μg litre^{-1} or less in the aqueous phase into chloroform (in some cases, less than 6 min was required for complete extraction). In general, the required shaking time was noted to increase with increasing metal concentration in solution. Sachsenberg and co-workers (1992), determining Cd, Cu, Pb, Ni in standard spiked seawater with final concentrations of 50 - 500 ng litre^{-1}, noted that the necessary shaking times were varying with different DIBK/ aqueous phase ratios.

Organic extracts can be directly analyzed, using techniques, such as AAS (St. John, 1970; Gomiscek et al., 1974; Kinrade and Van Loon, 1974; Kremling and Petersen, 1974; Anders and Hailer, 1976; Timperley, 1977; Pedersen et al., 1980; Pakalns, 1981; Zhuang et al., 1994). However, there are potential drawbacks associated with direct analyses, for instance, the solvent is easily volatile and the metal complexes in the organic phase are relatively unstable; therefore, the extracts are not suitable for storage. Sturgeon and co-workers (1979) and Sachsenberg and co-workers (1992) remarked that when GFAAS was applied, the low surface tension of organic solvent, such as MIBK, might make sample delivery (of μl volumes) difficult. The solvent may also creep along the length of the furnace tube. These problems lower reproducibility and could worsen the standard deviation of the metal analyses. Sturgeon and co-workers (1979) further noted that the analytical response from organometallic compounds was often different from that of inorganic salts, making the determination difficult unless organometallic standards and the same solvent were used (in a study of Gomiscek and co-workers (1974) is reported the behaviour of metal-dithiocarbamate complexes in various solvents during atomization in GFAAS). Sturgeon and co-workers (1979) also noted that other problems often encountered when MIBK was used included the variation of analytical response with volume of MIBK injected into the furnace (for the same absolute mass of metal) and possible pre-atomization losses of volatile metal chelates or their decomposition products. A final acidic aqueous solution is thus considered more suitable matrix for final measurements. Magnusson and Waterlund (1981) noted that such a solution can be obtained by evaporating the organic solvent of the extract, digesting the residue and dissolving it in a small amount of dilute acid. This procedure, as noted by the authors, easily gives a concentration factor up to 100, but it is rather time-consuming. Another way of obtaining a final aqueous solution is to use back-extraction, i.e., extraction of metals from an organic phase to an aqueous solution. Several researchers use nitric or hydrochloric acids, with varying concentrations in the back-extraction step to decompose the metal complexes or the complexing agent (Danielsson et al., 1978; Jan and Young, 1978; Sturgeon et al., 1979; Magnusson and Waterlund, 1981). Jan and Young (1978) reported that for most of the metals investigated (i.e., Ag, Cr, Cu, Fe, Ni, Pb), lower relative standard deviation values were obtained for the back-extraction analysis of dilute nitric acid extract than for direct analysis of MIBK phase. In a determination of Cd, Cu, Fe, Ni, Pb, Zn, and Co in spiked seawater by Magnusson and Westerlund (1981), the results from back-extraction with different acids revealed that nitric acid was more effective than HCl. The authors speculated that the decomposition mechanism was probably different because of the oxidizing power of nitric acid. It was found that with the use of 0.3 M nitric acid, all metals, except Co, could be quantitatively recovered when the extract was allowed to stand overnight. This suggested that some metal-dithiocarbamate complexes were relatively stable against nitric acid, and it took long reaction time for complete decomposition. Sachsenberg and co-workers (1992) remarked that the necessity to use concentrated nitric acid as a back-extraction matrix might give problems in GFAAS analysis, because of the corrosive effects of oxidizing acids on the graphite and the following signal depression which gave a loss of sensitivity. In addition, any necessary dilution of the nitric acid extract will result in a lower preconcentration factor. Another back-extraction method based on ligand-exchange reaction has been proposed; it involves use of metals which form much stronger complexes with dithiocarbamate than the metals to be analyzed. Lo and co-workers (1982) proposed the use of dilute Hg(II) solution, instead of nitric acid, in back-extraction step in the determination of Cd, Cu, Co, Pb, Fe, Mn, Ni, and Zn, from seawater. This was based on the fact that the extraction constant of Hg(II) dithiocarbamate was much greater than those of the other metals under consideration. The authors noted that since Hg had a low atomization temperature, the presence of a low concentration of Hg(II) in the back-extracted solution did not cause any noticeable interferences. It was found that under the experimental conditions, all of the metals investigated with initial spiked concentrations of 100 μg litre^{-1} could be back-extracted from the organic phase ($CHCl_3$) into a small volume of 1000 ppm Hg(II) solution (prepared from HgO) at pH 1.6 (HNO_3) with > 95% recovery within 2 min. The authors also noted that those with initial 5 μg litre^{-1} in seawater required even shorter time, less than 0.5 min, for near total recovery. The reaction time for the back-extraction step was apparently much shorter than that required in the acid back-extraction procedure reported by Magnusson and Waterlund (1981). Lo and coworkers (1982) pointed out that mercury introduced as HgO or

$Hg(NO_3)_2$ gave better results (in terms of extraction efficiency) than other forms, such as $HgCl_2$. It was found that when a Hg(II) solution prepared from $HgCl_2$ was used in the experiment, the efficiency of back-extraction decreased for Co and Ni. The authors speculated that this could be due to Hg(II) forming stable chloride complexes, e.g., $HgCl_4^{2-}$ which could inhibit the replacement reaction ($Hg^{2+} + 2/m\ M(DTC)_{m(org)} \Leftrightarrow 2/m\ M^{m+} + Hg(DTC)_{2(org)}$) for both Co and Ni. It was also remarked that another possible source of incompletion of ligand exchange in back-extraction process might result from possibility that during the extraction of metal-dithiocarbamate complexes from seawater, trace amounts of Cl^- might end up in the organic phase. As a consequence, this Cl^- might complex with Hg(II) ions in the back-extraction process and thus reduce the Hg(II) ions available for the replacement of metals in the organic phase. The authors, therefore, suggested that keeping an excess amount of Hg(II) in the system could compensate for this potential loss. Sachsenberg and co-workers (1992) commenting on the use of Hg(II)-salts as back-extraction reagents (Lo et al., 1982; Backstrom and Danielsson, 1990) noted that the Hg concentrations required were relatively high. Hg is extremely toxic, is very corrosive to the metal parts of an analytical instrument, and may contaminate the laboratory environment. The authors thus proposed a back-extraction procedure using palladium salts. Pd has been known to form one of the strongest carbamate complexes of all metals with the exception of Au and the other Pt-group elements; the extraction constants of the thiocarbamate-Pd-complexes are in the order of 10^{47} - 10^{70}, depending on the stoichiometry of the complexes, which may be present as di or monocarbamates (Briscoe and Humphries, 1969). The authors, therefore, noted that only low concentrations of Pd were necessary and this metal ensured a rapid and quantitative back-extraction. In addition, Pd is a less common metal in analytical trace analysis; thus it may not give contaminant problems. The authors further remarked that a major advantage was that Pd simultaneously worked as a matrix modifier in GFAAS analysis, so that the small amounts of NaCl which might be remaining throughout the extraction procedure did not disturb the determination. The proposed back-extraction method was evaluated in the analysis of Pb, Cu, Ni, and Cd in seawater matrices. It was found that under the conditions of the experiment, the necessary minimum shaking time for back-extraction of all the metals investigated was only 30 s. The authors noted that the relation of total thiocarbamates to the palladium concentration in the back-extraction solution was an important factor. When the recommended palladium concentration (0.5 mM palladium(II) chloride in dilute nitric acid) was used, the authors remarked that the total thiocarbamate concentration should not have exceeded 2 mg for 100 ml seawater to be extracted, otherwise back-extraction for elements like Cu, or Ni, which form strong carbamate complexes, is incomplete, due to the excess of the complexing agent in the organic phase. It could be noted here a study of Hiraide and co-workers (1997) on collection of trace heavy metals complexed with APDC onto surfactant-coated alumina sorbents. Aqueous sample solutions containing trace metals, adjusted to different pH values, were mixed with APDC solution; the resulting solutions were passed through a column filled with the surfactant-coated alumina particles. It was found that all trace metals were recovered in > 97% yields over a wide pH range of 2 to 8. The metals were quantitatively desorbed from the alumina with dilute nitric acid, which left > 99% of the surfactant on the solid phase. The proposed method was found to successfully apply to the determination of traces of Fe, Co, Ni, Cd, Cu, and Pb, contaminated at the sub-$\mu g\ g^{-1}$ level in high-purity alumina sample. The authors noted that compared with conventional liquid-liquid extraction with APDC and chloroform, the proposed sorption method was directly compatible with ICP-MS, because the final nitric acid solution was suitable for the plasma.

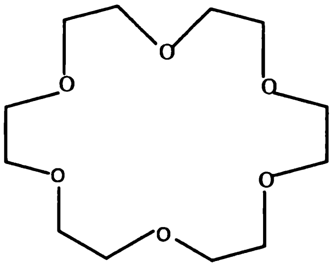
Based on the previous works on liquid-liquid extraction and ligand-exchange reaction outlined above, it is possible that when an organic phase containing a metal-dithiocarbamate complex comes into contact with a slightly acidic aqueous phase containing Pb ions, the metal ions will readily exchange, provided that Pb forms a more stable complex with the dithiocarbamate ligand than the original metal in the complex does. In this study, a metal-dithiocarbamate complex, $Zn(PDC)_2$, in MIBK is to be applied (see also the work of Schriner (1996), mentioned earlier in *subsection 1.6.6.*, on the application of this chelating system to redistribution problem of Cu). For a complete recovery of Pb, the amount of $Zn(PDC)_2$ to be added into the system may need to take into account the presence of other ions (whose amount may be significant in relation to that of Pb) in the aqueous phase since they may interfere with the complexation of Pb with the dithiocarbamate. Possible interfering ions include Fe and Mn (contributed from solid samples, such as goethite and hausmannite). For the APDC-MIBK system, the effective pH values for extractions of Fe and Mn are similar (i.e., 2 - 5) and in the same effective pH range as that used for Pb (the pH range of aqueous extraction solutions planned to be investigated is about 4). Pb-dithiocarbamate complex (in MIBK) needs to be adequately stable to allow for a complete back-extraction into dilute acidic aqueous phase, using a metal ion with stronger affinity for dithiocarbamate ligand than the Pb. In this study, palladium solution will be used at the back-extraction step. In this proposed multi-step extraction procedure, a good separation of aqueous and organic phases, at the end of each extraction step, is of importance for the overall accuracy of the Pb recovery, and this may be achieved by centrifugation with sufficient speed and time.

Macrocyclic ligands are polydentate ligands containing their donor atoms either incorporated in or attached to a cyclic backbone, and as usually defined, the ligands contain at least three donors atoms and the macrocyclic ring should consist of a minimum of nine atoms (including all hetero atoms) (Melson, 1979; Lindoy, 1989). Dietrich and co-workers (1993) classified ring systems, cyclo $(CH_2)_n$, into four groups: small rings ($n = 3, 4$), normal rings ($n = 5, 6, 7$), medium rings ($n = 8 - 11$), and large rings ($n \geq 12$). Well-recognized natural macrocyclic rings include porphin, the parent compound of a number of substituted derivatives known as porphyrins, which are major constituents of biologically important complexes (e.g., haemoglobin and chlorophyll) (Bell, 1977). Macrocyclic compounds are well-known for their abilities to selectively complex metal ions (Melson, 1979; Patai, 1980; Lindoy, 1989; Hancock, 1992; Dietrich et al., 1993; Martell et al., 1994; Dhillon et al., 1994) (two macrocyclic ligand type compounds used in this present study are outlined below). The hole size of a macrocyclic ligand is a fundamental structural parameter which usually influences, to a degree, complexation with a metal ion, making it stronger than that observed in the corresponding non-cyclic ligands. In overall terms, the hole size of a cyclic ligand is very often determined by the number of atoms in the macrocyclic ring; other factors include the nature (e.g., size) and the hybridization of the donor atoms (Lindoy, 1989). Relative to their open-chain analogues, macrocycles have additional stereochemical constraints resulting from their cyclic nature. These constraints influence the positions of the donor atoms both with respect to each other and to the central metal ion. Such constraints are often also further evidenced by a limitation of the possible coordination modes and/ or conformations of the coordinated macrocycle. When the metal is too large to fit into the available macrocyclic hole, then, provided complexation occurs, the macrocycle will either fold or the metal will be displaced from the donor plane of the ring. For sterically rigid rings, such ligand folding will be energetically unfavourable relative to displacement of the metal ion from the donor plane of the ring. In this case the metal is very often also bound to an axial ligand. In macrocyclic complexes, however, donor atom to metal-ion bond lengths which are shorter or longer than expected, unusual angular relationships between such bonds, and the formation of less common coordination geometries of macrocycles for particular metal ions have all been reported. Very often the macrocyclic complex will exhibit enhanced thermodynamic stabilities relative to the corresponding nonmacrocyclic complex; this is termed the "macrocyclic effect". For polydentate including macrocyclic ligand systems, metal-ligand formation reactions could be several orders of magnitude slower than related reactions involving monodentate ligands. Complexation in particular of the multidentate ligands often includes a series of intermediate steps like substitution of one or several solvent molecules from the inner coordination shell of the metal ion and/ or internal conformational rearrangements of the ligand (Vogtle and Weber, 1980). A range of factors including the nature of the solvent, steric and electrostatic effects, as well as the possibility of ligand protonation may all influence which step in a multi-step reaction is rate-limiting (Lindoy, 1989). Relative to the corresponding open-chain complexes, slow kinetics of dissociation is a characteristic of a large number of macrocyclic systems.

Structural diversity of macrocyclic ligands is influenced by several parameters, including number of ether oxygen atoms, substitution by other heteroatoms (N, S), ring size, length of the $(CH_2)_n$ bridge, and introduction of aromatic (e.g., benzene, biphenyl, napthalene) and heteroaromatic systems (e.g., pyridine, furan, thiophene) in the ring. A vast variety of macrocyclic ligand structures and synthetic strategies are shown in many publications, such as those of Pedersen (1967), Vogtle and Weber (1980), Lindoy (1989), Dietrich and co-workers (1993). Examples of macrocyclic structures include monocyclic ("coronands"), cage macrocycles ("cryptands"), "octopus" molecules with "many-armed" or pendant functional groups, interlocked macrocyclic ligands, and binucleating macrocycles. Based on donor atom type, macrocyclic ligands can be considered to span two extreme categories (Lindoy, 1989): (i) those chiefly containing N, S, P, and/ or As donors, and (ii) those consisting of a large group of cyclic compounds incorporating numbers of ether functions as donors. The first category of macrocycles tends to have considerable affinity for transition and other heavy metal ions; this ligand type usually show much less tendency to form stable complexes with ions of the alkali and alkaline earth metals. In contrast, the second category, "crown" polyethers (a typical structure, which is used in this study, is shown below), usually show strong complexing ability towards alkali and alkaline earth ions, which, in certain cases, are stable in aqueous solution; they also yield stable complexes of a range of non-transition metal ions but tend to bind less strongly to transition metal ions than the first category (Pedersen, 1967). Pedersen (1967) showed that crown ether rings incorporating between five and ten oxygen atoms tended to form the most stable complexes and complexes with some or all of the following metals were isolated: Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Au^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^+, Hg^{2+}, La^{3+}, Tl^+, Ce^{3+}, and Pb^{2+}; in such compounds the ether-oxygen interactions with the metal cation were considered to be essentially electrostatic. Many researchers, such as Lamb and co-workers (1979), Vogtle and Weber (1980) and Lindoy (1989) have summarized factors generally influencing the selectivity of many crown polyethers (and other macrocyclic ligands) for metal ions and corresponding complex stabilities. Factors frequently referred to include the following: (i) donor atom type; substitution of ether oxygen by N or S donor sites tends to reduce binding ability toward alkali/ alkaline earth metal ions, but raise stabilities of heavy metal complexes, (ii) number of donor atoms; a match between the coordination number of the particular cation and number of donor atoms of the ligand could enhance the ligand selectivity and the complex stability (optimum coordination number of cations is estimated by coordination numbers with water molecules) and their arrangement (i.e., crown ethers, in which the oxygen dipole ends are not ideally located in the ring center, show lower complex stability for cations), (iii) cavity size and shape; stability constant, K_s, for metal-ligand complex is frequently found to be highest when the diameter of the metal cation roughly matches the hole diameter of the ligand; this may be that the metal ion is able to occupy the cavity in an unstrained manner and the electrostatic interaction is enhanced, (iv) rigidity, flexibility and conformational changes of a ligand skeleton before and after complexation; rigid ligands give definite and only slightly alterable coordination cavities, while flexible, conformationally labile ligand can form cavities of variable dimensions; in other words, the rigid skeletons should exhibit higher cation selectivities. (In the case of large-ring crowns which are able to wrap around the cation to form a three-dimensional structure, the concept of a cavity is no longer applicable.), (v) ring substituents; lipophilicity of the ligand shields cation from the medium and decreases the stability of the complex (lipophilic character is contributed from the nature of the hydrocarbon constituents forming the ligand framework or attached to it), (vi) an interaction between anion and the complexed cation (ion-pair effects); in highly solvating media, the charged complex and the counterion are separately solvated; no anion effect on complex stability is found; however in poorly solvating media, ion pairing gains weight increasingly in the form of complexed or ligand-separated ion pairs; anion effects can be observed, and (vii) an interaction of the cation with solvent; in aqueous solution, most ligands are less selective and the complexes less stable than in less polar solvents, like methanol. Complexes of crown ethers with alkali metal ions are mostly found to display a 1 : 1 ligand/ salt stoichiometry (Vogtle and Weber, 1980). Lindoy (1989) remarked that the stoichiometry of a given crown-metal complex could be influenced by several factors including the charge density on the metal, the nature of the anion, and the relative strain energies of the crown in different conformations. Complexation involving the crowns is usually accompanied by marked changes in solubility. Many simple crown ethers are moderately soluble in water, when complexed the hydrophilic interior of such molecules is masked. Thus, surrounding a Lewis acid such as Na^+ or K^+ with a crown gives an increase in the lipophilicity of the system. This tendency of the complexed cation to have a greater solubility than the uncomplexed ion pair in non-polar solvents has led to various applications in both analytical (see examples below) and synthetic organic chemistry. Apart from metal ions, many crown polyether compounds also exhibit complexing ability and often specificity for other entities, such as organic cations and neutral molecules (complexes such as these, which contain species incorporated in the macrocyclic cavity, are usually known as inclusion complexes; the general area covering the binding of all types of substrates in molecular cavities often being referred to as host-guest chemistry).

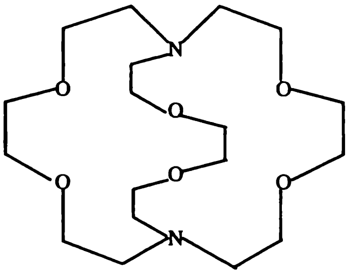
Cryptands (Greek: *cryptos* = cave) refers to three-dimensional polycyclic ligand systems (Lindoy, 1989) (see a common structure below). Whereas two-dimensional crown-like macrocyclic ligands form a complex by encirculation of metal ions, cryptand ligands form a complex by encapsulation of metal ion in the cyclic ring. The resulting metal-cryptand complexes are called cryptates. The cage topography of the cryptands results in them yielding complexes with considerably enhanced stabilities relative to analogous macromonocyclic crown ligands; this enhanced stability is referred to as the "cryptate effect" (a special case of the "macrocyclic effect"). In reviews by Hancock and Martell (1988) and Martell and co-workers (1994) on chelate, cryptate and macrocyclic effects, the authors remarked that the factors which contributed to the higher stability of macrocyclic complexes over the complexes of open-chain donors were also responsible for the still higher stability of the cryptate complexes over the corresponding macrocyclic compounds; these involve many factors, such as greater intrinsic basicity induced in donor atoms of the cryptand due to the additional alkyl bridges, greater reduction in the freedom of motion of the ligand and donor atoms, and a low degree of solvation (per donor group) due to the proximity of the polar cryptand donor groups to each other (examples of the thermodynamics of the cryptand effect can be found in the reviews). Rigid macrobicyclic ligands are found to display "peak selectivity" for metal ions; however, there is evidence that the larger, more flexible, ligands (e.g., above the size of cryptand 2.2.2, see below) tend to exhibit "plateau" selectivity--a reflection that a number of the larger metal ions are accommodated by the cryptand (without major variation in binding energy) (Lamb et al., 1979). Lamb and co-workers (1979), however, noted that ligands that were not flexible but were too small to accommodate the metal ion may form 2 : 1 complexes which would greatly alter selectivity patterns.

In this study, 18-crown-6 and cryptand 2.2.2 will be assessed for potential usefulness in counteracting Pb redistribution (the ligand structures are shown below). Typical syntheses of the ligands can be found in the literature, for examples those of Pedersen (1967), and Dietrich and co-workers (1993). Trivial names of crown ethers are based on, in order, the number and kind of attached hydrocarbon rings, the total number of atoms in the polyether ring, followed by the class descriptor "crown" and the total number of donor oxygen atoms in the main ring; in the case of the cryptand ligand, every cipher generally represents one bridge and gives the number of oxygen donor atoms (Vogtle and Weber, 1980). The pronounced selectivity (outlined below), semi-internal binding site, and bulky structure of these macrocyclic ligands are of potential advantage for application in this study since they imply that these reagents may be poor direct extractants of Pb from the solid phase but good scavengers of Pb in the solution.



18-crown-6

(1,4,7,10,13,16-Hexaoxacyclooctadecane)



cryptand 2.2.2

(4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo-[8,8,8]-hexacosane)

18-crown-6, a typical macrocycle, in the solid state and in solvents of low dielectric constant, is folded in on itself to minimize dipole-dipole repulsions (Martell et al., 1994). Thus the folded ligand would have to open up considerably to form the configuration which is necessary to complex metal ions (complex conformations for metals, such as Na^+, are illustrated in the literature; e.g., Lamb and co-workers (1979) and Vogtle and Weber (1980)). If 18-crown-6 is dissolved in water, it is likely that solvation lessens the dipole-dipole repulsions, and conformation like the one shown above is adopted (Martell et al., 1994). In this case, the water of solvation would have to be displaced before complex formation could occur. The conformation shown above is noted to have estimated values for the radius of 1.38 Å (Lindoy, 1989) or 1.45 Å (Vogtle and Weber, 1980). In a summary by Vogtle and Weber (1980) of thermodynamic data for the complexation of several 18-crown-6 type ligands with various metal ions in water at 25 °C, it was shown that 18-crown-6 had a high affinity for Pb^{2+} (log K_s 4.27 (Izatt et al., 1976)) (Pb^{2+} ionic radius 1.18 Å) over Ca^{2+} (log $K_s < 0.50$) (ionic radius 1.00 Å). Ca^{2+} is of interest because it is a prevalent ion in the systems under investigation in this study. 18-crown-6 forms its most stable alkali metal complex with K^+ (log K_s 2.03) (ionic radius 1.33-1.38 Å) and its most stable alkaline earth complex with Ba^{2+} (log K_s 3.87) (ionic radius 1.33 Å) (both in water medium and at 25 °C) (Lindoy, 1989). In a kinetic investigation of Liesegang and co-workers (1976), it was proposed that the complexation of K^+ and Cs^+ by 18-crown-6 followed the overall two-step mechanism involving a rapid ligand conformational rearrangement which was then followed by a stepwise substitution of the coordinated solvent by the ligand. However, in a set of subsequent kinetic studies of complexation of Li^+, Na^+, Rb^+, Tl^+, Ag^+, NH_4^+, and Ca^{2+} with the crown, it appeared that the corresponding reactions were more complicated (Liesegang and co-workers, 1977).

Cryptand 2.2.2 has an estimated cavity radius of ≈ 1.4 Å (Vogtle and Weber, 1980; Lindoy, 1989). Series of cryptands with the "parent" structure of cryptand 2.2.2 (e.g., varying in numbers of $-O(CH_2)-$ on the ring structure) are able to exist in three isomeric forms since the lone pair at the bridgehead nitrogens may be orientated inwards or outwards with respect to the molecular cavity, thus giving rise to three isomers: "endo-endo", "endo-exo" and "exo-exo" (an illustration is provided in Lamb and co-workers (1979)); these forms may interconvert rapidly via nitrogen inversion. However, the free cryptand 2.2.2 in solid state is shown to exist in the "endo-endo" conformation (Metz et al., 1976). Metz and co-workers (1976) remarked that in all the known cryptates of this ligand, the configuration was also endo-endo with the metal ion inside the cavity (in Martell and co-workers (1994) is shown a conversion ("swollen up") from a natural structure of cryptand 2.2.2 ligand to a structure that will allow it effectively to coordinate the central metal ion). Metz and co-workers (1971) noted a progressive opening-up of the cavity of cryptand 2.2.2 with torsion of the ligand around the N/N axis for complexations with metal ions with increasing radius: $Na^+ < K^+$, $Rb^+ < Ca^{2+}$. Metz and Weiss (1974), based on data from X-ray crystallography for the Pb-cryptand 2.2.2 complex, $C_{18}H_{36}O_6.Pb(SCN)_2$, revealed that Pb occupied a central position in the cavity of the ligand and the arrangement of the heteroatoms around the Pb atom approximates a trigonal-capped irregular hexagonal pyramid. Aza cryptands are noted for offering a wide range of complexation selectivities; based on a summary by Vogtle and Weber (1980) on stabilities (log K_s) of cryptand 2.2.2 and some aza analogues with various alkali/ alkali earth and heavy metal ions, in water at 25 °C, the ligands exhibit very strong complexation with toxic heavy metals Cu^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} but form rather weak complexes with the biologically important metals Na^+, K^+, Mg^{2+}, Ca^{2+}, and Zn^{2+}. Replacement of the ether oxygen on the cryptand 2.2.2 structure by $N-CH_3$ favourably influences the complexation with heavy metals but weakens the coordination of alkali metal ions; as a result, the substitution enhances the discrimination between the toxic and the alkaline/ alkaline earth metals; for example, log K_s of cryptand 2.2.2 for Pb^{2+} and Ca^{2+} are 12.7 and 4.4, respectively, while log K_s of analogues with four $N-CH_3$ substitutions on the outer bridges for Pb^{2+} and Ca^{2+} are 15.5 and 1.5, respectively. The stability constant (log value) of cryptand 2.2.2 for Pb^{2+} is also reported to be 12.0 at 25 °C and 0.1 M ionic strength (generally used KNO_3 or $NaClO_4$), and slightly higher, 12.36, at the same temperature but in tetraalkylammonium salt electrolyte solution (Martell and Smith, 1974a). Cukrowski and co-workers (1995), using pulse polarography to determine the formation constants of Pb^{2+} with cryptand 2.2.2 at ionic strength 0.5 M and 25 °C in the presence of sodium ions, reported the formation constant (log value) of 12.9 for PbL^{2+}, and 20.51 and 23.75 for the two labile new complexes, namely $PbL(OH)^+$ and $PbL(OH)_2$, respectively (in this work is also shown the species distribution as a function of pH). Cryptand 2.2.2 appears to be superior to 18-crown-6 for complexing Pb, under similar conditions, however the selectivity of the cryptand for Pb relative to the alkai/ alkaline earth metals (as expressed by the ratio of the corresponding stability constants) may not necessarily be greater than that of the crown (e.g., (i) the ratio of log K_s Pb^{2+} : Ca^{2+} for the cryptand is about 2.9; whereas that for the crown is at least 8.5, and (ii) the ratio of log K_s Pb^{2+} : Na^{2+} for the cryptand is about 3.2; whereas that for the crown is about 5.3) (see individual log K_s for other elements in Martell and Smith (1974a) and Vogtle and Weber (1980)). Cryptand 2.2.2, like 18-crown-6, forms its strongest alkali metal complex with K^+ and its strongest alkaline earth complex with Ba^{2+} (Vogtle and Weber, 1980; Lindoy, 1989); however, under similar conditions (water, 25 °C), the values of log K_s of the cryptate complexes appear to be higher than those of the crown complexes (i.e., for K^+ cryptate 5.4 vs crown complex 2.03; and for Ba^{2+} cryptate 9.5 vs crown complex 3.87). From a summary of Vogtle and Weber (1980) based on a study of Cox and co-workers (1978) on the kinetics of metal complexation by cryptand 2.2.2 and related cryptands with the same "parent" structure (in methanol, 25 °C), the remark was made that for a given metal ion the complexation rate (k_f) increases with increasing cavity size of the cryptands (i.e., comparably less rigid structures exchange cations more quickly). It was further shown that the k_f values of cryptand 2.2.2 for Na^+, K^+, Rb^+, and Cs^+ were in the range of 2.7×10^8 to $\approx 9 \times 10^8$ (l $mol^{-1}s^{-1}$); whereas, the decomplexation reaction constants (k_d) increased with increasing metal ion size (e.g., k_d of Na^+ is 2.87 l s^{-1} vs that of Cs^+ is $\approx 4 \times 10^4$ l s^{-1}).

18-crown-6 and cryptand 2.2.2, as well as their analogues, have been utilized for their abilities to selectively complex metal ions over a wide range of conditions (an application of these ligands in the form of solvent-impregnated resin has been outlined in the previous *subsection 1.7.1*. The applications of the ligands in both dissolved and solid forms (e.g., synthetic polymeric resins and other types of solid matrix will be presented here)). Kolthoff (1979) provides a comprehensive review of the applications of macrocyclic compounds in chemical analysis up to 1979. Since then, these ligands have seen extensive use in analytical and environmental chemistry as selective complexation agents for metal ion separation and determination (Lamb et al., 1980; Szczepaniak and Juskowaik, 1982; Sanz-Medel et al., 1984; Gomis et al., 1985; Sakai et al., 1986; Vibhute and Khopkar, 1989; Gomis and Garcia, 1990; Gandhi and Khopkar, 1991; Andres et al., 1994; Ion et al., 1994; Srivastava et al., 1994; Francois et al., 1995; Mathew and Khopkar, 1995; Chiou and Shih, 1996; Hankins et al., 1996; Srivastava et al., 1996; Tavakkoli and Shamsipur, 1996; Akhond and Shamsipur, 1997; Bol'shoi et al., 1997; Vaidya et al., 1997; Wood et al., 1997). Lamb and co-workers (1980) reported the use of dibenzo-18-crown-6 as a carrier (and an anion as a counter ion) in selective transport of metal ions across a bulk liquid membrane into an aqueous receiving phase (the rate of transport was anion-dependent). Gomis and co-workers (1985) used a solvent extraction into chloroform of the ion-pair formed between the positively-charged cryptate of Pb with cryptand 2.2 2 and eosinate anion dye, in combination with a spectrofluorimetric method, to determine ultratraces of Pb in solution. The method was found to be highly selective for the extraction and allowed determination of Pb in the presence of other cations, including alkali/ alkaline earths, of up to 1000-fold molar excess to Pb. The proposed method was also tested for determination (without a preconcentration step) of Pb in various soft drinks; the results were found to be consistent with those obtained by the extractive atomic-absorption method, which requires a ten-fold preconcentration with ammonium tetramethylene dithiocarbamate and MIBK. The authors noted that in relation to a previous preliminary investigation, the mercury cryptate was not extracted under the same experimental conditions as Pb, suggesting that although the stability constant of the Hg binary complex is very high, the extent of its complexation (interference) depends also on the nature of the solvent and the type of the counter-ion used. Ion and co-workers (1994) prepared dibenzo-18-crown-6- phosphomolybdic acid/ polystyrene supported on glass balls and applied this material as an adsorbent for Ag^+, Pb^{2+}, and Cd^{2+}; the adsorption was found to decrease in the order $Ag^+ > Pb^{2+} > Cd^{2+}$. The authors noted that the size of Ag^+ ion (diameter 2.56 Å) matched with the cavity (2.42 Å) of dibenzo-18-crown-6, while Pb^{2+} and Cd^{2+} were slightly smaller. Tavakkoli and Shamsipur (1996) used dibenzopyridino-18-crown-6 as ion-selective components (ion carriers) in a membrane electrode for the determination of Pb. Based on the potential responses of six different ion-selective electrodes, it was found that the sensitivity of the potential responses decreased in the order $Pb^{2+} > Ba^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$. The authors remarked that the observed trend in the sensitivity seemed to follow the order of decreased stability of the resulting 1:1 complexes with the macrocyclic ionophore. This was attributed to the fact that although the ionic radius of Ba^{2+} (1.35 Å) was more suited than that of Pb^{2+} (1.19 Å), the stronger soft-soft interaction of the latter cation with the pyridine nitrogen of the ring was expected to result in a higher stability of the Pb^{2+}-crown complex in comparison with Ba^{2+}-crown complex. The authors further noted that the stability order of other cations with much smaller sizes (i.e., 0.77 Å for Cu^{2+}, 0.75 Å for Co^{2+}, 0.69 Å for Ni^{2+}, and 0.95 Å for Cd^{2+} ions) than the cavity of the crown ligand followed the Irving-Williams order. The electrode also exhibited comparatively good selectivities for Pb^{2+} with respect to the presence of interfering ions, i.e., alkali, alkaline earth and some transition and heavy metal ions. The performance characteristics of the selective electrode on the response of the Pb^{2+} were found to be influenced by factors such as the composition of the membrane (e.g., the crown ligand/ PVC/ a plasticizer). Wood and co-workers (1997) used an organic extraction solution composed of 4', 4', (5')-di-(t-butyldicyclohexo)-18-crown-6 and tributyl phosphate to simultaneously remove Pb and Sr from nitric acid solutions and simulated acidic hazardous waste streams containing relatively high concentrations of alkali metals (simulated nuclear industrial waste solutions) (the crown derivative is the same extractant used in the work of Horwitz and co-workers (1994), mentioned in the previous *subsection 1.7.1.*, in the form of chromatographic resin). The extraction was found to be dependent upon extractant concentration, the aqueous nitrate concentration, and the identity of the predominant anion in the aqueous phase. The extraction procedure was found to be highly efficient, with the use of dilute solutions of ammonium citrate and nitric acid as stripping reagents for Pb and Sr, respectively. In a geochemical application, Bracke and co-workers (1995) used cryptand 2.2.2 and Li (as the exchanging cation) for the selective exchange of interlayer K, Rb, and Sr cations from three natural mica-type minerals. The proposed method was found to result in higher exchange of the cations than the use of only water alone or combination of the cryptand and water. It was found that complete exchange (> 95%) of K^+, Rb^+, and Sr^{2+} in two samples was achieved after two days; similar results for the exchange in the third sample but the exchange rate was apparently slower.

The aminopolycarboxylic acids, also known as "complexones", are highly effective chelating ligands; they are essentially derived from the simple amino acid glycine (Bell, 1977). The most widely used complexones are EDTA and nitrilotriacetic acid (NTA). In this study, NTA, ($N(CH_2COOH)_3$), a quadridentate open-chain synthetic chelating agent is to be used. As mentioned earlier in *subsection 1.6.6.*, Howard and Shu (1996) had tested NTA for a potential usefulness for counteracting redistribution during a modified sequential extraction of natural samples containing organic matter in the range of 2 - 6%. However, in this study, an initial aim will be to test the potential usefulness of NTA during the extraction of synthetic soil systems containing high concentration of scavenging phases, i.e., humic acid, and hausmannite.

NTA is widely known for its ability to form stable, water-soluble complexes with several metal ions (Perrin, 1970; Martell and Smith, 1974b; Bell, 1977); for instance, Pb^{2+} with stability constants (log K_1) of 11.34, at 0.1 M ionic strength (KNO_3 or $NaClO_4$), 25 °C or 11.39, at the same ionic strength but 20 °C, and Ca^{2+} with log K_1 of 6.41 at 0.1 KCl, 20 °C (Martell, 1964) or 6.39 at 0.1 M ionic strength (KNO_3 or $NaClO_4$), 25 °C (Martell and Smith, 1974b). (Bell (1977) remarked that the ability of NTA and EDTA to form stable complexes with Ca and Mg ions was the basis of analytical methods for the determination of hardness in water caused by the salts of these two metals). Bell (1977) noted that the dissociation of protons from the two carboxyl groups occurs in an aqueous solution of quite low pH, but the betaine proton was not lost until the solution is appreciably alkaline. Over the pH range of 4 - 8, the ligand exists almost entirely in the form HX^{2-}; the reaction with metal ions proceeds: $M^{n+} + HX^{2-} \Leftrightarrow MX^{(n-3)+} + H^{+}$. The stoichiometry of the complexes is the same as that of EDTA complexes. NTA, however, acts at best as a quadridentate ligand, coordination of one X^{3-} ion can satisfy completely only those metals which normally show a coordination number of 4 (when all the donor atoms of NTA are coordinated to a metal, three chelate rings are formed, each with a five-membered ring size). It is, therefore, not unusual to find that some metals react with excess NTA with the formation of bis complexes, $MX_2^{(n-6)+}$. In acidic media, the carboxyl groups can become protonated, leading to the production of complexes such as $MHX^{(n-2)+}$. In alkaline solutions, hydroxo complexes like $MX(OH)^{(n-4)+}$ can exist.

A wide range of potential uses of NTA have been reported. NTA found a major use as a replacement of phosphate builders in detergents (Allen and Boonlayangoor, 1978; Howe-Grant, 1993). Recent applications of NTA include its use as a potential extracting reagent for treatment of both metal-contaminated soils (prior to disposal by landfilling) (Elliott and Brown, 1989; Peters and Sham, 1992; Hong and Pintauro, 1996) and other materials, such as nuclear waste (Bolton et al., 1996). Other possible uses of NTA in soil applications include its use as a reagent for assessment of the potential leacheable or bioavailable fraction of soil metals (implied in a review by Pickering (1986)) (the most widely used chelants appear to be EDTA and DTPA), as models for natural ligand interactions with metals, and as micronutrient carriers for plants (implied by Shuman (1995)). NTA has also been applied in membrane technology for metal-ion separations (Walsh and Monbouquette, 1993; van Zanten et al., 1995). In a study by Elliott and Brown (1989) of a comparative evaluation of NTA and EDTA for extractive decontamination of a battery reclamation site soil containing about 21% Pb, the resulting relationship of pH, chelant concentrations, and percentage Pb recovery (using 5 h extraction time) revealed that, increasing chelant concentration generally resulted in greater Pb solubilization. For chelant concentrations below 0.04 M (representing a 1:1 chelant-to-total Pb molar ratio), EDTA released 10 to 30% more Pb than NTA. However, at greater than 1:1 chelant/ Pb ratios, the behaviours of NTA and EDTA were noted to be strikingly different. For higher EDTA levels, Pb recovery was enhanced; whereas a stoichiometric excess of NTA actually decreased Pb release for pH values less than about 8.5. The authors attributed this behavioural difference to the complexation characteristics of EDTA and NTA. EDTA, as a hexadentate ligand, fills all the available coordination sites of Pb^{2+}, as a result there is little opportunity for bridging to the soil surface. The authors remarked that in the case of NTA, (i) when 1:1 ligand/ Pb ratio was used, the complexation with Pb left two metal coordination sites available for interaction with the soil surface; therefore readsorption of the $PbNTA^-$ could occur through the coordination sphere of the metal (and the adsorption behaviour of the complex would be analogous to the free metal), and (ii) when a stoichiometric excess of NTA was added, some of the Pb released into solution could be bound as the 1 : 2 complex, $Pb(NTA)_2^{4-}$. The stereochemical arrangement of this complex species was considered to be such that two uncoordinated NTA functional groups were exposed to the solution; now, the complex might adsorb through the functional groups of the NTA (the result was referred to as "ligand-like" adsorption behaviour) (Elliott and Huang (1979) illustrate possible orientations of $CuNTA^-$ on a mineral surface). Elliott and Brown (1989) further found that the addition of $NaClO_4$ substantially suppressed Pb recovery by NTA for pH < 11, while it enhanced the recovery by EDTA for pH 5 to 12. The authors remarked that the reason(s) of the suppression of the metal recovery by NTA was not clearly understood. The ability of Pb to complex with NTA far outweighed any Na concentration advantage that might exist in the system (log K of $NaNTA^{2-}$ is only about 1.2); moreover, based on a previous study of the authors, the NTA-induced dissolution of Fe from the soil was so slow kinetically that competitive chelation by Fe was not important for these relatively short extraction times. In agreement with the observation of Elliott and Brown (1989), Peters and Shem (1992) reported that NTA exhibited lower efficiency than EDTA in removing Pb from contaminated soil. In addition, Peters and Shem (1992) found that extraction of Pb with EDTA was rapid, reaching equilibrium within a contact time of 1 h; whereas with the use of NTA, the extraction was slower, with a required contact time to reach equilibrium of approximately 3 h. Walsh and Monbouguette (1993) applied NTA in membrane technology (as a preliminary test for possible future use in effluent treatment). NTA was encapsulated in lipid vesicles harbouring a lipophilic ionophore (carrier) in the capsule wall; the resulting vesicles, mimicking a biological cell membrane, were then used as a means of selectively separating Cd^{2+} and Pb^{2+} from dilute aqueous solutions. NTA here provides the driving force for metal ion uptake mediated by the metal carriers; therefore, metal ion concentrations surrounding the vesicles can be driven very low. Two types of carriers were used: a natural antibiotic and a novel synthetic compound. A hollow-fibre membrane cartridge was chosen as a means of maintaining continuous contact between feed and vesicle solutions (this eliminates downstream separation of vesicles from the purified wastewater). It was found that vesicles containing the synthetic carrier showed selective uptake of Pb^{2+} over Cd^{2+} at pH 5.5 from a mixed solution. The authors remarked that the process model worked well for the case where the quantity of vesicles was large such that the moles of encapsulated NTA exceeded the initial moles of metal ion.

As a result of its various potential applications in metal complexation, the level of NTA released into the environment is of interest. Many studies have focused on assessing possible ecological effects of NTA by investigating potential mobilization of metals from soils and sediments by the ligand (Chau and Shiomi, 1972; Gregor, 1972; Allen and Boonlayangoor, 1978; Denduluri, 1993, 1994a,b; Shuman, 1995). In an investigation of Gregor (1972) on the possibility of NTA solubilizing Pb from suburban lake and reservoir sediments into drinking water, the samples, containing Pb in the range of 36 to 160 mg kg^{-1}, were shaken for varying periods of time with reservoir or lake water to which had been added different amounts of NTA (as the trisodium salt). It was found that NTA of only 2 ppm could raise Pb up to and above the 0.05-ppm maximum permissible level in public water supplied. Gregor (1972) noted that although some previous studies had reported that the use of 10 ppm NTA could solubilize Cu, Cd, and Zn but not Fe or Pb, sediments tested in such studies were taken from rural areas, which were presumably far from highways, therefore the Pb in such cases could have been in a refractive forms, contrasting in nature to that originating from automobile emissions (as assumed for the sample used in his study). Allen and Boonlayangoor (1978) remarked that in several previous studies of potential mobilization of metals by NTA, the concentrations of NTA used had generally been greatly in excess of those found in receiving waters and often had exceeded those present in treated or untreated effluents. Therefore, in their study, NTA concentrations selected were based on monitoring data from some rivers and sewage treatment plants. The authors found that an added NTA concentration of 0.75 mg $litre^{-1}$ (as H_3NTA), a concentration typical of effluent from activated sludge sewage treatment plants surveyed, resulted in few instances of metal mobilization under the experimental conditions employed (complete mixing of high ratios of sediment to water). In a study of Denduluri (1993) on the effects of NTA and EDTA on metal accumulation by plants, the plants were grown on soils spiked with Pb ranging from 0 to 1000 $\mu g\ g^{-1}$ with and without an addition of 10^{-2} M chelating agents, and irrigated with sewage water. It was found that the application of the chelating agents significantly reduced the uptake of Pb. At the 50 μg Pb g^{-1} soil exposure treated with NTA or EDTA, the accumulation of Pb was found to be not detectable in the roots, stems, leaves, and fruits of the plants; whereas at the same level of Pb exposure without the treatments with the chelating agents the accumulation of Pb in the roots, stems, leaves, and fruits were 6.7, 2.2, 0.6 $\mu g\ g^{-1}$ and not detectable, respectively. At elevated concentration of Pb exposure, e.g., 500 and 1000 $\mu g\ g^{-1}$ soil, less uptake of Pb was still observed in the systems containing the chelating agents, in comparison to those without the treatment. The authors attributed the reduction of plant uptake of Pb to the poor absorption of stable metal-chelate complexes by the plants, in comparison to metal in the ionic form (biodegradation of various metal-NTA complexes is discussed in Bolton and co-workers (1996)). Shuman (1995) studied the effects of NTA (1 mM) on the adsorptions of Zn, Pb, or Cd (0 to about 1 mM) by two different types of topsoils, in solutions of pH 5 with 5 mM $CaCl_2$ background electrolyte. The adsorption experiments were performed with and without NTA; the results were used to plot adsorption isotherms. It was found that the distribution coefficients (K_d) values (metal adsorbed/ total metal in solution) from experimental and equilibrium models of the three metals without the addition of NTA followed the order Pb > Cd > Zn; however, the trend with NTA was Cd > Zn > Pb. The author remarked that, according to the literature, substances with K_d values greater than 5 were not likely to be mobile in soils but ones with values less than 0.5 were likely to move in the soil profile; based on this criteria, the author deduced that none of the metals tested would be mobile where no NTA was added, but Zn and Pb would become borderline ($5 > K_d > 0.5$) for mobility in both soils with NTA added at 1 mM, whereas Cd would be mobilized by NTA to a smaller degree than Zn or Pb.

1.8. The objectives of this study.

The objectives of this study are to 1) construct a series of reasonable model soils based on the literature and use them to systematically determine the extent of redistribution of Pb, which may occur during two sequential extractions (that of the BCR and that of Tessier and co-workers), 2) devise and test a range of modifications to the extraction scheme(s) which might work to inhibit redistribution of Pb, should it occur, so as to improve the accuracy of the sequential extraction for Pb; and if possible to evaluate the effectiveness of the modified extraction scheme on environmental samples, and 3) assess the levels and distributions of Pb in roadside soil and street dust samples from Hamilton, New Zealand, in the period immediately surrounding the phasing out of leaded petrol, in order both to provide a benchmark for future studies in the area and to determine whether a reduction in Pb levels is detectable in the short term. Corresponding results obtained from the investigations are presented in chapters 3, 4, and 5, respectively.

Chapter 2. Materials and methods

In this chapter is described the experimental methodology used throughout this study. This involved the use of five synthetic solid phases and multi-phase model soils for an assessment of the extent of possible redistribution of Pb during the sequential extraction schemes of Tessier et al. and the BCR, and subsequent investigations of potentially useful approaches for counteracting the redistribution. The most promising approach was preliminarily applied on model soils and contaminated natural samples. Samples of kerbside top-soil and street dust were collected as part of a monitoring of Pb levels in soil and dust in Hamilton during the phasing-out of leaded-petrol, and details of the sample collections and preparations are given. Also described are methodologies relating to the analytical determinations of Pb and other relevant metals during the investigation, and details of an additional adsorption experiment, which was performed to supplement the work on the inhibition of Pb redistribution.

2.1. Assessment of the extent of lead redistribution during sequential extractions.

Five solid phases used in this study include calcium carbonate (AR), synthetic goethite and hausmannite, purified humic acid, and naturally-extracted halloysite. Each phase was spiked with Pb. Five synthetic model soils were prepared, with each being composed of a Pb-spiked phase and four clean phases, with an additional dilution using acid-washed sand.
The originally-spiked phase was used as a reference point for the release of the Pb (in the absence of the influence from other solid phases). Redistribution (by readsorption) of Pb among phases during the extractions was assessed by comparing the Pb recovery patterns of individually-spiked solid phases with those of the five-phase model soils, containing the corresponding spiked phases. In addition, redistribution was examined in systems comprising natural soils and a spiked synthetic phase.

2.1.1. Preparation and characterization of solid phases.

Calcium carbonate (AR) was used directly as obtained (BDH). Hausmannite (Mn_3O_4) was prepared by Schriner (1994), using a modified method of Wadsley (1950) for the preparation of birnessite. This involved the use of sodium hydroxide and manganese sulphate (Schriner, 1994). Goethite (α-FeOOH) was prepared following the method of Atkinson et al. (1967) using (AR) $Fe(NO_3)_3$ and 2.5 M (AR) KOH, with a mole ratio of 1 : 5. The precipitate was aged for 48 h at 60 °C. Halloysite (aluminosilicate), obtained as extracted from New Zealand China Clay Ltd. (batch EP 112693), was treated according to the methods of Mehra and Jackson (1960) to remove organic matter, amorphous coatings and crystals of free iron and manganese oxides. The removal of organic matter involved an oxidation with 5% hydrogen peroxide for 24 h (room temperature of ~ 20 °C), at pH 5.8 (500 ml of hydrogen peroxide per

10 g of halloysite). The slurry was centrifuged, then washed thoroughly with clean water before being subjected to a treatment for a removal of iron and manganese. This involved the use of (AR) sodium citrate ($Na_3C_6H_5O_7.2H_2O$), (AR) $NaHCO_3$, and (AR) sodium dithionite ($Na_2S_2O_4$) (with mole ratio of 4 : 1.6 : 1), at 80 °C (using a water bath) for about 20 min. After the mixture had cooled, a small volume of saturated (AR) NaCl solution was added to flocculate the clay. Aldrich humic acid was purified by dissolution under basic conditions (using (AR) NaOH), followed by reprecipitation under acidic conditions (using (AR) HCl), according to the method of Weber and Wilson (1975).

The precipitates of "clean" hausmannite, goethite, halloysite, and humic acid were washed thoroughly with distilled-deionized water using centrifugation, filtered, and oven dried (50 °C in the case of hausmannite (Schriner, 1994), and about 30 - 40 °C in the cases of the other phases). Calcite, and the oven-dried halloysite and humic acid, were lightly crushed using a mortar and pestle to a fine powder and homogenized, then stored in clean air-tight bottles. The oven-dried hausmannite and goethite were crushed using a tungsten carbide ring-mill to a fine powder and homogenized before storing in cleaned containers. In the case of goethite, the storing was under nitrogen to prevent any variation in adsorptive properties which may be caused by exposure to carbon dioxide (Barrow, 1987).

Solid phases were characterized with the use of Scanning Electron Microscopy (SEM) and Powder X-ray Diffraction (XRD) (the results are shown in *Appendices 2.1. and 2.2.*, respectively). With the exception of humic acid, all phases were of distinct morphology: goethite crystals were needles, those of halloysite had a tube-like structure, calcite particles were rhombohedral, and hausmannite crystals were tetragonal octahedral.

Adsorption of nitrogen (BET method) was used to measure surface areas of the phases. The mean surface area values are shown in Table 2.1. Each mean value is obtained from 3 to 6 replicate samples (given in *Appendix 2.3.*).

Phases containing adsorbed Pb were prepared by suspending 5 g solid in 25 ml of 400 mg litre^{-1} Pb (as (AR) lead (II) nitrate) at 25 °C for 72 h with mechanical shaking. Solutions were prepared from distilled-deionized water and were unbuffered. The main purpose of this was to construct a series of solid phases capable of releasing Pb to solution at different stages of the extraction (not to measure the relative extent of Pb adsorption on each phase at a given pH). Pb-sorbed phases were washed thoroughly with distilled-deionized water by centrifugation, filtered, and oven dried at 30 - 40 °C.

In order to assess the concentration of Pb ($\mu g\ g^{-1}$) on the sorbed phases, six replicates of each Pb-sorbed phase (except Pb-sorbed humic acid) were digested/ extracted, using a mixture of 25 ml 4 M nitric acid and 5 ml concentrated hydrochloric acid per 0.25 g solid. Six replicates of Pb-sorbed humic acid were completely oxidized using the oxidative conditions of Tessier et al.'s extraction scheme (see *section 2.1.4.*). Samples were analyzed for Pb by FAAS (*section 2.5.1.*). At least 3 replicates of each corresponding clean phase were also analyzed for Pb, by FAAS and/ or GFAAS. The concentrations of Pb sorbed on the individual phases used in this study are listed in Table 2.1. In all cases, the concentration of Pb in "clean" phases (at least 3 replicates per each clean phase) is less than 1% of that on corresponding sorbed phases (*Appendix 2.4.*).

Table 2.1. Mean surface area of solid phases and mean concentrations of Pb in the Pb-sorbed solid phases.

Phases	calcite	goethite	halloysite	hausmannite	humic acid
surface area ($m^2 g^{-1}$)	1	55	24	12	2
Pb ($\mu g\ g^{-1}$)[a]	1480	1820	946	1840	1470

[a] In all cases, %RSD was less than 6.

2.1.2. Preparation of model soils.

Five model soils were prepared by mixing (in each case) four of the clean phases with one of the Pb-spiked phases, followed by dilution with acid-washed silica sand.

Samples were weighed to a total of 2.0000 g ± 0.0002 g directly into cleaned plastic vials, mixed and agitated to ensure a thorough blending. All five model soils contained the same proportions of calcite, goethite, hausmannite, halloysite, humic acid, and silica sand. These portions were considered to be reasonably similar to those which could be found in natural soils (Luke, 1968). The compositions of the model systems are presented as percentages both by weight and surface area in Table 2.2.

Model soils containing 2 or 3 synthetic solid phases were prepared in a similar way to five-phase systems but without dilution with acid-washed sand.

Table 2.2. Phase breakdown of a model soil comprising five synthetic phases.

Phases	calcite	goethite	halloysite	hausmannite	humic acid
% by weight	5	10	15	10	20
% by surface area	0.5	51	33	11	4

Note: the remaining 40% of the weight was represented by silica sand.

2.1.3. Preparation of spiked natural soils.

Two natural soils containing typical background levels of Pb but with high organic or manganese contents were used in this study. They are classified as Te Rapa silty peat and Kainui silt loam (Hamilton silt loam) (Luke, 1968). Models comprising a natural soil and a Pb-spiked phase were prepared by mixing either (1) 0.4 g of each natural soil with 0.1 g of Pb-spiked calcite, or (b) 0.35 g of each natural soil with 0.15 g of Pb-sorbed halloysite. In each case, the ratio of a natural soil to a Pb-spiked synthetic phase was such that the Pb content of Te Rapa peat and Kainui silt loam was about 2% and 6% of the total Pb spiked in the mixtures, respectively. This allowed a prior knowledge of predominant Pb-containing phase before extraction.

Some relevant parameters of Te Rapa silty peats and Kainui silt loam are presented in Table 2.3. Prior to the mixing, the natural soil samples were air-dried for about 3 days, then sieved through a nylon sieve (< 2 mm). Subsamples were taken using the cone and quarter method. Ignition was carried out at 450 °C for 2 h on oven-dried (100 °C, 20 h) soil samples. Determinations of Pb, Mn, and Fe in aqua-regia extracts of the sieved Te Rapa silty peats and Kainui silt loam (3 replicates each) show percentage RSD values of below 6 in all cases, except for that of Pb analysis in Te Rapa extracts, which has RSD of approximately 14% (raw data is provided in *Appendix 2.5.*).

Table 2.3. Partial characterizations of Te Rapa silty peats and Kainui silt loam.

Soil types	approximate organic matter (%loss on ignition)	Pb ($\mu g\ g^{-1}$ soil)	Mn ($\mu g\ g^{-1}$ soil)	Fe ($\mu g\ g^{-1}$ soil)
Te Rapa	36	7	49	2780
Kainui	6	25	1250	35 900

After addition, final concentrations of Pb in these samples were in the range of 280 to 320 $\mu g\ g^{-1}$, figures which could be taken to represent Pb concentrations which may occur in soils and sediments at contaminated sites. Final Pb concentrations in the model soils are given in Table 2.4.

2.1.4. Sequential extraction methodology.

Subsamples of each five-phase model soil were weighed to 0.5000 g ± 0.0002 g for extraction. The same amount was taken from a model containing the natural soil and a spiked synthetic phase. In the case of individually Pb-spiked phases and the two-/ three-phase synthetic model soils, the subsamples were weighed according to their equivalent amounts in 0.5 g subsamples of the five-phase models, i.e., 0.025 g calcite, 0.05 g goethite, 0.075 g halloysite, 0.05 g hausmannite, and 0.1 g humic acid. Each subsample was weighed directly into a 50 ml, acid-washed polycarbonate centrifuge tube, with polypropylene screw closure (Nalgene®) (unless otherwise specified, this type of centrifuge tube was used throughout the study).

Table 2.4. Mean concentrations of Pb in five-phase model soils and spiked natural soils.

Samples	spiked phases	Pb concentration in spiked phase		Pb concentration in final mixture
		$\mu g\ g^{-1}$	$\mu g\ m^{-2}$	μg Pb g^{-1}
Model soil 1	calcite	1480	1480	74
Model soil 2	halloysite	946	39	142
Model soil 3	goethite	1820	33	186
Model soil 4	hausmannite	1840	153	186
Model soil 5	humic acid	1470	735	296
Te Rapa silty peats	calcite	1480	1480	302
Te Rapa silty peats	halloysite	946	39	288
Kainui silt loam	calcite	1480	1480	318
Kainui silt loam	halloysite	946	39	302

Two to four replicates of the individually spiked phases and the model soils were used in assessing the sequential extractions. The sequential extraction procedures of Tessier et al. and the BCR were slightly modified, and the schemes used are outlined in Table 2.5.

Both modifications related to final steps, where redistribution is no longer a possibility.
The original reagents for the "residual" phase of Tessier et al.'s scheme are a 5 : 1 mixture of hydrofluoric and perchloric acids (Tessier et al., 1979); this was replaced by a pseudo-total aqua regia digestion. A pseudo-total acid digestion of solid residues was also added as new step (where none previously existed) in the originally proposed BCR procedure (Quevauviller et al., 1994; Ure et al., 1993, 1995) in order to allow the assessment of Pb recoveries.
It should be noted here that in the preparation of the first extraction solution (1 M magnesium chloride) of Tessier et al.'s scheme, a small amount of (AR) MgO was added to adjust the pH of the $MgCl_2$ solution to about 7.

Wherever applicable, the mixtures were shaken at room temperature (~ 20 °C) using a rotary mechanical shaker at a speed of 40 rpm. This ensured continuous suspension of the mixtures.

The supernatants were separated from the solid residues by centrifugation at 10 000 rpm for about 20 - 25 min (unless otherwise specified). Supernatant solutions were transferred using micropipette into clean glass vials and were acidified with concentrated nitric acid when deemed appropriate, e.g., those from step 1 and 2 of Tessier et al.'s scheme. The solutions were analyzed as soon as possible after extraction, otherwise being stored at 8 °C prior to analysis.

Table 2.5. Tessier et al.'s and the BCR extraction procedures.

Step	Tessier et al.'s extraction conditions	Step	BCR extraction conditions
1	8 ml 1 M magnesium chloride, pH~7, shake 1 h	-	-
2	8 ml 1 M acetic acid/ sodium acetate, pH~5, shake 5 h	1	20 ml 0.11 M acetic acid, pH~3, shake 16 h
3	20 ml 0.04 M hydroxylamine hydrochloride in 25% v/v acetic acid, pH~2, @ 96 ° C, 6 h	2	20 ml 0.1M hydroxylamine hydrochloride, pH~2, shake 16 h
4	27% hydrogen peroxide, 3.2 M ammonium acetate in 20% v/v nitric acid	3	27% hydrogen peroxide, 1 M ammonium acetate, pH~2
5	4 M nitric acid + concentrated hydrochloric acid (aqua regia)	4	4 M nitric acid + concentrated hydrochloric acid (aqua regia)

Note:
The purposes of the first two steps in Tessier et al.'s scheme and the first step in the BCR procedure are generally comparable, i.e., selective to "exchangeable" and "acid- soluble" metal-bound phases. The steps 3 ("bound to Fe/ Mn oxides") and 4 ("bound to organic matter" fractions) in Tessier et al.'s scheme are parallel to the steps 2 ("reducing") and 3 ("oxidizing") in the BCR scheme, respectively. The original reagents for the "residual" phases in Tessier et al.'s scheme are replaced by aqua regia. An acid digestion is added as step 4 to the originally proposed BCR procedure.

Between steps of the extraction, solid residues were washed once with distilled-deionized water, also by centrifugation. The volume of rinse-water (8 or 10 ml) was kept to a minimum in order to avoid excessive loss of the metal and the solid residues, and washings were discarded.

Analysis of the solid digests and extracts is described in *section 2.5.1.*

2.1.5. Investigation of solid phases influencing Pb recovery patterns of five-phase model soils.

Various combinations of two-and/ or three-phase systems were subjected to the extraction schemes of Tessier et al. and BCR. A given solid phase was deemed dominating if its presence in the two-and/ or three-phase systems resulted in recovery patterns of Pb similar to those of the five-phase model soils, with corresponding spiked phases, using the same extraction scheme.

2.1.6. Investigation of the effects of the extraction conditions on Pb recovery patterns.

The differences between the extraction conditions of the "early" extraction steps of the schemes of Tessier et al. and BCR (where readsorption of Pb to the remaining solid phase(s) was still possible) were investigated in terms of their influences over the pattern of Pb recovered from five-phase system (spiked calcite). In most cases examined, humic acid was the phase of interest (further discussed in *Chapter 3 section 3.3.*).

It was considered possible that Mg (1 M $MgCl_2$ is the first extraction reagent for the "exchangeable" fraction of Tessier et al.'s scheme, Table 2.5.) saturated on solid phase(s) might deactivate the surface binding sites, and/ or Mg of high concentration in the solution might hinder readsorption of Pb on solid phase(s). The first possibility was tested by applying the BCR extraction scheme on duplicate samples of five-phase model soil comprising spiked-calcite, Mg-sorbed humic acid, and the other three clean phases (using the same ratio of each component, as previously described in *section 2.1.2.*). The Mg-sorbed humic acid was prepared using the first extraction step of Tessier et al.'s scheme.
This involved the addition of 1 M $MgCl_2$ solution into a centrifuge tube containing clean humic acid (with the ratio of 8 ml solution : 0.1 g solid). The mixture was subjected to mechanical shaking for 1 h, after which time, the Mg-sorbed humic acid was separated from the supernatant by filtration through Whatman #541 filter papers. After being thoroughly washed using clean water, the treated humic acid was allowed to air-dry on filter paper and then oven dried (at about 30 °C) for about an hour. The amount of Mg sorbed on the humic acid was assessed by complete destruction of duplicate samples of treated humic acid using the oxidation step of Tessier et al.'s scheme (Table 2.5.). This was performed concurrently with a complete oxidation of duplicate samples of untreated-clean humic acid.

Mean concentrations of Mg on the clean and treated humic acids were found to be 36 and 7162 μg g^{-1} solid, respectively (the former values is the mean of 38 and 33 μg Mg per g solid, and the latter value is the mean of 6888 and 7435 μg Mg per g solid). The second possibility, that a high concentration of Mg in solution may hinder readsorption, was tested by applying a "modified" BCR extraction scheme on duplicate samples of the five-phase model soil with spiked calcite. The BCR scheme was modified by using 1 M $MgCl_2$ / 0.11 M acetic acid as the first extraction reagent instead of acetic acid alone (magnesium chloride hexahydrate was dissolved in 0.11 M acetic acid to make $MgCl_2$ at final concentration of 1 M and final pH of about 4.75).

The possible effect of the high ionic strength of the second reagent in Tessier et al.'s scheme (1 M acetic acid/ sodium acetate) was assessed by substituting this reagent with the first extraction solution of the BCR procedure (0.11 M acetic acid); the "modified" BCR scheme was then applied on duplicate samples of the five-phase model soil which contained spiked calcite.

The possible influence of elevated temperatures and high acetate anion concentrations (which are used in the reducing step of Tessier et al.'s scheme (Table 2.5.) was examined by applying this reducing step in the place of the conventional reducing step in the BCR scheme (Table 2.5.); the "modified" BCR procedure was applied on duplicate samples of the five-phase model soil containing spiked calcite or halloysite.

The possible effect of the high temperature (96 °C) only (used in Tessier et al.'s reducing step) on retention of Pb on humic acid was tested by sorption of Pb onto clean humic acid from a solution of the reducing reagent (0.04 M hydroxylamine hydrochloride in 25% v/v acetic acid, pH 2) for 6 h at room temperature, and at 96 °C. Each 20 ml aliquot of the reducing reagent was added into two sets of two and three centrifuge tubes, each containing a 0.1 g clean humic acid. Into each tube, a 37 μl aliquot of stock 1000 ppm Pb was added (equivalent to amount of Pb released from a completely dissolved 0.025 g sample of spiked calcite). The first set (of two centrifuge tubes) was subjected to rotary mechanical shaking for 6 h at room temperature, whereas the second set (of three centrifuge tubes) was subjected to a temperature of 96 °C for 6 h, using a water bath (with occasional shaking). The second set of centrifuge tubes was allowed to cool, then loss by evaporation was countered by replenishing the tubes up to the mark of 20 ml, using the reducing reagent. In all cases, the supernatants were separated from the remaining humic acid by centrifugation at 10 000 rpm for 30 min. It was found that 237 and 98 μg (mean values) of Pb were retained on humic acid (1 g) at room temperature, and at 96 °C, respectively (tabulated results are shown in *Appendix 2.6.*).

Possible influence of 25% v/v acetic acid (used in the reducing step of Tessier et al.'s scheme) on retention of Pb on humic acid, was tested by sorption of Pb onto clean humic acid in 0.04 M hydroxylamine hydrochloride solution, in the absence of acetic acid, for 6 h, at room temperature and at 96 °C. The experiment was performed in duplicate with the assessment of the effect of high temperature (96 °C) on Pb retention on humic acid. It was found that 331 and 218 μg (mean values) of Pb were retained on humic acid (1 g) at room temperature, and at 96 °C, respectively (tabulated results are shown in *Appendix 2.6.*).

2.2. Inhibition of lead redistribution during the BCR sequential extraction.

All the clean and individually-spiked solid phases used in this section are those used in the previous experimental *section 2.1.* In the case of individually Pb-spiked phases and the two-/ three-/ four-phase synthetic model soils, each solid composition was weighed according to its amount in 0.5000 g ± 0.0002 g sample of a five-phase model (as mentioned earlier in *section 2.1.2.*). Five-phase model soils (unless otherwise specified) were prepared as previously, with a dilution with acid-washed sand, whereas models containing 2, 3, or 4 synthetic solid phases were prepared without the dilution. The solid systems were generally subjected to a modified BCR extraction scheme (as described in the following paragraph), in order of increasing complexity, i.e., a two-phase system was tested prior to three-/ four-/ and five-phase systems, respectively. In most multi-phase systems under investigation, Pb was originally introduced in the form of spiked-calcite and modifications to prevent redistribution were made to reagents in the first step. Recovery of the Pb released from complete dissolution of spiked calcite, at the modified step in the presence of other synthetic soil phases suggests effectiveness of the modification in counteracting Pb redistribution.

Two broad approaches, as previously outlined in *Chapter 1 section 1.7.*, were tested for their potential usefulness in inhibiting Pb redistribution. These involved a range of modifications at the first extraction step of the BCR scheme (where redistribution is possible), using (1) solid sequestering agents; and (2) dissolved complexing agents. The subsequent extraction steps of the BCR scheme (Table 2.5.) were applied in their unmodified forms.

2.2.1. Solid sequestering agents.

The solid sequestering materials assessed included (a) a commercial sulfonate ion exchange membrane strip; (b) SiO_2 gel and wool functionalized with dithiocarbamate; (c) a commercial thiol resin (RSH); (d) a commercial flame-retardant cotton fabric (Proban); (e) a thiol-derivatized SiO_2 gel; and (f) a phosphine-derivatized wool. The sources, preparations, and structures of these materials are listed in *Appendix 2.7.* Most of these materials were trialed concurrently.

The solid sequestering agents used were generally systematically tested, under the conventional BCR's first extraction step (0.11 M acetic acid, 16 h), for (1) their affinities for Pb (as $Pb(NO_3)_2$ in 1 M nitric acid or as Pb-sorbed calcite), in the absence of synthetic soil components; and (2) their abilities to capture Pb released from completely dissolved calcite, in the presence of humic acid and/ or other phase(s).

Various techniques used to separate/ remove the solid sequestering materials from the synthetic soil components involved (1) the use of a nylon sieve (1 or 6 μm pore size) or dialysis tube (Molecular Weight Cut Off of 12 000) to confine the sequestering agent(s) prior to their being inserted into a system; or (2) the use of a 100 μm pore sized nylon sieve to separate sequestering agent from synthetic soil phase(s), after the completion of an extraction. These two techniques were chosen over other possible separation methods (such as separation by density gravity or magnetism) as being the most practicable.

2.2.1. (a) Sulfonate ion exchange membrane strips.

The ion exchange membrane, supplied as square sheet, was soaked in clean water for about 24 h before use, as suggested by the supplier. The membrane was then cut into strips of 49 mm x 20 mm. Two strips of the 49 mm x 20 mm membrane (equivalent to a total reactive surface area of about 3900 mm^2) were considered to provide reactive surface sites in enough excess for Pb and Ca ions, which would be available in 0.11 M acetic acid as a result of the complete dissolution of 0.025 g individually spiked calcite. This estimate is partially based on the test using the same type of membrane by Sagger and co-workers (1990) that each membrane strip of 62.5 mm x 25 mm (equivalent to the total reactive surface area of about 3000 mm^2) has an approximate exchange capacity of 0.2 meq for Ca^{2+} (milliequivalent = mmole per charge of free ions). In this study, complete dissolution of the spiked calcite released 0.125 meq Ca^{2+} and an approximate 9×10^{-5} meq Pb^{2+} into the solution. The strip length of 49 mm was to ensure complete immersion in the 20 ml solution in the sample centrifuge tubes used. The strip width of 20 mm also facilitated convenient handling during insertion and withdrawal of the membrane. At the preliminary step, some tests of a possible Pb contaminant from the membrane itself were also performed. The control sample tubes contained new two membrane strips of 49 mm x 20 mm immersed in 0.11 M acetic acid, in the absence of solid phases.

After the systems containing only individually spiked calcite were tested, the two-phase systems consisting of (1) 0.025 g spiked calcite and 0.1 g humic acid; and (2) 0.025 g spiked calcite and 0.05 g hausmannite, were further investigated.

An increase in the amounts of the membrane strips was also performed, to assess the effect of more available active surface sites on capture of Pb from solution.

In the case of a two-phase system containing spiked calcite and humic acid, chopped membrane of about 39 000 mm^2 (equivalent to about 20 strips of the 49 mm x 20 mm membrane) contained in two dialysis bags (molecular weight cut off of 12 000) tied with an overhand knot enclosure, was immersed in the system to test for a possible technique for preventing direct contact between the remaining solid phase in the system and the membrane. Prior to the experiment, the dialysis tube was tested for its durability in acetic acid solution by being immersed in the solution and mechanically shaken for 16 h.

In these cases, the solid phases were weighed directly into polycarbonate centrifuge tubes, and this was followed by addition of 20 ml of the 0.11 M acetic acid extraction solution. Immediately after this, the required numbers of the membrane strips were inserted in the sample tube, using plastic tweezers. The samples were then mechanically shaken, as previously described in *section 2.1.4*. After a 16-h extraction, the membrane strips were taken out, then rinsed with a small amount of clean water to remove any possible free Pb and (in some cases) other solid particles retained on the membrane strip. The rinse-water was discarded (it was previously established that addition of the rinse-water in the extraction solution made no significant difference to the total recovery of Pb). In the cases where solid phase material still remained in the system (e.g., the two-phase system) after the extraction, the supernatant was separated from the solids by centrifugation as described in *section 2.1.4*. The Pb-sorbed membrane strips were transferred to a new cleaned centrifuge tube and the Pb sorbed on the membrane strips was eluted by being mechanically shaken with either
(1) 20 ml 0.5 M nitric acid, 3 h, and followed by 20 ml 1 M nitric acid, 24 h; or
(2) 20 ml 1 M nitric acid and 0.5 M NaCl, 24 h. The Pb in the eluants and in the extractant solution (0.11 M acetic acid) was then analyzed by FAAS, as described in *section 2.5.1*.

2.2.1. (b) SiO_2 gel and wool functionalized with dithiocarbamate.

The dithiocarbamate-functionalized SiO_2 (hereafter "dSiO_2") and the derivatized wool were tested as received. Three sets of duplicate systems were prepared. The first contained about 0.1 g dSiO_2 + 20 ml acetic acid; the second about 0.1 g dSiO_2 + 37 μg Pb (37 μl of stock 1000 ppm Pb, in 1 M nitric acid) + 20 ml water; and the third 37 μg Pb (from the stock 1000 ppm Pb) + 20 ml water. These were used to assess the contribution of Pb from the dSiO_2 under acetic acid extraction conditions, the affinity for Pb of the dithiocarbamate functional group under the slightly acidic conditions, and the significance of Pb adsorption onto the wall of the tube, respectively. All the systems were mechanically shaken for 16 h.

The separation of the $dSiO_2$ and the supernatant as well as the subsequent washing and elution steps are as described in the following paragraph.

The $dSiO_2$ was weighed to about 0.1 and 0.5 g into two polycarbonate centrifuge tubes, each containing 0.025 g Pb-spiked calcite. The tubes were shaken to ensure reasonably good blending and 20 ml of 0.11 M acetic acid was added. The mixtures were then mechanically shaken for 16 h. The solid and supernatant were separated using centrifugation (as described in *section 2.1.4.).* The $dSiO_2$ was then washed twice, with 20 ml clean water by centrifugation (12 000 rpm for 5 min). The rinsings were discarded. A 20 ml aliquot of 1 M nitric acid was added to extract any Pb possibly retained on the resin. The extraction conditions and the separation of the sequestering agent(s) from the system, as well as the washing and the elution steps, described here, were also applied to all of the following systems tested, unless otherwise specified.

Two materials, dialysis tubing (as previously used in *section 2.2.1. (a)*) and nylon sieves, were tested as possible means of separating the $dSiO_2$ from the synthetic soil component(s). A section of dialysis tubing was made into a bag using an overhand knot. The bag, containing about 0.1 g $dSiO_2$, was inserted into a centrifuge tube containing Pb-spiked calcite and goethite prior to an addition of acetic acid. Both 1 μm and 6 μm pore-sized nylon sieves were made into bags, each with a dimension of about 1 cm × 2 cm. Each nylon bag, containing about 0.1 g resin, was inserted into a centrifuge tube, in the absence of other solid phase(s), after which acetic acid was added. Another 1 μm pore-sized nylon bag of the same dimension containing about 0.1 g $dSiO_2$ was also tested with the individually spiked-calcite system. In all cases, the dialysis and nylon bags, containing the $dSiO_2$, were wetted with acetic acid prior to insertion into the centrifuge tubes. At the end of the extraction step, the bags were removed from the tubes and washed thoroughly with clean water. The bags were then cut open and the resin was transferred (using clean water) to a new clean centrifuge tube. The resin was further washed with about 10 ml clean water and was then separated from the supernatant prior to undergoing the elution step.

Wool coated with dithiocarbamate binding sites was tested in a similar sequence to the $dSiO_2$. The fuctionalized-wool (of weight about 0.2 g) was put into a tube containing Pb-spiked calcite prior to the addition of 20 ml 0.11 M acetic acid. At the end of the extraction step, the wool was taken out of the tube and washed thoroughly with clean water (using a water bottle) then allowed to dry for a few minutes on a clean filter paper. The wool was then transferred to a new tube for the subsequent elution step. Only the 1 μm pore-sized nylon bag was tested for its usefulness in separating the wool from other solid phase(s). About 0.5 g wool, sealed in a nylon bag (with a dimension of about 1.5 cm × 5 cm) and previously wetted with acetic acid, was inserted into a tube containing 0.025 g Pb-spiked calcite; then acetic acid was added. The subsequent steps were handled as outlined above.

In accordance with observations made during the work, nylon bags with a 1 μm pore- size were used for separation when testing the 5-phase system containing spiked calcite. Three 1 μm pore-sized nylon bags, containing in total about 3 g of the wool, were used in combination with a nylon bag, containing about 2 g of the resin, to test with a five-phase system (spiked calcite). Subsequent steps were as previously described, except that (1) the bags were simultaneously eluted with the sequestering agents and (2) the wash- water of the sequestering agents and the bags was added to that of the remaining solid phases (so that the synthetic soil particles being washed out from the sequestering agents and the bags were recovered).

2.2.1. (c) Thiol resin (RSH).

In all cases, thiol resin (supplied in water) was allowed to dry for a few minutes on clean filter paper before weighing (wet weight). The resin was weighed to about 1 g directly into a polycarbonate centrifuge tube, containing 0.025 g Pb-spiked calcite. Another 1 g of the resin was weighed and confined in a dialysis bag (MWCO 12 000) before being inserted into a tube containing the same amount of Pb-spiked calcite. Acetic acid (0.11 M) was then added to both tubes. The mixtures were mechanically shaken for 16 h. The elution and rinsing steps were as described in the previous sections. In the system comprising the resin in the dialysis bag, only the resin was eluted with nitric acid.

In the case of a system comprising about 0.5 g resin + Pb-spiked calcite + humic acid + hausmannite, a small amount of chloroform was added to test for its potential usefulness as an aid to separation of the resin from the remaining solid phases by density.

A 100 μm pore-sized nylon sieve was tested as a possible means of filtering the resin from synthetic soil phases in a five-phase system (spiked calcite) at the end of the extraction step. Prior to the preparation of the five-phase system, humic acid and sand were sieved through a clean 100 μm pore-sized nylon sieve (goethite, hausmannite, halloysite, and spiked-calcite were not sieved since they are already very fine particles). Portions of humic acid and sand which passed through the sieve were then weighed to 0.1 and 0.2 g, respectively (corresponding to their weight ratios in a five-phase system as outlined in *section 2.1.2.*) and directly mixed with other phases in a clean centrifuge tube. Prior to the mixing of the resin with the five-phase system, the resin (particle size of about 300 - 1200 μm) was rinsed with water through a clean 100 μm pore-sized nylon sieve. This was to ensure that any resin particles of smaller size than 100 μm were separated out. The resin retained on the sieve was then transferred to a clean filter paper and allowed to dry for a few minutes. This resin ($\geq$ 100 μm) was weighed to about 5 g directly into a tube, containing the five-phase system (spiked calcite). Acetic acid (0.11 M) was added to the tube and the mixture was then mechanically shaken for 16 h. After this time the supernatant was separated from the solid phases by centrifugation, and the remaining solid phases were fractionated by transferring them (with the aid of water) to a clean 100 μm pore-sized nylon sieve funnel. The material in the funnel was rinsed several times with clean water to facilitate good separation of the smaller particles of the synthetic soil components from the resin. The filtrate containing the synthetic soil component was collected and centrifuged in order to recover the solid, with the supernatant being separated using a micropipette. The solid remaining in the tube was then subjected to the subsequent (reducing, oxidizing, and aqua regia) extraction steps. The resin retained on the nylon sieve was then transferred to a new clean tube using a plastic spoon and a small volume of clean water. After pipetting out the remaining water, the resin was eluted using the procedures described earlier.

2.2.1. (d) Chemically-activated flame retardant Proban, thiol-derivaized silica gel, and phosphine-derivatized wool.

A chemically-activated cotton cloth (Proban), as received, was cut to provide a strip of dimensions about 2 cm x 5.5 cm. The strip was then inserted into a polycarbonate centrifuge tube containing 0.025 g Pb-spiked calcite. Proban of about the same dimension was inserted into a tube containing humic acid, goethite and hausmannite, followed by an addition of 0.11 M acetic acid.

A sample of the dried wool-THP, Wool-N-CH_2-$P(CH_2OH)_2$,was weighed to about 0.5 g into a clean tube, immediately after being prepared. This was followed by addition of 20 ml clean water and 37 μl of stock 1000 ppm Pb solution (which would yield an equivalent amount of Pb to the 37 μg Pb released from 0.025 g completely dissolved Pb-spiked calcite). Another 2 g of the wool was inserted into a second clean tube, containing 0.025 g Pb-spiked calcite, into which was also added 20 ml 0.11 M acetic acid. About 4 g of the derivatized-wool was also tested with a five-phase system (spiked calcite).

In the case of thiol-functionalized silica gel, SiO_2-$(CH_2)_3SCH_2CHOHCH_2SH$, about 0.1 g was added into a polycarbonate centrifuge tube containing 0.025 g Pb-spiked calcite, and this was followed by an addition of 20 ml 0.11 M acetic acid.

In all of the above cases in this section, the conditions of the extraction, separation, and elution steps were as described in the earlier sections.

2.2.2. Dissolved sequestering agents.

Four different dissolved complexing agents: (a) Aerophine® 3418A promoter; (b) 18-Crown-6; (c) Zinc dithiocarbamate; (d) Cryptand 2.2.2; and (e) NTA, were assessed in this section of the study; the experimental details will be outlined in this chronological order. Each of these ligands, except the Zn dithiocarbamate, was separately dissolved in the conventional first extraction reagent (0.11 M acetic acid, pH ~ 3) of the BCR scheme to obtain the required concentration of the ligand. Each modified extraction solution was then added into the solid systems under investigation. For Zn dithiocarbamate (freshly prepared according to the procedure described in *subsection 2.2.2. (c)*), the complexing agent was introduced into the system via an organic phase in contact with the acetic acid solution.

In general, the modifications made to the first extraction step involved a combination of various concentrations of the complexing ligands in the acetic acid (or in the organic phase in the case of the Zn dithiocarbamate) with variation in the extraction times. Generally, the "modified" extraction conditions were initially applied to a sample of individually-spiked calcite, to ensure they were capable of causing complete dissolution of the calcite, prior to further application on more complex systems (i.e., multi-phase systems).

Once again, in all cases unless otherwise indicated, the amount or ratio of each synthetic solid phase was the same as that used individually and as a component in multi-phase systems (shown in Table 2.2. and described in *subsections 2.1.2.* and *2.1.4.*). Unless otherwise specified, each experiment was generally performed on a single sample replicate, in order to facilitate screening and identification of the most promising approaches.

2.2.2. (a) Aerophine® (a phosphine derivative)

Aerophine (50% w/v, pH ~ 10) as supplied was diluted with 0.11 M acetic acid, clean water and absolute ethanol to make up various "modified" extraction solutions. The alcohol was added to help ensure the complete dissolution of a white precipitate which was otherwise observed. The compositions of the "modified" extraction solutions and their relevant characteristics are summarized in Tables 2.6. and 2.7.

Each 20 ml of the "Original" extraction solution (2.5% w/v Aerophine in acetic acid, pH ~ 4) was added into two centrifuge tubes, one containing individually-spiked calcite, and another containing a two-phase system comprising individually-spiked calcite and clean humic acid. The two centrifuge tubes were then mechanically shaken for 16 h. In the case of the tube containing the two-phase system, at the end of the extraction, the remaining humic acid was separated from the solution by centrifugation at 12 000 rpm for 30 min. The residual humic acid was then washed with about 10 ml of clean water. This washing was discarded and the humic acid was then oxidized using H_2O_2 (BCR's oxidizing step). The aerophine supernatants collected from both systems (pH ~ 4) were not further acidified (since acidification caused some white precipitation), but were analysed as soon as possible (no later than 1 day after the collection). In preparation of standard solutions for FAAS analysis, the "Original" solution with a small volume of absolute ethanol added was used as the background matrix. In all cases, the pH values of the standard solutions were about 4.

Table 2.6. Compositions of the "modified" extraction solutions containing Aerophine.

"modified" extraction solutions	Aerophine as supplied (50% w/v solution)	0.8M acetic	Absolute EtOH	Water
"Original"	10	100	90	-
	"Original"solution	0.4M acetic	Absolute EtOH	Water
"Diluted"	50	100	60	-
"Diluted-1"	20	55	65	60
"Diluted-2"	5	55	80	60
"Diluted-2"	5	55	75	50

Table 2.7. Relevant characteristics of the "modified" extraction solutions containing Aerophine

	"Original"	"Diluted"	"Diluted-1"	"Diluted-2"
% Aerophine	2.50%	0.60%	0.25%	0.06%
final conc. of acetic acid	~0.4M	~0.19M	~0.11M	~0.11M
pH of the mixture	~4	~3.5	~3.3	~3.3

Under these conditions, the analytical determinations of Pb in the standard solutions and the aerophine extracts by FAAS were found to be highly problematic (this is further discussed in *Chapter 4 subsection 4.2.1.*). In an attempt to resolve these problems, a new set of standard solutions (containing Pb and other relevant metals: Fe and Mn) was prepared in 100 ml beakers using the "Original" solution, with additions of 10 ml 4 M nitric acid and 2 ml concentrated HCl. The mixtures were then refluxed on a steam bath for about 90 min. After cooling, the mixtures were filtered through Whatman #541 filter papers (pre-washed with 4 M nitric acid), and the filtrates were collected. However, refluxing the aerophine solutions with the acid caused an unexpected chemical reaction, involving the appearance of an oily solid, and it was therefore deemed not appropriate to further use the filtrates to prepare standard solutions (discussed further in *Chapter 4 subsection 4.2.1.*).

Due to the difficulties encountered in attempting direct analysis of solutions containing aerophine, in subsequent tests, the parameter measured was the amount of Pb left on the remaining solid phase(s) in the system(s) at the end of the "modified" extraction step. Thus it was still possible to evaluate the potential usefulness of the Aerophine in counteracting Pb redistribution.

The "Original" solution was further tested for its ability to act as an extractant in its own right with single sample of three individually-spiked phases: humic acid, hausmannite, and goethite. In these cases the "Original" solution (20 ml) was added into each system, and the mixtures were mechanically shaken for 16 h. Remaining solid phases were separated from the aerophine matrix and thoroughly washed using the same procedure as described above. The remaining humic acid was completely oxidized using H_2O_2, whereas the goethite and hausmannite were totally digested by hot aqua-regia. In the case of the hausmannite, a reduction using hydroxylamine hydrochloride was also tried. The determinations of Pb in these matrices by FAAS were as routinely performed, i.e., the standard solutions were prepared in matrices and with acid strengths as similar as possible to those of the samples.

The approach of determining of Pb left on remaining solid phases was also applied to the same solid systems (i.e., the individually-spiked phases and the mixture of clean humic acid and spiked calcite) subjected to the following range of different "modified" extraction conditions: (1) the "Original" solution for 5 h and 1/2 h; (2) the "Diluted" solution (0.60% Aerophine) for 16 h and 1/2 h; as well as (3) the "Diluted-1" (0.25% Aerophine) and the "Diluted-2" solutions (0.06% Aerophine), each for 1/2 h.

Based on the comparison of the percentages of Pb recovered from the individually spiked phases and the two-phase system (clean humic acid + spiked calcite) by the different "modified" extraction conditions (discussed in *Chapter 4 subsection 4.2.1.*), the 0.06% "Diluted-2" solution and the extraction time of 1/2 h were deemed most suitable and therefore further tested on following multi-phase systems.

Two 20 ml aliquots of the "Diluted-2" solution was added into two duplicate centrifuge tubes, each containing 0.5 g of a five-phase model soil with spiked calcite (37 μg Pb). The samples were then mechanically shaken for 1/2 h. The remaining solid phases were separated from the aerophine matrix and washed with water as described above, and then subjected to the reduction, oxidation, and acid digestion steps. It should be noted here that these subsequent extraction conditions are those of the BCR scheme except for the reducing step, which is that of Tessier et al.'s scheme (Table 2.5.). This adjustment was based on an observation that a portion of the individually-spiked hausmannite (after being extracted by the "Original" solution and then washed with clean water) was not completely reduced by hydroxylamine hydrochloride under the room temperature conditions specified in the BCR scheme.

The determination of Pb in the samples containing the "Diluted-2" matrix collected from the above duplicate samples of the five-phase systems was performed using the FAAS.
The standard solutions were prepared fresh (final pH ~ 4), as previously described.
The aerophine extracts (all pH ~ 4 and without acidification) and the standard solution were kept in a 4 °C cool room for 7 days before analysis (this slight delay being due to factors outside the author's control). The analyses of Pb in the other extracts (of the unmodified reduction, oxidation, and acid digestion steps) were as previously described. The test on a five-phase system containing spiked calcite (37 μg Pb) using the "Diluted-2" extraction solution was repeated once more using an identical procedure as described here, except that in this case the aerophine extracts were analyzed on the same day as they were collected (against freshly prepared standard solutions) instead of 7 days later.

The FAAS determinations of the Pb in the aerophine extracts collected from the above four replicates of a five-phase model soils containing spiked calcite (37 μg Pb) were still found to be subject to an unusual reproducibility problem (discussed in *Chapter 4 subsection 4.2.1.*). To further investigate this analytical problem, 1/2 h extractions with the "Diluted-2" solution were performed on the following systems: (1) a sample of five-phase soil model with spiked calcite (37 μg Pb) (a repeat of the above experiment); (2) duplicate samples of a five-phase system with 0.05 g spiked calcite (74 μg Pb); and (3) duplicate samples of a 0.05 g individually-spiked calcite (74 μg Pb). All the parameters concerning the handlings of the extractions of these samples were kept consistent with the previous trials. The determinations of Pb in the aerophine extracts using FAAS were performed as already described, but with the additional use of atom traps (Ti and quartz) to help enhance the absorbance signals. In many cases, the analytical determinations were performed several times on the same extracts.

In addition to the above investigation of the analytical problem, some fresh aerophine-containing solutions were sent to R.J. Hill Laboratory Ltd. for independent Pb analysis by ICP-MS and GFAAS. These samples included (1) the "Diluted-2" aerophine extracts collected from the extraction of new duplicate samples of a five-phase model soil with spiked calcite (37 μg Pb); (2) an aerophine blank; and (3) a 2 ppm Pb standard solution.
The samples were sent out on the same day of the collections and were analyzed by the lab within a few days of their being received.

2.2.2. (b) 18-Crown-6.

18-Crown-6, as purchased from Sigma Chemical Company, Ltd., was dissolved in 0.11M acetic acid to make up five "modified" extraction solutions at the following concentrations: 9×10^{-6}; 9×10^{-5}; 9×10^{-4}; 9×10^{-3}; and 9×10^{-2} M. In order to assess the dissolution of calcite, 20 ml aliquots of the "modified" solutions (pH ~ 3 - 4) were added into each of 5 centrifuge tubes, each containing 0.025 g of individually-spiked calcite (in all cases, a complete dissolution of the calcite was observed within less than 10 min after the additions of the solutions and the systems were subjected to a vigorous shake). In addition, 20 ml aliquots of the 9×10^{-6}; 9×10^{-5}; and 9×10^{-3} M solutions were added into three sets of 3 centrifuge tubes, each containing 0.125 g of a two-phase system comprising spiked calcite and clean humic acid. The first set (of 3 centrifuge tubes) was then mechanically shaken for 1/2 h, the second and the third sets were shaken for 5, and 16 h, respectively.

A 20 ml aliquot of the 9×10^{-2} M solution was added into a centrifuge tube containing a 0.125 g sample of the two-phase system, and the tube was mechanically shaken for 1/2 h. In addition, a shorter extraction time of 15 min was tested using two of the modified extraction solutions (9×10^{-4} and 9×10^{-3} M). Each 20 ml aliquot of the 9×10^{-4} and 9×10^{-3} M solutions was added into (1) two centrifuge tubes each containing 0.1 g of an individually-spiked humic acid, and (2) two tubes each containing the sample of the two-phase system. At the end of the extraction, the remaining humic acid in the systems which were subjected to the 1/2, 5, and 16 h extraction was separated from the solution by centrifugation at 12 000 rpm for 1/2 h, whereas the remaining humic acid in the systems which were subjected to the 15 min extraction was separated out by centrifugation at 13 000 rpm for 10 min. In all cases, the crown extracts were acidified with concentrated nitric acid and the residual humic acid was washed with about 10 ml of clean water.

This washing was discarded (except that of the 9×10^{-3} M solution (with 1/2, 5 and 16 h extraction) which was later analyzed for Pb) and the humic acid was then oxidized using the H_2O_2 step of the BCR scheme. Analysis of Pb was performed for both the crown extracts and the solutions of oxidized humic acid. The standard solutions for the analysis of Pb in the crown extracts were prepared in the corresponding crown extraction solutions with similar acid strength to those of the extracts. To test for a possible effect of a high concentration of Ca (from dissolved calcite) on the absorbance readings of Pb, a mixture containing known amounts/ volumes of Pb (from stock Pb solution), clean calcite, conc. nitric acid, and the 9×10^{-5} solution was analyzed for Pb against the standard solutions, which were prepared in the same matrix but without the presence of calcite. This "simulated-extract" sample was prepared in such a way as to be as similar as possible to the above 9×10^{-5} extract of the two-phase system (i.e., in terms of the concentration of Ca, and acid strength) but with a final Pb concentration of 0.5 ppm.

2.2.2. (c) Liquid-liquid extraction using Zn dithiocarbamate in MIBK.

As in the previous sections, the experiments reported in this section are in chronological order, although, it was later found that if certain experiments had been performed earlier than they were, a conclusion would have been reached more quickly regarding the potential usefulness of the liquid-liquid extraction approach for inhibiting redistribution of Pb.

However, the sequence of the experiments reported here does not alter the final conclusion about this modified method.

Since almost all of the experiments required quite a detailed description, each experiment was numbered as to aid in the follow up.

Unless otherwise specified, all chemicals used were of analytical grade or better.
$PdCl_2$ (with maximum Pb contamination of 0.001%) was purchased from PGM Chemicals (Pty) Ltd. A palladium chloride solution was prepared by dissolving the required amount in 0.7% nitric acid. The MIBK used in the first five experiments was a single fraction distilled at 117 - 118 °C from drum grade, whereas that used in all the subsequent trials was of AR grade. Stock Zn solution of 1000 ppm was prepared by dissolving (AR) $ZnSO_4.7H_2O$ in 1 M nitric acid. All dilutions from the stock Zn solution were prepared freshly using clean water. Stock Fe solution of concentration 1000 ppm was prepared by dissolving AR $Fe(NO_3).9H_2O$ in 1 M HNO_3, whereas a 1000 ppm Mn solution was purchased as a manganous nitrate standard solution for AAS from BDH.

Unless otherwise indicated, each experiment was performed in a single replicate.
The centrifuge tubes used for work with MIBK were made of polypropylene copolymer with polypropylene screw closures (Nalgene®) (in contrast to the polycarbonate tubes normally used, which are not resistant to MIBK). All the sample extracts were acidified by addition of a small volume of concentrated nitric acid prior to analysis for Pb and other relevant metals. Analyses were performed as soon as possible; otherwise the extracts were kept in the cool room, according to routine practise.

In general, the complexing agent $Zn(PDC)_2$ in MIBK was prepared daily, by dissolving a required amount of APDC in clean water using a volumetric flask. The solution was then pre-cleaned by shaking with MIBK (25 ml APDC : 5 ml MIBK). This was done by passing the APDC solution through filter papers (to separate any particulate impurities) into a separating funnel, to which the MIBK had previously been added. The separating funnel was manually shaken for about 5 - 10 min, then left for about 5 min (until both layers were completely separated and the solutions were clear). The lower layer of aqueous APDC was run off into an acid-washed beaker. A required volume of the pre-cleaned APDC solution was pipetted into a cleaned separating funnel, in to which was then added the required volume of a dilute solution of Zn. The separating funnel was manually shaken for about 5 min (a white precipitate was observed when the two solutions came into contact), then the required volume of MIBK was added. The shaking was resumed for 10 more minutes, after which time the white precipitate was completely dissolved. The liquids were allowed to separate by standing for about 5 - 10 min. The top layer of the $Zn(PDC)_2$ in MIBK was carefully removed using a pipette and without disturbing the interface. The solution of Zn complex was retained in an acid-washed glass reagent bottle prior to use.

In the first three preliminary systems (described in the following paragraph) the ability of Pb to migrate from the aqueous to the organic phases (in substitution for Zn in the complex), and of palladium to recover the Pb back into an aqueous solution, were assessed in the absence of solid. An attempt was also made to optimize the concentrations/ volumes of the Zn complex and $PdCl_2$ as well as the handling of the extraction procedures. Some relevant parameters (e.g., amount of Pb, concentration of Fe contributed from goethite, etc.) were kept as similar as possible to those of the more complex multi-phase solid systems further investigated.

In the first preliminary experiment (*Expt.1*, carried out in duplicate), $Zn(PDC)_2$ (in MIBK) was prepared by using 5 ml of freshly-prepared pre-cleaned 2% w/v APDC (and 4% w/v APDC), 40 ml of 8 ppm Zn solution, and 20 ml MIBK. For each duplicate run, a 12 ml aliquot of $Zn(PDC)_2$ (in MIBK) was added into a clean-separating funnel, containing 20 ml 0.11 M acetic acid and 37 μl 1000 ppm Pb stock solution (the mole ratio of Zn : Pb was about 17). The separating funnels were manually shaken for about 15 min and the solutions were allowed to separate by standing for 10 - 15 min. The lower aqueous-layer was carefully run off (without disturbing the interface) into a polypropylene tube, then, acidified with a small volume of concentrated nitric acid and kept in the cool room prior to the analyses for Zn and Pb.

In order to assess the concentration of Fe (a potential interference in the metal exchange process between Pb and Zn) possibly contributed from a partial dissolution of the goethite phase by acetic acid (*Expt. 2*), separate 20 ml aliquots of 0.11 M acetic acid were added into three sets of two centrifuge tubes, each containing clean goethite (0.05 g). The first set was mechanically shaken for 1/2 h, and the second and third sets were shaken for 5 and 16 h, respectively. The supernatants were separated from the solid using a centrifugation at 10 000 rpm for 30 min. The solutions were then acidified prior to the analysis for Fe. The concentration of Fe at 16 h extraction was found to be 5 ppm (the Fe concentrations at 1/2 h, and 5 h extraction times, were found to be 4, and 4.7 ppm, respectively).

In the next experiment (*Expt. 3*, shown schematically, in Fig. 2.1.), the setting of the system tested was basically similar to that in the *Expt.1*, except that (1) a 2% APDC solution was used to prepare the $Zn(PDC)_2$ (in MIBK) reagent; and (2) the acetic acid layer contained 100 μl of the 1000 ppm Fe stock solution, in addition to 37 μl stock Pb solution. The final Fe concentration in the acetic acid layer of about 5 ppm was the maximum concentration observed from *Expt. 2*. At the end of the extraction, the acetic acid layer was run off and the MIBK phase (presumably containing Pb complex) of 10 ml was removed from the funnel using a pipette, into a cleaned separating funnel. Twenty ml of 10^{-3} M Pd solution was then added into the new funnel. The separating funnel was manually shaken for about 10 min, and the solutions were allowed to separate for about 10 min. The aqueous phase was run off into a clean glass vial, and acidified. All the aqueous extracts were analyzed for Pb, Zn, and Fe.

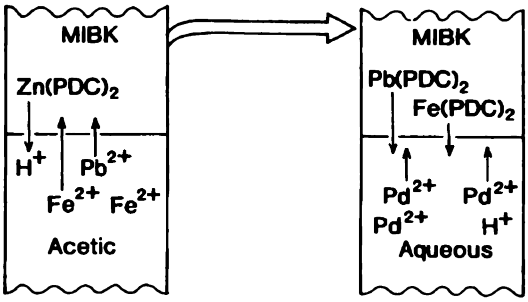


Fig. 2.1. Schematic representation of the use of $Zn(PDC)_2$ in MIBK in the absence of solid phase, but containing Fe in acetic acid solution (*Experiment 3*).

The above extraction and back-extraction scheme was applied on the subsequent systems containing solid phase(s). Prior to testing multi-phase systems, a two-phase system containing clean humic acid and spiked calcite was investigated (*Expt. 4*). In order to assess a suitable extraction time for complete dissolution of the spiked calcite, 20 ml of 0.11 M acetic acid was added into each of three centrifuge tubes, each containing 0.025 g ± 0.0002 g spiked calcite; the first tube was subjected to a mechanical shaking for 15 min, and the second and the third tubes were subjected to the same treatment for 1/2 h and 1 h, respectively. In all cases, at the end of a centrifugation at 10 000 rpm for 30 min, it was found that the calcite was completely dissolved.

It was decided that for *Expt. 4*, the extraction time used would be 1/2 h (with a centrifugation time of 30 min). In this experiment (shown in Fig. 2.2.), a solution of $Zn(PDC)_2$ (in MIBK) was prepared using 5 ml of freshly-prepared pre-cleaned 2% APDC solution, 40 ml of 16 ppm Zn solution, and 12 ml MIBK. A 20 ml aliquot of 0.11 M acetic acid was added into a centrifuge tube, containing spiked calcite and clean humic acid. This was immediately followed by addition of an 8 ml aliquot of the $Zn(PDC)_2$ (in MIBK) (the mole ratio of Zn : Pb was about 39). The centrifuge tube was then vigorously shaken using a mechanical shaker (horizontally-orbital) at about 225 rpm for 30 min. After centrifugation at 10 000 rpm for 30 min, the organic phase (5 ml) was removed from the system using a micropipette, into a cleaned separating funnel. The interface of the organic and the aqueous phases, containing some solid colloidal particles, was removed using a glass dropper. The colloidal particles were added back to the remaining humic acid which was then subjected to a thorough washing with clean water, using centrifugation. The washing was discarded and the remaining solid was later oxidized using hydrogen peroxide. The acetic acid layer was removed from the centrifuge tube, using a micropipette, into a cleaned glass vial and later analyzed for Zn and Pb. Back extraction was performed by adding a 10 ml aliquot of palladium solution (10^{-3} M) into the separating funnel previously containing the 5 ml organic phase. The separating funnel was manually shaken for about 10 min, and the solutions were allowed to separate for about 15 min (the rate of exchange observed from a shift in colour occurred within a few minutes). The lower aqueous layer (clear solution) was carefully run off into a glass vial and the solution was also analyzed for Zn and Pb. In the analysis of the metals in the palladium aqueous extract, two sets of standard solutions were prepared, both containing a range of 1 - 4 ppm Pb: the first set also contained the 10^{-3} M palladium solution without further alteration; the second set contained palladium solution (10^{-3} M) which had previously been in contact with fresh clean MIBK for about 15 min. This was to assess a possible matrix effect which might result from a slight solubilization of MIBK in the palladium matrix solution.

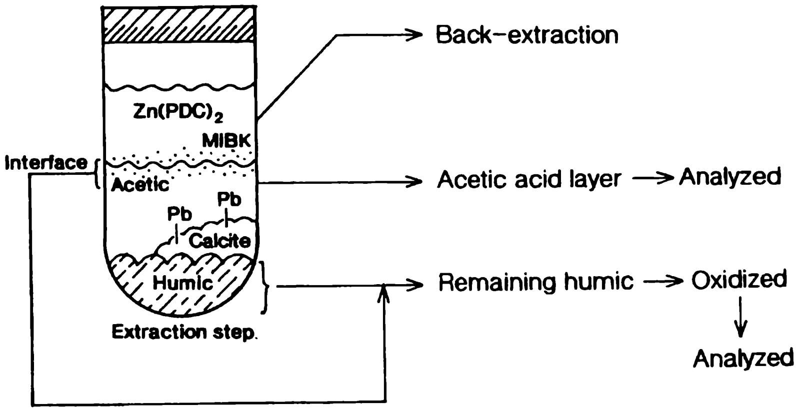


Fig. 2.2. Schematic of the application of Zn(PDC)$_2$ in MIBK on a mixture of spiked calcite and humic acid (*Experiment 4*).

The modified extraction scheme was subsequently applied on a five-phase system containing Pb-spiked calcite (*Expt. 5*). All mole-ratios of relevant metals as well as the extraction times and the handlings were as in *Expt. 4*, except that (1) in this experiment, a control tube containing no solid phase was used concurrently, in order to assess any possible contamination of Pb along the multi-step modified procedure; (2) separation of remaining solid phases and the supernatants was performed by centrifugation at 12 000 rpm (instead of 10 000 rpm, previously used). The aim of this was to improve the settling of the particles observed at the interface of the two immiscible phases. Under these conditions a small number of solid particles still remained in the interface region after centrifugation, however, their amount was considered insignificant, and therefore, these colloidal particles were later discarded; (3) for both the control and sample systems, the analyses of Pb, Zn, Fe, and Mn were performed for (a) the palladium extracts, (b) the aqueous APDC solution (used for a preparation of the Zn-complex (in MIBK)), and (c) the remaining acetic acid layer (except in the case of Mn). The analyses of the metals in the palladium extracts were initially performed against two sets of standards (1 - 4 ppm Pb range), as described in *Expt. 4*. However, in both *Expt. 4* and *Expt. 5*, it was found that the absorbance readings of Pb in the palladium extracts determined against the two standard curves were similar. Therefore, in subsequent experiments in which Pb in palladium extracts were not exceeding 1 - 4 ppm range, Pb determinations were performed against standard solutions containing only the palladium solution, which had not been in previous contact with MIBK; (4) the washwater of the remaining solid phase at the end of the first modified extraction step, was retained and analyzed for Zn and Pb; and (5) extracts of all the reducing, oxidizing and acid digestion steps were analyzed for Pb and Zn.

A good recovery of Pb at the modified extraction step of the *Expt. 5* was seen to be promising (further discussed in *Chapter 4 subsection 4.2.3.*). In *Expt. 4* and *Expt. 5*, acetic acid was added into centrifuge tubes containing the solid phases, before addition of $Zn(PDC)_2$ (in MIBK). It was therefore considered possible that Pb released from dissolved calcite was quickly sequestered by the remaining solid phases in the system, before it had a chance to come into contact with the organic phase and substitute with Zn in the complex. Therefore, it was thought possible that if the $Zn(PDC)_2$ (in MIBK) was available in the system at the time that Pb was first released into the solution, Pb would have more chance to exchange with the Zn (with the result that more of the Pb would be recovered at the modified extraction step).

In the next experiment (*Expt. 6*) the modified first extraction scheme used was that of the *Expt. 5*, except that (1) $Zn(PDC)_2$ (in MIBK) was added into a centrifuge tube containing the sample of the five-phase system (spiked calcite) first, and this was followed by addition of the acetic acid; (2) no control experiment was carried out (it was deemed unnecessary); and (3) only Pb and Zn were determined in the palladium extracts, the aqueous APDC solutions (used in the preparation of the Zn-complex (in MIBK)), and the remaining acetic acid phase (at the end of the modified extraction step one). The remaining solid phases in the system were subjected to the subsequent reduction, oxidation, and acid digestion steps. However, the results of *Expt. 6* revealed that addition of the organic phase into the system prior to the aqueous acetic acid phase did not improve the recovery of Pb at the modified extraction step (further discussed in *Chapter 4 subsection 4.2.3.*). Therefore, in all following experiments, acetic acid was added into multi-phase solid systems first, and this was immediately followed by addition of the $Zn(PDC)_2$ (in MIBK).

The modified first extraction step as performed in *Expt. 5* was then applied on a sample of a five-phase system, this time containing spiked halloysite (*Expt. 7*). In this experiment, the mole ratio of Zn (from 8 ml of $Zn(PDC)_2$ (in MIBK)): Pb (from the total amount originally on the halloysite) was 19. The centrifuge tube containing the solid phases, acetic acid, and $Zn(PDC)_2$ (in MIBK) was subjected to mechanical shaking for 5 h. This extraction time of 5 h was selected on the basis of the percentages of Pb recovered in acetic acid extracts of replicate samples of an individually-spiked halloysite at different extraction times of 15 min, 1/2 h, 3, 5, and 16 h (centrifugation time of 30 min, at 10 000 rpm was applied in all cases) (further discussed in *Chapter 4 subsection 4.2.3.*). All the succeeding steps of the modified first extraction step were as of those in *Expt. 5*. Determinations of Pb and Zn were performed for palladium extracts and for all the extracts from the subsequent extraction steps.

Despite use of the same modified first extraction step (except for the extraction time), the recovery patterns of Pb obtained from *Expt. 5* (five-phase system, with spiked calcite) and *Expt. 7* (five-phase system, with spiked halloysite) were found not to be in agreement. In the system containing the spiked halloysite, none of the Pb was recovered at the modified step, whereas in the system containing the spiked calcite, a significant amount of Pb was recovered (at the same step) (discussed further in *Chapter 4 subsection 4.2.3.*). Since this was not the result expected, it was therefore deemed appropriate to repeat *Expt. 5*. However, the recovery pattern of Pb observed in this repeated experiment (*Expt. 8*) was found to be very similar to that obtained from the first run of *Expt. 5*. As a consequence, the difference between the Pb recovery patterns obtained by using the same modified first extraction step (apart from the extraction time) on the 2 five-phase model systems; one with spiked calcite (*Expt. 5* and *8*), another with spiked halloysite (*Expt. 7*), was confirmed. Therefore, in the following experiments, the possible effect which different extraction times might have on the recovery pattern of Pb was investigated.

In the next set of four experiments (*Expt. 9* to *Expt. 12*), the modified first extraction step of the *Expt. 5*, with varying extraction times, was applied on five-phase model soils, all containing spiked calcite. Separate 20 ml aliquots of 0.11 M acetic acid were added into four centrifuge tubes, each containing the model soil. This was immediately followed by addition of an 8 ml aliquot of $Zn(PDC)_2$ (in MIBK). The first tube was subjected to mechanical shaking for 5 h, and the second, the third, and the fourth tubes were subjected to the same treatment for 1 h, 45 min, and 15 min, respectively (in all cases, the centrifugation was performed at 12 000 rpm for 1/2 h). Determinations of Pb and Zn were performed for the palladium extracts; it was found that the longer the extraction time, the less Pb was recovered (discussed further in *Chapter 4* Fig. 4.3.). The remaining solid phases in the system were subjected to the succeeding steps of the sequential extraction scheme, and the extracts were analyzed for Pb and Zn.

Based on the observation (*Expt. 9 to 12*) that the length of the extraction time of the modified step did in fact influence the percentage recovery of Pb, the extraction times of 1/2 h and 15 min were therefore applied in the cases of two subsequent experiments of five-phase model soils with spiked halloysite (*Expt. 13* and *14*) (discussed further in *Chapter 4 subsection 4.2.3.*). However, a further modification was also made; this involved the addition of a second 5 ml aliquot of fresh $Zn(PDC)_2$ (in MIBK) into the system (after the removal of the first aliquot of the organic phase during which the interface region was left undisturbed). At the end of the extraction and centrifugation, the second aliquot (4 ml) of the organic phase was transferred using a micropipette into a separating funnel, containing 8 ml of palladium solution. Determination of Pb was separately performed for each of the two palladium extracts. All the subsequent extraction steps were as described for *Expt. 5.*

From a comparison of the percentages of Pb recovered at the modified first extraction step from the five-phase system containing spiked halloysite, using three different extraction times of 5 h, 1/2 h (twice), and 15 min (twice) (*Expt. 7*, *Expt. 13* and *Expt. 14*), it was considered possible that successive addition of fresh $Zn(PDC)_2$ (in MIBK) solution into the system at the shortest time interval of 15 min might improve the recovery of Pb at this modified step (discussed further in *Chapter 4 subsection 4.2.3.*).

A modified first extraction step incorporating successive addition of fresh $Zn(PDC)_2$ (in MIBK) was applied on a sample of a five-phase model soil, containing spiked halloysite (*Expt. 15*, shown in Fig. 2.3.). In the preparation of $Zn(PDC)_2$ (in MIBK), the mole ratios of 2% w/v pre-cleaned APDC : Zn (diluted solution from the stock Zn) were the same as specified for *Expts. 4* and *5*. A solution of 0.11 M acetic acid (20 ml) was added into the centrifuge tube containing the solid phase, and this was followed by addition of the initial 8 ml aliquot of the $Zn(PDC)_2$ (in MIBK). The tube was then mechanically shaken at 225 rpm for 15 min. At the end of the extraction, the tube was subjected to centrifugation at 13 000 rpm for 10 min. A 6 ml aliquot of the top organic layer was transferred using a micropipette into a clean glass vial in such a way as to leave interfacial region undisturbed. A fresh 6 ml aliquot of $Zn(PDC)_2$ (in MIBK) was immediately used to replenish the system. This extraction procedure using fresh $Zn(PDC)_2$ (in MIBK) was repeated 12 more times (discussed further in *Chapter 4 subsection 4.2.3.*) (and at the final repeated step, the interface region was discarded). Concurrently, a 10 ml aliquot of palladium solution was added into the glass vial containing 6 ml of the organic layer (with the Pb complex). The glass vial was vigorously shaken (using the mechanical shaker) for about 10 min. The two immiscible phases were then left to separate for about 10 min (the phases were clearly separated within a few minutes). The organic upper layer was removed from the vial using a micropipette, and later discarded, whereas the aqueous lower layer was transferred into a clean vial, and later acidified. A control experiment was later performed for possible contamination of Pb during the procedure of back-extraction of Pb from the organic phase to the aqueous layer, using the palladium ($PdCl_2$ solution), as described below in *Exp. 17*. Each of the 13 palladium aqueous extracts was separately analyzed for Pb, using the FAAS with a quartz or titanium atom-trap assembly to help enhance the absorbance signals. The remaining solid phase components in the system were subjected to subsequent extraction steps, as previously described.

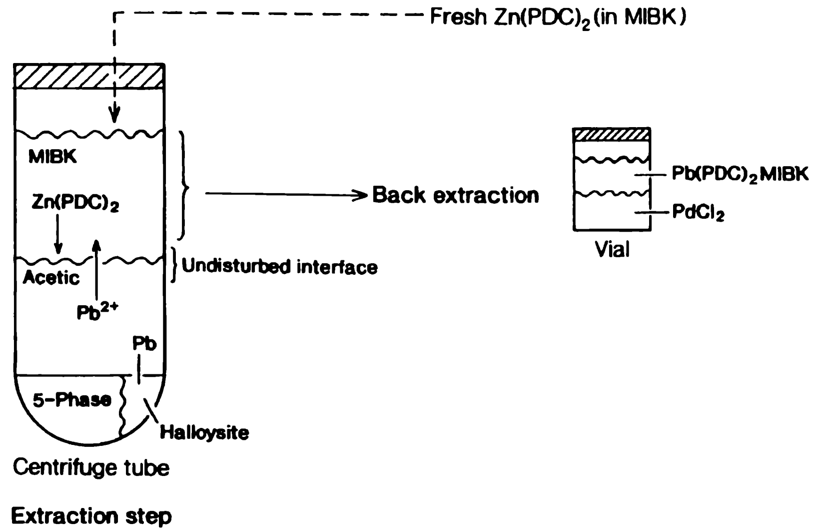


Fig. 2.3. Successive application of $Zn(PDC)_2$ in MIBK onto a five-phase model soil with spiked halloysite (*Experiment 15*).

The results from the above successively modified extractions were found to be promising. Therefore, the modified scheme was further applied on a sample of a mixture of Te Rapa soil and spiked halloysite (*Expt. 16*). The total amount of Pb in this system was 144 μg (the natural soil and the spiked halloysite contributed Pb of 2 and 142 μg, respectively). The modified scheme of 13 successive extractions was further adjusted for *Expt. 16*, with changes being as follows: (1) an initial 9 ml aliquot of $Zn(PDC)_2$ (in MIBK) was added into the centrifuge tube containing the solid phases and acetic acid; and (2) at the end of the first extraction and the centrifugation, a 7 ml aliquot of the upper organic phase was removed, using a micropipette, and immediately replaced with a fresh 7 ml aliquot of $Zn(PDC)_2$ (in MIBK). Each of the 13 palladium extracts was separately analyzed for Pb, using the FAAS with a quartz or titanium atom-trap assembly to help enhance the absorbance signals. In addition, two sets of standard solutions containing two different palladium matrices: with and without previously shaking with MIBK, with the range of Pb from 2 to 8 ppm, were used for determinations of Pb.

The modified first extraction step with the successive extractions used in *Expt. 16* was applied on a sample of a mixture of Te Rapa soil and spiked calcite (*Expt. 17*). The total amount of Pb in this system was 151 μg (the natural soil and the spiked halloysite contributed 3 and 148 μg Pb, respectively). For a control experiment during back-extraction for Pb, aliquots of 7 ml $Zn(PDC)_2$ (in MIBK) and 10 ml $PdCl_2$ solution were added into a clean glass vial. The vial was then shaken for 10 min, and the two phases were left to separate for 10 min. After separation, the lower aqueous layer was acidified and analyzed for Pb. The determinations of Pb in the 13 palladium aqueous extracts were performed against two sets of standard solutions, prepared as previously described in *Expt. 16*, except that the range of Pb was from 2 to 12 ppm.

The modified extraction scheme used in the above *Expt. 17*, but with only 6 successive steps, was applied on a sample (0.5 g) of a contaminated dust (fraction 100 μm < size of particle < 1 mm), collected from Steele Park (Hamilton) in Nov 1995, containing 457 μg Pb g^{-1} dried dust, as determined using aqua regia pseudo-total digestion, described in *subsection 2.4.2.*) (*Expt. 18*). Prior to the trial, the amount of Pb released from the dust sample (0.5 g) by 0.11 M acetic acid (20 ml) at the extraction times of 15 min, and 1 h, 5 h, and (the conventional) 16 h, was assessed. The supernatants were separated from the solid using centrifugation at 13 000 rpm for 10 min. During the stepwise extractions of the dust sample in acetic acid and $Zn(PDC)_2$ (in MIBK) phases, a strong dark brown colour in the organic phase was observed. Each 6 ml extract of the aqueous solution was separately analyzed for Pb.

The occurrence of strong colour in the organic layers observed in *Expt. 18* was regarded with some suspicion. It was thought possible that the organic phase may have solubilized some compartment of the dust sample (discussed in *Chapter 4 subsection 4.2.3.*). To assess this possibility, a synthetic soil system was used. Individual 9 ml fresh aliquots of $Zn(PDC)_2$ (in MIBK) were added into four centrifuge tubes which each contained some individually-spiked phases and 20 ml 0.11 M acetic acid; the first two tubes contained a sample of spiked humic acid (Pb 147 μg Pb) (*Expt. 19*), the third and fourth ones contained samples of spiked hausmannite and goethite (93 μg Pb each) (*Expt. 20* and *21*), respectively. The first two tubes, each containing humic acid, were mechanically shaken, one for 15 min and the other for 5 h. The tubes containing hausmannite and goethite were subjected to mechanical shaking for 15 min. At the end of the extraction, all the tubes were centrifuged at 13 000 rpm for 10 min. The upper organic layers (7 ml) were transferred to clean glass vials, using a micropipette, and 10 ml aliquot of $PdCl_2$ solution were added to each of the four vials. The vials were mechanically shaken (vigorously) for 10 min, then left to stand for 8 min to allow separation of the two phases. The upper organic layers were then removed using a micropipette. The lower aqueous layer was transferred into a clean glass vials, acidified, and analyzed for Pb. The residual solids in the system were subjected to an oxidation using H_2O_2 (in the case of humic acid) and an acid digestion (in the cases of goethite and hausmannite); the solutions were later analyzed for Pb.

In the case of the individually-spiked humic acid (*Expt. 19*) at the end of even the short extraction (15 min extraction and 10 min centrifugation), most of the Pb was recovered from the palladium aqueous phase implying that although $Zn(PDC)_2$ was held in the organic phase, it was capable of directly extracting Pb from the humic acid. It was therefore possible that the significant recoveries of Pb observed at the modified first extraction step in most of the earlier experiments might reflect direct Pb extraction rather than a real potential usefulness of the approach in counteracting the Pb redistribution (discussed further in *Chapter 4 subsection 4.2.3.*). For instance, some Pb released from calcite could have been sequestered by the humic acid and then re-extracted by the $Zn(PDC)_2$. This would introduce the problem of distinguishing between Pb held in early phases and that held on humic acid during extraction of real systems. At this point, it was therefore decided to set aside this approach in favour of the next possible one.

However, it should be noted here that two additional sets of preliminary experiments were assessed for possible factor(s) influencing a stability of $Pb(PDC)_2$ complex (in MIBK).
In the first set of experiments (*Expt. 22*), 0.025 g of spiked calcite was added into each of four centrifuge tubes. This was followed by additions of 20 ml 0.11 M acetic acid, and 9 ml $Zn(PDC)_2$ (in MIBK). The first tube was mechanically shaken for 15 min, and the second, the third, and the fourth tubes were shaken for 45 min, 1.5 h, and 5 h, respectively.
At the end of the extraction, all the tubes were centrifuged at 13 000 rpm for 10 min.
The organic phases (7 ml) were removed from the systems and subjected to the back-extraction procedure for Pb using 10 ml palladium solution, as previously described in *Expt. 17*. Determinations of Pb were performed both for all palladium aqueous extracts, and the remaining acetic acid solution.

In the second set of the experiments (*Expt. 23*), 20 ml aliquots of 0.11 M acetic acid were added to each of four centrifuge tubes. This was followed by addition of 37 μl of the stock 1000 ppm Pb, and 9 ml $Zn(PDC)_2$ (in MIBK), respectively, into each tube. The tubes were then subjected to the same treatment as described in *Expt. 22*.

2.2.2. (d) Cryptand 2.2.2.

Cryptand 2.2.2, as purchased from Aldrich, was dissolved in 0.11 M acetic acid to make up three "modified" extraction solutions at the following concentrations: 9×10^{-6}; 9×10^{-4}; and 9×10^{-3} M. In order to assess the dissolution of calcite, 20 ml aliquots of the "modified" solutions (pH ~ 3 - 4) were added into 3 centrifuge tubes, each containing 0.025 g individually-spiked calcite. The centrifuge tubes were vigorously shaken at room temperature (~ 20 °C), using a mechanical shaker (horizontally-orbital) at a speed of 250 rpm for 15 min, then subjected to centrifugation at 13 000 rpm for 10 min (at the end of the procedure, a complete dissolution of the 0.025 g spiked-calcite was observed in all cases). The total length of contact time of 25 min (extraction time of 15 min and centrifugation time of 10 min) was applied for all the systems further tested. The decision to decrease the contact time (relative to the original BCR time) to 25 min was also supported by previous results from the use of 18-crown-6 (*Chapter 4 subsection 4.2.2.*) and the result of a sorption experiment between Pb and humic acid (*Chapter 4 section 4.3.*).

In order to assess a suitable concentration of cryptand in the modified extraction solutions for further use in counteracting Pb redistribution in more complex multi-phase model soils, two sets of experiments were performed concurrently. In the first set of the experiments, individual 20 ml aliquots of the modified extractants, containing cryptand at concentrations of 9×10^{-6}; 9×10^{-4}; and 9×10^{-3} M, were added into 3 centrifuge tubes, each containing 0.1 g of individually-spiked humic acid. In the second set, the same volume of each modified extraction solution was added into another 3 centrifuge tubes, each containing a sample of a two-phase system (0.025 g spiked-calcite + 0.1 g clean humic acid). All tubes were vigorously shaken for 15 min, then the supernatants were separated from the solid residues by the centrifugation, as described above. The determinations of Pb were performed for both the extracted supernatant and the solutions obtained by complete oxidization of the residual humic acid using H_2O_2 (the oxidation step of the BCR scheme).

Based on the comparison of the amount (and percentages) of Pb recovered from the above two sets of experiments, it was considered that cryptand at a concentration of 9×10^{-3} M was the most suitable for further investigation on the potential usefulness of this complexing agent in counteracting Pb redistribution in the more complex solid systems. This decision was related to the ability of the cryptand to act as a direct extractant at the various concentrations (discussed further in *Chapter 4 subsection 4.2.4. (a)*). Prior to application of the cryptand (9×10^{-3} M) on multi-phase model soils, 20 ml aliquots of the cryptand solution were added to each of 3 centrifuge tubes: the first one contained 0.075 g individually-spiked halloysite; the second and the third ones contained 0.05 g spiked-goethite, and 0.05 g spiked-hausmannite, respectively. The systems were then subjected to the 15 min extraction and 10 min centrifugation procedures, as described above. After washing with clean water by centrifugation at 13 000 rpm for 10 min, the remaining halloysite and goethite in the systems were digested by acid extraction, using aqua regia, whereas residual hausmannite was subjected to the BCR's reduction, using hydroxylamine hydrochloride. All the extracts and the solutions from complete destruction of the solid phases were analyzed for Pb. In all cases (including trials of both the individually-spiked phases and the following systems), the BCR's conventional first extraction step was also applied concurrently on duplicate samples (using the same centrifugation procedure).

The cryptand (9×10^{-3} M) solution was subsequently applied on the two-/ three-/ four- and five-phase systems, each containing spiked-calcite. For each system, each solid composition was weighed according to its amount in 0.5 g sample of a five-phase model, i.e., 0.025 g calcite, 0.05 g goethite, 0.075 g halloysite, 0.05 g hausmannite, and 0.1 g humic acid. In the cases of the two-phase systems, the remaining halloysite, goethite, and hausmannite in the systems (at the end of the modified first extraction step) were subjected to acid digestion or reduction steps, as outlined above. In the cases of the three-/ four- and five-phase systems, the remaining solid phases in the systems (at the end of the modified step 1) were subjected to the subsequent extraction steps: reduction, oxidation, and acid digestion.

The recovery patterns of Pb from the above multi-phase soil models suggested that the presence of both hausmannite and humic acid in the systems significantly decreased the percentages of Pb recovered by the 9×10^{-3} M cryptand solution (results are discussed further in *Chapter 4 subsection 4.2.4. (b)*). In order to assess the limitations of the cryptand (9×10^{-3} M) solution in counteracting Pb redistribution in the five-phase soil models, the percentages of hausmannite and humic acid present in the systems were systematically varied. In the five-phase systems comprised spiked calcite with various percentage by weight compositions of humic acid and hausmannite, the amount of acid-washed sand was varied to bring the total weight to 0.5000 g ± 0.0002 g. The systems were subjected to the modified first extraction step using the cryptand and the remaining solid phases were then treated according to the subsequent BCR extraction steps, as described earlier.

It should be noted here that the silica sand diluent was experimentally proved inert (i.e., not involved in adsorbing any significant Pb). This involved addition of a 20 ml aliquot of 0.11 M acetic acid into each of two centrifuge tubes: the first one containing spiked-calcite + halloysite + goethite and diluted to 0.5 g total weight using the sand; and the second tube containing the same synthetic soil components but without the dilution. The tubes were then subjected to the mechanical shake and centrifugation, as described above. The remaining solids in the systems, after the extraction step 1, were treated by reduction, oxidation, and acid digestion steps, respectively, and Pb recovery patterns of the two systems tested were found to be similar (noted in *Appendix 4.14.*).

The 9×10^{-3} M cryptand solution was then used in the extraction of four sets of five-phase model soils, all of which contained spiked-calcite. For the first set of experiments, 6 five-phase model soils were prepared, each containing 10% hausmannite, but with humic acid contents of 0%, 2%, 5%, 10%, 15%, and 20%. A 0.5000 g ± 0.0002 g portion of each model soil was weighed into a centrifuge tube, to which was added 20 ml of the cryptand (9×10^{-3} M) solution. The tubes were then vigorously shaken for 15 min and proceeded to the subsequent steps as previously described (the results are depicted in *Curve A* in *Chapter 4* Fig. 4.8.). The second set of experiments comprised 3 five-phase model soils, each containing 20% humic acid, but with 0%, 5%, and 10% hausmannite. The third and fourth sets of experiments related to 6 five-phase model soils, each containing no hausmannite, but with 0%, 2%, 5%, 10%, 15%, and 20% humic acid; and 4 five-phase model soils, each containing 10% humic acid, but with 0%, 1%, 2%, and 4% hausmannite, respectively. Each solid system was subjected to the modified first extraction condition and subsequent extraction steps, as described earlier. (The results of the second, third, and fourth experiments of five-phase systems, with different phase compositions, are illustrated in *Curves B*, *C*, and *D*, in *Chapter 4* Fig. 4.8.).

2.2.2. (e) Nitrilotriacetic acid (NTA).

NTA (as the disodium salt, purchased from Aldrich), was dissolved in 0.11M acetic acid to make up five "modified" extraction solutions at the following concentrations: 1×10^{-4}; 1.6×10^{-4}; 2.4×10^{-4}; 5×10^{-4}; 9×10^{-4} and 9×10^{-3} M. The modified extraction solutions were assessed with respect to their capacity to completely dissolve the calcite, as well as for a suitable concentration for further use investigating their ability to counteract Pb redistribution (discussed further in *Chapter 4 subsection 4.2.4.*), as described in the earlier investigations of the cryptand 2.2.2. In all cases, the modified extraction conditions used and the separations of supernatants from residual solids, were as described in the previous experiments on the cryptand 2.2.2 (*subsection 2.2.2. (d)* (with the exception that NTA was now used instead of the cryptand).

Based on the results of the investigation for a suitable concentration of NTA (in acetic acid), it was considered that 1×10^{-4} M was the most appropriate concentration of the ligand (results are discussed further in *Chapter 4 subsection 4.2.4. (a)*). The NTA (1×10^{-4} M) solution was then applied on the two-/ three-/ four- and five-phase systems, each containing spiked-calcite, as previously summarized in the *subsection 2.2.2 (d)* for cryptand 2.2.2. The results from the application of the NTA solution on the multi-phase model soils were in agreement with those obtained by use of the cryptand solution, in that the presences of hausmannite and humic acid in the model soils were again found to be limiting factors affecting the percentage recoveries of Pb by the ligands (discussed further in *Chapter 4 subsection 4.2.4. (c)*).

In order to assess the limitation of the NTA (1×10^{-4} M) solution in counteracting Pb redistribution in the five-phase soil models, the modified extraction solution was systematically applied to two different sets of five-phase model soils containing various compositions of humic acid and hausmannite; the first one being the 6 distinct five-phase model soils containing a fixed 10% hausmannite, with 0%, 2%, 5%, 10%, 15%, and 20% humic acid; the second set being 3 different five-phase model soils with a fixed 5% humic acid and 0%, 1%, and 2% hausmannite. A 0.5000 g ± 0.0002 g portion of each model soil was weighed into a centrifuge tube, into which a 20 ml aliquot of the NTA (1×10^{-4} M) solution was then added. All the tubes were then subjected to the modified first extraction step and afterward proceeded to the later reduction, oxidation, and acid digestion steps, as outlined in *subsection 2.2.2. (d)* for the cryptand.

2.3. Application of the modified extraction scheme to environmental samples.

Based on the results obtained from the previous experiments outlined in *subsection 2.2.2 (d)*, cryptand at the concentration of 9×10^{-3} M showed the greatest potential usefulness (relative to *2.2.2 (a)* to *2.2.2 (e)* approaches) in counteracting Pb redistribution in a multi-phase model soil, containing limited amounts of humic acid and hausmannite (discussed further in *Chapter 4*). In order to assess the effectiveness of the cryptand (9×10^{-3} M) in a natural system, the ligand was applied on the following systems; (1) a mixture of a synthetic soil and a natural Kainui soil, and (2) contaminated kerbside top soil (< 1 mm) and street dust (100 μm < dust < 1 mm). The Kainui soil contained 25 μg Pb g^{-1} (partial characterization is shown in Table 2.3.). The contaminated kerbside top soil and the street dust were collected in April 1996, from Melville, and Steele Parks, Hamilton, respectively (these are two of the sites used in the environmental survey of Pb concentrations, described in *section 2.4.*). Mean concentrations of Pb in the two fractions of the soil and dust were 81 and 347 μg g^{-1}, respectively (shown in *Appendix 2.8. (a)*). In addition, the content of organic matter in the soil and dust samples were both found to be about 12% (as determined from weight loss during ignition described in *subsection 2.1.3.*).

The spiked-natural soil system comprised 0.05 g spiked calcite, 0.2 g Kainui soil, and 0.25 g acid-washed sand. Total amount of Pb in this system was 79 μg (of which 94%, was from the spiked calcite, and 6% was from the Kainui soil). 20 ml aliquots of cryptand (9×10^{-3} M) and acetic acid (0.11 M) were added into each of two centrifuge tubes, each containing a 0.5 g portion of the spiked-natural soil system. This was performed in duplicate. The four tubes were then vigorously shaken, using a mechanical shaker at a speed of 250 rpm, for 15 min. At the end of the extraction, the supernatants were separated from the remaining solid phases using centrifugation at 13 000 rpm for 10 min (it should be noted here that under the modified extraction solutions and total contact time of 25 min, a complete dissolution of 0.05 g calcite was previously observed). After washing with clean water, using centrifugation, the remaining solid phases in the systems were subjected to the reduction, oxidation, and acid digestion steps of the BCR scheme.

Four 20 ml aliquots of the 9×10^{-3} M cryptand and 0.11 M acetic acid were added into two sets of two centrifuge tubes: the first set each containing a 0.5 g portion of the kerbside soil sample (41 μg Pb), and the second set each containing a 0.5 g portion of the dust sample

(174 μg Pb). Samples in all 8 centrifuge tubes were then subjected to the modified first extraction step, followed by the later conventional steps, as outlined above.

2.4. Monitoring lead levels in soil and dust in Hamilton.

2.4.1. Site description.

Four Parks were selected for monitoring Pb levels in soil and street dust in Hamilton, during the period of phasing-out of leaded-petrol in New Zealand. The sampling sites were (1) the University's sport field on Knighton road, (2) Melville Park on State Highway 1, (3) Milne Park on Victoria street, and (4) Steele Park on Grey street. The locations of the parks are illustrated in Fig. 2.4.

The sampling sites were chosen according to the following criteria (which are not necessarily in order of priority): (1) convenient accessibility; (2) unlikelihood of the soil being disturbed throughout the intended sampling period (Gill, 1995; Thompson, 1995); (3) absence of other known forms of contamination (e.g., Pb-based painted houses or industries); (4) availability of some supplemental information (e.g., traffic flow densities, prevailing wind directions, and soil types); and (5) location near busy roads, e.g., average daily flows were around 20 000 vehicles per day alongside the State Highway 1 and Victoria street sites (Robins, 1995).

Soil from the Ruakura Agricultural Research Center (see Fig. 2.4.) was collected and analysed for Pb in order to provide a reference point as to "background" levels. This soil is considered largely indistinguishable from soil at more remote sites (e.g., native bush) with respect to the ability to detect anthropogenic contributions to Pb levels (Roberts, 1995). The samples included three prevalent soil types found in Hamilton, i.e., Te Kawhai silt loam (gley), Hamilton Clay (Brown Granula Loam), and Horotiu Sandy Loam; these were collected from Paddy no. 25, no. 38, and no. 5B, respectively. In all cases the samples were taken at distances greater than 100 m from roads.

2.4.2. Sampling procedure and sample preparation.

Sampling for determination of background Pb levels was performed once, in November 1995. At each of the three sampling sites at the Ruakura Agricultural Research Center, two to three soil cores of 3 cm diameter were obtained to a depth of 6 - 10 cm, with the use of a clean metal core-pipe (open-ends) (peripheral soil in contact with the inside of the metal-core was later removed using a clean plastic knife). The samples were then kept in clean plastic bags and transferred to the lab as soon as possible, where each core sample was divided into 2 lengths from the top: 0 - 2 cm and 2 - 6 cm, using a clean plastic knife. Each section of core samples was then oven dried at 65 °C for 24 h. The dried soil was crushed and passed through a clean nylon sieve (1 mm-pore size). The fine-fractions of < 1 mm were thoroughly mixed using a clean plastic spatula, then stored in acid-washed (and dried) bottles. The dried samples were analyzed for Pb (as described at the end of this *subsection*), as soon as possible.

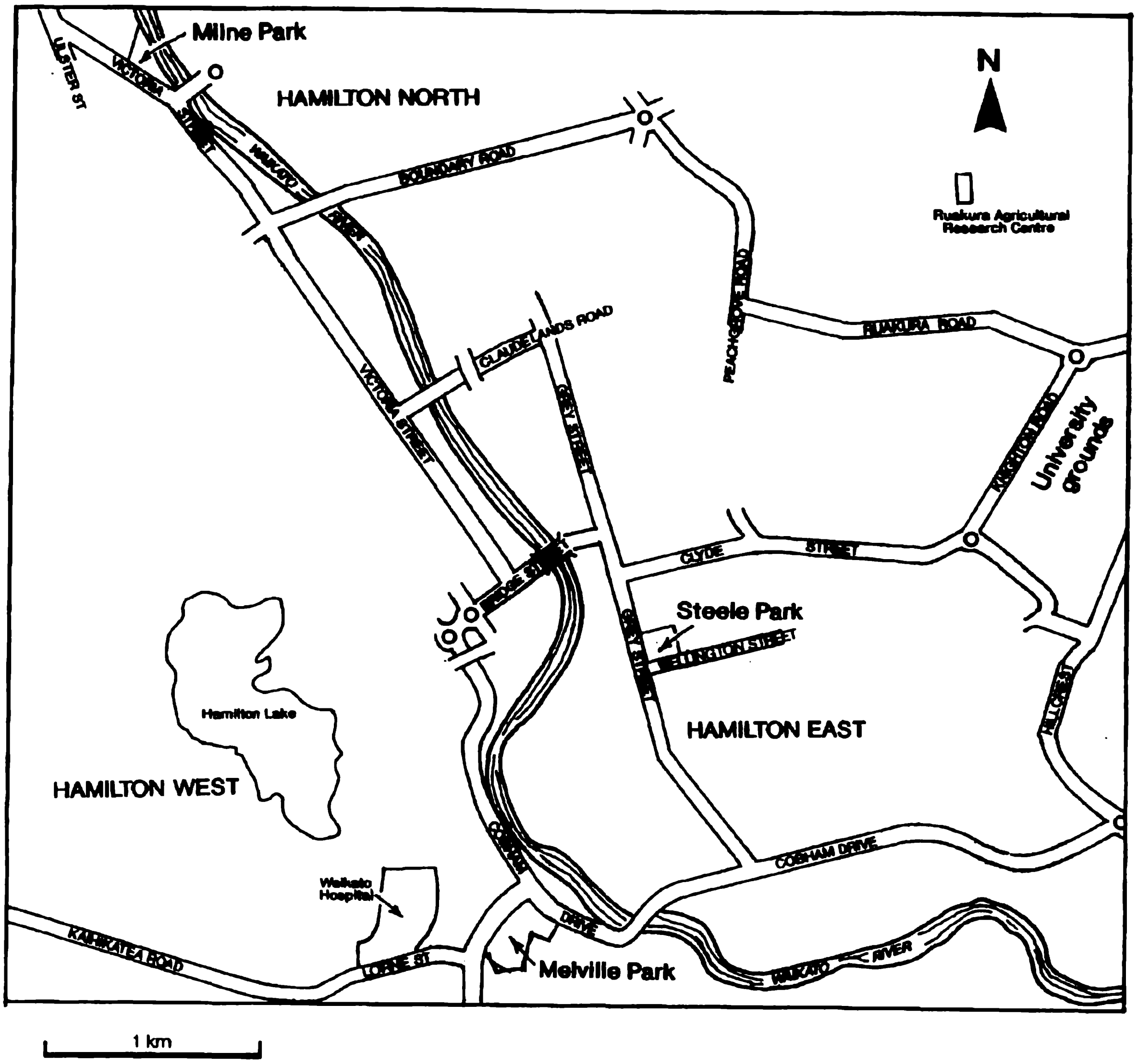


Fig. 2.4. Locations of parks sampled in Hamilton City.

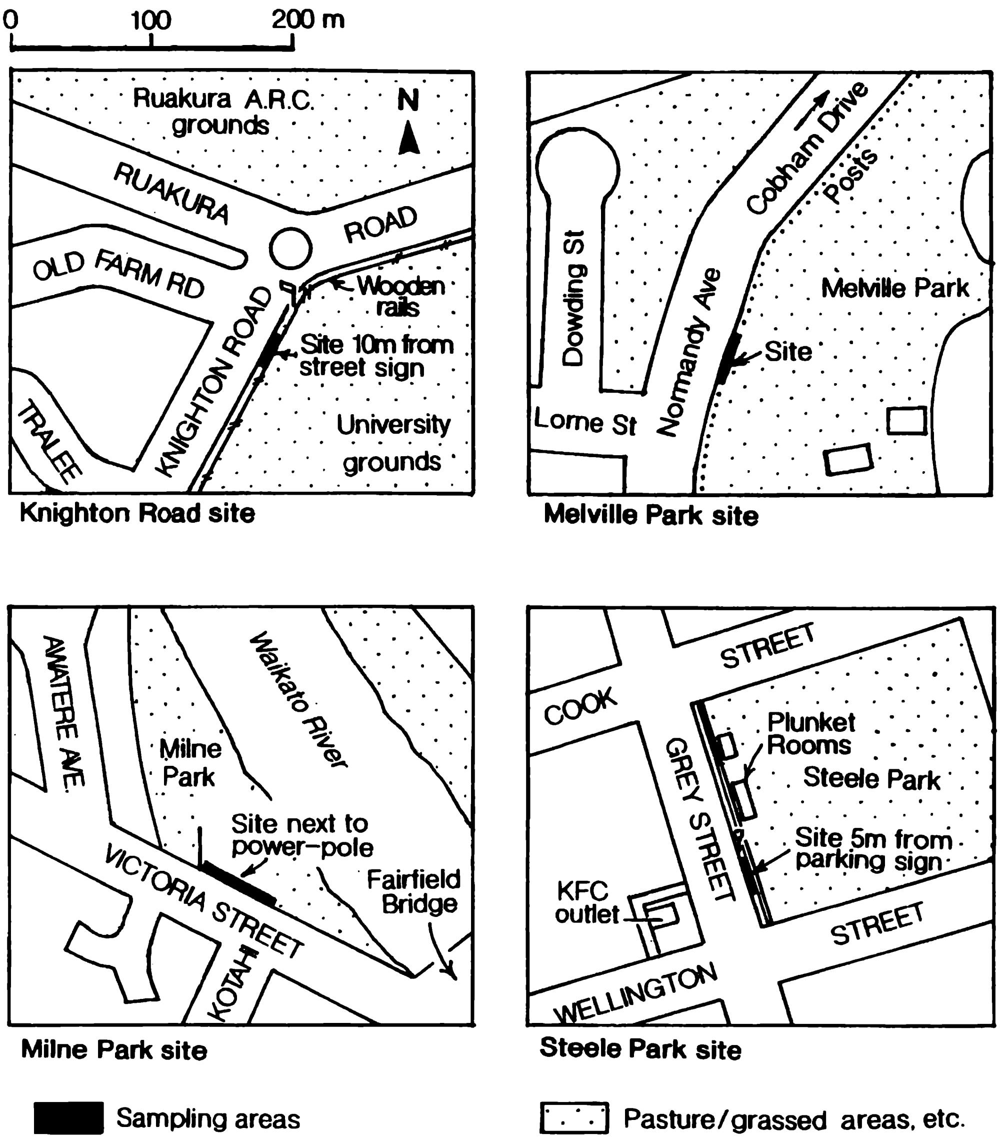
Core samples of kerbside top 2 cm soil were collected from the four parks once in each sampling period of November 1995; and February, April, and September 1996. Street dust samples were concurrently collected from the gutter and roadside (near the sampling stations of kerbside soils), with an additional sampling in June 1996. The sampling periods covered the commencement of the legal phasing out of leaded-petrol on the New Zealand market (Nov 1995), the date of no import or production of leaded-petrol (January 1996), and the date according to the legislation that no leaded-petrol should be offered for sale in the country (September 1996).

The core soil samples were collected with the use of a clean metal core-pipe (open ends) (6 cm in diameter and 10 cm in length). At each park, 5 individual core soil samples were collected along the kerbside, at an interval of about 5 m. The sampling stations for all the parks are illustrated in the Fig. 2.5.

In the first sampling (Nov. 1995) of all the parks, core soil samples were collected at kerbsides as well as along transects extending from the kerbsides into the fields. In the case of the University's field, the additional sampling spots were at 10, 25, and 50 m, and in the cases of Melville, Milne, and Steele Parks, they were at 25 and 50 m; 10, 20, and 50 m; and 6, 10, and 20 m, respectively. The differences in the distances of various sampling points at each park were due to the difference in size of the parks and the accessibility of the sampling stations. At each sampling point along the transects, 5 individual core soil samples were taken, within about a 5 meter interval. Care was taken to prevent possible contamination by collecting samples at the far distance before collecting at the kerbside. In the subsequent sampling periods, only kerbside top soil core samples were collected.

Core soil samples (about 10 cm in length) were handled using clean plastic gloves, stored in clean plastic bags, and transferred to the lab as soon as possible after collection. After the removal of covering vegetation and peripheral soil which had been in contact with the body of the metal-cores (both using a clean plastic knife), each core soil was divided into 2 cm lengths from the top. It should be noted here that in the case of almost all of the cores taken during the first sampling period, the soil below a depth of about 2 cm was collapsed during the attempt to divide the cores (due to loosely-bound structure and dry nature of the soil). Therefore, it was decided that in subsequent samplings, only the top 2 cm of each soil core would be proceeded and analyzed. This was not likely to present any problem with respect to assessing any effects of the removal of leaded-petrol, as lead from this source is deposited on the soil surface in any case. Migration of lead through most soils is known to be slow (Fergusson, 1990). Soil samples were oven-dried at 35 to 40 °C for 24 h. The dried soil was crushed and sieved through a clean nylon sieve of 1 mm-pore size. The fine-fraction of < 1 mm soil was thoroughly mixed using a clean plastic spatula, then stored in clean plastic bags (with seals), prior to the analyses for Pb (as described at the end of this *subsection*) which was carried out as soon as possible.

Samples of street dust were collected in clean plastic bags, using a clean plastic brush and pan. Four to five sample replicates were collected from each park, per sampling period. The dust samples were then oven-dried (35 to 40 °C for 24 h) and sieved through a clean nylon sieve (1 mm pore-size). Coarse and large particles (e.g., gravel and grass) were thereby separated out. The < 1 mm fraction was then passed through a clean fine nylon sieve (100 μm). The two dust fractions thus produced (< 100 μm and 100 μm < dust < 1 mm) were separately stored in clean plastic bags (with seals), prior to determinations for Pb.



Knighton Road site

Melville Park site

Milne Park site

Steele Park site

■ Sampling areas

▨ Pasture/grassed areas, etc.

Fig. 2.5. Locations of sampling stations for all the parks.

Pseudo-total digestions using concentrated acids, as modified from the procedure recommended by Ure (1990) for assessment of soils contaminated with heavy metals, were applied to all samples collected. The digestion involved the use of about 2 g solid sample per 5 and 15 ml aliquots of conc. nitric and hydrochloric acids, respectively.
The slurry was left in a fume hood for about 1 h, with occasional shaking. A 10 ml aliquot of clean water was then added into the slurry prior to refluxing for about 2 h. Care was taken by adding a small volume of clean water when the solution became too low to prevent loss of Pb due to dryness. The extracted solution was separated from the solid phase by filtering through filter papers (Whatman # 541). The filtrates were made up to 100 ml using clean water. Along with each batch of the samples, one or two samples of a GBW07401 certified reference soil material were extracted using the same modified pseudo-total digestion procedure. This reference material was purchased from Laboratory of the Government Chemist, England, and has a specified Pb content of 98 ± 3 $\mu g\ g^{-1}$. Determinations of Pb in all extracts were performed as described in *subsection 2.5.2.*

2.5. Analysis of lead and some other relevant elements.

2.5.1. Elemental analysis during an investigation of sequential extraction.

Analysis of Pb in some "clean" solid phases was carried out using a GBC 905 Graphite Furnace AAS (GBC Scientific Equipment Pty Ltd., Victoria, Australia) at 217.0 nm, with deuterium background correction. The solid digests and extracts were analyzed using a GBC 909 Flame Atomic Absorption Spectrophotometer (FAAS) at the same wavelength, with deuterium background correction, the slit width at 1 nm, the lamp current at 5.0 mA, and an air-acetylene (oxidizing) flame type. A stock standard solution of 1000 ppm Pb was prepared by dissolving AR $Pb(NO_3)_2$ in 1 M AR nitric acid. Unless otherwise specified, standards used for AAS analyses were made up in matrices and acid strengths as identical as possible to those of the digests and extracts themselves. When deemed appropriate, a quartz or titanium atom-trap assembly was used on the FAAS to help enhance the absorbance signals. No reference material was used during the study on the sequential extraction section, firstly because the BCR-certified reference was not at the time commercially available, and also because total recoveries could easily be assessed by comparison of the known amounts of Pb added by spiking with amounts determined as the sum of Pb recovered over all extract steps. Recoveries are generally shown in individual Tables relating to given results. In most extracts of individually spiked phases and multi-phase systems recoveries were consistently close to 100%, suggesting that overall accuracy in the Pb determinations was good. A typical calibration curve is illustrated in *Appendix 2.9. (a)* ; in most cases, correlation coefficients (r^2) of calibration curves were not less than 0.997. Relative standard deviations (RSD) of the determination of Pb in each extract or solid digest were typically $\leq$ 3% for Pb concentrations of $\geq$ 1 ppm, and generally $\leq$ 10 %. RSD values between repeated determinations of Pb were usually found to be low, e.g., $\leq$ 1% for extracts containing Pb of about 2 ppm in the presence of NTA. The absorbance readings were in all cases within the acceptable calibration range.

Where applicable, Fe and Mn were analyzed using the GBC 905 Graphite Furnace AAS or the GBC 909 FAAS, both with deuterium background correction, at wavelengths of 248.3 and 279.5 nm, respectively. Additional FAAS conditions for the analysis of Mn included slit width 0.2 nm, lamp current 5.0 mA, and air-acetylene (stoichiometric) flame type; while the corresponding conditions for the analyses of Fe were 0.2 nm, 5.0 mA, and air-acetylene (oxidizing), respectively.

2.5.2. Elemental analysis of environmental samples.

Determination of Pb in the acid extracts of soil and dust samples was performed by use of the GBC 909 FAAS, at 217.0 nm, with deuterium background correction. The samples were normally analyzed immediately after extraction, otherwise being kept in a 4 °C cool room prior to analysis. Standard solutions were prepared in the acid matrix as similar as possible to those of the sample solutions. An extract of the GBW07401 certified reference material (described in *section 2.4.2.*) was analysed for Pb simultaneously with every batch of sample determinations. The results of the Pb analyses in the reference samples were used to construct a control chart and this is illustrated in *Appendix 2.9. (b)*. This also shows good accuracy, with the mean (94 μg Pb g^{-1}) of the 16 determinations being about 96% of the mean (98 μg Pb g^{-1}) of the certified value. All of the Pb determinations are within twice the value of the standard deviation.

As a further check on accuracy, an inter-laboratory comparison for Pb was performed in two samples of a kerbside-top soil and a street dust, collected in April 1996, from Melville Park and Steele park, Hamilton, respectively (these are two of the sites used in the environmental survey of Pb concentrations, *Chapter 5*). The acid extracts of the sub-samples of the soil and dust (4 and 5 sub-samples, respectively) were analyzed by this laboratory (using FAAS) and R.J.Hill Laboratory Ltd. (using ICP-MS). The results of the Pb determinations (shown in *Appendix 2.8. (a)*) show good agreement between laboratories, with the overall coefficients of variation (100 × SD/ mean) for the soil and dust being 2 and 5%, respectively.

The extracts sent to R.J. Hill Laboratory Ltd, were also analysed for Ca, Br, Fe, Mn, Al, Cd, Cr, Cu, Ni, and Zn (the results are shown in *Appendix 2.8. (b)*), using either ICP-MS or ICP-OES (*Appendix 2.8. (c)*).

2.6. Sorption of Pb onto humic acid.

In this supplemental experiment, the rate of adsorption of Pb on humic acid was assessed. Twenty ml aliquots of 0.11M acetic acid were added into each of four centrifuge tubes, each containing 0.1000 g ± 0.0002 g clean humic acid. This was followed by addition of 37 μl 1000 ppm Stock Pb solution (equivalent to 37 μg Pb total) in to each tube. The first tube was vigorously shaken, using a mechanical shaker (horizontally-orbital) at a speed of 250 rpm, for 3 min. The second, third, and fourth tubes were subjected to the same shaking for 5, 10, and 15 min, respectively. The supernatants were separated from the remaining humic acid using a quick centrifugation (12 000 rpm) of 2 min (this includes the time taken for the machine to stop spinning). The solutions were then acidified with a small volume of concentrated nitric acid. The remaining humic acid was washed using clean water, then subjected to an oxidation using the H_2O_2 procedure of the BCR scheme.

Determinations of Pb were performed for both the remaining acetic acid solutions and the extracts of completely oxidized humic acid. A control tube, containing acetic acid and Pb solution in the absence of humic acid, was concurrently tested.

2.7. General preparations of reagents and glassware.

All reagents used were of analytical grade (AR). All glassware and polycarbonate and polyethylene copolymer centrifuge tubes were acid-washed with 4 M nitric acid, and thoroughly rinsed with clean water prior to use. Water used in this study was distilled then passed through a four-stage MilliQ system comprising cation and anion exchange resins and activated carbon filters, to a final resistivity of greater than 18 Mohm cm^{-1}. This is referred to as distilled-deionized water.

Chapter 3. Assessment of the extent of lead redistribution during sequential extraction by the Tessier et al. and the BCR schemes

(Publication note: the research results outlined in this chapter have been published in the journal Analytica Chimica Acta, Vol. 332 (1996) p. 1 - 14. A reprint of this paper is provided in a pocket on the inside back cover of this thesis)

3.1. Recovery patterns of Pb from the individually spiked phases and five-phase synthetic model soils.

Percentages of added Pb found in each extract of the individually spiked phases and five-phase model soils as determined by Tessier et al.'s scheme are shown in Table 3.1. A typical distribution pattern, in this case of five-phase model soil containing Pb-spiked calcite, is shown in Fig. 3.1. Corresponding results of the BCR procedure are presented in Table 3.2.

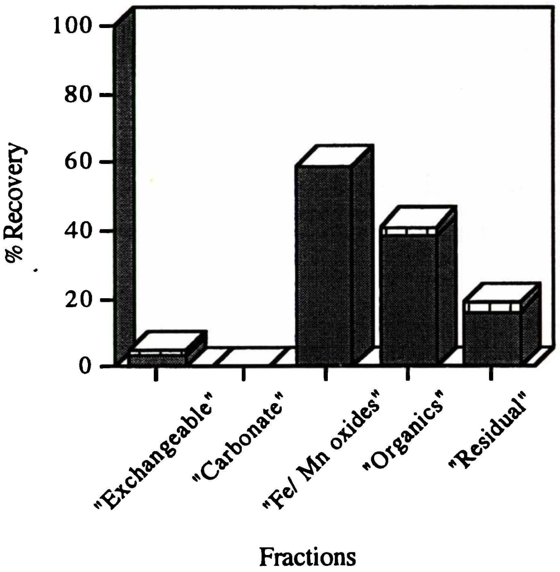


Fig. 3.1. Observed distributions of Pb from the five-phase model soil containing spiked calcite as determined using the sequential extraction protocol of Tessier et al. (regions of overlap relate to duplicate determinations).

The distribution patterns of the individually spiked phases show that in general, the extraction conditions of both schemes do not provide an unequivocal indication of the origin of Pb. The sum of Pb recovered at step 1 (1 M magnesium chloride) and step 2 (1 M acetic acid/ acetate) of Tessier et al.'s scheme should be fairly equivalent to that recovered at step 1 (0.11 M acetic acid) of the BCR scheme. Step 1 of the BCR scheme is designed to liberate "exchangeable", and "water and acid-soluble" metals. Similarly, steps 1 and 2 of Tessier et al.'s scheme are designed to release "exchangeable" and "bound to carbonate" metals, respectively. However, in the case of individually spiked humic acid, nearly 80% of the Pb was recovered at steps 1 and 2 of Tessier et al.'s scheme, whereas none was extracted at (the supposedly equivalent) step 1 of the BCR scheme (Table 3.1. vs Table 3.2.). When step 2 of Tessier et al.' s scheme was applied alone, it was found that only 20% of the Pb was recovered from individually spiked humic acid, compared with a combined recovery of about 80% when step 1 is followed by step 2 (*Appendix 3.1.*). This finding indicates that the 1M Mg^{2+} solution in Tessier et al.'s scheme has an important role in removing Pb from humic acid in that case. The BCR extraction falls short in this respect. Arunachalam and co-workers (1996) used a different sequential extraction scheme to extract trace elements from forest soil samples and observed close agreements between (i) the sum of step 1 (ammonium acetate) and 2 (acetic acid) with the release of the elements with the second reagent alone, and (ii) the sum of steps 1, 2 and 3 (hydroxylamine hydrochloride in acetic acid) with the release with the third reagent alone.

About 40% of the Pb was recovered from Pb-spiked humic acid at the reducing (rather than oxidizing) step of the BCR scheme (Table 3.2.). Whalley and Grant (1994) similarly observed that about 20 to 40% of Ni and Zn were released from (Merck) humic acid by hydroxylamine hydrochloride in the BCR scheme. These authors suggested that the metal release might be determined by relative binding capacities, rather than chemical degradation of the humic acid itself. Overall, with respect to Pb on humic acid, the oxidizing step of Tessier et al.'s scheme liberates only a small amount (11%) of residual Pb, as most is extracted at earlier steps. By contrast, the oxidizing step of the BCR scheme extracts significant (70%), although significant amounts are also released during reduction.

In the case of individually spiked goethite, the highest Pb recovery (~ 60%) was at the step 3 (the reducing step) in Tessier et al.'s scheme (Table 3.1.) whereas the highest Pb recovery (~ 50%) was at step 1 (acetic acid) of the BCR scheme (Table 3.2.). It is possible that dissolution of amorphous iron oxides films is a reason why Pb is lost from the goethite under the acidic conditions (pH~ 3, acetic acid) of step 1 of the BCR scheme, but not until later in the scheme of Tessier et al. Kedziorek and Bourg (1996) reported increasing solubilization of Pb, Ni, and Cd from their synthetic amorphous ferric oxyhydroxide as the pH of the systems investigated decreased below the value of 6. Thus, as with humic acid, there is a disparity between the schemes in exactly which step Pb is liberated from the iron oxide, and this needs to be borne in mind when making comparisons.

By contrast, hydroxylamine hydrochloride used in both extraction schemes (at step 3 in Tessier et al.'s and at step 2 in the BCR protocol) appears to selectively dissolve the manganese oxide phase (hence, releasing Pb originally retained on it). This is in agreement with the observations of several investigators, such as Chao (1972), Shuman (1982), and Arunachalam and co-workers (1996). Reagent selectivity for Pb on hausmannite is therefore good; Pb is liberated at the "designated" step (reducible) and this result is consistent between the extractions.

Table 3.1. Percentages of Pb recovered from individually spiked phases and five-phase model soils using the extraction of Tessier et al. (values are given for each of two duplicate determinations).

	Step 1 "Exchangeable"		Step 2 " Bound to Carbonate"		Step 3 "Bound to Fe/ Mn oxides"		Step 4 "Bound to Organics"		Step 5 "Residual"		Total % Recovery	
Individually spike phases												
Calcite	112	108	9	9	-	-	-	-	-	-	121	117
Halloysite	78	70	21	23	6	7	1	0	0	1	106	101
Goethite	7	7	28	27	57	59	10	10	11	12	112	114
Hausmannite	0	0	0	0	91	94	-	-	-	-	91	94
Humic acid	70	71	6	6	17	16	11	11	1	1	105	105
Model soils												
Model soil 1 (Spiked calcite)	3	5	0	0	59	57	38	41	16	19	116	121
Model soil 2 (Spiked halloysite)	3	3	1	1	52	44	31	31	13	13	100	92
Model soil 3 (Spiked goethite)	2	3	1	1	48	40	37	38	27	22	116	104
Model soil 4 (Spiked hausmannite)	0	1	1	1	57	49	35	38	12	12	104	101
Model soil 5 (Spiked humic acid)	3	2	4	5	52	48	41	41	10	11	108	107

Note: A recovery of zero percent has been applied to the concentrations of below a detection limit. An empty position (-) refers to a discontinued extraction (due to the complete dissolution of solid phases).

Table 3.2. Percentages of Pb recovered from individually spiked phases and five-phase model soils using the BCR sequential extraction protocol (values are given for each of two duplicate determinations).

	Step 1 "Exchangeable and Carbonate bound" & "Water soluble"		Step 2 "Reducible" (e.g., Fe and Mn oxides)		Step 3 "Oxidizable" (e.g., Organics)		Step 4 "Residual"		Total % Recovery	
Individually spiked phases										
Calcite	131	126	0	0	-	-	-	-	131	126
Halloysite	86	86	6	6	0	1	0	0	92	92
Goethite	50	54	21	21	17	17	10	10	98	102
Hausmannite	0	0	109	109	-	-	-	-	109	109
Humic acid	1	0	38	38	69	70	2	1	110	110
Model soils										
Model soil 1 (Spiked calcite)	0	0	1	2	84	90	9	10	94	102
Model soil 2 (Spiked halloysite)	0	0	0	0	69	76	8	8	77	84
Model soil 3 (Spiked goethite)	0	0	0	1	78	68	18	16	96	86
Model soil 4 (Spiked hausmannite)	0	0	0	0	88	78	11	10	99	88
Model soil 5 (Spiked humic acid)	0	0	1	0	107	93	10	9	117	102

Reagent selectivity for Pb originally bound on calcite and the clay mineral (halloysite) is also consistent between the extractions. Pb is liberated from both phases primarily at step 1 of the respective schemes. (In the case of calcite in the BCR scheme this is because the phase (calcite) dissolves).

In summary, extraction of Pb from calcite, halloysite, or hausmannite alone results in similar outcomes between the two sequential schemes; whereas extraction of Pb from humic acid or goethite results in different outcomes. Although these results are reproducible, interpretive errors are likely to occur if the reducing and oxidizing steps are taken to exclusively represent Pb bound to iron oxides and organic matter, respectively. From the point of view of assessing redistribution, the exact behaviour of individual spiked phases under extraction conditions supplies the necessary benchmark data.

It should be noted that the observed Pb redistributions (discussed in the following section) obtained from these extractions of artificially-spiked individual phases will not necessarily describe the behaviour of analogous phases under natural conditions. For example, under natural conditions, calcite typically accounts for a comparatively small fraction of the available Pb, and that which is on calcite is, therefore, likely to be associated with higher-energy sites. The main purpose of these individually spiked phases is to serve as reference points for Pb release at particular steps of each extraction. Comparison of the results for each mixed-phase system containing one spiked phase with its respective single phase reference allows one to directly assess the extent of redistribution under actual sequential extraction conditions. In this sense, the mineral that Pb was released from in each case is less relevant than the fact that it is released, and the primary question focused on in this present study is the fate of Pb initially released to solution during a given step.

3.2. Redistribution of Pb in the synthetic model soils and solid phases influencing the Pb recovery patterns.

The recovery patterns of Pb in all five-phase model soils are found to be almost identical for each extraction scheme, but are independent of the origins of Pb in the corresponding individually spiked phases in both extraction procedures (Tables 3.1. and 3.2.). Pb released in the early stages of both extraction procedures was detected in the later stages when the five-phase model soils were extracted. In the BCR scheme, the highest recovery of Pb occurs at the oxidizing step, whereas in Tessier et al.'s extraction, the highest recovery is observed in the reducing step. Lopez-Sanchez and co-workers (1993) previously observed different distribution patterns of heavy metals extracted from contaminated sediment using Tessier et al.'s and BCR schemes (however, the authors did not carry on testing possible factors contributing to the observation). In this present study, the mean of total recoveries of Pb in the 40 determinations presented in Tables 3.1. and 3.2. was found to be 104% with a relative standard deviation of 12%. There was no major loss of Pb from the systems. Rather, readsorption of Pb during extraction occurred. This finding is consistent with that of Rendell and Bartley (1980) that nearly all of Pb spiked into extractants with final pH ~ 4 - 5 was adsorbed onto river sediment samples. Strong redistribution of Pb has also been observed in Tessier et al.'s extraction by Kheboian and Bauer (1987) and Shan and Chen (1993).

The finding that the distribution patterns of the five-phase model soils for each extraction procedure are similar regardless of the origin of the spiked Pb is a significant one. It implies that both sequential extractions will give inherently unreliable results for Pb distribution.

However, there are significant differences between the schemes in the exact manner in which Pb redistributes. These differences are illustrated for the case of spiked calcite in Figures 3.1. and 3.2., respectively (the latter figure is shown in *section 3.4.* below). The observation that the reducing step in Tessier et al.'s scheme is selective toward hausmannite and goethite (Table 3.1.), can be taken to imply that either one or both of these phases dominated the redistribution in this scheme. In addition, as about 40% of Pb is recovered at the oxidizing step in Tessier et al.'s scheme, the oxidizable humic acid is likely to participate in the redistribution. In keeping with these results, Kheboian and Bauer (1987), Ajayi and Vanloon (1989) as well as Shan and Chen (1993) observed that "Mn/ Fe oxides" and "organics" were the "destination" phases in the redistribution of Pb in Tessier et al.'s procedure. In the BCR procedure, although no Pb was recovered at the reducing step, it is suspected that hausmannite and/or goethite nevertheless play an intermediate part in the distribution of Pb in this scheme. By contrast, during the extraction of the Tessier et al.'s scheme, humic acid appears to be "deactivated" in some way, so that the amount of Pb is extracted under the reducing conditions is greater.

Phases governing redistribution and contributing to the difference between the two schemes were investigated experimentally in further detail. Tessier et al.'s procedure was performed on various combinations of 2 phases and 3 phases; the results of these experiments are presented in Tables 3.3. and 3.4.

The two-phase model comprising Pb-spiked humic acid and clean goethite yielded a very similar distribution pattern of Pb to that of the individually spiked humic acid, i.e., about 70% of Pb was recovered in the first extractant and most of the remainder appeared in the reduction step. This similarity indicated that the presence of goethite had little effect on extraction and redistribution.

By contrast, the two-phase model which contained Pb-spiked humic acid and clean hausmannite (Table 3.3.) yielded a very similar distribution pattern of Pb to that observed in five-phase model soils. This suggests that hausmannite may directly sequester Pb released from humic acid, and that it exerts a dominant role in the redistribution of Pb in five-phase model soils.

Table 3.3. Percentages of Pb recovered from two-phase models using the extraction of Tessier et al. (values are given for each of two duplicate determinations).

Mixtures	Step 1		Step 2		Step 3		Step 4		Step 5		Total % Recovery	
	"Exchangeable"		" Bound to carbonate"		"Bound to Fe/ Mn oxides"		"Bound to organics"		"Residual"			
Spiked humic acid + Goethite	67	67	6	5	21	20	12	11	2	3	108	107
Spiked humic acid + Hausmannite	0	0	0	0	59	58	37	36	8	7	103	101
Spiked hausmannite + Humic acid	0	0	0	0	57	53	33	33	9	8	99	93
Spiked goethite + Hausmannite	0	0	0	0	76	82	6	7	12	14	94	103
Spiked calcite + Hausmannite	0	0	0	0	116	117	0	0	0	0	116	117
Spiked halloysite + Hausmannite	0	0	0	0	90	89	3	3	0	0	93	92
Spiked hausmannite + Goethite	0	0	0	0	101	95	0	0	0	0	101	95

Table 3.4. Percentages of Pb recovered from three-phase models using the extraction of Tessier et al. (values are given for each of two duplicate determinations).

Mixtures	Step 1 "Exchangeable"		Step 2 " Bound to Carbonate"		Step 3 "Bound to Fe/ Mn oxides"		Step 4 "Bound to Organics"		Step 5 "Residual"		Total % Recovery	
Spiked goethite + Hausmannite + Humic	0	0	0	0	43	41	34	33	20	22	97	97
Spiked hausmannite + Goethite + Humic	0	0	0	0	52	53	34	32	12	13	98	99
Spiked humic + Hausmannite + Goethite	2	2	0	0	54	54	34	35	12	12	102	102
Spiked hausmannite + Humic + Calcite	0	0	0	0	49	49	37	35	10	10	96	93
Spiked humic + Hausmannite + Calcite	1	1	4	4	48	49	33	32	9	9	95	97
Spiked calcite + Hausmannite + Humic	0	0	0	0	47	49	40	40	10	10	97	100
Spiked hausmannite + Humic + Halloysite	1	1	0	0	48	53	41	35	11	12	100	100
Spiked humic + Hausmannite + Halloysite	1	1	0	0	51	50	43	42	11	10	106	103
Spiked halloysite + Hausmannite + Hhumic	0	0	0	0	46	48	32	31	13	12	91	91

The addition of clean humic acid to spiked hausmannite resulted in a notable increase of Pb at the oxidizing step and a proportional decrease of Pb at the reducing step (Table 3.1. vs Table 3.3.). The similarity of the distribution patterns for this two-phase model system of spiked clean humic acid and hausmannite and five-phase model soils suggests that humic acid also has a major part to play in the redistribution of Pb.

The results of these experiments suggest that hausmannite, rather than goethite, is responsible for the recovery of most Pb at the reducing step in Tessier et al.'s procedure. This was further confirmed by the redistribution of Pb from fraction 1 and 2 of the individually spiked halloysite, calcite, and goethite to the reducing fraction when clean hausmannite was added (Table 3.1. vs Table 3.3.). The distribution patterns of these two-phase mixtures are the same as those of the individually spiked hausmannite. Moreover, the distribution pattern of Pb obtained from the mixture of clean goethite and Pb-spiked hausmannite was identical to that of individually spiked hausmannite.

Further evidence for the dominant roles of hausmannite and humic acid in Tessier et al.'s scheme is provided by the similarity between the distribution patterns obtained from three-phase models, shown in Table 3.4. with those of the five-phase model soils (Table 3.1.). All of these three-phase mixtures contained humic acid and hausmannite.

Although at this stage it can not be specified whether it is primarily hausmannite or humic acid (or both) which take up Pb when the metal was first released to solution, it can be concluded that in Tessier et al.'s procedure, both hausmannite and humic acid participate in the redistribution of Pb in the five-phase model soils. A similar finding has been reported by Tu and co-workers (1994b), who found that humic acid and a manganese oxide (pyrolusite) exerted a combined influence on recovery of Pb during a single extraction using acetic acid/ acetate solution of model soil samples; the manganese oxide was noted to have the major control on the retention of Pb.

In the present study, hausmannite was responsible for Pb recovered at the reducing step and humic acid dominated the recovery of Pb at the oxidative fraction. The observation that hausmannite is more efficient at adsorbing Pb than the iron oxide under the extraction conditions has some support in the literature. McKenzie (1980) found that although very little of the Pb adsorbed on synthetic birnessite (manganese oxide) was extractable by dilute acid, the same conditions could remove most (~ 90%) of that sorbed on synthetic goethite.
In addition, McKenzie (1981) found that at medium pH values, iron oxides were positively charged whereas manganese oxides were negatively charged; therefore, there was a much stronger tendency for the adsorption of metals to occur at lower pH values onto the manganese oxides.

In the BCR scheme, humic acid has the most major influence on Pb redistribution (i.e., the highest Pb was recovered at the oxidizing step) (Table 3.1.). However, by performing the BCR scheme on two combinations of two phases (shown in Table 3.5.), an intermediary role of hausmannite in the transfer of Pb to humic acid is also indicated. The addition of clean hausmannite caused shifts of Pb from fraction 1 of the individually spiked calcite and halloysite to the reducing fraction, showing that hausmannite is capable of participating in redistribution in the BCR scheme. These results are also consistent with the Tessier et al.'s extraction on the same phase combination (Table 3.3.).

Table 3.5. Percentages of Pb recovered from two-phase models using the BCR sequential extraction protocol (values are given for each of two duplicate determinations).

Model systems	Step 1 "Exchangeable and "Carbonate bound" & "Water soluble"		Step 2 "Reducible"		Step 3 "Oxidizable"		Step 4 "Residual"		Total % Recovery	
Spiked calcite + Hausmannite	0	0	106	104	3	3	-	-	109	107
Spiked halloysite + Hausmannite	0	0	77	74	15	15	0	0	93	90

3.3. Effect(s) of the extraction conditions on Pb recovery patterns (see also *Chapter 2 subsection 2.1.6.*).

Based on the observation that the readsorption occurred during "early" extraction steps in both schemes, investigation of the factors contributing to the dissimilar final distribution patterns of Pb (Tables 3.1. and 3.2.) centered on the differences in extraction conditions of the "exchangeable", "carbonate bound", and "reducible" fractions of the two schemes.
The dissimilarity is evidently related in some way to the presence of humic acid, since the redistribution pattern of the BCR scheme resembled that of Tessier et al. in the absence of this phase (Tables 3.3. and 3.5.).

The effect of Mg (used in step 1 of Tessier et al.'s scheme) was tested by performing the BCR extraction (in duplicates) on a five-phase model soil containing Pb-spiked calcite, Mg-saturated humic acid and 3 other clean phases. If sorption of Mg was responsible for deactivation of the humic acid, substantial Pb would be recovered at the reducing step, as observed in Tessier et al.'s scheme, but not in the BCR scheme. However, in this system, readsorption to humic acid still occurred, with no Pb being recovered at the reducing step (i.e., 94 and 98% of the Pb spiked were recovered in the oxidizable fraction, and about 6% (from each duplicate sample) was recovered in the residual fraction). Therefore, it can be stated that Mg sorbed on humic acid is not what inhibits the sorption of Pb by this phase during the course of Tessier et al.'s extraction. It could be that Mg and Pb were bound to different sites in the humic acid or that the mechanisms of binding were different for the two metals.

The application of the BCR scheme with a "modified" first extraction solution where Tessier et al.'s reagent was incorporated (i.e., using a mixture of 1 M $MgCl_2$ and 0.11 M CH_3COOH) on the five-phase model soil with Pb originally spiked on calcite (duplicates), was found to result in Pb in this system still emerging at the oxidizing step; no Pb was recovered at the reducing step (i.e., 90 and 86% of the Pb spiked were recovered at the oxidizable step, and 17 and 20% were recovered at the acid extraction step). It is, therefore, apparent that the inability of humic acid to readsorb Pb in Tessier et al.'s scheme (compared with the BCR outcome) is not a result of the competitive effect of high concentrations of Mg^{2+} being utilized in the former scheme. In support of these results, Ladonin and Margolina (1997) have recently observed that sorption of Pb onto humic acid was independent from the presence of a major ion, such as Ca^{2+}; this was attributed to specific adsorption of the metals.

The next parameters tested were the possible effect of high concentrations of a potential competing cation (Na^+) and complexing ligand (acetate) in the second step of Tessier et al.'s extraction. The application of a "modified" BCR scheme with a substitution of its first extraction solution by the second reagent of Tessier et al.'s procedure (i.e., a mixture of 1 M acetic acid and 1 M sodium acetate, pH ~ 4.75), on five-phase model soil containing Pb-spiked calcite (duplicates) was again found to result in a similar distribution pattern to that of the unmodified BCR extraction (i.e., 93 and 83% of the Pb spiked were recovered in the oxidizable fraction, and 14% (from each duplicate samples) was recovered in the residual fraction). It is, hence, apparent that high concentration of Na^+ ions and acetate anions do not significantly inhibit retention of Pb by humic acid either.

The third aspect examined was differences in the exact reducing conditions employed in each extraction. The application of a "modified" BCR scheme with a substitution of its reducing conditions with those of the Tessier et al.'s scheme on the five-phase model soils with Pb originally spiked on calcite (duplicates), was found to result, for the first time, in a substantial recovery of 49 and 48% of the Pb at the reducing step, with 48 and 58% at the oxidizing step, and 8 and 7% at the acid extraction step. This is consistent with the result of the application of the "modified" BCR scheme on the five-phase model soils with Pb-spiked halloysite, i.e., 48 and 55% of the spiked Pb were recovered at the reducing step, 45 and 42% at the oxidizing step, and 7 and 8% at the acid extraction step. Apparently, the key to the differences in the redistribution outcomes of the two schemes lies with their different reducing steps. Specifically, the reducing condition in Tessier et al.'s scheme decreases the sorptive capacity of humic acid, therefore, Pb is more likely to be recovered at the reducing step. The main differences between the two scheme's reducing steps relate to temperature and acetate ion concentration (Table 2.5. *Chapter 2*). In further trials, it was found that the sorptive capacity of humic acid was significantly less (more than 50%) as a result of the high temperature (96 °C), 6 h in Tessier et al.'s extraction (in comparison to the room temperature, 16 h in the BCR scheme) (*Appendix 2.6.*). The much darker supernatant from the heated system indicated degradation. Previous workers have noted the structural degradation of humic substances when subjected to high temperature (Kawamura and Kaplan, 1987; Boles et al., 1988). Retention of Pb on humic acid in the presence of acetic acid in the reducing solution was found to be 30% less (unheated) to 50% less (heated) (237 μg Pb g^{-1} vs 331 μg Pb g^{-1} unheated; 98 μg Pb g^{-1} vs 217 μg Pb g^{-1} heated) (*Appendix 2.6.*). It is evident that the high concentration of acetate ions, therefore, also serve to retain Pb in solution, preventing it readsorbing on the humic acid. Acetate is known for its ability in this respect; Bermond and Eustache (1993) reported that an extraction solution containing acetic acid could extract more Cd and Cu from a soil sample than a solution containing nitric acid. The authors attributed this to complexing ligand properties of the acetate anion.

It can be concluded that the differences in the distribution patterns of Pb for the BCR and Tessier et al.'s extractions are due to the combined effects of the presence of high temperature (96 °C) and 25% v/v acetic acid in the reducing step of Tessier et al.'s scheme. Based on this finding, Tessier et al.'s procedure could be considered to inhibit to a certain extent the redistribution of Pb which might otherwise occur if a sample contains Mn/ Fe oxide-bound Pb and organic matter. On the other hand, if a sample contains high amounts of organic-sorbed Pb, Tessier et al.'s extraction will provide a misinterpretation by extracting humic-bound Pb in the reducing extractant, where it would be interpreted as having originated from the Fe/ Mn oxides compartment.

3.4. Redistribution of Pb in spiked natural soils during the BCR extraction.

A linkage between the results for the synthetic model systems and behaviour of real systems was provided by performing the extractions on natural soils (i.e., Kainui, and Te Rapa peat) spiked with Pb in one added synthetic phase. The Pb was spiked in such a way that in no case did the Pb contribution from the original soil exceeded 6% of the total Pb in each system (see also *Chapter 2 subsection 2.1.3.*).

The results for Pb-spiked calcite and halloysite added to the two soils show that substantial redistribution occurred, since the majority (~70 - 80%) of Pb was not recovered at the first step of BCR extraction. The results of the system containing spiked calcite is illustrated in Fig. 3.2. (Tabulated data for both systems (i.e., spiked calcite and spiked halloysite) are provided in *Appendix 3.2.*). In the case of the Kainui soil, the highest recovery of Pb occurred at the reducing step, suggesting a major role of Mn/ Fe components. This is consistent with the presence of comparatively high concentration of manganese in this soil

(Table 2.3. *Chapter 2*). By contrast, the organic fraction appears to dominate readsorption in the Te Rapa peat, the highest amount of Pb is recovered at the oxidative fraction (Fig. 3.2.).

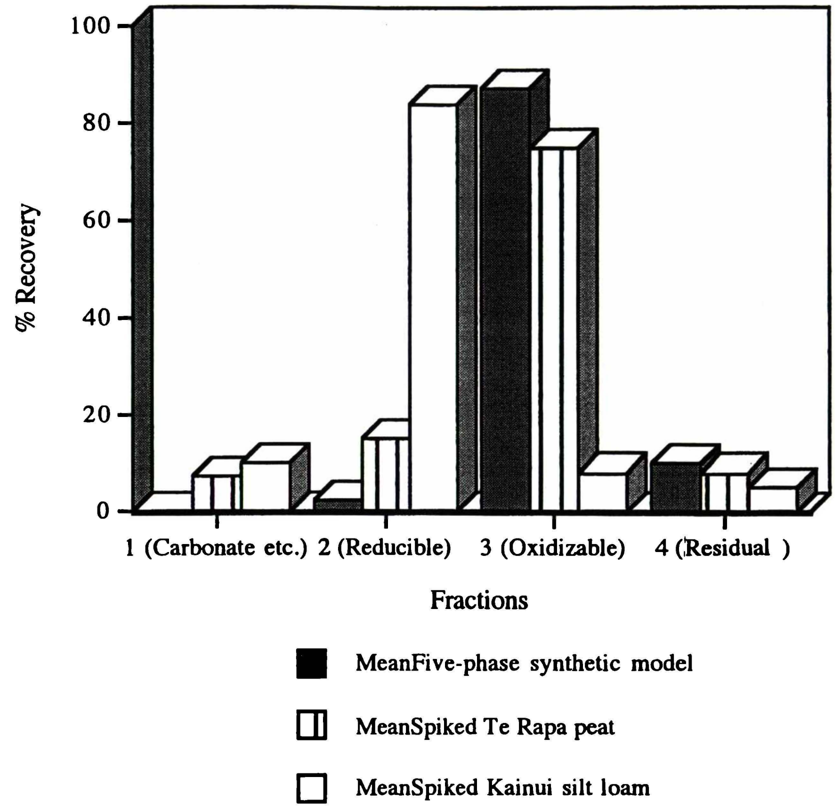


Fig. 3.2. Observed distributions of Pb from model soils containing spiked calcite as determined using the BCR sequential extraction protocol (values shown are means of duplicate determinations).

The Te Rapa peat soil had an organic matter content of about 25 - 29% (by weight), which was close to that of 20% in the synthetic five-phase model soils, whereas the mixture of Kainui soil and the Pb-spiked phase had organic matter content of only about 4 - 5%. The comparative outcomes of the BCR extraction on these two soils suggest that in a real soil sample containing organic matter of not less than 20% and Pb-bound calcite or clay, the organic fraction might be expected to dominate the redistribution of Pb, provided that other important Pb-sorbing phases are insignificant (e.g., less than 0.2% w/w of Fe and Mn, as in the case of the mixture of Te Rapa peat).

A similar interpretation can be made for the mixture of Kainui soil and a Pb-spiked phase. It is apparent that a manganese content of only about 0.1% (by weight) and iron content of only ~ 3% (compared to 10% each in the synthetic five-phase system) is sufficient to play a major role in the redistribution of Pb. Thus, it is suggested that during BCR extraction of a real soil sample containing Pb-bound calcite or clay and low amounts of manganese and iron, the Mn/Fe fraction might influence the redistribution of Pb, provided that other important Pb-sorbing phases are insignificant (e.g., less than 4% w/w of organic matter, as in the case of the mixture of Kainui). Otherwise, organic matter will probably dominate. In a sense, these distinctions could be seen to be academic, as redistribution is operative in either case, and both experimentally-determined phase distributions would be inaccurate.

3.5. Summary and conclusion.

Substantial redistribution of Pb was observed with both Tessier et al.'s and the new BCR sequential extraction procedures for both synthetic model systems and spiked natural soils. Hausmannite and humic acid were found to dominate the redistribution in both extraction schemes. However, whereas Tessier et al.'s procedure yielded the highest recovery of Pb at the reducing step, the three-stage BCR procedure generated the highest Pb at the oxidizing step. The high temperature of the reducing reagent (96°C) and the presence of acetic acid (25% v/v) in Tessier et al.'s scheme were found to be the main factors contributing to the difference between the distribution patterns obtained from the two schemes. Redistribution of Pb during the BCR extraction is likely to be a problem in real systems for samples which contain normal to high amounts of organic matter or manganese oxides, where Pb is originally associated with "exchangeable", "water-soluble" or "acid-soluble" fractions.

Clearly redistribution is still likely to be a serious issue for some metals in even the new BCR sequential extraction, and further research is warranted along the lines of potential modifications to extraction conditions which could be employed in order to inhibit it.
Pb redistribution is very strong, and it is suspected that if the problem of redistribution is solved for Pb, it will also be solved for other metals (such as, Cd (Kim and Fergusson, 1991)) which have shown little or less severe redistribution during sequential extraction.

Until a redistribution-free extraction is developed, it would seem inadvisable to attempt to monitor natural redistribution of Pb which may occur with time at contaminated sites.
For example, Pb initially deposited as a carbonate could be extracted and interpreted as being associated with iron and manganese oxides (Tessier et al.'s scheme) or organic matter (BCR scheme) at all times after deposition.

Chapter 4. Inhibition of Pb redistribution during the BCR sequential extraction of soil models

(Publication note: research results relating to the ligands cryptand 2.2.2 and NTA which are detailed in this chapter have been published in the journal Analytica Chimica Acta, Vol. 347 (1997), p. 313-323. A reprint of this paper is provided in a pocket on the inside back cover of this thesis.)

4.1. The use of solid sequestering agents.

The results of the assessment of potentially useful solid sequestering agents for counteracting Pb redistribution are provided in the following.

4.1.1. Trials of a sulfonate ion exchange membrane strip.

In Table 4.1. is listed the percentages of Pb recovered from spiked calcite and a two-phase system containing spiked calcite and humic acid, in the presence of sulfonate ion exchange membrane strips.

In a preliminary control experiment, two strips of membrane with a dimension of 49 mm x 20 mm (equivalent to the total reactive surface area of 3920 mm^2) were immersed in acetic acid, in the absence of a solid phase (Table 4.1.). No Pb was found in either the acetic acid or elution solutions. This suggests that under the extraction and elution conditions, the membrane did not contribute any detectable Pb into the system.

In the presence of Pb-spiked calcite, 80% of the Pb liberated from the completely dissolved calcite was recovered from two membrane strips (3920 mm^2), with about 35% of the Pb remaining in the acetic acid solution (the reason the sum of these figures exceeds 100% is that recoveries are based on the results of two separate analyses in relation to how much lead was initially in the system. Calculated in relation to total recovered Pb, the ratios are 70% (membrane strips) to 30% (solution)). This suggested that the reactive binding sites on the membrane were capable of capturing the Pb in the presence of high concentrations of Ca. Increasing the total surface areas to 7840 and 11 760 mm^2 resulted in none of the Pb remaining in the acetic acid solutions, and all of the Pb being recovered from the membranes. This indicates that the membrane with the total reactive surface area of 3920 to 7840 mm^2 is capable of retaining all the Pb (in the absence of other sequestering phase(s)).

Table 4.1. Percentages of Pb recovered from individually spiked calcite systems and the two-phase systems comprising spiked calcite and humic acid, by the sulfonate ion exchange membrane strips.

System tested	μg Pb in the systems	Total area (mm^2) of the membrane used	% Pb left in the conventional 0.11 M acetic acid, 16 h	% Pb recovered from the membrane strips	Total % Pb recovered from the acetic acid solution and the membrane
control(1)	-	3920	0	0(2)	0
Pb-calcite(1)	37	3920	35	80(2)	115
Pb-calcite	37	7840	0	114(2)	114
Pb-calcite	37	11 760	0	126(3)	126
Pb-calcite + humic acid	37	3920	0	10(2)	10
Pb-calcite + humic acid	37	5880	0	16(2)	16
Pb-calcite + humic acid	37	35 280	0	97(4)	97

Note: (1) The experiments were done in duplicate. The values reported are the averages of the determinations;

(2) The values reported are the sum of the Pb recovered from two elution solutions (20 ml 0.5 M nitric acid, 3 h, followed by 20 ml 1 M nitric acid, 24 h);

(3) The elution solution used was a 20 ml mixture of 1 M nitric acid and 0.5 M NaCl, 24 h;

(4) The values reported are the sum of the Pb recovered from two elutions with a 20 ml mixture of 1 M nitric acid and 0.5 M NaCl, 24 h.

In the two phase systems comprising spiked calcite and humic acid, only about 10 - 16% of the Pb was recovered from the membrane with the total reactive area of 3920 and 5880 mm^2, and none of the Pb remained in the acetic acid solution (Table 4.1.). This suggested that humic acid had still taken up the majority of the Pb. However, based on the earlier observation in the case of individually spiked calcite, that an increase in the membrane surface area could result in more Pb being captured from solution, it was considered possible that addition of more membrane (more sulfonate binding sites) into the two-phase system could increase its ability to successfully compete with the humic acid for Pb. The approach proved successful; when a total reactive surface area of 35 280 mm^2 was added into the system, almost all (97%) of the Pb was recovered from the membrane. This, together with the observation of no visible retention of humic acid particles on the membrane, showed that a large amount of membrane (the total reactive area of 35 280 mm^2, which was equivalent to 18 strips of 49 mm x 20 mm) was successfully counteracting the Pb readsorption, previously observed during the course of the first extraction step of the BCR scheme. However, at this stage, it was realized that the use of a sulfonate ion exchange membrane strip might not be feasible for the more complex multi-phase model soils because a substantial amount of the membrane would be required.

In a further experiment, membrane of total area 21 560 mm^2 was immersed into a two-phase system comprising hausmannite and spiked calcite. In this case, it was evident by direct observation that a significant amount of hausmannite was being retained on the membrane. This could not be removed by centrifugation or a selection of other physical methods. Interaction of the hausmannite particles with the membrane resulted in its changing from its initial colour (brown) to black. This suggested a possible reaction between sulfonate binding groups on the membrane and the hausmannite particles (in the system containing only Pb-spiked calcite and hausmannite in acetic acid solution, the brown colour of hausmannite was unchanged). In addition, about 80% of the Pb was found to be still retained on the remaining hausmannite in the system. These results imply that the membrane was indeed not practicable for the use in this system, and suggest that attempts to counteract readsorption by direct immersion of exchange membranes in environmental extract solutions may be impractical due to (at least) manganese oxides causing membrane deactivation.

To test a possible means of preventing direct contact between the membrane and the solid phase(s) in a system, membrane of total area about 39 200 mm^2 was placed in a cellulose dialysis bag and immersed in a two-phase system comprising spiked calcite and humic acid (the dialysis tube was initially tested and had proved durable under the extraction conditions). However, it was found that in this case, none of the Pb was recovered from the membrane. This together with the earlier result (that about the same total area of membrane used in the same solid system but in direct contact with the Pb in the solution, could take up almost all of the Pb) suggested that the dialysis bags were imposing kinetics limitations on the rate of Pb uptake. Howard (1988) speculated that the poor performance of a polydithiocarbamate resin held in dialysis bags in capturing Zn, Ni, Cu, and Pb from solubilized calcite, might due to kinetics of Pb permeation through the dialysis membranes and/ or a thermodynamic effect of the resin. It seems likely that Pb was sequestered by the humic acid soon after being liberated from calcite, and did not have the opportunity to pass through the pores of the dialysis bag and come in to contact with the binding sites on the membrane.

In a preliminary experiment, the membrane was also applied to a system containing Te Rapa soil and spiked calcite (the same system used in *Chapter 3 section 3.4.*). In this case, the membrane of total area 31 200 mm^2 was found to recover only 8% of the total Pb (151 μg) in the system, with small amounts of Pb left in acetic acid solution and most of the Pb later recovered at the oxidizing step. The Pb recovery of about 10% at the first modified extraction step was close to that of 7% recovered in conventional first extraction step of the BCR from the same model soil system (*Chapter 3 section 3.4.* Fig. 3.2.). Possible reasons for the membrane's failure to sequester the Pb in this instance are (a) the number of reactive sites on the membrane might not be sufficient for competing with the organic matter (about 25 - 29% by weight) present in the sample, and (b) manganese oxides (or other agents capable of membrane deactivation) may have "poisoned" the membrane surface.

At this point, trials on the sulfonate ion exchange membrane was set aside in favour of more promising approaches. Such membranes may still have a use in similar systems, but the results of this work have highlighted a number of significant limitations which would have to be overcome or otherwise accommodated. These are: (1) a considerable and impractical amount of the membrane was needed to compete with the humic acid; (2) a large amount of the membrane did not significantly compete for the Pb in the presence of hausmannite, possibly due to membrane fouling; (3) a notable amount of hausmannite was retained on the membrane which was a potential error in assessing an accurate amount of Pb captured by the membrane; and (4) a separation technique involving use of a dialysis bag appears to result in Pb being kinetically hindered from reaching the membrane.

4.1.2. Trials of SiO_2 gel and wool functionalized with dithiocarbamate.

In the system comprising only the SiO_2 functionalized with dithiocarbamate (hereafter "$dSiO_2$") and acetic acid, no Pb was recovered from the $dSiO_2$ or left in acetic acid solution (Table 4.2.). This implied that under the extraction and elution conditions tested, the $dSiO_2$ did not contribute any detectable Pb into the system.

Table 4.2. Percentage recovery of Pb from sets of duplicate systems using dithiocarbamate-functionalized SiO_2 ($dSiO_2$).

Systems tested	% Pb left in acetic acid or water	% Pb recovered from the $dSiO_2$ by 20 ml, 1M nitric acid, 24 h	Total % Pb recovery
0.1185 g $dSiO_2$ + 20 ml acetic acid	0	0	0
0.1055 g $dSiO_2$ + 20 ml acetic acid	0	0	0
0.1150 g $dSiO_2$ + 37 μg Pb* + 20 ml water	35	63	98
0.1103 g $dSiO_2$ + 37 μg Pb + 20 ml water	12	81	93
37 μg Pb + 20 ml water (1)	100	-	-
37 μg Pb + 20 ml water (2)	100	-	-
0.0252 g Pb-spiked calcite + 0.1040 g $dSiO_2$ + acetic acid	0	98	98
0.0254 g Pb-spiked calcite + 0.5114 g $dSiO_2$ + acetic acid	0	100	100

* 37 μg Pb is equivalent to the amount of Pb from completely dissolved 0.025 g Pb-spiked calcite.

In the system containing the $dSiO_2$ + 37 μg Pb (37 μl of the stock 1000 ppm Pb) in clean water, an average of about 70% of the Pb was recovered from the 0.1 g $dSiO_2$, whereas in the system containing only 37 μg Pb and water, all the Pb was left in the solution (Table 4.2.). The first result implies that the dithiocarbamate binding group survived and can retain a significant amount of the Pb under the slightly acidic conditions, and the second result demonstrates that under these conditions, Pb was not being lost from the system by adsorption onto the wall of the centrifuge tube. In the systems comprising Pb-spiked calcite, the $dSiO_2$ of weight about 0.1 and 0.5 g, and acetic acid, no Pb was found in the acetic acid, and generally all the Pb was recovered from the $dSiO_2$. The sites on the $dSiO_2$ apparently could retain Pb under the extraction pH of about 4. In addition, about 0.1 g of $dSiO_2$ is sufficient for capturing Pb released from completely dissolved 0.025 g calcite, in the absence of other solid phase(s).

The size (60 - 120 μm) and density of the $dSiO_2$ mean that it is not possible to separate it from sand (a diluent phase in a more complex synthetic soil models) and also probably from other solid phase(s), if these solids are to come into direct contact. Therefore, a dialysis membrane with MWCO of 12 000 and nylon sieves of 1 and 6 μm pore sizes were made into bags to confine the resin prior to immersing it into the system. These procedures are outlined in *Chapter 2 section 2.2.1.(b)*. The results of these trials are as follows; some observations are outlined in Table 4.3.

The 1 μm pore-sized nylon bag, proved capable of retaining the resin throughout the mechanical shaking extraction period, and was then tested with the individually spiked calcite system. It was found that in the case of 0.14 g $dSiO_2$ retained in the nylon bag, about 30 % of the Pb still remained in the acetic acid extractant and about 70% of the Pb was recovered from the $dSiO_2$ in nitric acid elution solution. It is apparent that the 1 μm pore-sized nylon decreased the percentage of Pb being captured by the $dSiO_2$ (comparing with the near 100% Pb recovered by a similar amount of the $dSiO_2$, but in the absence of the membrane) (Table 4.2. vs Table 4.3.). It is possible that a nylon sieve allowed less mechanical mixing of the $dSiO_2$ confined in it with the solution. Results from the use of the $dSiO_2$ in combination with the derivatized wool are presented in Table 4.4.

About 0.2 g of the dithiocarbamate-derivatized wool sequestered about 80% Pb released from dissolved calcite, whereas in the same system, 0.1 g of the $dSiO_2$ could retain 98% of the Pb) (Table 4.4. vs Table 4.2.). In the case of using 0.5 g of the wool sealed in a nylon bag, no Pb was found in the acetic acid, but about 90% was recovered from the wool (Table 4.4.).

Table 4.3. The use of dialysis tube and nylon bag to retain 0.1 g dithiocarbamate-functionalized SiO_2 ($dSiO_2$).

system tested	weight of the $dSiO_2$ (g) and separation medium used	Observation after 16 h mechnical shaking
0.025 g Pb-spiked calcite + 0.1 g goethite + acetic acid	0.1000 g in dialysis tube with overhand knot *	leakage of resin through overhand knot & significant amount of yellow particles (goethite) retained on both the $dSiO_2$ and the membrane
acetic acid only	0.1000 g in 6 μm pore-sized nylon bag sealed by nylon thread	leakage of the $dSiO_2$
acetic acid only	0.1000 g in 1 μm pore-sized nylon bag sealed by nylon thread	no noticeable leakage of the $dSiO_2$
0.025 g Pb-spiked calcite + acetic acid	0.1400 g in 1 μm pore sized nylon seive sealed by nylon thread	no noticeable leakage of the $dSiO_2$

* In this case, a plastic clip is not practical for enclosing the dialysis tube.

Table 4.4. Percentages of Pb recovered from individually spiked calcite systems by the dithiocarbamate-functionalized wool and from a five-phase system (spiked calcite) by the dithiocarbamate-derivatized wool and -SiO_2 ($dSiO_2$).

Systems tested	weight of the wool (g)	weight of the $dSiO_2$ (g)	% Pb left in acetic acid	% Pb recovered from the sequestering agent(s) by 20 ml, 1M nitric acid, 24 h	Total % Pb recovery
0.0251 g Pb- spiked calcite	0.2332	-	30%	80%	111%
0.0250 g Pb- spiked calcite	0.5057 g in a nylon bag (1 µm pore size)	-	0%	87%	87%
0.5000g five-phase (spiked calcite)	2.3387 g in 3 nylon bags (1 µm pore-size)	3.3896 g in a nylon bag (1 µm pore-size)	0%	17%	-

Up to this stage, it is apparent that at least 0.1 g of the $dSiO_2$ or 0.5 g of the wool, both sealed in 1 μm pore-sized nylon bag(s), are required for an individually Pb-spiked calcite system if the Pb recovery by these sequestering agent(s) were to be higher than about 70% (Table 4.4.). The 0.1 μm bags are preferable to 6 μm, because the latter allowed significant leakage of the $dSiO_2$ particles (Table 4.3.). It was decided to apply the highest possible practical amount of the $dSiO_2$ and the wool to a five-phase model (containing spiked calcite), this being dictated by the available volume in the centrifuge tubes. In this case, however, it was found that significant amounts of fine particles of goethite (yellow), hausmannite (brown), and humic acid (black/dark brown) were able to pass through the pores of the nylon sieve and were retained on the $dSiO_2$, the wool, and also the bags. This was despite the fact that the $dSiO_2$, the wool, and the bags were all thoroughly washed with water. Less than 20% of the Pb was recovered from both the sequestering agents and the bags; however, it is considered likely that a significant portion of this < 20% came from direct desorption of Pb captured by these solid particles, particularly as the colour due to the synthetic soil particles retained on and in the bags noticeably faded during the elution step. The majority of the remaining Pb was later recovered at the oxidation step (none was recovered at the reduction step), indicating that even under these optimal conditions, the sequesterant systems were not strong enough to compete with humic acid for available Pb.

Although prior to the test with the five-phase system, the $dSiO_2$ and the wool, sealed in nylon bags, were not tested in less complex systems (such as two-phase system comprising Pb-spiked calcite and humic acid or hausmannite or goethite) the above observation that there is significant retention of the particles on to both sequestering agents and the nylon bags suggests that this type of approach to resolve the problem is not likely to be successful, even in a simple two-phase system. However, one positive finding which may be applicable to future work is that the 1 μm nylon sieve (the smallest pore size available) is sufficiently large as to permit Pb in the solution to reach the binding sites available on the surfaces of the $dSiO_2$ and the wool.

At this point, trials on the dithiocarbamate resin and wool were abandoned in favour of more promising approaches.

4.1.3. Trials of a thiol resin (RSH).

In the system containing Pb-spiked calcite and the thiol resin in a dialysis bag, no noticeable leakage of the resin (particle size of about 300 - 1200 μm) through the overhand knot of the bag was observed throughout the extraction step (Table 4.5.). Therefore, the recovery of about 78% from the confined resin (about 16% less than that from about the same amount of the unconfined resin) implied that presence of the dialysis bag prevented the resin from sequestering some of the Pb. This is despite the fact that the original system was shaken for 16 h; however the result appears unequivocal as the Pb absent from the resin was present in the solution (Table 4.5.). The result is also consistent with the earlier results of the sulfonate ion exchange membrane strip, and dithiocarbamate-derivatized silica gel, that both dialysis tubing and nylon mesh, are capable of preventing a portion of the Pb from being captured by sequestering agents confined in these material(s). In the case of the dialysis bags, possible reasons for this effect include (a) a kinetic limitation to transport of $Pb^{2+}_{(aq)}$ across the membrane, and (b) inhibition of simple mechanical mixing of the solutions inside and outside the bag due to the presence of the bag itself. In the case of 1 μm nylon mesh, it would seem unlikely that the first possibility would apply, because the mesh is significantly larger than hydrated Pb ions. However, the second inhibitory effect could still be operative.

Table 4.5. Percentages of Pb recovered from individually spiked-calcite systems, using thiol resin.

System tested	% Pb left in acetic acid	% Pb recovered in elution solution (20 ml 1 M nitric, 24 h mechanical shaking)	Total % Pb recovery
0.0253 g Pb-spiked calcite + 1.0870 g resin	0%	94%	94%
0.0250 g Pb-spiked calcite + 1.0054 g resin in a dialysis bag *	17%	78%	95%

* closed by overhand knot

In a polycarbonate tube containing Pb-spiked calcite + humic acid + hausmannite + 0.5013 g of free resin with a small amount of chloroform added into the system at the end of the extraction step, it was found that density separation using this organic solvent did not assist in isolating the resin from the particles of humic acid and hausmannite. In fact the resin and an emulsion containing the synthetic soil particles aggregated at the interface of the organic and the aqueous phases. In addition, the polycarbonate centrifuge tubes were found to have poor resistance to chloroform.

In the system comprising 5.0133 g previously-sieved resin and 0.5003 g of the five-phase mixture (spiked calcite) with previously-sieved humic acid and sand, it was observed that at the end of the acetic acid extraction step, particles of goethite (yellow) and hausmannite (brown) were retained on the resin. In addition, none of the Pb was either recovered in the nitric acid elution solution (from the recovered resin) or remained in the acetic acid extraction solution. Rather, 20% and 50% of the Pb was later recovered at the reducing and oxidizing steps, respectively. This result confirmed that humic acid dominated the sequestering of Pb in the system. A low total recovery of only 70% was observed in this case (no Pb was recovered at the final aqua regia extraction) and this was probably due to a significant loss of synthetic soil particles during the separation of the resin from the mixture at the end of the extraction step. Several ml of clean water was used to wash the synthetic soil particles through the nylon sieve. The finest particles of the synthetic soil suspended in the rinsed water may not have been completely recovered.

By this point in the trials it had become clear that use of the thiol resin to counteract the redistribution of Pb was limited by the same inter-related problems observed during the earlier assessment of other solid sequestering agents; specifically, (1) the resin particles themselves sequestered significant quantities of the solid phases; and (2) a separation of the resin from solution using an artificial membrane inhibited it from capturing a significant quantity of the Pb, even in systems lacking humic acid as a competing sequesterant. Furthermore, when bags were not used, attempts to separate the free resin after an extraction on the basis of size or density were both not practical and unsuccessful.

4.1.4. Trials of functionalized cotton fabric with P-reactive group, SiO_2 gel functionalized with thiol groups, and phosphine derivatized wool.

Table 4.6. Percentages of Pb remaining in the solution in the systems, using Proban, wool-THP, and $SiO_2(CH_2)_3SCH_2CHOHCH_2SH$.

System tested	% Pb left in acetic acid or water
0.0250 g Pb-spiked calcite + 11 cm^2 Proban + acetic acid	85%
37 μg Pb + 0.4940 g wool-THP+ 20 ml water	60%
0.0249 g Pb-calcite + 1.859 g wool-THP + acetic acid	10%
0.0253 g Pb-calcite + 0.1201 g $SiO_2(CH_2)_3SCH_2CHOHCH_2SH$+ acetic acid	93%

A small amount of the Pb (about 15%), released from completely dissolved calcite, was sequestered by 11 cm^2 chemically activated Proban under the mildly acidic conditions (Table 4.6.) This figure is low, and although it could perhaps be enhanced by increasing the amount of Proban to the point where the tubes was up to its capacity, another observation reveals that Proban is unlikely to be a useful agent for counteract the Pb redistribution in the more complex system(s). This was because when Proban was incorporated in to a system containing humic acid, goethite, and hausmannite, it was found to sequester a significant amount of the these solid phases, and this behaviour would introduce major problems in determining the readsorbed-phase(s) of the Pb. For this reason, work on chemically-activated Proban was discontinued.

In the system comprising 37 μg Pb (37 μl stock 1000 ppm Pb in 1 M nitric acid) and about 0.5 g wool-THP in water, about 60% of the Pb still remained in the solution, showing that under slightly acidic conditions, this quantity of the THP-functionalized wool was capable of retaining over twice the amount of Pb as the tested quantity of Proban (Table 4.6.).
In addition, in the system comprising Pb-spiked calcite and about 2 g wool-THP in acetic acid, only about 10% of the Pb was left in the acetic acid extraction solution. The difference between these two figures (from 40% retained to 90% retained) is probably mainly due to greater quantity of wool used in this case. However, further trials on the THP-functionalized wool were abandoned at this stage because (1) in comparison with the dithiocarbamate-functionalized wool, about 8 times more of the wool-THP was used in a similar system to give similar results (Table 4.4. vs Table 4.6.) (therefore, the dithiocarbamate-functionalized wool was deemed the preferred sequestering agent of the two); and (2) once again, the wool-THP in acetic acid solution retained a significant quantity of the solid phases (i.e., humic acid, hausmannite, and goethite) as previously observed in the earlier tests on the dithiocarbamate-functionalized wool and other solid sequestering agents. This proved to be the consistent major limitation with direct use of these solid-sequesterant in these systems, and has been shown to apply over quite a range of functional groups (sulfonate, dithiocarbamate, and thiol) and over a few matrix materials (reins, wool, and silica gel).

In the system comprising Pb-spiked calcite and $SiO_2(CH_2)_3SCH_2CHOHCH_2SH$ in acetic acid, almost all of the Pb remained in the acetic acid solution (Table 4.6.). By comparison, the dithiocarbamate-functionalized SiO_2 (of about the same amount and in a similar system) could sequester almost all of the Pb (Table 4.2.). The SiO_2 derivatized with thiol groups was, therefore, identified as the inferior sequestering agent of the two, and further tests on this sequesterant were not performed.

4.1.5. Summary of the use of solid sequestering agents for potentially counteracting Pb redistribution.

All solid sequestering agents tested were able to capture Pb released from completely dissolved calcite under the acidic extraction conditions, in the absence of other synthetic solid phase(s). However, these sequestering agents have a common limitation for counteracting Pb redistribution in the more complex model soil systems, especially the five-phase system. This limitation is that the solid sequestering agents themselves also sequestered significant quantities of the synthetic solid phase(s). This phenomenon would seem likely to happen if these solid sequestering agents were to be applied to counteract the redistribution problem which may be observed in other sequential extractions. A secondary and inter-related problem is that physical separation of the sequestering agents from other solid phase(s) in the solution using dialysis membranes or nylon sieves significantly inhibits the Pb from being sequestered by the agents. It is shown in subsequent experiments (*section 4.3.*) that a significant amount of Pb initially in acetic acid solution is sequestered by humic acid within as short a period of time as 10 min; therefore it seems likely that the separation approach, in which a physical barrier is put between the solid sequestering agents and the Pb in solution, will fail.

4.2. The use of soluble complexing agents.

The results of the investigations of potentially useful soluble complexing agents are chronologically outlined in the following discussion.

4.2.1. Trials of the soluble phosphine derivative (Aerophine®).

Determinations of Pb in the "Original" aerophine extracts of both a system comprising individually spiked calcite, and a two-phase system comprising clean humic acid + spiked calcite, were found to be problematic and prone to significant error. Specifically, absorbance signals were both low in absolute size and highly variable, with significant differences evident between repeat runs of the same standards and samples. The low and variable absorbance signals observed were not consistent with the experimental variation normally obtained from the analysis of Pb by the FAAS used in this study. It was speculated that these interferences were likely to be somehow connected to the presence of aerophine in solution, either through its ability to modify surface tension and alter the characteristics of aerosol droplet formation in the nebuliser (aerophine is a surfactant), or perhaps by formation of stable chemical species with Pb which persist in the flame. To test this speculation, a portion of aqua regia was added into a series of beakers containing the "Original" aerophine solution and different volumes of stock Pb solution and the mixtures were refluxed, with the intention being that the aqua regia would degrade the (organic compound) aerophine and release Pb from the complex. However, during the refluxing, an unexpected side-reaction occurred which involved formation of a significant amount of oily coloured-solid residue, which separated out from a quite clear yellowish solution and stayed in upper layer of the solution. After the separation, the solid was retained on the filter paper. It was very likely that the filtrates obtained would incur a significant error in the Pb determination if they were to be used as standard solutions. As a result, this approach of using a strong acid to resolve the analytical problem was abandoned.

Due to the difficulty in the analysis of Pb in the aerophine matrix, a determination of Pb retained on remaining solid phase(s) in the systems (after being treated with an aerophine-containing extractant) was considered an appropriate alternative approach for assessing the potential usefulness of the Aerophine in counteracting Pb redistribution. Therefore, the "direct" Pb determination was temporarily abandoned and the "indirect" analysis was performed for subsequent samples comprising individually-spiked phases and a two-phase system. A pre-requisite of the modified extraction system is that it allows the retention of most or all of the Pb on the individually-spiked solid phases, since this would suggest that over the extraction period the "modified" extractant does not significantly directly attack the non-target solid phases (i.e., the extractant is selective). However, for the two-phase system comprising clean humic acid and spiked calcite, the retention of Pb on the remaining humic acid would suggest that the "modified" extraction conditions allow redistribution of Pb to occur. Therefore, the two boundary conditions used to define a useful extraction system are that the system causes minimal removal of Pb from the individually-spiked solid phase (except calcite), while at the same time encouraging minimal retention of Pb on the humic acid in the two-phase system.

In Tables 4.7. and 4.8. are shown the percentages of Pb recovered from the residues of the individually-spiked phases and the remaining humic acid in the two-phase systems, after the "modified" extractions using various aerophine-containing solutions: 2.5% ("Original"), 0.60% ("Diluted"), 0.25% ("Diluted-1"), and 0.06% ("Diluted-2") over different extraction times. (Exact compositions of the various solutions are outlined in Table 2.6.)

Table 4.7. Percentages of Pb retained on the residual solid after extraction using a "modified" extraction solution containing 2.5% Aerophine ("Original" solution) over three different extraction times.

System tested	% (1)Pb retained on residual solids after extraction using the "Original" solution		
	16 h	5 h	1/2 h
Individually spiked phases			
Pb-Calcite	no solid left in the system	no solid left in the system	no solid left in the system
Pb-Humic acid	11	30	41
Pb-Hausmanite	0	5	6
Pb-Goethite	84	70	88
Two-phase system			
Pb-Calcite+clean Humic	0 (2)	0	0

Note: (1) Percentages of Pb shown are based on the amount of Pb originally retained on the spiked phases. Total amounts of Pb in the systems of individually spiked-calcite, humic acid, hausmannite, and goethite are 37, 148, 93, and 93 μg, respectively.

(2) Refers to no Pb being recovered from the remaining humic acid.

In the cases of individually-spiked calcite (Tables 4.7. and 4.8.) all of the various extraction conditions assessed completely dissolved the calcite, and as a result all the Pb originally sorbed on it was released into the solutions.

Table 4.8. Percentages of Pb retained on the residual solid after extraction using the "modified" extraction solutions containing 0.6%, 0.25%, and 0.06% Aerophine ("Diluted", "Diluted-1", and "Diluted-2" solutions, respectively) over varying extraction times.

System tested	% Pb retained on residual solids after extraction using the "modified" extraction solutions			
	"Diluted" 16 h	"Diluted" 1/2 h	"Diluted-1" 1/2 h	"Diluted-2" 1/2 h
Individually spiked phases				
Pb-Calcite	no solid left in the system	no solid left in the system	no solid left in the system	no solid left in the system
Pb-Humic acid	50	77	87	72
Pb-Hausmanite	0	70	88	92
Pb-Goethite	66	92	83	80
Two-phase system				
Pb-Calcite+clean Humic	43	23	31	22

In the case of individually-spiked humic acid (Table 4.7.), the percentages of Pb directly desorbed by the 2.5% ("Original") solution were decreased (more of the Pb was retained on the remaining humic acid) by moving to a shorter extraction time. It was also noticed that the extract was becoming darker in colour over a longer extraction time, suggesting the dissolution or fragmentation of the humic acid. Irrespective of whether the extraction time was 1/2 h or 16 h, the percentages of Pb removed from the humic acid by the diluted 0.60% ("Diluted") solution were less than those removed by the more concentrated 2.5% solution (Table 4.7. vs Table 4.8.). Nevertheless, the diluted 0.60% solution removed Pb at a shorter rate than the concentrated solution, with only about 20% of the Pb being removed from the humic acid over 1/2 h in comparison to about 50% over the longer time of 16 h (Table 4.8.). Over the same extraction time of 1/2 h, however, further decreasing the aerophine concentrations from 0.60% to 0.25% ("Diluted-1") and 0.06% ("Diluted-2") did not seem to result in significant reduction in the percentages of Pb being desorbed from humic acid.

In the cases of individually-spiked hausmannite, the "Original" solution was capable of desorbing almost all of the Pb from the hausmannite within a short extraction time of only 1/2 h (Table 4.7.). This observation is reproducible but seemed difficult to explain when comparing it with the results from using the same "Original" solution on the above humic acid and on the individually-spiked goethite later tested. The extractant removed about 60% of the Pb from the humic acid over 1/2 h and desorbed only about 20% of the Pb from the goethite (Table 4.7). In addition, based on the previous findings (*Chapter 3* 's summary and conclusion), hausmannite and humic acid have been identified as the two main sequestering solid phases in the multi-phase model soils, so it would perhaps be expected that hausmannite and humic acid would retain Pb more effectively than goethite. However, the reaction mechanism involving the readsorption of already dissolved Pb onto the remaining solid phase(s) might be different from that involving the direct desorption of Pb from each individually-spiked solid phase by the Aerophine. Despite the above observations, the hausmannite responded to the combination of the aerophine concentrations and extraction times by showing a similar trend to the humic acid, i.e., (1) at the same concentration of the Aerophine ("Diluted" solution), the shorter the extraction time, the less Pb was removed from the solid phase (Table 4.8.), and (2) over the same extraction time of 1/2 h, a kinetic effect was evident where the percentages of Pb removed by the "Diluted" solution were less than those extracted by the more concentrated "Original" solution (Table 4.7. vs Table 4.8.). However, it appeared that over the same extraction time of 1/2 h, the "Diluted-2" solution was the most favourable in terms of allowing the least desorption of the Pb from the hausmannite.

In the cases of individually-spiked goethite, the percentages of Pb being directly removed were generally insensitive to changes in the aerophine concentrations or the extraction times (Tables 4.7. and 4.8.). However, over the same extraction time of 16 h, the 0.60% solution was able to remove more of the Pb from goethite than the more concentrated 2.5% solution did (34% removed vs 16%). This observation was obviously not consistent with the rest of the results of goethite, as well as with those of the individually-spiked humic acid and hausmannite (which generally showed a trend that more concentrated solution removed more of the Pb). In addition, the inconsistent result was based on a single replicate (although the FAAS analysis has been reproducible). Therefore, it is likely that this single contradictory result was not real. It should also be noted here that under the conventional first step of the BCR scheme (0.11 M acetic acid, 16 h), about 50% of Pb was retained on goethite (*Chapter 3* Table 3.2.) which was notably less than the retention of Pb of about 80 - 90% on the goethite under the "modified" extraction conditions investigated here (Tables 4.7. and 4.8.). However, this might be a consequence of a coating of the aerophine onto the goethite.

In the cases of two-phase systems comprising clean humic acid and spiked calcite, over all the different extraction times, the "Original" solution was capable of retaining all of the Pb in the solution (none of the Pb was sequestered by the humic acid) (Table 4.7.). Although this suggested a potential usefulness of the "Original" solution for counteracting Pb redistribution, this 2.5% solution was also capable of significantly removing Pb from the individually-spiked humic acid and hausmannite. Therefore, the "Original" extractant was deemed unsuitable for further tests on more complicated multi-phase soil models. More diluted aerophine solutions, however, allowed some retention of Pb originally spiked on the humic acid (Table 4.8.). The 0.6% "Diluted" solution allowed about 40% retention of the Pb on the remaining humic acid over the 16 h extraction, but the percentage retention was decreased to about half over 30 min. Over the same extraction time of 30 min, the more diluted solutions (0.25 and 0.06%) did not significantly improve this result, with much the same percentage of Pb being sequestered by the remaining humic acid.

Among all the combinations of aerophine concentrations and the extraction times investigated, the use of the 0.06% "Diluted-2" solution for 1/2 h extraction appeared to be the best compromise for all the solid systems tested. This "modified" extraction system was capable of completely dissolving the spiked calcite (the original phase of Pb in the more complex multi-phase soil models), while not being so strong as to cause a significant removal of Pb from other non-target phases (i.e., humic acid, hausmannite, and goethite). In addition, under these conditions redistribution of Pb to humic acid was significantly counteracted (as observed in the two-phase system).

This extraction system (0.06% aerophine over 1/2 h), which represents the best compromise, was then further applied on a five-phase system with spiked calcite (37 μg Pb).

The following figures illustrate the percentages of Pb recovered at each extraction step from two identical sets of duplicate samples of the five-phase system.

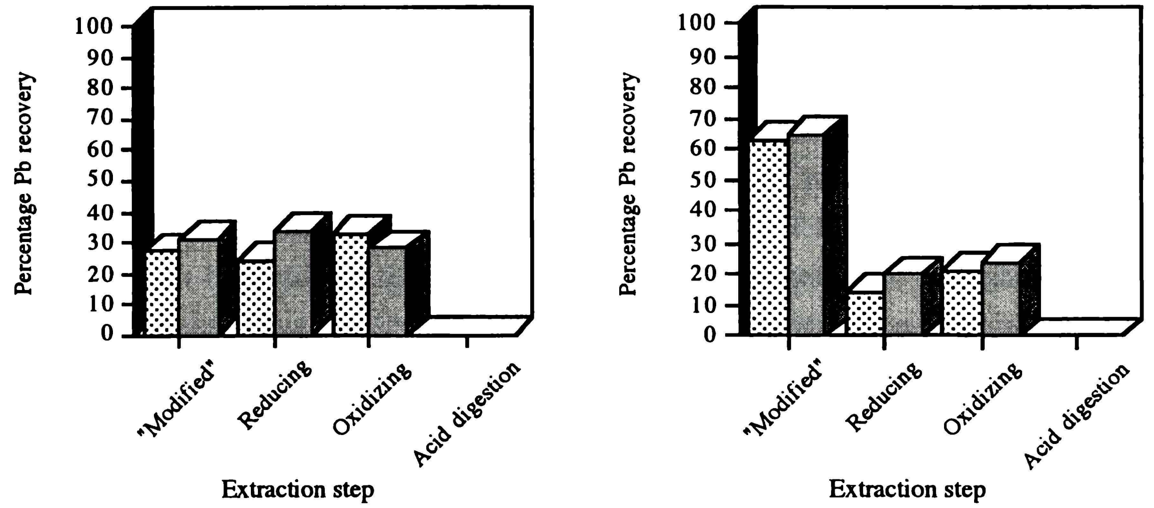


Fig. 4.1. Percentages of Pb recovered from the five-phase model soils (spiked calcite), using the modified 0.06% aerophine solution and a 1/2 h extraction (data shown duplicate experiments)

In these experiments, Pb in the diluted-aerophine extracts was directly determined using the FAAS (Fig. 4.1). Lead in the aerophine extracts reported for the first set was analyzed about 7 days after the collections, whereas that illustrated for the second set was immediately determined. During the determinations of Pb in all these diluted aerophine extracts, the unusual variations of the absorbance signals (previously observed during the analysis of the more concentrated "Original" solutions) were still persisting. However, an attempt was made to counteract this problem by use of statistical averaging; each percentage of Pb recovered at the first modified extraction step reported here is the average value of a few repeated determinations. For all the replicates, the total recovery of near 100%, suggested no significant loss of Pb from the systems. However, although the percentages of Pb in the aerophine extracts within each set of the data were in good agreement, the difference between the average values of the two data sets were significantly beyond that which could be expected on the basis of experimental variability. This lack of reproducibility in the determinations of

Pb in the "Dilute-2" aerophine matrix (which contained about 40 times less aerophine than the "Original" solution) was also observed in the following systems: (1) a sample of a five-phase soil model with spiked calcite (37 μg Pb) (a repeat of the above experiment); (2) duplicate samples of a five-phase system with 0.05 g spiked calcite (74 μg Pb); and (3) duplicate samples of a 0.05 g individually spiked calcite (74 μg Pb). The percentages of Pb found in the aerophine extracts of these three systems also varied widely, with ranges of 36% to 92%, 33% to 65%, and 75% to 112%, respectively (*Appendix 4.1.*). Each percentage of Pb in the aerophine extracts reported here was an average of repeated determinations with and without the use of the atom-trap assembly on the FAAS.

The lack of reproducibility in the determinations of Pb in the "Dilute-2" aerophine matrix was also found in duplicate samples of a five-phase soil model with spiked calcite (37 μg Pb) and aerophine-containing standard solutions (blank and 2 ppm Pb) sent to R.J.Hill Laboratory Ltd for different methods of analysis for Pb (*Appendix 4.2.*). Intriguingly, the results from ICP-MS analysis were found to differ depending on the amount of the dilution, an effect which the analysts involved had not encountered previously (R.J. Hill Analytical Laboratory Ltd, 1995). As previously mentioned, this unusual result might be related to the effect of Aerophine (which is a surfactant) on the surface tension of the solution, which would have the consequence of modifying the formation of droplets in the nebuliser. It might also be possible that some components of the synthetic soils combined with Aerophine to produce a significant difference between the matrix of the standards and extracts. In contrast to ICP-MS, analysis at the external laboratory by GFAAS (which is independent of the nebuliser) resulted in detection of no Pb in any of the samples, despite the fact that the 2 ppm standard was over 100 times higher than the instrument's normal working range. In this case, it is possible that the total suppression of the GFAAS signals might due to a loss through volatilization of the Pb-aerophine complex during the GFAAS ashing step and prior to atomization.

In summary, Aerophine may be a potentially useful ligand for inhibiting redistribution; but its solutions are subject to unusual analytical interferences which make it difficult to accurately determine the concentration of Pb. These were observed during many attempts at the University laboratory and also when sent for analysis at an independent external laboratory. During method development, this problem could be circumvented by direct analysis of Pb left on the solid phases, but this option would not be available during a normal sequential extraction. Although the use of Aerophine revealed some promising results and the high variation in the determination of Pb in the aerophine matrix might be resolvable (e.g., a method which allows a complete destruction of Pb-aerophine complex without loss may be possible), a considerable time might be needed for resolving the analytical problem and this was not considered justifiable at this stage in the research, given that other ligands were available but untested. Work involving the aerophine was therefore discontinued at this point.

(It should be noted in closing that two obvious options for destroying the aerophine prior to analysis are oxidation with a strong acid system, or dry ashing. The former was shown to result in an unexpected side reaction. GFAAS results suggest that the latter method would simply result in loss of the Pb-aerophine complex.)

4.2.2. Trials of the soluble ligand 18-Crown-6.

In Table 4.9. is shown the percentages of Pb recovered from a two-phase system comprising spiked calcite and clean humic acid using different concentrations of the ligand 18-crown-6 and a range of extraction times. In all cases, the percentages of Pb reported here were an average of several determinations.

Over the extraction time of 1/2 h, an increasing ligand concentration seemed to result in more retention of Pb in the solution, and this was particularly apparent in comparing the cases of the 9×10^{-6} vs 9×10^{-2} M solutions (12% recovery vs 50%). However, over the longer extraction times of 5 and 16 h, increasing the ligand concentration did not seem to improve the recovery of Pb in the solution. At the concentrations of 9×10^{-6} and 9×10^{-5} M, an increase in the extraction time from 1/2 h to 5 and 16 h did not seem to affect the recovery of Pb in the solutions, whereas at a more concentrated solution of 9×10^{-3} M, an increasing extraction time resulted in a reduction in recoveries of Pb. These results suggest that the more concentrated crown-ether solution and the shorter (1/2 h) extraction time would best favour retention of Pb in the solution (i.e., reducing Pb redistribution to the humic acid in the two-phase systems tested). However, solutions of the crown-ether more concentrated than 9×10^{-2} M were not investigated. This was based on the observation that increasing the ligand concentration by 10^4 times (from 9×10^{-6} to 9×10^{-2} M) could only improve the percentage of Pb recovery in the solution by about 4 times. Moreover, in the preparation of a crown-ether solution more concentrated than 9×10^{-2} M would require large amount of the ligand, which was not feasible due to its high cost (Table 4.9). In addition, as a practical matter, during a preparation of the 9×10^{-2} M solution, a fairly large amount of the crown ligand was required, and some difficulty was experienced in getting this to dissolve in the 0.11 M acetic acid (therefore, it was speculated that it would be even more difficult to dissolve a larger amount).

Most of the total percentage recoveries of Pb (i.e., range: 73 - 97% with a mean of 82%) reported here, although not particularly poor, were nevertheless lower than the majority of those normally obtained from the systems subjected to a single-step extraction. It was thought possible that the absorbance signal of Pb might be suppressed by a high concentration of Ca (from completely dissolved calcite) and/ or a significant loss of solid was occurring during the washing at the end of the extraction step.

Table 4.9. Percentages of Pb recovered from a two-phase system comprising spiked calcite and clean humic acid (37 μg Pb), in "modified" extraction solutions containing the ligand 18-Crown-6.

Concentrations of 18-Crown-6 (M) in 0.11 M acetic acid	Percentages of Pb recovered in the solution			Percentages of Pb recovered from the remaining humic acid			Total percentages of Pb recovery		
	Extraction times			Extraction times			Extraction times		
	1/2 h	5 h	16 h	1/2 h	5 h	16 h	1/2 h	5 h	16 h
9×10^{-6}	12	6	8	68	74	72	80	80	80
9×10^{-5}	10	6	5	71	67	70	81	73	75
9×10^{-3}	34	12	8	63	75	76	97	87	84
9×10^{-2}	50	-	-	-	-	-	-	-	-

Note: Total contact time = Extraction time + centrifugation time of 1/2 h (@12 000 rpm)
In all cases, various extraction conditions assessed completely dissolved the calcite.

However, the FAAS determination of Pb in a "simulated-extract" sample containing a high concentration of Ca in the 9 × 10^{-5} M crown matrix with a final Pb concentration of 0.500 ppm, against the standard solutions prepared in the same matrix but containing no Ca, resulted in an average Pb concentration (from a few determinations) of 0.498 ppm. This suggested that the high concentration of Ca did not significantly reduce the absorbance signal of Pb in the crown matrix. In addition, all wash water samples (~ 8 - 10 ml), collected at the end of the extraction of the two-phase system using 9 × 10^{-3} M solutions, were found to contain no detectable Pb. Since the handling of all the systems tested here was consistent, therefore, it was believed that loss of solid materials (i.e., humic acid particles) through the washing was not a significant factor in these slightly low recoveries observed. Although a cause(s) of the lower total recoveries of Pb was not resolved, it was decided not to investigate this issue any further, since this was not crucially relevant to a main observation that increasing the crown-ether concentration from 9 × 10^{-6} to 9 × 10^{-2} M significantly improves the percentage Pb recovery in the solution.

In Table 4.10. is presented percentages of Pb recovered from an individually-spiked humic acid system and a two-phase (spiked calcite + clean humic acid) system, in the extraction solutions containing 18-crown-6 (at concentrations of 9 × 10^{-3} to 9 × 10^{-4} M). The extraction time used in these experiments was reduced to 15 min. This brought the total contact time (extraction + centrifugation) of solid and solution to 25 min.

Table 4.10. Percentages of Pb recovered from the individually-spiked humic acid (147 μg Pb), and the two-phase system comprising spiked calcite and clean humic acid (37 μg Pb), in two "modified" extraction solutions containing 18-Crown-6 ligand, over the extraction time of 15 min.

Concentrations of 18-Crown-6 (M) in 0.11 M acetic acid	Percentages of Pb recovered from individually spiked humic acid in the extraction solution	Percentages of Pb recovered from the two-phase system in the extraction solution
9 × 10^{-4}	0	24
9 × 10^{-3}	0	46

Note: Total contact time = extraction time + centrifugation time of 10 mins (@13 000 rpm)
In all cases, the extraction conditions assessed completely dissolved the calcite.

Over the extraction time of 15 min, neither crown-ether solution (concentrations of 9 × 10^{-3} and 9 × 10^{-4} M) was capable of removing Pb from the individually-spiked humic acid. In the case of the two-phase system, the more concentrated 9 × 10^{-3} M solution was apparently able to retain more Pb in the solution (i.e., counteracting Pb redistribution onto the humic acid) than the less concentrated solution did (Table 4.10.). Over the total contact time (extraction time + centrifugation time) of 25 min, 46% of the Pb was retained in the 9 × 10^{-3} M crown solution (Table 4.10.) whereas over the longer total contact time of 1 h, less of the Pb (34%) was retained in the solution (Table 4.9.). This supports the earlier observation that in the two-phase system, decreasing the extraction time (and therefore the total contact time) would be likely to assist the retention of Pb in solution (provided that the shorter time still allowed a complete dissolution of the spiked calcite). Therefore, it was possible that over a short (15 min) extraction time, the most concentrated crown solution of 9 × 10^{-2} M tested here would be able to retain more than 50% of the Pb in solution (Table 4.9.). However, it was decided that further investigation of the 18-crown-6 ligand would be set aside in favour of the macrobicyclic crown-like ligand (cryptand 2.2.2). The potential usefulness of the crown-ether solutions over the short extraction time of 15 min is discussed in a later section, where comparison is made between the crown-ether and the cryptand (*subsection 4.2.4.* of this *Chapter*).

4.2.3. Trials of Zn dithiocarbamate in MIBK.

In Table 4.11. is shown the percentages of metals (Pb, Zn, and Fe) recovered from the three preliminary systems when utilizing the Zn-dithiocarbamate method detailed in *section 2.2.2. (c) Chapter 2*, in the absence of any synthetic solid.

In the system initially comprising only Pb in the acetic acid phase (*Expt. 1* Table 4.11.), the non-detectable Pb and the recovery of 80% Zn in the acetic acid phase suggested that Pb was completely transferred from the acetic acid layer to the MIBK phase, and that Zn was concurrently released from the $Zn(PDC)_2$ complex in the organic phase into the acid phase. In the presence of Fe (5 ppm) in the acetic acid phase (*Expt. 2* and *3* Table 4.11.), it appeared that some of the Pb (20%) was still retained in the acetic layer, but the majority (77%) was recovered by back-extraction using palladium, implying it had been transferred to the organic phase. The recovery of 115% Fe in acetic acid layer seems a little inconsistent with this result, as it might be expected that some of the Fe would have replaced some of the Pb transferring over to the organic phase. However, this might be a marginal thing, and more importantly the result suggests that for the extraction and back-extraction scheme used, Fe does not significantly interfere with the transfer of Pb from the aqueous acetic layer to the organic MIBK phase (from where it was later recovered into the aqueous palladium layer).

Percentages of Pb and Zn recovered from a two-phase solid system, comprising Pb-spiked calcite and clean humic acid (*Expt. 4*), are shown in Table 4.12.

Table 4.11. Percentages of metals (Pb, Zn , and Fe) recovered in acetic acid layer and palladium solution with the Zn pyrrolidine dithiocarbamate method, in the absence of solid phase.

Experiment number	Introduction of metals in the system			% Recovery of metals in					
				Acetic acid layer (after extraction)			Palladium aqueous layer (after back-extraction)		
	Pb	Zn	Fe	Pb	Zn	Fe	Pb	Zn	Fe
1	37 μg in acetic acid	$Zn(PDC)_2$ (a) in MIBK	-	0%	82%	-	-	-	-
2 & 3	37 μg in acetic acid	$Zn(PDC)_2$ (a) in MIBK	100 μg (b) in acetic acid	20%	115%	115%	77%	-	0%

(a) $Zn(PDC)_2$ (in MIBK) contained Zn equivalent to 195 μg (about 1 μg Zn was remaining in the aqueous APDC solution)

(b) Equivalent to 5 ppm Fe

Table 4.12. Percentages of Pb and Zn recovered from a two-phase solid system, comprising Pb-spiked calcite and clean humic acid, using the Zn pyrrolidine dithiocarbamate method.

Elements	% Recovery in			Total % recovery
	Acetic acid layer (after extraction)	Palladium aqueous layer(*) (after back-extraction)	Residual humic acid	
Pb	0%	112%	0%	112%
Zn	44%	24%	27%	95%

(*) Each percentage of Pb and Zn reported is an average of two determinations, using two sets of palladium standard solutions (with and without previous shaking with MIBK).

In this experiment, it was found that 112% of the Pb was recovered in the aqueous back-extraction solution, but none was recovered from the remaining humic acid (*Expt. 4.* Table 4.12.). This result establishes that the modified extraction scheme successfully counteracts Pb redistribution to humic acid in this system, which would otherwise be observed within a total contact time of 25 min (as evidenced in *subsection 4.2.4.*).
The mechanism by which redistribution is prevented may be through either direct exchange of solubilized lead with zinc in the $M(PDC)_2$ complex (as planned) or direct extraction of Pb from humic acid after it has been sequestered (or a combination of the two). At the time of doing this experiment, the second possibility seemed very unlikely, because the extraction system was set up in such a way as to minimize contact between the complexing agent (held in the organic phase) and the humic acid (held in the aqueous phase). However, later trials revealed that, despite these precautions being taken, the complexing agent was capable of directly extracting Pb from humic acid, a factor which would complicate interpretation in more complex systems. Whatever the precise mechanism, in this system, redistribution of Pb to humic acid was prevented. Therefore, it was decided that this modified scheme would be applied on more complex solid systems. At the same time, it was thought likely that parameters such as the total contact time and amounts of Zn and Pd required could be fine-tuned without compromising the percentage recovery of Pb in the palladium aqueous solution. Decreasing the extraction time to 15 min (with the same mode of mechanical shaking and 30 min centrifugation), still allowed complete dissolution of 0.025 g calcite, as shown in *Appendix 4.3.*

It should also be noted at this stage that the absorbance readings of Pb determined for the palladium aqueous extracts obtained from the two sets of standard solutions (prepared with and without previous contact with MIBK) were not significantly different from each other (*Appendix 4.4.*). This suggested that there was no matrix effect resulting from (possible) slight dissolution of MIBK into the aqueous palladium solution. As a consequence, at concentration ranges of 1 - 4 ppm Pb (as determined in this Expt.) in palladium extracts of subsequent trials, the background matrix of standard solutions comprised palladium chloride solution which had not been in previous contact with MIBK.

Application of the BCR extraction scheme with the above modification at the first extraction step (with 30 min extraction and 30 min centrifugation time), on a sample of five-phase model soil with spiked calcite (*Expt. 5.*), resulted in the significant Pb recovery of 77% at the modified first step, as shown in Fig. 4.2. (tabulated data is provided in *Appendix 4.5.*). This result again suggested the effectiveness of the modified extraction procedure in counteracting Pb redistribution, by whatever mechanism was in operation.

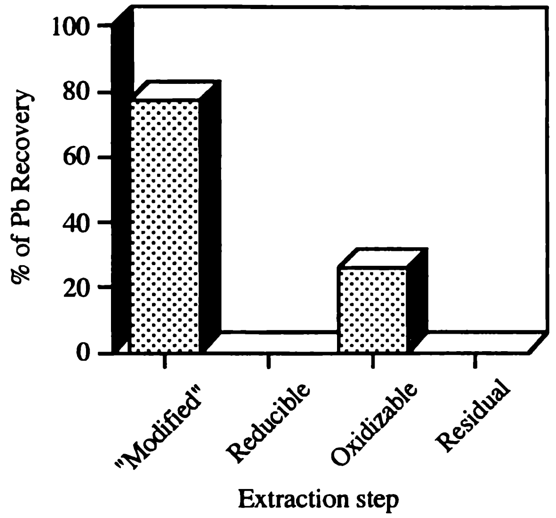


Fig. 4.2. Percentages of Pb recovered using $Zn(PDC)_2$ in MIBK from a five-phase model soil containing spiked calcite, with a 30 min extraction time at the "modified" first step.

It should be noted here that in the control system performed for the modified extraction step, to which no Pb had been added, (run concurrently with the five-phase solid system), no Pb was detected in (1) the aqueous APDC solution (used in a preparation of $Zn(PDC)_2$ (in MIBK)); (2) the remaining acetic acid (after the extraction); or (3) the palladium solution (after the back-extraction). This suggested that throughout the several handling steps of the modified first extraction step, possible contamination by Pb was not significant. It was found that a high speed centrifugation at 12 000 rpm for 30 min satisfactorily settled the solid particles from the interface region (of the MIBK and acetic acid). In addition, losses of Pb were negligible. In the five-phase system, no Pb was detected in wash-water of the remaining solid phases (at the end of the extraction step 1). This is reflected in the good overall Pb recovery of near 100% (recoveries of Zn and Fe are reported in *Appendix 4.5.*). It was also again confirmed that possible "solvent effect" of MIBK on the determination of Pb (0 - 4 ppm) in palladium aqueous solution was not significant (*Appendix 4.4.*).

In an attempt to improve the percentages of Pb recovered at the modified extraction step, the order of addition of the extraction solutions was reversed, i.e., the solution of $Zn(PDC)_2$ (in MIBK) was added into a five-phase model soil (containing spiked calcite) prior to the acetic acid (*Expt. 6*). In this case, however, it was found that none of the Pb was recovered at the modified step (via back-extraction using palladium solution), with most (90%) being recovered at the oxidation step (tabulated data of the recoveries of Pb and Zn are shown in

Appendix 4.6.). This undesirable outcome might due to a breaking down of the Zn complex on contact with the solid material. Based on this observation, in the further systems investigated, the aliquot of acetic acid solution was added into the solid systems first, and was then followed by the Zn complex (in MIBK).

The ($Zn(PDC)_2$ (in MIBK)) modified BCR scheme, with a 5 h extraction time at the first step, was next applied to a five-phase model soil containing spiked halloysite (*Expt. 7*). Surprisingly, it was found that none of the Pb was recovered in the first fraction, with the majority being recovered at the oxidation step (tabulated data are shown in *Appendix 4.7.*) (The pattern of Pb recovery was similar to that obtained from an application of the conventional BCR scheme (0.11 M acetic acid, 16 h) on the same system, where redistribution was known to be operative (illustrated in *Chapter 3* Table 3.2.). This result was not consistent with the previous finding from the application of the same modified extraction procedure on a five-phase system containing spiked calcite (Expt. 5), discussed above. On the basis of the results from the spiked-calcite experiment, it was speculated that a significant amount of Pb would be recovered at the modified step from the five-phase model soil with spiked halloysite, as Pb is released from halloysite at the first step of the conventional BCR extraction (*Chapter 3* Table 3.2.). However, there were two other differences between the experiments involving spiked calcite and spiked halloysite. Firstly, the original amount of Pb in the two systems were different, 71 μg in the cases of spiked halloysite and 37 μg for spiked calcite. Secondly, and perhaps more significantly, there was quite a difference in the time allowed for the modified extraction step (i.e., the time the solid phases were in contact with acetic acid and Zn $(PDC)_2$ in MIBK). The longer first step extraction time of 5 h used for the five-phase system with spiked halloysite was based on the efficiency with which Pb could be extracted from individually spiked-halloysite in the conventional 0.11 M acetic acid reagent at various extraction times (*Appendix 4.8.*); in particular, the percentage of Pb recovered at an extraction time of 5 h (83 % of the total 71 μg originally sorbed on the halloysite) was very close to that recovered at 16 h (86%) (therefore, the shorter extraction times of the two was selected). In the case of spiked calcite (*Expt. 5*), a shorter 30 min extraction time was sufficient to completely dissolve the calcite and release the Pb. It was, therefore, decided to further investigate the influence of the extraction time on the recovery pattern of Pb. However, prior to this, application of the modified extraction procedure on a five-phase system with spiked calcite was repeated (*Expt. 8*). The recovery pattern of Pb from the repeated trial (i.e., 82% at the modified first step, and 0%, 41%, and 0%, at the reducing, oxidizing, and acid digestion steps, respectively) was found to be in good agreement with the previous trial, using the modified scheme on the same system (*Expt. 5*). This confirmed that the different recovery patterns of Pb between the five-phase system which contained spiked calcite and the one which contained spiked halloysite, were real.

In Fig. 4.3. is shown recovery patterns of Pb from five-phase model soils containing spiked calcite with four different extraction times (with the same centrifugation time of 30 min) (*Expts. 9* to *12*) (tabulated data of Pb and Zn determinations shown in *Appendix 4.9.*).

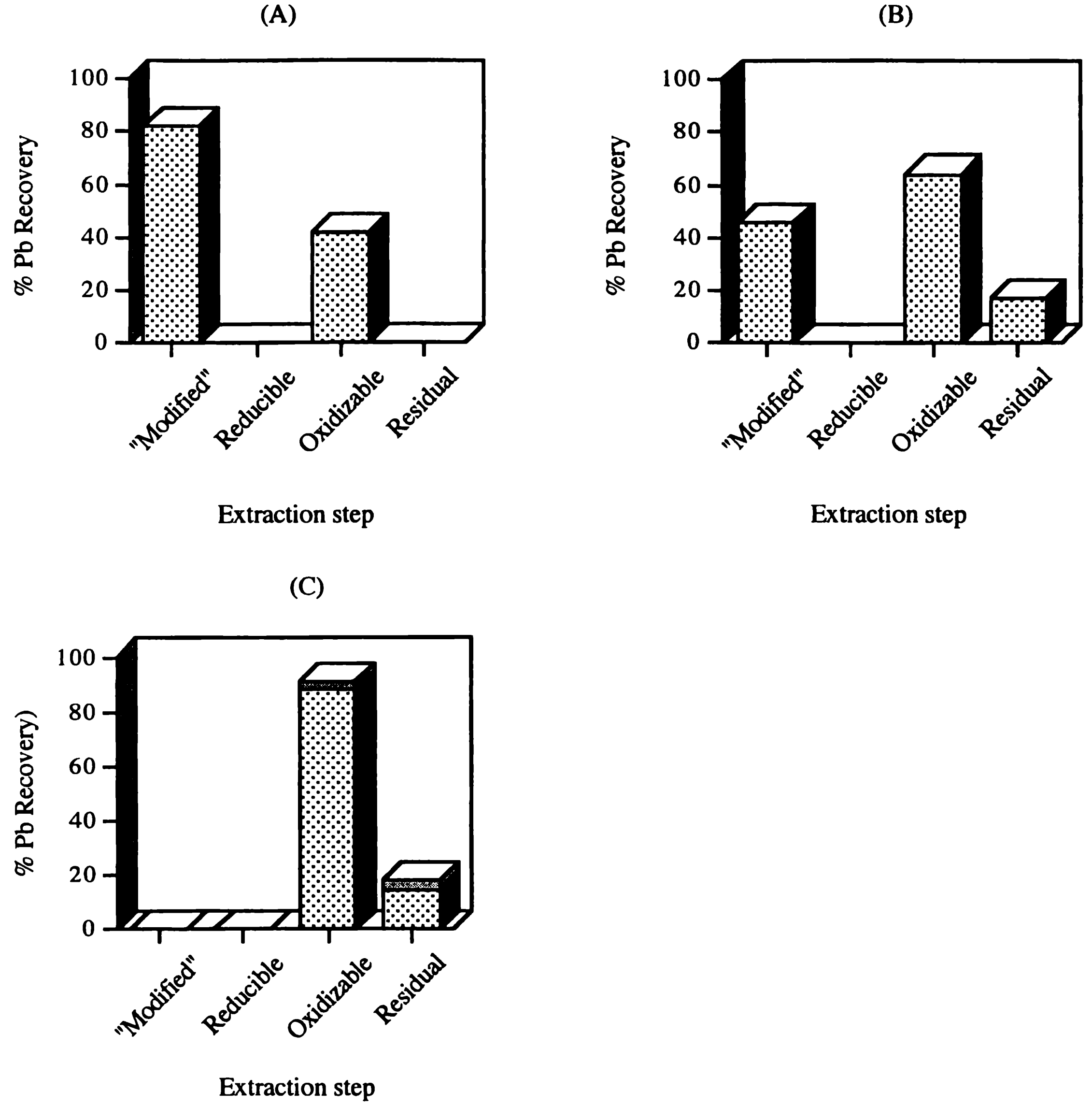


Fig. 4.3. Percentages of Pb recovered from five-phase model soils containing spiked calcite, with the $Zn(PDC)_2$ in MIBK "modified" first step, at the extraction times of (A) 15 min, (B) 45 min, and (C) 1 and 5 h.

The influence of the length of the extraction time on the recovery of Pb, at the first (modified) step is shown in Fig. 4.4. (derived from the data given in Fig. 4.3.).

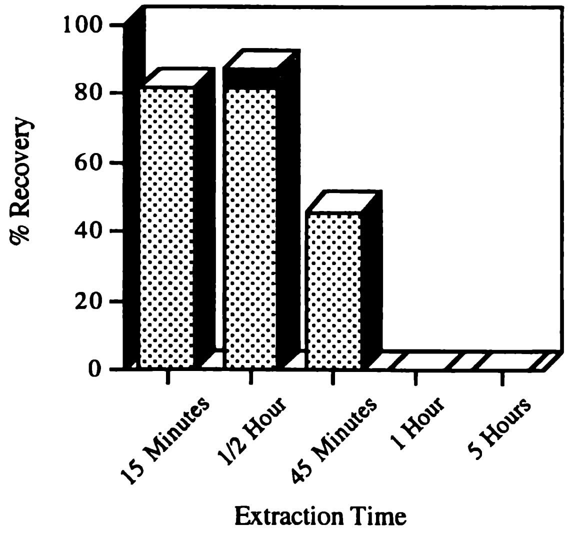


Fig. 4.4. Percentage recoveries of Pb at the first ("modified") step vs extraction time from a five-phase model soil containing spiked calcite.

(Notes: 1. Duplicates shown for 1/2 extraction time, 2. No Pb recovered at 1 and 5 h)

The results of these experiments reveal that the highest recovery of Pb occurs at the modified step with the shortest extraction time of 15 min (Fig. 4.4). The Pb recovery decreases the longer the extraction time, with none of the Pb being recovered after 1 h. It might be possible that the longer extraction times provide an opportunity for $Pb(PDC)_2$ (in MIBK) to partially decompose, releasing Pb back into the acetic acid layer (which would then reassociate with the remaining solid phases in the system, and be released at later steps in the extraction scheme when the solid phases were completely dissolved). Alternatively, Pb sequestered as $Pb(PDC)_2$ (in MIBK) may slowly "leak" back over to any more stable binding sites it encounters on humic acid as the latter bridges the interface between the aqueous and organic layers during shaking. Whatever the mechanism, the observation suggests that in the case of five-phase model soil with spiked halloysite (*Expt. 7*), a short extraction time of 15 or 30 min at the modified step might improve the Pb recovery (provided that time is sufficient to allow significant initial extraction of Pb).

The modified extraction steps with extraction times of 15 and 30 min (with the same centrifugation time of 30 min) were therefore applied on a five-phase model soil containing spiked halloysite; the recovery patterns of Pb obtained are shown in Fig. 4.5. (*Expt. 13* to *14*, tabulated data shown in *Appendix 4.10.*). It should be noted that based on extractions of individually spiked halloysite using the conventional reagent (0.11 M acetic acid), 63% and 66% of the 72 μg Pb originally sorbed on the halloysite were recovered at extraction times of 15 and 30 min, respectively (*Appendix 4.8.*).

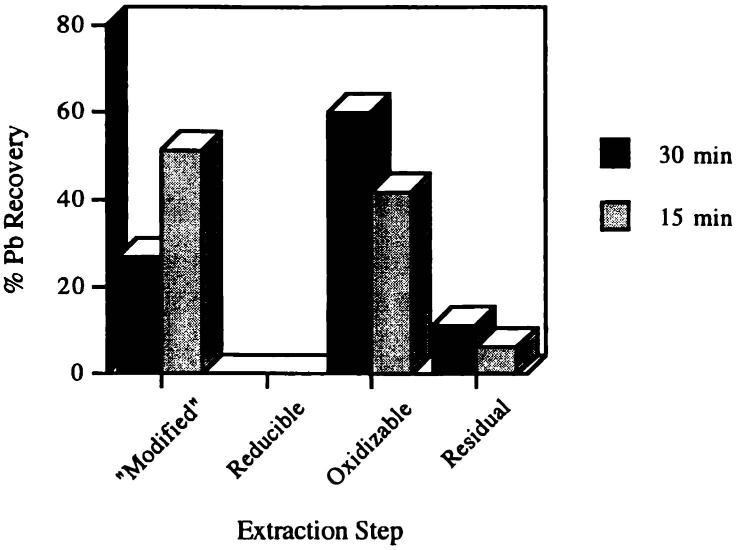


Fig. 4.5. Percentages of Pb recovered from five-phase model soils containing spiked halloysite, with the Zn(PDC)$_2$ in MIBK "modified" first step, at the extraction times of 30 and 15 min.

In Fig. 4.6. is shown the percentages of Pb recovered from the five-phase model soil containing spiked-halloysite, at three different extraction times (15 min (twice), 30 min (twice), and 5 h) of the modified step (derived from the data from *Expt. 7* and from Fig. 4.5.).

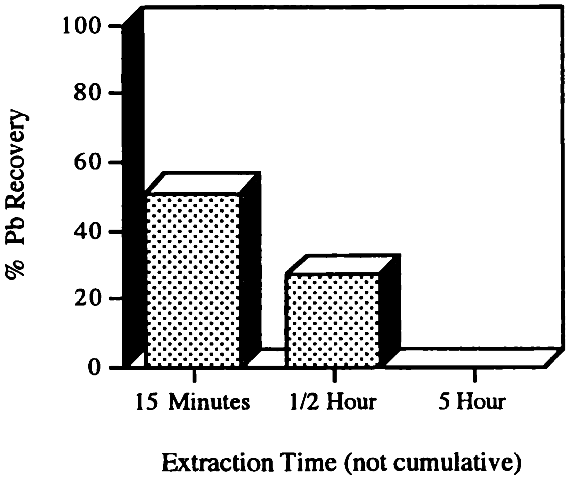


Fig. 4.6. Percentage recoveries of Pb at the modified first extraction step vs extraction times from 5-phase model soils containing spiked halloysite.

The effect of the length of the extraction time of the modified step on Pb recovery patterns in the five-phase model soils containing spiked halloysite, is readily apparent (Fig. 4.6.). About 50% of the 73 μg Pb originally sorbed on spiked halloysite, was recovered at the end of the extraction time of 15 min (and 30 min centrifugation). This 50% Pb recovery was equivalent to about 80% of the Pb (45 μg) available in the acetic acid (an estimate based on the amount known to be extractable from halloysite over 15 min) (*Appendix 4.8.*). However, the recovery of Pb was significantly decreased to about 20% at an extraction time of 30 min.

In general terms, these results are similar to those obtained from the systems containing spiked calcite (*Expts. 9* to *12*). However, in terms of their exact time-dependence, the recovery patterns at the extraction times of 15 and 30 min appear to be inconsistent with each other (Fig. 4.4. vs Fig. 4.6.). Specifically Pb from halloysite is already being lost to redistribution after 30 min, whereas Pb from calcite is not. This difference might be due in part to differences in the release-rates of Pb from the originally sorbed calcite and halloysite phases. In the system containing spiked calcite, the total Pb originally sorbed on calcite was available in the solution within a few minutes of the calcite being placed in contact with acetic acid reagent, whereas in the case of halloysite, Pb was being released from the original phase at a slower rate. If the release rate of Pb is fast, the exchange between Pb and Zn in the PDC complex (in MIBK) is likely to be completed before the concentrations of other possible competing ions, such as Fe^{2+} and Mn^{2+}, increase significantly. Fe and Mn are known to form complexes with most ligands which approach those of Pb in terms of their stability (Martell, 1964), and the differences in time-dependencies observed may provide evidence that these two metals may compete with Pb for PDC.

Based on the observation that decreasing the extraction time at the modified first extraction step increased the percentage of Pb recovered from five-phase model soil containing spiked halloysite, it was speculated that a series of successive extractions using fresh $Zn(PDC)_2$ (in MIBK), each at a short extraction time of 15 min, might improve Pb recoveries.

A modified first extraction step using 13 successive additions of fresh $Zn(PDC)_2$ (in MIBK), each lasting 15 min (with a 10 min centrifugation), was applied on a five-phase model soil containing spiked halloysite (*Expt. 15*). The recovery of Pb with each successive extract is shown in Fig. 4.7. (tabulated data are provided in *Appendix 4.11.*).

A significant amount of Pb (54%, of 73 μg Pb originally on the spiked halloysite) was recovered from the first aliquot of $Zn(PDC)_2$ (in MIBK), at the end of first 15 min extraction (and 10 min centrifugation time) (Fig. 4.7.). The sum of Pb recovered from the succeeding 8 extracts was found to be around 23% (no detectable Pb was recovered in the last 4 extracts of the successive scheme). Therefore, the total Pb recovered, at the end of the extraction time of 3 h 15 min (total contact time of 5 h 25 min), was found to be 77% (56 μg Pb). This was equivalent to about 90% of the Pb released from spiked halloysite into the acetic acid reagent at approximately the same extraction time (*Appendix 4.8.*). After subjecting the residue to the subsequent BCR steps, it was found that none of the Pb was recovered at the conventional reducing step, and only about 10% and 3% (of the total 73 μg) was recovered at the oxidizing, and acid digestion steps, respectively. This suggested that the modified first extraction step using the successive addition of fresh $Zn(PDC)_2$ (in MIBK) at short time-intervals of 15 min, could effectively counteract the Pb redistribution which would otherwise be observed in the five-phase model soil containing spiked halloysite (none of the Pb was recovered at the conventional acetic acid (with 15 min extraction and 10 min centrifugation) and reduction steps, 68% and 18% were recovered at oxidation, and acid digestion steps, respectively).

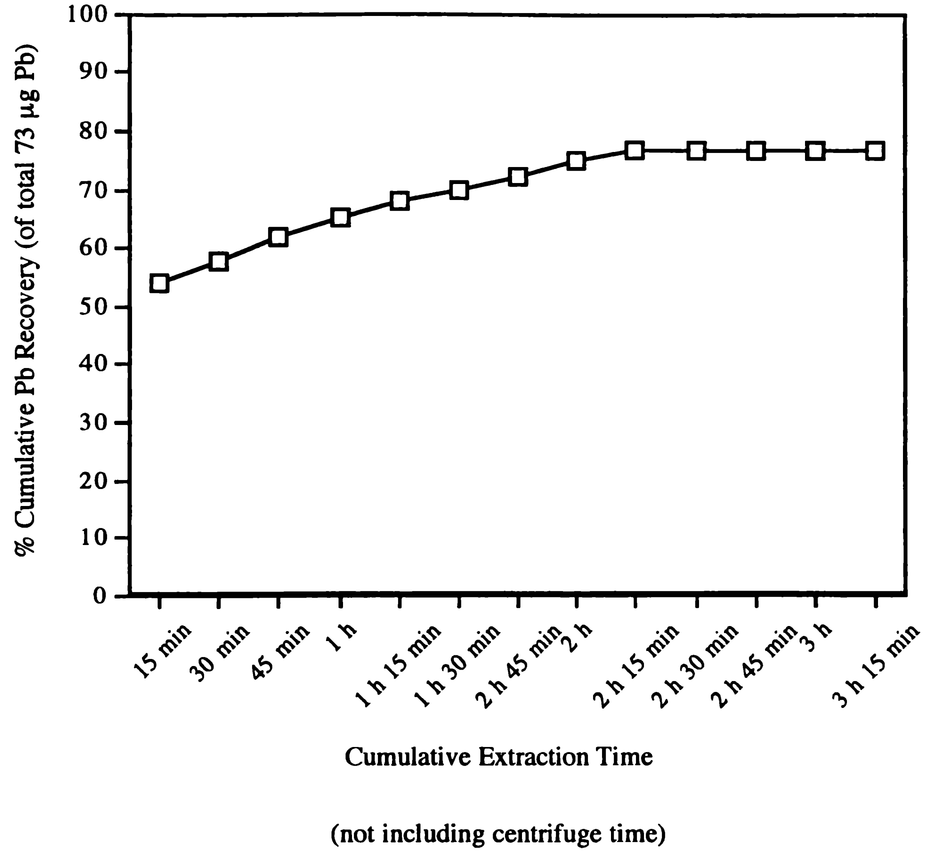


Fig. 4.7. Percentage cumulative recovery of Pb using successive $Zn(PDC)_2$ extractions from a five-phase system containing spiked halloysite.

The successive extraction scheme was then applied on a mixture of Te Rapa soil with spiked halloysite (*Expt. 16*). In this case the recovery pattern of Pb at the modified successive extraction scheme was found to be similar to that illustrated in Fig. 4.7. Most of the Pb (64%, of the total 144 μg, in the system) was recovered from the first aliquot of $Zn(PDC)_2$ (in MIBK), at the end of first 15 min extraction (and 10 min centrifugation time). The sum of Pb from the subsequent 6 extracts was found to be around 20% (an insignificant amount of Pb was recovered in the last 6 extracts of the successive scheme) (tabulated data for this experiment are shown in *Appendix 4.12.(a)*). Therefore, the total Pb recovered during the modified step was about 85% (122 μg Pb), at the end of the extraction time of 3 h 15 min (total contact time of 5 h 25 min). It should be noted here that Pb in the first two aqueous extracts (back-extracted from $Zn(PDC)_2$ (in MIBK)) was determined against two sets of standard solutions (i.e., the matrix of the standards were prepared with and without previous contact with MIBK). The results (2 - 8 ppm range) were found to be in agreement (i.e., there was no significant "solvent effect" in the Pb determination) (*Appendix 4.12.(b)*). It was found that none of the Pb was recovered at the conventional reducing step, and only about 6%

and 3% (of the total 144 μg) was recovered at the subsequent oxidizing, and acid digestion steps (*Appendix 4.12.(a)*). In this system, therefore, the modified extraction scheme, involving successive additions of $Zn(PDC)_2$ (in MIBK) at the first step, was successful in counteracting Pb redistribution.

The successive extraction scheme was further applied on a mixture of Te Rapa soil with spiked calcite (*Expt. 17*). Here it was found that almost all of the Pb (99%, of the total 151 μg in the system) was recovered from the first aliquot of $Zn(PDC)_2$ (in MIBK)), at the end of first 15 min extraction (and 10 min centrifugation time). A few percentages of Pb were recovered from the second to fourth aliquots from the organic phase, and no Pb was recovered at the subsequent unmodified extract steps of the BCR scheme (tabulated data are shown in *Appendix 4.13.*).

At this stage it was considered appropriate to apply the modified successive extraction scheme on a contaminated natural soil. A street dust sample was, therefore, subjected to the successive extraction (*Expt. 18*). During the successive extraction, a strong dark colour was observed in the organic extracts. A significant amount of Pb (26%) (of the total 229 μg Pb retained on the dust sample (as determined using aqua regia)) was recovered from the first aliquot of $Zn(PDC)_2$ (in MIBK)). The sum of Pb recovered from the first five aliquots of the organic phase was found to be 40%, at the end of the total extraction time of 1 h 30 min (total contact time of 2 h 30 min). These results can be compared with those based on the preliminary tests on the dust, where only about 10% (of the total 229 μg Pb) was recovered in aliquots of the conventional 0.11 M acetic acid reagent, at various extraction times of 15 min, 1 h, 5 h, and 16 h (in all cases, the centrifugation time was 10 min); and where all the acetic extracts were also clear and colourless. The percentage of Pb recovered by the use of the modified first extraction step was therefore much higher than that recovered by the use of conventional first extraction reagent (40% vs 10%). However, in this case, the original phase associations of the Pb were unknown (as the experiment involved an entirely natural system). This complicates the interpretation of the result, which could be due to (a) the successful inhibition of redistribution, as seen previously, and/ or (b) direct extraction of Pb by the $Zn(PDC)_2$ (in MIBK) from another solid phase present in the sample. The second possibility was initially thought unlikely, because the system was set up in such a way as to minimize contact between the ligand and the solid phases. However, observation that a strong dark-colour developed in the organic phase during extraction of the natural dust sample suggested that the ligand might be capable of direct extraction of Pb from solid components.

In order to assess the possibility that Pb might be directly desorbed from solid particles by the complexing agent in the organic phase, samples of individually spiked phases (humic acid (147 μg Pb); and hausmannite, and goethite (93 μg Pb each) were subjected to the modified extraction procedure, using the extraction time of 15 min (total contact time of 25 min) (*Expts. 19* to *21*). In Table 4.13. are listed the percentages of Pb recovered from these individually spiked phase systems.

Table 4.13. Percentages of Pb recovered from individually spiked phases, using the $Zn(PDC)_2$ in MIBK modified extraction procedure, with 15 min extraction time (and 10 min centriguation time)

Individually spiked phases		Percentage recoveries of Pb in		Total percentage Pb recoveries
	Acetic acid layer	Back-extraction solution	Residual solids	
humic acid*	0%	77%	42%	119%
hausmannite	0%	8%	93%	101%
goethite	0%	26%	68%	94%

* At the extraction time of 5 h (and 10 min centrifugation time), none of Pb was recovered in acetic acid layer and in back-extraction solution, but 92% was recovered from the remaining humic acid.

In the case of individually-spiked humic acid, a significant percentage of Pb (77%) was recovered from the organic phase, and only 42% of the Pb was retained on the remaining humic acid at the end of the extraction time of 15 min (Table 4.13.), suggesting that Pb was significantly directly desorbed from humic acid by $Zn(PDC)_2$ (by comparison, none of the Pb was recovered from individually spiked humic acid, using the conventional first extraction reagent, 0.11 M acetic acid, at the end of the extraction time of 15 min (also shown in Table 4.17. of the subsequent *subsection 4.2.4.* on cryptand) or 16 h (*Chapter 3* Table 3.2.) (However, the observation that at the extraction time of 5 h, 92% of Pb was recovered from the remaining humic acid seemed difficult to explain. A possibility which might account for this is that Pb may have been desorbed from "weak" sites on humic acid and transferred to the organic phase to form $Pb(PDC)_2$), which was then broken-down with time or simply exchanged upon encountering "stronger" sites on humic acid, as previously observed.)

In the case of individually-spiked hausmannite, the majority of Pb remained on the residual hausmannite, suggesting that the organic phase did not significantly directly desorb Pb from the hausmannite particles (none of the Pb was recovered from individually-spiked hausmannite, using the conventional first reagent, at the end of the extraction time of 15 min (shown in Table 4.17. of the subsequent *subsection 4.2.4.* on cryptand) or 16 h (*Chapter 3* Table 3.2.). In the case of individually spiked goethite, about 30% of the Pb was recovered from the organic phase, and most of the Pb (about 70%) remained on the residual solid, results which were in agreement with those obtained from spiked goethite, subjected to a conventional reagent for 15 min (Table 4.17.). This suggested that the $Zn(PDC)_2$ in MIBK phase did not significantly remove Pb from spiked goethite.

Based on the finding that notable amount of Pb originally retained on humic acid was removed by the use of the modified extraction procedure, involving a 15 min extraction using the complexing agent introduced via an organic phase (Table 4.13.), it is quite possible that the significant recoveries of Pb at the modified extraction step, previously observed from the multi-phase model soils (containing either spiked calcite or halloysite) and contaminated dust samples, could partly result from direct desorption of Pb from the non-target humic acid phase. In the case of the multi-phase model soils, some Pb released from the original solid phase during the 15 min extraction time, may have been sequestered by the solid phase (i.e., humic acid), while other Pb simultaneously migrated into the organic layer (in exchange with Zn); and the above finding (from the extraction of individually spiked humic acid) suggests that any Pb being sequestered by the humic acid could be subsequently removed by the ligand in the organic layer (over a 15 min extraction time). This possibility is not a desired phenomena, since the aim of the modified procedure was to complex only the Pb released from the originally-spiked phase by 0.11 M acetic acid, and thereby inhibit the liberated Pb from being readsorbed onto remaining solid phase(s) in the system. The capacity of $Zn(PDC)_2$ in MIBK to act as an efficient extractant in its own right (in the case of Pb bound to humic acid) would complicate the interpretation of any such extraction applied to a natural systems as there would be uncertainty as to whether the liberated Pb originated on an "early" phase or with the organic components. Although further refinements to the method could possibly yield more unequivocal results, it was decided not to investigate this possibility at this stage, but set it aside in favour of testing a macrobicyclic crown-like ligand (cryptand 2.2.2).

In a preliminary assessment of the stability of $Pb(PDC)_2$ (in MIBK), it was found that at extraction times of 15 min, 45 min, 1.5 h, and 5 h (in all cases the centrifugation time was 10 min) all of the Pb was recovered from the MIBK phase from the system comprising spiked calcite, acetic acid and $Zn(PDC)_2$ (in MIBK) (*Expt. 22*), as shown in Table 4.14.

Table 4.14. Percentages of Pb recovered from the system containing spiked calcite, acetic acid, and $Zn(PDC)_2$ (in MIBK), at different extraction times.

Extraction times	Percentages of Pb recovered in		Total percentage recoveries of Pb
	Acetic acid	Back-extraction solution	
15 min	0%	96%	96%
45 min	0%	98%	98%
1.5 h	0%	100%	100%
5 h	0%	101%	101%

From these results, it appears that increasing extraction time alone does not reduce the percentage recovery of Pb (in back-extracted solution). At first glance, this seems inconsistent with the observation from five-phase model soils, comprising either spiked calcite or spiked halloysite (Figs. 4.4. and 4.6.) that the recovery of Pb from the organic phase decreased as extraction time increased. The difference in the patterns of Pb recoveries, however, suggests that the presence of solid phase is a necessary precondition to loss of Pb from the complex. A solid phase might in some way induce breakdown of the Pb complex in the organic layer or may simply act to sequester Pb from the complex as high-energy sites are presented at the aqueous/ organic boundary. However, contradictory results were obtained from a system containing only 37 μl stock Pb of 1000 ppm, acetic acid, and $Zn(PDC)_2$ (in MIBK) (*Expt. 23*), where percentages of Pb recovered from the organic phase were found to decrease as the extraction time increased, as shown in Table 4.15.

Table 4.15. Percentages of Pb recovered from the system containing Pb solution, acetic acid, and $Zn(PDC)_2$ (in MIBK), at different extraction times.

Extraction times	Percentage of Pb recovered in		Total percentage recoveries of Pb
	Acetic acid	Back-extraction solution	
15 min	0%	79%	79%
45 min	0%	79%	79%
1.5 h	11%	77%	88%
5 h	63%	20%	83%

The difference between the two sets of results (Table 4.14. vs Table 4.15.) is not easy to explain, given the similarity conditions and the systems may warrant further investigation at a future date. It might be possible that the inconsistency of the Pb recovery patterns of the two systems is due to the slight difference in pH of the systems (the presence of calcite in the *Expt. 22* system caused a slightly higher pH than that of the system in *Expt. 23*, (pH 4.47 vs 3)).

In summary, the use of $Zn(PDC)_2$ (introduced via MIBK) to counteract Pb redistribution otherwise observed in five-phase solid systems, containing either spiked calcite or halloysite, was not regarded as successful. This is not because redistribution was not counteracted in the model systems (it was) but because the mechanism by which this inhibition occurred in the models may have included a component of direct extraction by the complexing ligand.
This would complicate interpretation of results in natural systems, where the reagent would concurrently sequester dissolved Pb while directly extracting Pb from humic components.
It therefore appeared that the selectivity of the reagent was poor, i.e., a significant amount of Pb originally retained on humic acid was removed. Although it might be possible that the approach might be useful for systems containing no humic acid, it should be borne in mind that the modified extraction procedure was also tedious and not practical for handling more than 1 or 2 samples at a time. However, the results from this investigation suggested that Pb originally in aqueous solution of pH around 4 containing high concentration of Fe, could be recovered using an excess amount of a complexing agent in the form of $Zn(PDC)_2$.

Parameters possibly affecting the stability of $Pb(PDC)_2$ (in MIBK) include extraction time (or total contact time) and the presence of other solid phases. Another factor which influences extraction efficiency is the rate at which Pb is initially released from the solid phase involved.

4.2.4. Trials of cryptand 2.2.2 and NTA.

Results of trials of cryptand 2.2.2 and NTA are concurrently discussed in this section. In all cases, either when using only 0.11 M acetic acid as the first extractant, or when using the modified extractants containing cryptand or NTA, the total length of contact time of 25 min (extraction time of 15 min plus centrifugation time of 10 min) was proven to be sufficient for complete liberation of Pb from calcite (i.e., all 0.025 g calcite was completely dissolved, as shown in *subsection 4.2.4. (b)*). The decision to decrease the contact time to 25 min was also based on the earlier results that in the case of two-phase system comprising spiked calcite and humic acid, the percentage of Pb recovered by a mixed solution of 0.11 M acetic acid and 18-crown-6 (a macrocyclic ligand) notably decreases with time (Table 4.9. *subsection 4.2.2.*), and that in the case of Pb initially available in 0.11 M acetic acid, a majority of the Pb was scavenged by humic acid within a contact-time of only 10 min (*section 4.3.*). Thus, in the absence of a soluble ligand, opportunity for substantial Pb readsorption is afforded within even the shortened time-scale of 25 min. An additional reason for favouring short contact-times is that initial adsorption of Pb by humic acid may be predominantly to low-energy sites, and thus, more reversible in nature than would be the case when Pb has been allowed to properly equilibrate with all available sites on the humic phase. The modified contact-time is therefore considered sufficient to enable complete release of Pb from calcite while at the same time minimize irreversible readsorption of Pb onto a major sequestering solid phase.

4.2.4. (a) Determination of suitable concentrations of the complexing agents.

In Table 4.16. is shown percentages of Pb recovered from individually spiked humic acid and a two-phase model soil, comprising spiked calcite and clean humic acid, by solutions of cryptand and NTA.

Within this concentration range, cryptand 2.2.2 did not remove Pb originally retained on humic acid. By contrast, although low concentrations of NTA did not remove the Pb, higher concentrations extracted increasing amounts. At a concentration of 9×10^{-3} M, NTA extracted about 50% of the Pb. For the two-phase system, the higher the concentrations of the complexing agents, the more Pb was recovered, with NTA being more effective at retaining Pb than the cryptand at a given concentration.

Table 4.16. Percentages of Pb recovered from individually spiked humic acid (147 μg Pb) and a two-phase model soil comprising spiked calcite (37 μg Pb) and clean humic acid by solutions of complexing agents in 0.11 M acetic acid.

Concentration of a complexing agent (M) in 0.11M acetic acid	Percentages of Pb recovery of spiked humic acid		Percentages of Pb recovery of the two-phase system	
	Cryptand 222	NTA	Cryptand 222	NTA
9.0×10^{-3}	0	47	62	110
9.0×10^{-4}	0	7	12	85
5.0×10^{-4}	-	3	-	76
2.4×10^{-4}	-	2	-	65
1.6×10^{-4}	-	2	-	54
1.0×10^{-4}	-	0	-	42
9.0×10^{-6}	0	-	0	-

Note: Some values represented the means of two determinations.

Once again, a suitable concentration of a complexing agent is considered to be the lowest concentration, in the conventional 0.11 M acetic acid, that substantially retains Pb in the solution, and as a consequence, prevents readsorption of the Pb onto the two main scavenging phases (humic acid and hausmannite). In addition, at this concentration, the ligand should not be good at directly removing Pb originally bound on the non-target solid phases.

At the concentrations of 9×10^{-4} and 9×10^{-3} M, cryptand did not extract Pb from individually spiked humic acid, but also enabled retention of about 12% and 60% of the Pb in the solution of the two-phase systems, comprising spiked calcite and humic acid (Table 4.16.). It may be the case that at concentrations of higher than 9×10^{-3} M, cryptand may retain more than 60% of the Pb in the solution of the two-phase systems, without significantly removing Pb from the individually spiked humic acid. However, due to the high cost of the cryptand ligand and the significant percentage of Pb recovery (60%) from the two-phase system, cryptand at the concentration of 9×10^{-3} M was considered suitable for assessing its usefulness in preventing the Pb redistribution in the more complex multi-phase model soils.

At the concentration of 1×10^{-4} M, NTA removed none of the Pb from the individually spiked humic acid, and enabled retention of 40% of the Pb from the two-phase system (Table 4.16.). At concentrations of higher than 1×10^{-4} M, NTA appears to directly remove Pb from the spiked humic acid, it was decided that NTA at a concentration of 1×10^{-4} M would be used for further investigation on its potential effectiveness.

At the concentration of 9×10^{-3} M, NTA removed about 50% of the Pb from the individually spiked humic acid, whereas cryptand did not extract Pb from the solid phase. This suggests an effect of the structural difference between cryptand and NTA, considering that the complexing stability constant of cryptand for Pb (in the range of $10^{12.0}$ - $10^{12.7}$) is only slightly higher than that of NTA ($10^{11.34}$ - $10^{11.39}$) (Martell and Smith, 1974a,b; Handcock, 1992). It is probable that the bulky structure and semi-internal binding sites of cryptand could sterically hinder it from extracting Pb directly from the solid phase.

In the two-phase systems, at the concentrations of 9×10^{-4} and 9×10^{-3} M, NTA retained significantly more of the Pb in the solution than cryptand did. This might be attributable to the greater number of potential binding sites on NTA than on cryptand.

The influence of the complex stability constants over the recovery of Pb from individually spiked humic acid and the two-phase systems, containing spiked calcite and humic acid, is demonstrated by comparison with the results from the previous test on 18-crown-6, a macrocyclic ligand with semi-internal binding sites (*subsection 4.2.2.*). Using the same solid phases with identical extraction and centrifugation times, it was found that the crown ligand at the concentration of 9×10^{-3} M, in 0.11 M acetic acid, did not remove Pb from individually spiked humic acid but recovered 46% of the Pb from the two-phase system. The fact that 18-crown-6 has the lowest stability constant for Pb ($10^{4.27}$) of the three complexing agents (Izatt et al., 1976), corresponds to the experimental observation that it recovers less Pb than the other ligands.

It should be noted here that the ratios of the solid phases used in this section of the study (0.025 g spiked calcite, and 0.1 g clean or spiked humic acid) and the volumes of the modified extraction solutions (20 ml cryptand or NTA) corresponded to those used in more complex multi-phase systems. As a consequence, the amount of Pb in the system containing the spiked humic acid (147 μg Pb) is higher than that in the model comprising spiked calcite and humic acid (37 μg Pb). However, these differences are not significant in terms of the choice of suitable concentrations of both complexing agents, as this choice was based on the absolute amount (μg) of Pb available in solution.

4.2.4. (b) Investigation of the potential usefulness of cryptand (9×10^{-3} M) and NTA (1×10^{-4} M) in preventing Pb redistribution

In Table 4.17., is shown % of Pb recovered from the individually spiked phases, by the conventional and the modified BCR procedure (using the cryptand and NTA).

For the modified extraction time of 15 min and centrifugation time of 10 min, all the Pb was recovered from the individually spiked calcite by both the conventional 0.11 M acetic acid and the modified extraction solutions (9×10^{-3} M cryptand and 1×10^{-4} M NTA) (Table 4.17.). In the case of individually spiked halloysite, the addition of each ligand resulted in more Pb being extracted and this result suggests that cryptand and NTA are still capable of acting as mild extractants in their own right for an "exchangeable" fraction of Pb retained on the clay mineral halloysite. It is also possible that the lowering of the free Pb concentration in solution caused by complexation may have induced more Pb to desorb from the surface. In the case of individually spiked goethite, about 40% of the Pb was recovered by both conventional 0.11 M acetic and cryptand. This suggests that the remaining Pb might be strongly bound on goethite. However, the Pb recovery of about 25% in the NTA solution from the same system is not expected, as it indicates that acetic acid + NTA is a worse extraction system than acetic acid by itself. This result remained unaccounted for. For the individually spiked hausmannite and humic acid, none of the Pb was recovered at the step 1 of the extraction scheme; this Pb was recovered later when the solid phases were completely dissolved at reducing and oxidizing steps, respectively. This indicates that at the concentrations used, the cryptand and NTA did not act as extractants for the Pb originally retained on hausmannite and humic acid.

In Table 4.18., is shown percentages of Pb recovered from the multi-phase model soils, containing spiked calcite.

In the case of the two-phase systems comprising spiked calcite and goethite/ halloysite, the full recoveries of Pb by 0.11 M acetic acid (Table 4.18.) are consistent with the earlier finding that goethite and halloysite are not the major sequestering solid phases in multi-phase model soils (*Chapter 3*) (the recovery of all the Pb by cryptand and NTA, therefore, can not be taken to suggest the effectiveness of the complexing agents in counteracting the Pb readsorption).

In the case of two-phase systems comprising spiked calcite and humic acid/ hausmannite, the retention only 0 - 10% Pb in the 0.11 M acetic acid solution confirms the dominant sequestering roles of the humic acid and hausmannite for Pb (*Table 4.18.*). In these cases, the addition of each of the complexing agents resulted in significant increases in the percentage of Pb recovered at the first step. In the system comprising spiked calcite and humic acid, about 60% and 40% of the Pb was recovered in the cryptand and NTA solutions, respectively. For the systems containing spiked calcite and hausmannite, about 30% of the Pb was retained by both cryptand and NTA. These results revealed that cryptand (9×10^{-3} M) and NTA (1×10^{-4}M) are indeed capable of counteracting readsorption of Pb onto the humic acid and hausmannite, the major scavenging solid phases in the model systems.

Table 4.17. Percentages of Pb recovered from individually spiked phases, using 0.11 M acetic acid, and solutions of complexing agents in 0.11M acetic acid.

Individually spiked phases	Step 1			Step 2: 0.1M $NH_2OH.HCl$			Step3:H_2O_2			Step 4 : aqua regia			Total % Recovery		
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
Calcite	109	106	113	-	-	-	-	-	-	-	-	-	109	106	113
Halloysite	57	106	68	-	-	-	-	-	-	36	5	28	93	111	96
Goethite	42	42	25	-	-	-	-	-	-	68	58	78	110	100	103
Hausmannite	0	0	0	105	95	100	-	-	-	-	-	-	105	95	100
Humic acid	0	0	0	-	-	-	92	91	103	-	-	-	92	91	103

Note: The complexing agents are added at step 1 only. (A) 0.11 M acetic acid, (B) 9×10^{-3} M cryptand in 0.11 M acetic acid, (C) 1×10^{-4} M NTA in 0.11 M acetic acid. Percentages of Pb recovery shown are relative to those originally on individually spiked phases.

Table 4.18. Percentages of Pb recovered from multiphase-phase model soils, with spiked calcite, using 0.11 M acetic acid, and solutions of complexing agents in 0.11M acetic acid.

Systems tested	Step 1			Step 2: 0.1M $NH_2OH.HCl$			Step3:H_2O_2			Step 4 : aqua regia			Total % Pb Recovery		
	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)	(A)	(B)	(C)
spiked calcite + humic acid	8	62	42	-	-	-	80	37	54	-	-	-	88	99	99
spiked calcite + goethite	110	107	105	-	-	-	-	-	-	0	0	9	110	107	114
spiked calcite + hausmannite	0	33	27	108	80	93	-	-	-	-	-	-	108	113	120
spiked calcite + halloysite	107	101	112	-	-	-	-	-	-	12	0	0	119	101	112
spiked calcite + humic + hausmannite	0	16	6	0	17	0	104	77	97	-	-	-	104	110	103
spiked calcite + humic + goethite	10	72	27	14	7	25	85	35	65	10	0	0	119	114	117
spiked calcite +humic + hausmannite + goethite	0	25	0	0	12	8	89	62	89	20	10	16	109	109	113
five- phase system (spiked calcite)	0	20	0	0	14	0	92	67	86	21	11	16	113	112	102

Note: The complexing agents are added at step 1 only. (A) 0.11 M acetic acid, (B) 9 ×10^{-3} M cryptand in 0.11 M acetic acid, (C) 1 × 10^{-4} M NTA in 0.11 M acetic acid.
Percentages of Pb recovery shown are relative to that of originally on spiked calcite.

By comparing the difference between the percentages of Pb recovered from the two-phase systems containing spiked calcite and humic acid/ hausmannite (Table 4.18.), it is apparent that in the presence of hausmannite, the complexing agents are less effective at retaining the Pb in the solution. This implies that hausmannite is better than humic acid at competing for the Pb with the soluble ligands.

In the presence of both hausmannite and humic acid in the three-/ four-/ and five-phase systems, irrespective of the presence or absence of goethite and halloysite, the percentage of Pb recoveries at the first step were depressed to about 20% in the cryptand solution, and almost none in the NTA solution (Table 4.18.). This suggests that at the concentrations used, the coexistence of humic acid and hausmannite are limiting factors in counteracting Pb readsorption in multi-phase model soils.

Regarding the degree of reproducibility in the results obtainable from these model systems, the numbers of replicate experiments carried out in this section of the study were less than those in the previous section assessing redistribution itself (*Chapter 3*). This is because cryptand 2.2.2 is relatively expensive. However, in most cases the data show good internal consistency by describing various trends, and the (good) overall percentage recoveries act as a further internal check that all the Pb added could be accounted for. In cases where replicate experiments were carried out (such as extraction of the 5-phase system with spiked calcite), recovery patterns were found to be in good agreement with previous results.

4.2.4. (c) Limitation of the effectiveness of the complexing agents in counteracting Pb readsorption in the five-phase soil models (spiked calcite).

As an alternative to increasing the concentrations of cryptand and NTA (in the conventional 0.11 M acetic acid), which would present a higher risk of directly desorbing Pb from a non-target phase, it was decided to adjust the percentages of hausmannite and humic acid present in the five-phase systems to assess the limitation of cryptand (9×10^{-3} M) and NTA (1×10^{-4} M) in counteracting Pb redistribution in the five-phase soil models.

Percentages of Pb recovered, at step 1 of the extraction scheme, from five-phase model soils containing spiked calcite and various compositions of humic acid and hausmannite, by cryptand (9×10^{-3} M) and NTA (1×10^{-4} M), in 0.11 M acetic acid, are summarized in Figs. 4.8 and 4.9. (Relevant data including percentages of Pb recovered from the corresponding solid phases using only 0.11 M acetic acid reagent are shown in *Appendices 4.14.* and *4.15.*, respectively. Also presented are percentage Pb recoveries at subsequent extraction steps.)

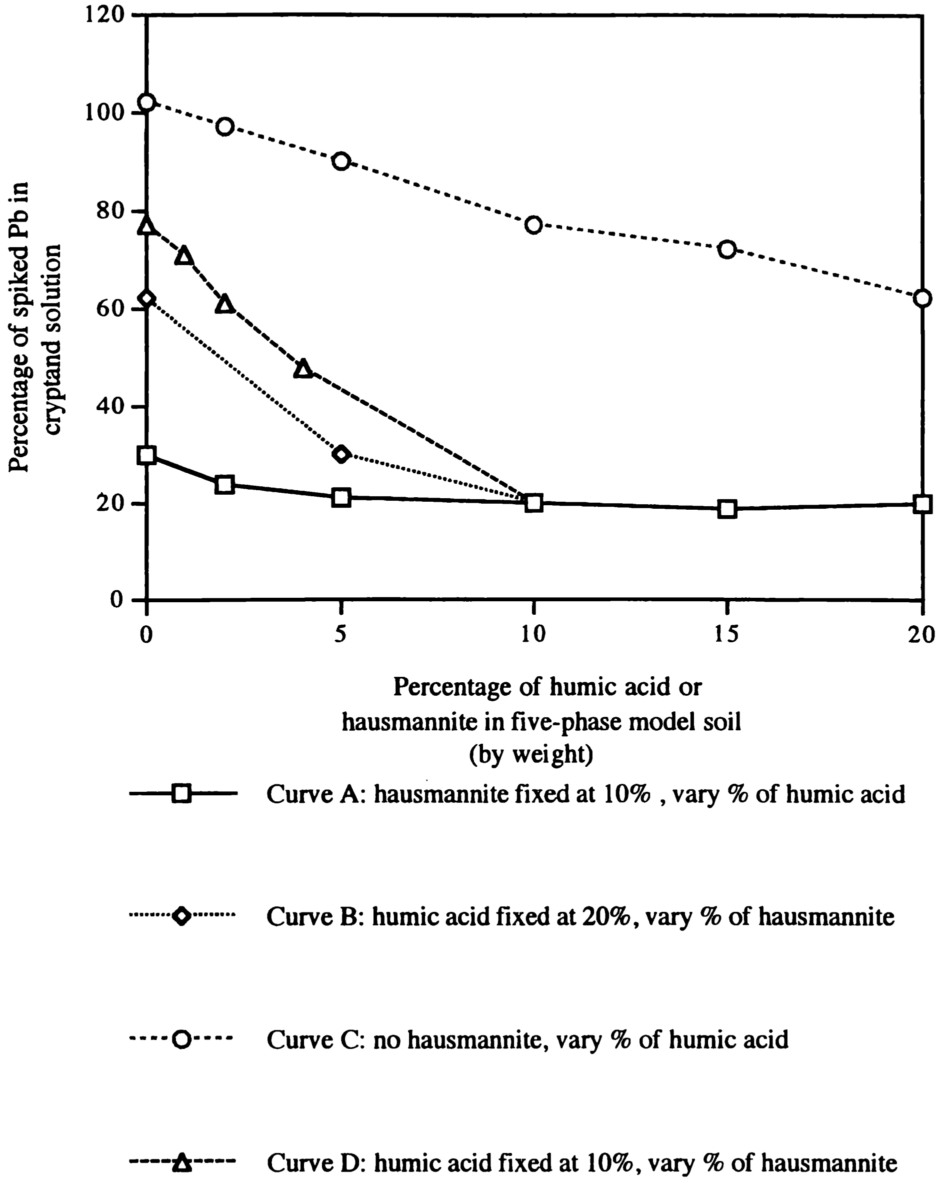


Fig. 4.8. Percentages of Pb recovered at the modified first extraction step, using cryptand at 9×10^{-3} M in 0.11 M acetic acid, from five-phase model soils containing spiked calcite and various compositions of humic acid and hausmannite.

In general, the results from both complexing agents are in agreement that in the presence of 10% hausmannite, the decrease in the percentage of humic acid did not significantly improve the percentage of Pb recovery (*Curve A* in Fig 4.8 and *Curve E* in Fig. 4.9.). In contrast, in the models comprising fixed percentages of humic acid, the reduction of the percentage of hausmannite results in a marked improvement in the percentage of Pb recovery (*Curves B* and *D* in Fig. 4.8. and *Curve F* in Fig. 4.9.). In the presence of 10% hausmannite, the percentage of Pb recovery appears to be independent of the percentages of humic acid in the systems (*Curves A, B* and *D* in Fig. 4.8. and *Curves E* and *F* in Fig. 4.9.).

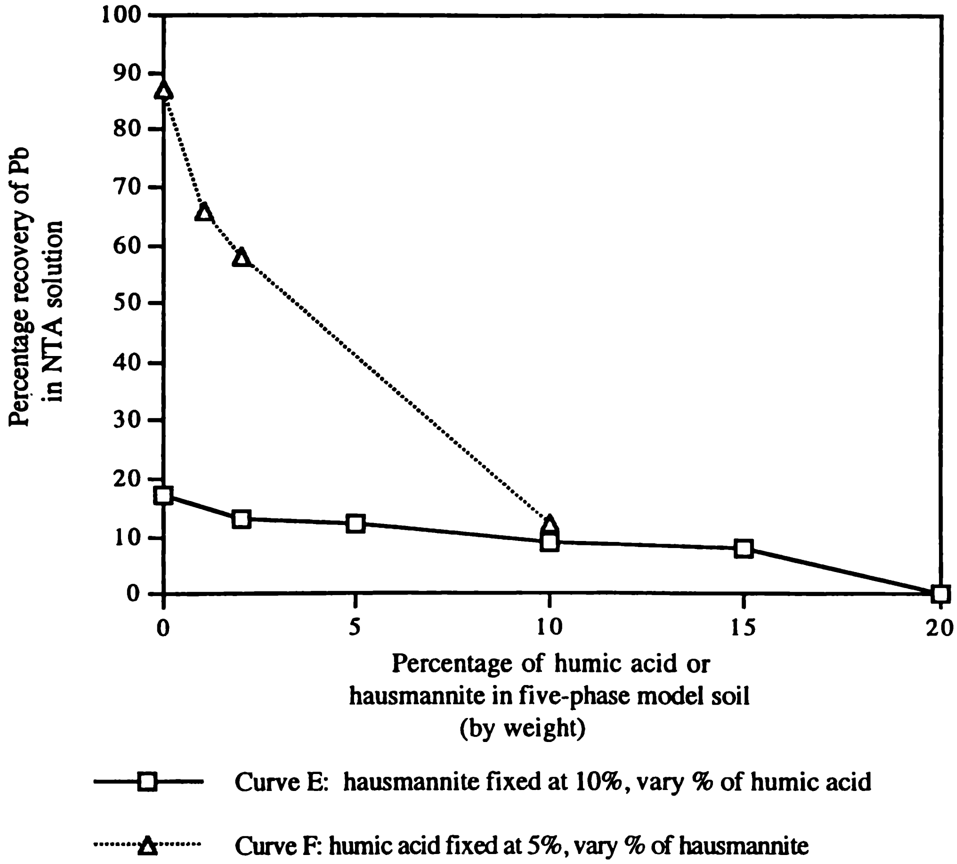


Fig. 4.9. Percentages of Pb recovered at the modified first extraction step, using 1 × 10^{-4} M NTA in 0.11 M acetic acid, from five-phase model soils containing spiked calcite and various compositions of humic acid and hausmannite.

In the absence of both humic acid and hausmannite in the systems, all Pb from the dissolved calcite was recovered in the cryptand solution (*Curve C* in Fig. 4.8.). However, in the system containing 5% humic acid (by weight) but no hausmannite, about 90% of the Pb was recovered in the NTA (*Curve F* in Fig. 4.9.).

The recovery of Pb by cryptand (9 × 10^{-3} M) is very sensitive to the presence of hausmannite in the systems (Fig. 4.8.). For every 1% (by weight) hausmannite added in the systems containing 10% and 20% humic acid, the percentage of Pb recovered in cryptand solution decreases about 6 - 10% (*Curves B* and *D*), whereas for every 5% humic acid added in the system containing 10% hausmannite, the percentage of Pb recovery does not change (*Curve A*). It is apparent that, irrespective of the percentage of humic acid in the system, the presence of hausmannite at 10% governs the percentage recovery of the Pb (*Curves A, B,* and *D*). The dominant role of hausmannite over the humic acid is further supported by the 70% improvement in the percentage of Pb recovered from the five-phase systems containing (1) no humic acid and 10% hausmannite vs (2) no humic acid and no hausmannite (*Curves A* and *C*), in comparison with the 40% increase in the percentage of Pb recovered from the systems containing (1) no hausmannite and 20% humic acid vs (2) no hausmannite and no humic acid (*Curve C*).

The sensitivity of the percentage of Pb recovery by NTA (1×10^{-4} M) to the presence of hausmannite is found consistent with recoveries by the cryptand (9×10^{-3} M) (Fig. 4.9.). In the system comprising 5% humic acid, an addition of every 1% hausmannite decreases the percentage recovery of Pb about 15% (*Curve F*). However, in the presence of 10% hausmannite in the system, an addition of humic acid does not significantly decrease the percentage of Pb recovered (*Curve E*).

From the strategy of adjusting the percentage composition of humic acid and hausmannite in the five-phase soil models, cryptand at the concentration of 9×10^{-3} M was found to retain about 60% of the Pb in solution of the systems containing (1) 20% humic acid and no hausmannite (*Curve B*), and (2) 10% humic acid and 2% hausmannite (*Curve D*). The NTA concentration of 1×10^{-4} M could retain about 60% of the Pb in the system comprised 5% humic acid and 2% hausmannite (*Curve F*).

In summary, the results of this investigation suggested that cryptand 2.2.2 and NTA, added in the conventional first extraction solution of the BCR sequential extraction scheme, are useful in counteracting Pb redistribution in five-phase synthetic soil models, with Pb originally retained on calcite. However, at the concentrations used, the effectiveness of these ligands is dependent on the amounts of hausmannite and humic acid in the soil models. In the presence of 10% hausmannite, the recovery of Pb by each complexing agent at the concentrations used is deemed unsuccessful. However, in the presence of hausmannite of no more than 2%, both cryptand and NTA could satisfactorily recover about 60% of the Pb, provided that the percentages of humic acid in the systems are not higher than 10% and 5%, respectively. The Pb recovery appears to be more sensitive to the presence of hausmannite than humic acid.

4.2.5. Preliminary trial of a modified extraction scheme on environmental samples.

In Table 4.19. is shown percentages of Pb recovered from an application of "modified" first extraction step, using a cryptand concentration of 9×10^{-3} M, on samples of a natural Kainui soil spiked with Pb-sorbed calcite, contaminated kerbside top soil, and street dust (in the cases of unspiked contaminated soil and dust, the percentages of Pb recovery presented are those of the mean Pb values determined from aqua regia extracts of replicate samples, by this laboratory and R.J. Hill Laboratory Ltd (*Appendix 2.8. (a)*).

Table 4.19. Percentages of Pb recovered from (i) a mixture of Pb-spiked calcite + Kainui soil + sand; (ii) roadside soil; (iii) street dust, using 0.11 M acetic acid and 9×10^{-3} M cryptand 2.2.2 in acetic acid.

Systems tested	Step 1				Step 2: 0.1M $NH_2OH.HCl$				Step3:H_2O_2				Step 4 : aqua regia				Total Recovery			
	(A) acetic acid		(B) cryptand/ acetic acid		(A)		(B)		(A)		(B)		(A)		(B)		(A)		(B)	
Spiked calcite + Kainui + sand (79 µg)	4 2%	44%	98%	101%	66%	66%	13%	14%	8%	0 %	0%	0%	0%	0%	0%	0%	116%	110%	111%	115%
Soil (41 µg)	0%	0%	0%	0%	46%	41%	39%	37%	29%	32%	34%	29%	27%	22%	27%	20%	102%	95%	100%	85%
Dust (174 µg)	2%	2%	10%	6%	37%	32%	54%	58%	32%	23%	35%	32%	19%	16%	22%	25%	90%	75%	121%	121%

In the case of spiked natural soil, Pb was fully recovered by the modified first extraction reagent, whereas only about 40% of the Pb was recovered by the conventional reagent (Table 4.19.). This suggested that at the concentration of 9 × 10^{-3} M, cryptand significantly counteracted Pb redistribution, which would have otherwise occurred in the system.
It should be noted here that the increase in Pb recovered at the first modified extraction step corresponds with the decreased recovery at the subsequent reducing step; this supports the role of an iron reducible component, present at high levels in the natural Kainui soil, in sequestering Pb (*Chapter* 2 Table 2.3.).

However, by comparison, the outcomes of an application of the modified extraction reagent to the unspiked contaminated soil and dust are ambiguous. In the cases of unspiked contaminated soil, it was found that no Pb was recovered at step 1 by either the acetic acid reagent or cryptand solution; whereas in the case of the dust sample, the percentages of Pb recovered by the conventional and the modified extraction reagents were not significantly different (this judgement is made in relation to the fact that the total recovery of Pb for the dust replicate samples are found to be notably different, both in terms of the sum of amount of Pb recovered at each extraction step, and total percentage recovery (comparing with 174 μg Pb)). These results suggest (at least) two possibilities: (1) the cryptand solution at the concentration used failed to counteract Pb redistribution, and/ or (2) Pb was not actually present in an "early" phase in either sample in the first place (perhaps as a result of natural redistribution).

4.2.6. Summary of the use of soluble sequestering agents for their potential to counteract Pb redistribution in model soils, and contaminated natural samples.

Among a combination of various concentrations of the soluble complexing ligands and various extraction times investigated, cryptand 2.2.2 of 9 × 10^{-3} M and NTA of 1 × 10^{-4} M (each in 0.11 M conventional first extraction solution) with the extraction time of 15 min (total contact time of 25 min) were found to be the most promising extraction conditions for counteracting Pb redistribution observed in models soils containing spiked calcite. This was based on three criteria that within the contact time: (i) the spiked calcite is completely dissolved in the "modified" extraction solution (thus, releasing Pb into the solution); (ii) the modified extraction solution does not desorb (or removes negligible amount/ percentage of) Pb from non-target individually spiked solid phases; and (iii) Pb is significantly retained in the solution during the extraction of multi-solid phase systems.
The second criteria also implies something about the mechanism by which redistribution is prevented; specifically, direct sequestering of solubilized Pb (from the dissolved calcite) by the complexing agents is desired, in contrast to an undesired phenomena of Pb being directly extracted from the main solid sequestering phases (humic acid and/ or hausmannite) after the metal has been sequestered by them. Despite the fact that these systems contained different original amounts of Pb, e.g., multi-phase systems comprising spiked calcite (37 μg),

vs an individually spiked humic acid (147 μg), the criteria was deemed to be on the conservative side; for instance, Pb on humic acid could be present at a number of binding sites from weak to strong, therefore in the spiked humic acid, the first Pb to be extracted would be that which is bound least strongly, followed by Pb bound more strongly. However, when Pb is released from calcite, the smaller amount (of 37 μg) available in solution may be taken by higher-energy sites on the humic acid (more strongly bound). In natural systems, proportionately more of Pb may be on the higher-strength sites (if "natural" redistribution has already occurred), therefore, it is possible that the "modified" extraction solution containing the cryptand or NTA would not actually extract as much Pb from natural humic-Pb as it did from synthetic humic-Pb. In this sense, the initial tests on synthetic humic-Pb may over-estimate risk of directly desorbing Pb from non-targeted phase(s); however, erring on the side of caution is reasonable given that the origin(s) and variation of retention modes of natural Pb are not known.

The results of this section of the study suggest that a soluble ligand with a high stability constant for Pb and possessing a semi-encapsulated metal binding site is potentially useful in counteracting metal redistribution in the systems tested. In addition, the decrease in the extraction time of the first step in the BCR scheme was found to assist in reducing the opportunity for redistribution of Pb.

Once again, Pb has exhibited a strong redistribution during sequential extraction. Therefore, given that a significant degree of Pb redistribution was inhibited using cryptand 2.2.2 and NTA, it seems likely that the effect of soluble ligands on inhibiting redistribution of other metals could be even greater.

4.3. Supplemental experiment on sorption of Pb onto humic acid.

In Table 4.20. are shown the percentages of Pb remaining in the acetic acid solution in the presence of humic acid

Table 4.20. Pb sorption on humic acid vs time.

Extraction time (minutes)	Total time (minutes) (extraction time + centrifugation time)	Pb left in acetic acid (%)	Pb retained on humic acid (%)	Total % recovery
3	7	43	54	97
5	9	30	65	95
10	14	10	80	90
15	19	0	83	83
15(control)	19	96	-	96

These results, which are based on analysis of both the solution and the solid, reveal that a significant amount of Pb initially in 0.11 M acetic acid was sequestered by humic acid within as short a period of time as 10 min. This suggested that if the Pb available in solution, could be intercepted immediately after being released under the conditions of the first extraction step, then it is possible that the problem of Pb redistribution observed in the model soils would be resolved.

Chapter 5. Behaviour of lead in roadside soils and dust after the removal of leaded-petrol from the New Zealand market

The objectives of the investigation of behaviour of Pb in roadside soils and dust after the removal of leaded-petrol from the New Zealand market, and relevant background literature are outlined in *Chapter 1 sections 1.8.* and *1.3.*, respectively. Methodology is outlined in *Chapter 2 section 2.4.* (site description, sampling procedure, and sample preparation) and *subsection 2.5.2.* (elemental analysis). In this chapter, the results are presented and discussed.

In Figures 5.1. to 5.5. are presented graphs of Pb levels in street dust and the top 2 cm of roadside soils collected from four parks in Hamilton, NZ: Milne, Melville, Steele, and the University's sport field on Knighton Road, during the period November 1995 (before the regulatory phasing-out of Pb from petrol sold in NZ) to September 1996. Data points shown in Fig. 5.1. are concentrations of Pb (μg g^{-1}) in top 2 cm of soils collected from the four parks during 24/ 11/ to 8/ 12/ 95; the Pb concentrations are illustrated in relation to distances (m) from the kerbside of roads (zero distance refers to kerbside site). Values of Pb illustrated in all the figures are arithmetic means of sampling replicates (tabulated data and the corresponding statistical analysis are shown in *Appendices 5.1.*, and *5.2.*). Analytical quality control including the analyses of the soil reference material, and the interlaboratory comparison are previously outlined in *Chapter 2 subsection 2.5.2.*; in short, the accuracy and precision both appear good, and were regarded as acceptable (see also the corresponding tabulated data in *Appendices 2.8. (a)* and *2.9.(b)*).

The exponential reductions of Pb in top soils with respect to increasing distance from the road are typical for roadside top soils (Fig. 5.1.), as also observed by several researchers, for example, Fergusson and co-workers (1980), Collins (1984), and Piron-Frenet and co-workers (1994). This reverse relationship confirms the significance of automobiles as the source of Pb in this present study. In all cases, the most dramatic decline in Pb concentrations occurs within 10 m from the road, then gradually decreases, and in two parks had reached levels near the background concentration at a distance of 50 m (the mean background concentration of Pb, determined from 7 replicates of samples from the surface soil collected from the Ruakura Agricultural Research Center at distances far from roads, is 19 μg g^{-1}, with a 95% confidence error of 5 μg g^{-1}). From a public health point of view, planting trees along the roadside or allocating children's playground equipment away from the road and further back into the field would be preferable. Levels of Pb (mean ± 95% confidence interval) in top 2 cm of soils collected at kerbsides of Milne Park, the sport field on Knighton Road, and Steele and Melville Parks in November and December, 1995 were found to be: 929 ± 386, 698 ± 94, 494 ± 105, and 130 ± 60 μg g^{-1}, respectively.

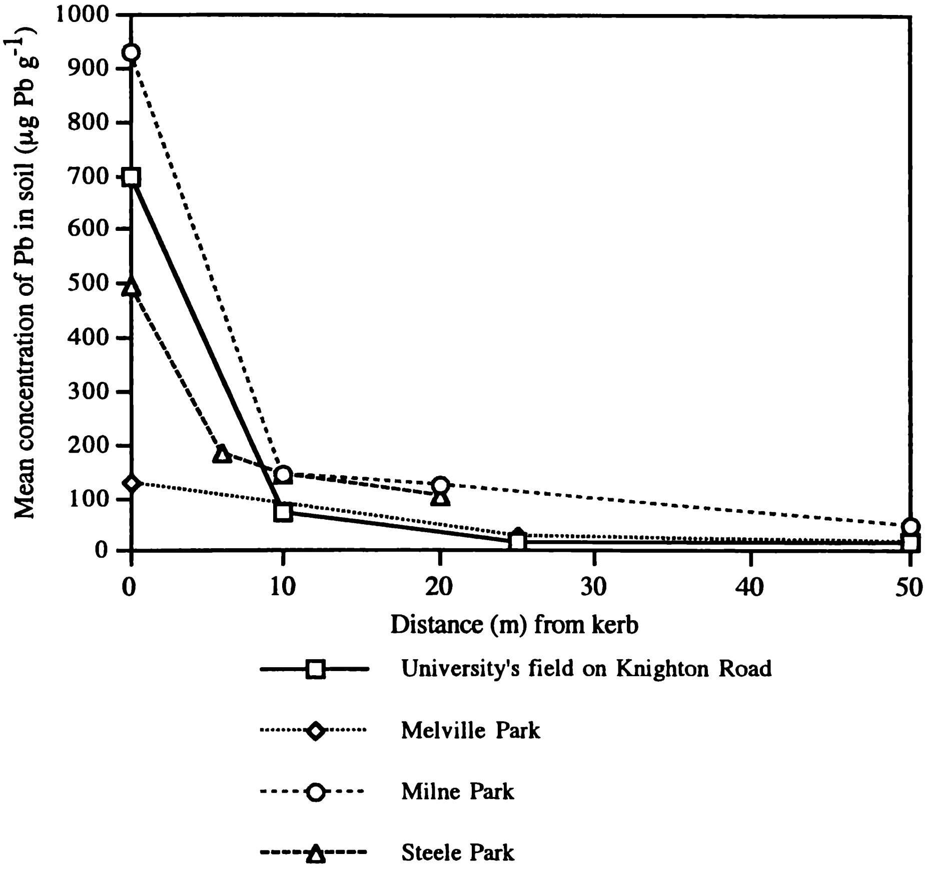


Fig. 5.1. Concentrations of Pb in top 2 cm soil (µg g^{-1}) vs distance (m).

It was initially speculated that the concentrations of Pb in kerbside top soil would exhibit a positive relationship with traffic density; however, in this case parks situated near apparently smaller roads were found to have higher Pb concentrations in their top soil than parks near a busy highway (e.g., the field on Knighton Road vs Melville Park) (Fig. 5.1.). Each of the sampling sites was generally facing the prevailing wind and their general surroundings seem to be similar to each other (e.g., intersection or roundabout nearby). Therefore, the lack of general correlation between the level of Pb and traffic density observed is possibly influenced by other factors, such as the history of the sampling sites (e.g., origins of the top soils/ initial Pb concentrations in them, and soil treatment). The mean concentrations of Pb found within a distance of 10 m in each park are generally comparable with those reported in NZ for the top 2 to 4 cm of roadside soils at similar distances from busy roads (see, for example, Fergusson et al., 1980; Collins, 1984).

In Figures 5.2. to 5.5., the concentrations of Pb in the top-2 cm of soil shown for Nov 1995 are the same ones as those illustrated in Fig. 5.1. Error bars represent the sample standard error, SD/√N; where SD is standard deviation of Pb levels in sampling replicates, and N is the number of sampling replicates. In some cases, error bars are not shown; this is due to the scale of the plotting.

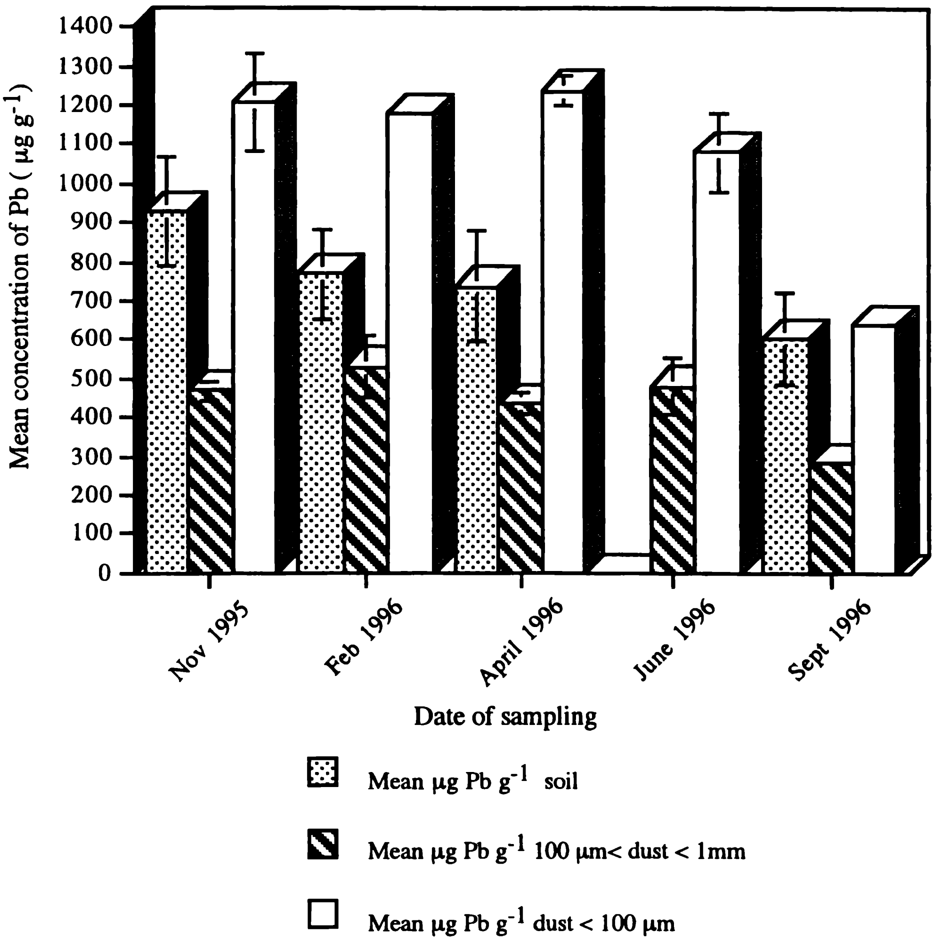


Fig. 5.2. Milne Park: Mean concentrations of Pb in top 2 cm kerbside soil and the two sized fractions of road dust

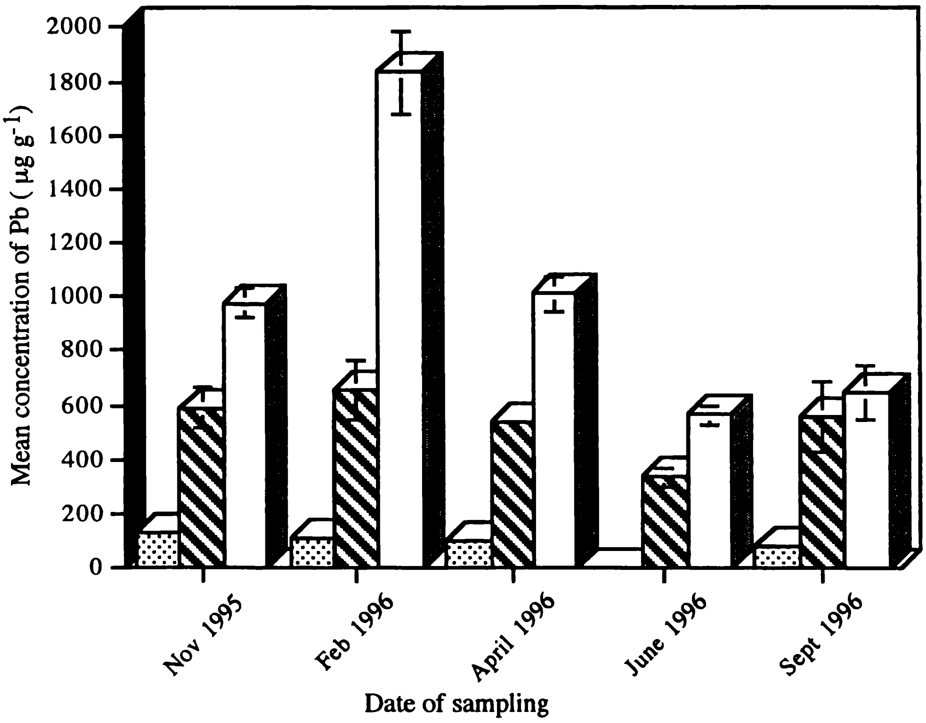


Fig. 5.3. Melville Park: Mean concentrations of Pb in top 2 cm kerbside soil and the two sized fractions of road dust.

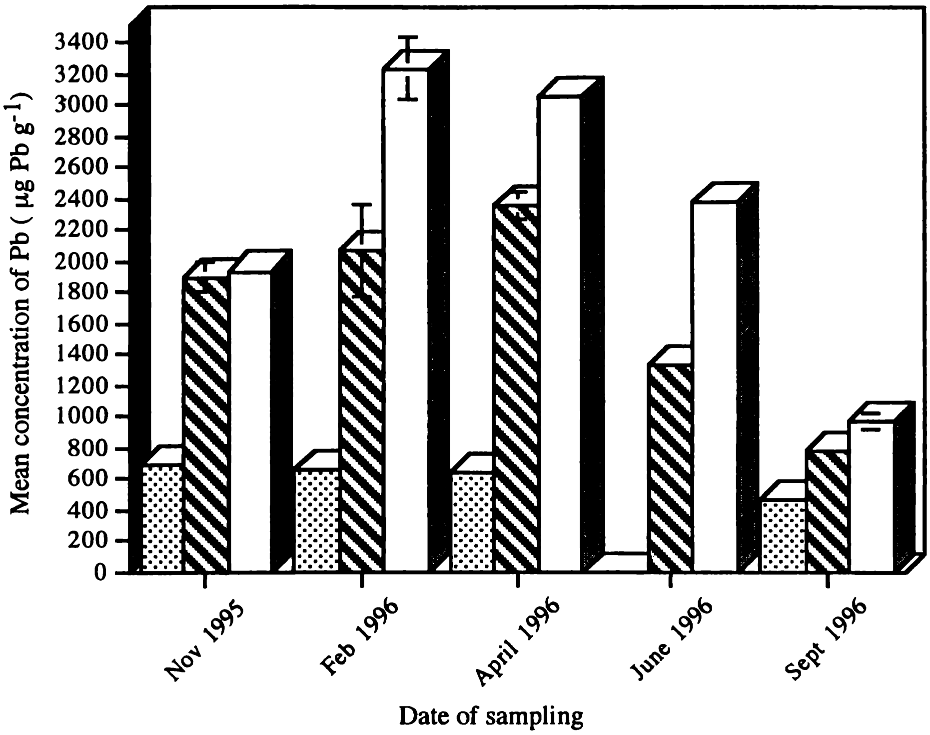


Fig. 5.4. Knighton Field: Mean concentrations of Pb in top 2 cm kerbside soil and the two sized fractions of road dust.

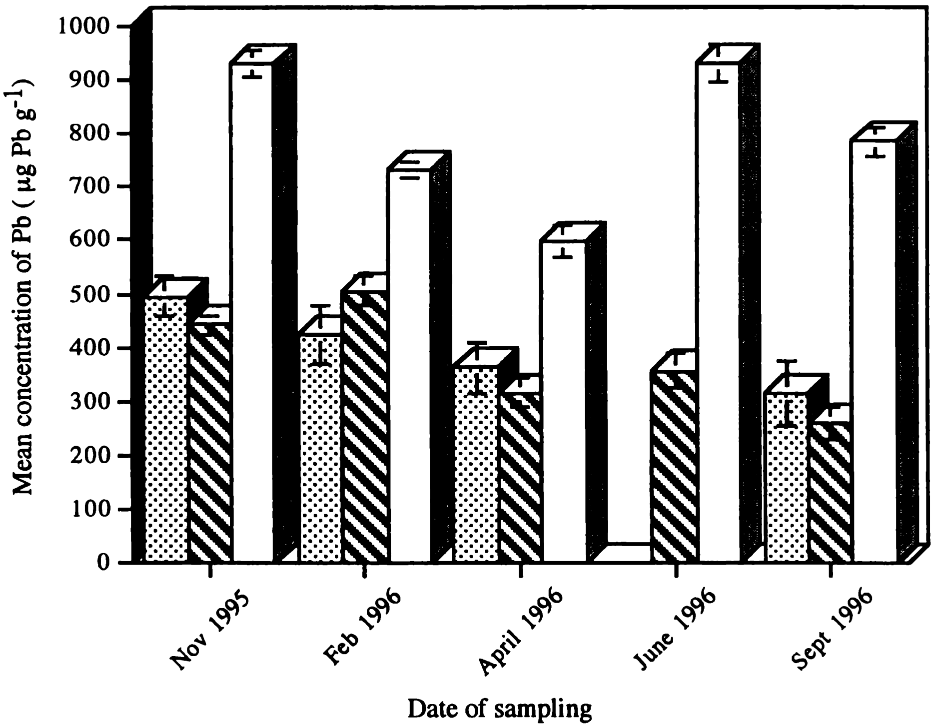


Fig. 5.5. Steele Park: Mean concentrations of Pb in top 2 cm kerbside soil and the two sized fractions of road dust.

Among the three sample types derived from each park (Figures 5.2. to 5.5.), the highest concentrations of Pb are generally found to be associated with the fine fraction (< 100 µm) of street dust. However, it should be noted that the total mass of Pb in the fine fraction of the dust might not necessarily be the largest mass of Pb in the sample. The mean concentrations of Pb in dusts (both fractions) of all the parks measured throughout the monitoring period (*Appendix 5.2.*), are found to be comparable to the mean levels of Pb (2790 μg g^{-1}) in road dust (< 1 mm) in the center city area of Christchurch, reported by Fergusson and co-workers (1980); however, the mean values of this present study are found to be lower than the levels of Pb (6340 μg g^{-1}) in dust (< 250 μm) sampled from a busy intersection in Christchurch, reported by Fergusson and Simmonds (1983). Although it is often remarked that direct comparison of the levels of Pb (and other heavy metals) in dust is difficult or inappropriate, because the type of environment might be markedly different, both studies referred to here have similar sampling and analytical methods to the present study.

According to the schedule of the reduction of Pb in petrol estimated for Hamilton (previously mentioned in *Chapter 1 subsection 1.3.2.*), it was expected that in April 1996, when the level of Pb in petrol sold had become only about 5% of that of Nov, 1995 (the commencement of the monitoring), the levels of Pb in dust (in particular the fine fraction) would begin to decline. However, it appears that throughout the sampling period, the levels of Pb in both fractions of street dusts at all the sampling sites were found to be variable, to an extent which masked possible underlying trends, at least over the duration of the sampling programme. In a long-term monitoring of levels of Pb in street dust at a busy intersection in Christchurch, NZ by Fergusson and Maata (1987) (unpublished data, referred to in Fergusson and Kim, 1991, and Fergusson, 1993), it was illustrated that subsequent to a reduction of Pb in NZ petrol from 0.82 to 0.43 g $litre^{-1}$ the concentrations of Pb (assuming the mean value since it was not specified) in street dust sampled had notably decreased from a level of about 9000 μg g^{-1} in around middle of 1986 to about 7000 μg g^{-1} in 1987. As previously mentioned in *Chapter 1 subsection 1.2.4.*, Ho (1990) found that a 70% reduction of Pb in Hong Kong petrol had at the end of the 6 year span resulted in a decrease of about 67% in the mean concentrations of Pb in street dust. In both studies, the percentage Pb reduction in the dust samples were less than those of the petrol. High variability of Pb levels in dust observed in this present study may reflect normal variability in dust, and it is possible that in order to identify a distinct trend over 10 months, it would be necessary to sample a much greater number of sites, and rely on statistical averaging. In the 6 year Hong Kong study, a total of 37 sites were sampled. It is also possible that resuspension of Pb-containing dust might occur, resulting in the same dust particles remaining in the street for quite some time (therefore, the Pb found might not reflect the most recent accumulation in the dust).

In contrast, the mean concentrations of Pb in the top kerbside soils from all four parks generally exhibit a downward trend over time, and this illustrated in Fig. 5.6.

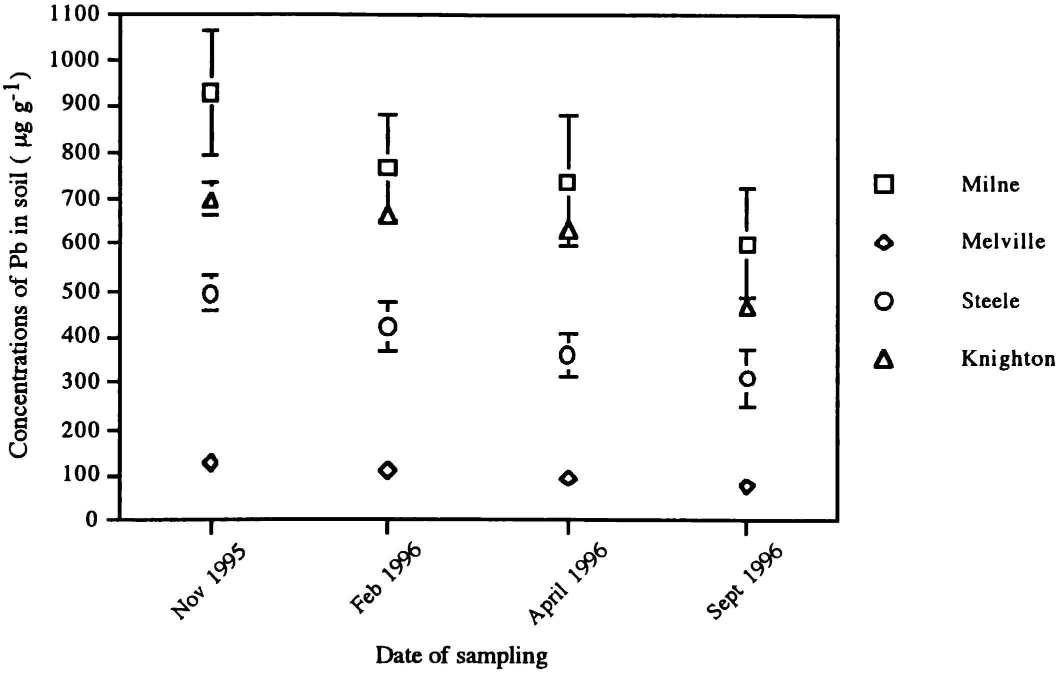


Fig. 5.6. Concentrations of Pb in the top 2 cm kerbside soils (μg g^{-1}) of the four parks.

The concentrations of Pb in the soils are found to be consistent with those of the first sampling in November, 1995, i.e., in the order: Milne > Knighton > Steele > Melville. This supports the idea that real differences of Pb levels exist between the sampling sites (and can also be seen as a support to the previous remarks that the levels found in this study are likely to be influenced by more factors than only traffic density). The results of the Student t-test of each pair of the mean concentrations of soils (of each park) (*Appendix 5.2.*) reveal that in the case of Knighton field, there is a statistically significant difference between the first mean (November 1995) and the final mean (September 1996) at a 95% confidence level. Linear regression performed on all (18 or 20 data points for each park) soil analyses show negative slopes (the following Fig. 5.7.); the highest r-value of 0.822 was obtained from the data set of the Knighton field; this corresponds to a probability of $p < 0.001$. The correlation coefficients for Melville Park and Steele Park also indicate that the relationships are statistically significant, although progressively less so ($p < 0.01$ and $p < 0.02$, respectively).

The least-squares line for Milne Park still has a negative slope; however, the relationship is not statistically significant in this case. It is interesting to note, however, that the slopes of all four relationships follow the same order as the original Pb concentrations, declining more at those sites with more initial Pb. Initial 0 - 2 cm Pb concentrations and apparent loss rates indicated by the slopes both follow the order Milne Park (930 μg g^{-1}, slope = -31) > Knighton field (698 μg g^{-1}, slope = -24) > Steele Park (494 μg g^{-1}, slope = -18) > Melville Park (130 μg g^{-1}, slope = -5) (see Fig. 5.8.). The result itself suggests that the rate of Pb loss from these soils on phasing out of leaded-petrol is likely to progressively decline with time, rather than being linear. This may reflect a tendency for Pb to become bound to progressively weaker binding sites in soil as the concentration increases.

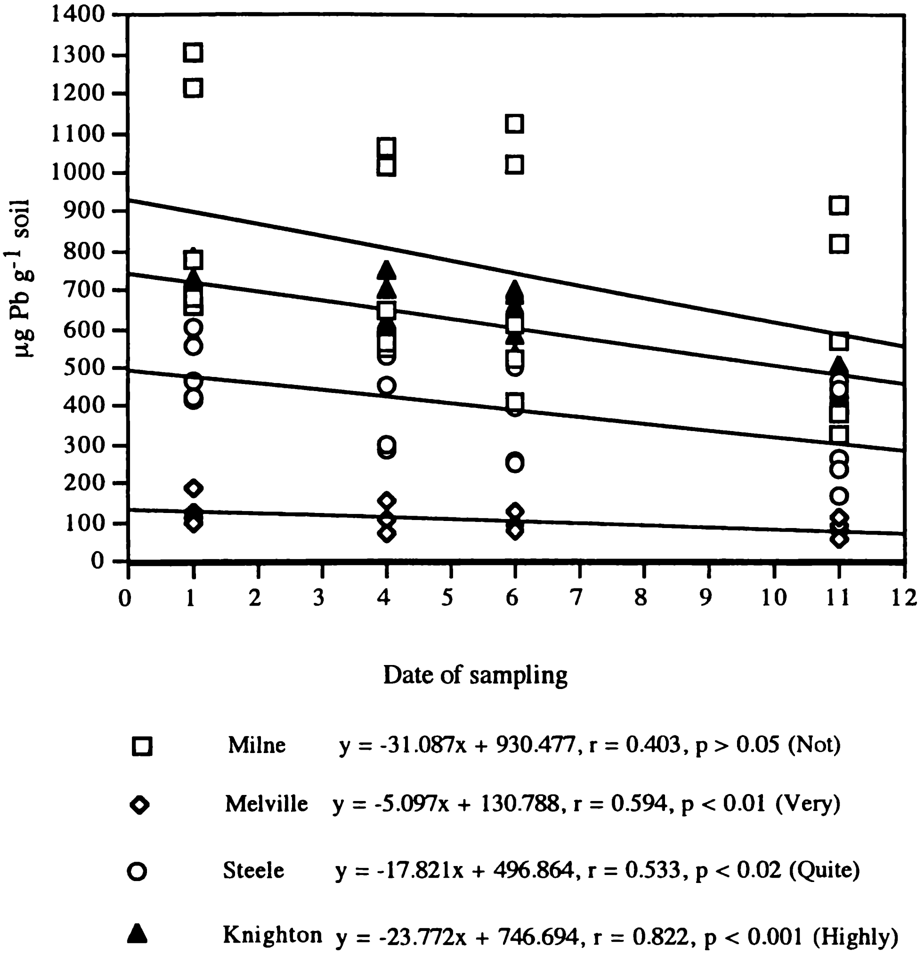


Fig. 5.7. Concentrations of Pb (µg g^{-1}) in top 2 cm kerbside sampling soil replicates of the four parks.

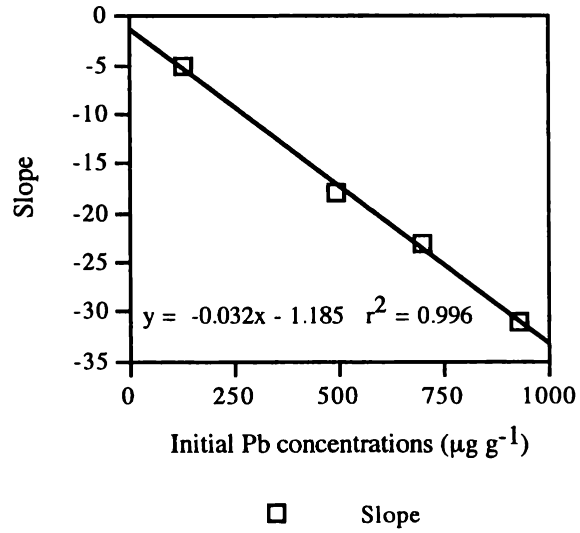


Fig. 5.8. Relationships between the estimated decline rate of Pb concentrations in top 2 cm soil and initial Pb concentrations of the four parks.

Relative to the initial Pb concentrations, the absolute amount which Pb declined in the soil over 10 months is not large. For example, at Knighton field, the decline represents 33% of the original amount (i.e., 698 ± 94 $\mu g\ g^{-1}$ in Nov 1995 and 466 ± 31 $\mu g\ g^{-1}$ in Sept 1996). Using a linear estimate, and based on the current rate of loss of Pb from the Knighton field soil, a rough estimate of 19 months from the last sampling in Sep 1996 would be required for Pb to reach background level (assumed 20 $\mu g\ g^{-1}$). Rough estimates for Pb in soils collected from Milne, Melville, and Steele to reach the assumed background levels are 19, 12, and 17 months, respectively. However, for the reasons given above, these figures are likely to represent the shortest possible times, since it is more likely that the rate of loss declines with time. Byrd and co-workers (1983) have noted a significant reduction of mean Pb in roadside topsoil after about 6 years of their monitoring during a stepwise reduction of petrol Pb consumption in US.

Chapter 6. Summary, conclusion, and recommendations for further work

In this study, redistribution of Pb in the sequential extraction protocols of Tessier et al. and the BCR was investigated using synthetic model soils, prepared by mixing a spiked solid phase with four "clean" phases, and an acid-washed sand (an inert diluent). The assessment for each extraction scheme was achieved by comparing Pb recovery patterns obtained from single spiked solid phases with those from the corresponding model soils. In general, Pb recovered from the individually spiked phases was found at "early" extraction steps, whereas the majority of the metal from the corresponding model soils was found at later steps. The resulting Pb recovery patterns of the five-phase model soils, therefore, did not provide an indication of the origin of the metal in the systems. These observations suggested that Pb liberated from its original phase by the early extraction solutions used in each extraction scheme, could reassociate with the remaining solid phases in the model systems, during the time-scale of the extraction. When subjected to the same extraction scheme, all five-phase model systems (containing different spiked phases) were found to give very similar Pb distribution patterns; however, recovery patterns of Pb obtained from Tessier et al.'s and the BCR protocols were found to be notably different, i.e., the highest Pb recovery of the former scheme was at the reducing step, whereas that of the latter scheme was at the oxidizing step. Possible factors influencing this difference were systematically investigated; these included some extraction conditions in Tessier et al.'s scheme, namely, the presence of Mg in the first extraction solution, the high ionic strength of the second reagent, and a combination of high temperature (96 °C) and the presence of 25% v/v acetic acid in the reducing step. The extraction conditions of the reducing step in Tessier et al.'s scheme were found to be the main factors contributing to the differences; the elevated temperature reduced the sorptive capacity of humic acid by more than 50%; in addition, more of the Pb was retained in solution by acetate ions. Additional results from the extractions of a series of multi-phase model soils (e.g., two-/ three- phases) suggested that humic acid and hausmannite were the dominant phases responsible for the redistribution observed in both extraction schemes. Redistribution phenomena, similar to those observed in the synthetic model soils, were also evidenced in two natural soils (with high organic content or Fe/ Mn content) spiked with a Pb-bearing solid phase during the extraction using the BCR protocol.

With the ultimate aim to improve the accuracy of the conventional BCR extraction protocol in determining Pb distribution in the model soils, two broad approaches were investigated for their potential usefulness in inhibiting/ counteracting the redistribution phenomena earlier observed. These involved an addition of different sequestering agents in either solid or dissolved forms into the model soils at the conventional first extraction step where the redistribution occurred. Solid sequestering agents assessed included (i) a commercial sulfonate ion exchange membrane strip, (ii) SiO_2 gel and wool functionalized with dithiocarbamate, (iii) a commercial thiol resin (RSH), (iv) a commercial flame-retardant cotton fabric (Proban), (v) a thiol-derivatized SiO_2 gel, and (vi) a phosphine-derivatized wool. In general, the use of solid sequestering agents was found to be unsuccessful. They were commonly found to retain significant amounts of the solid particles (such as, the hausmannite) (this complicated the quantification of Pb available in the solution being captured by the sequestering agents). In addition, physical separation of the solid sequestering agent from the synthetic soil particles using membranes was found to notably reduce the amount of Pb being captured by the sequestering agents; this was likely to be due to kinetic limitations induced by the use of the membranes. Dissolved sequestering agents investigated included (i) Aerophine® 3418A promoter; (ii) 18-Crown-6, (iii) Zinc pyrrolidine dithiocarbamate, (iv) Cryptand 2.2.2; and (v) NTA. Among the dissolved sequestering agents assessed, a macrobicyclic compound, cryptand 2.2.2, and a quadridentate open-chain aminocarboxylic chelating agent, NTA, were found to be the most effective. Aerophine was found to pose an unusual analytical problem, while the Zn-dithiocarbamate method was found to directly remove a significant amount of Pb originally sorbed on a non-target humic acid phase. The effectiveness of the cryptand and NTA, however, was found to depend on concentrations of the complexing agents, reaction time, and abundance of model soil components, i.e., hausmannite, and humic acid. With the cryptand and NTA at concentrations of 9×10^{-3} and 1×10^{-4} M, respectively, and the total contact time between the soil particles and the modified extraction solution shortened to 25 min, the cryptand and the NTA could satisfactorily recover about 60% of the Pb from the systems containing (i) no more than 2% hausmannite (by weight), and (ii) percentages of humic acid of no higher than 10% and 5%, respectively. Two important characteristics of potentially useful complexing agents implied by the results of the investigation were high affinity for the metal of interest and the presence of an internal binding site. A preliminary application of the modified extraction procedure using the modified extraction solution containing cryptand on a natural soil with spiked calcite was found to be successful in that all (98 - 101%) of the Pb in the system was retained in the modified extraction solution (as expected if the redistribution is prevented). However, an application of the modified extraction scheme on samples of unspiked roadside top soil and street dust did not result in a significant increase in the recovery of Pb in the modified first extraction solution relative to the use of the conventional extraction solution; this was possibly due to little Pb being present in the early phase at the outset. Increasing the concentration of the cryptand used was, however, deemed to present a high risk of directly desorbing Pb from the non-target phase(s) remaining in the systems.

Given that 9×10^{-3} M cryptand 2.2.2 was found to be useful in counteracting the Pb redistribution in the BCR extraction (of the synthetic model soils and a spiked environmental sample), it is of interest to further assess the usefulness of this complexing agent in counteracting Cu redistribution under the same experimental conditions (Cu redistribution was previously reported by Schriner (1994), using similar model soils, but in Tessier et al.'s scheme). In addition, an extraction of model soils containing a spiked phase with both metals using the modified extraction scheme is a possible approach to assess the effect of simultaneous metal extraction on the ability of such a ligand to inhibit redistribution (the affinity of cryptand 2.2.2 for Pb is reported to be 10^6 times greater than its affinity for Cu, Patai (1980)). Supplementary experiments could involve individual and simultaneous adsorptions of the metals under extraction solutions.

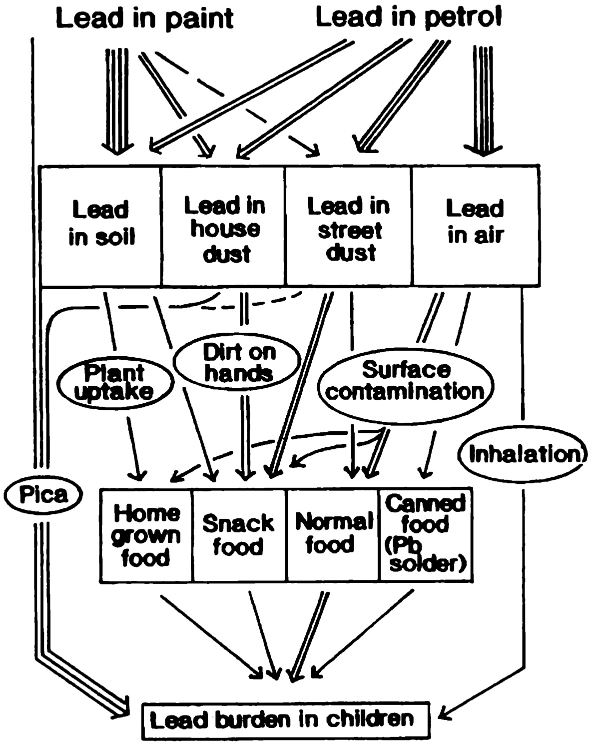
Although the application of the modified BCR extraction scheme using the cryptand on the contaminated soil and dust did not produce a successful outcome, the ambiguous result might reflect the natural distribution of Pb in these samples. It is, therefore, of interest to further assess the effectiveness of the modified extraction scheme using natural samples containing Pb from a range of contamination sources (e.g., soils near battery factory, and in the vicinity of lead mine). It is also interesting to see whether the resulting Pb distribution patterns are distinct from site to site, and whether there is any relationship between the recovery patterns and relative abundance of various solid components of the sample.

Regarding the monitoring of Pb in roadside top soil and street dust collected from four parks in Hamilton, NZ, during the phasing out of leaded petrol, it was found that the Pb levels in the soils generally exhibited a slight downward trend, while those in the dust showed no clear trend. It is of interest to further monitor Pb levels in soils and street dust from these four parks. Further monitoring of the sites could be carried out in order to establish longer-term estimates of the rate of decline of Pb to background levels. In addition, migration of Pb from top soil to the lower depth may warrant investigation; this could be estimated by use of a soil column and simulated rainfall. Samples taken during the present work have been appropriately stored; it would therefore be possible to use the modified extraction scheme (containing the cryptand) developed in this study to further investigate whether redistribution of Pb occurs during the phasing out of leaded-petrol or not.

Appendices

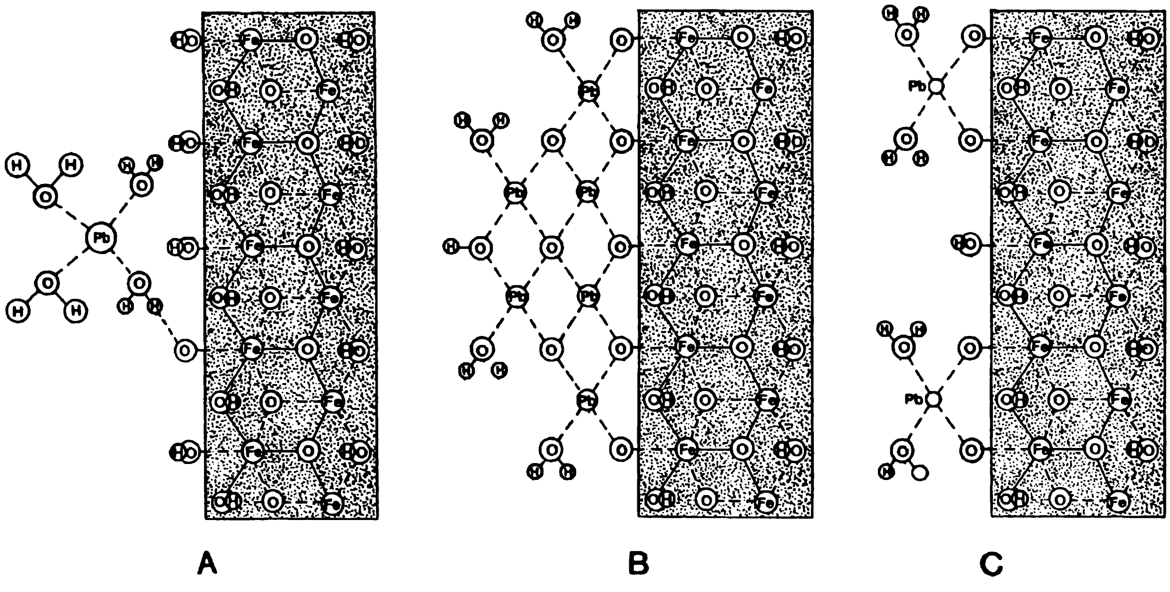
Apppendix 1. Supplemental information referred to in Chapter 1

Appendix 1.1. Sources and pathways of Pb intake of children.



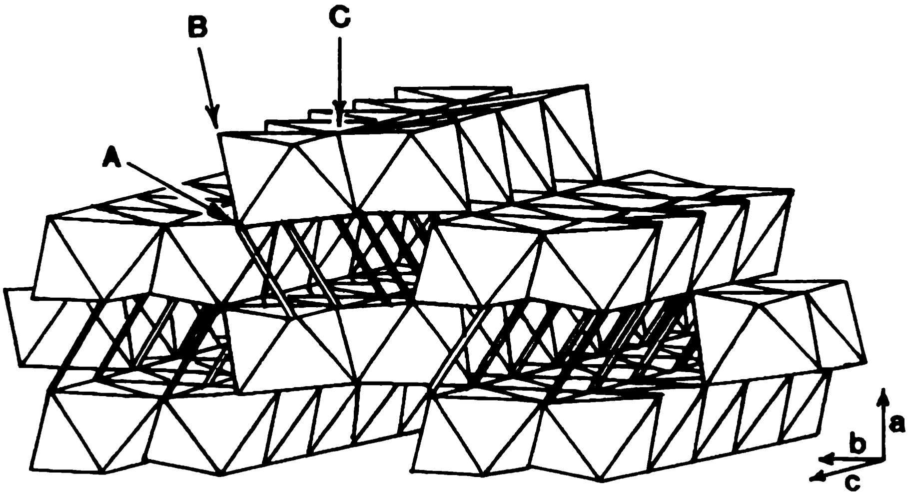
(Redrawn from Fergusson, 1986) The more lines, the stronger the pathway.

Appendix 1.2. Schematic representation of various structural models of Pb sorption.

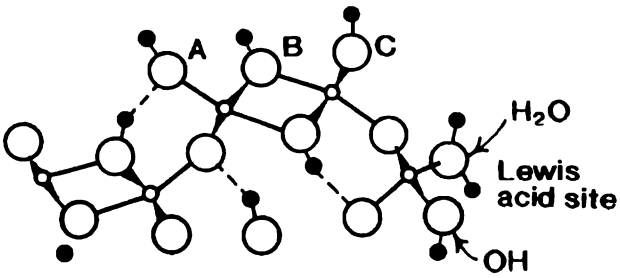


A: outer-sphere surface complex model; B: surface precipitate model; C: inner-sphere surface complex model. (Redrawn from Roe et al., 1991)

Appendix 1.3. Structure of goethite.

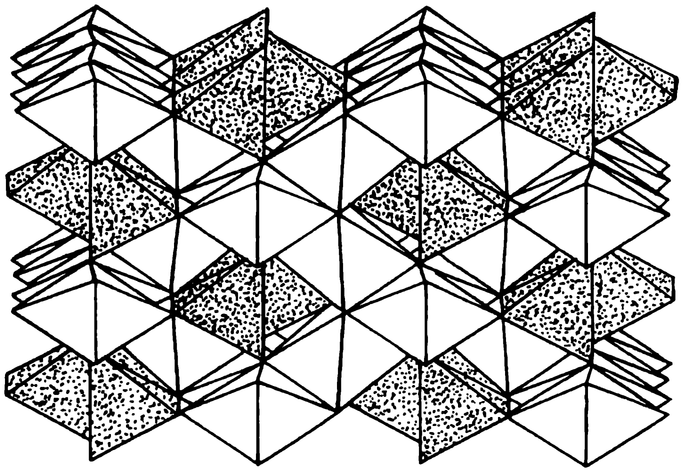


(Redrawn from Stucki et al., 1988) illustrates an octahedral model with three types of surface hydroxyl groups (Sposito, 1984). Hydrogen bonds are represented by small bars.



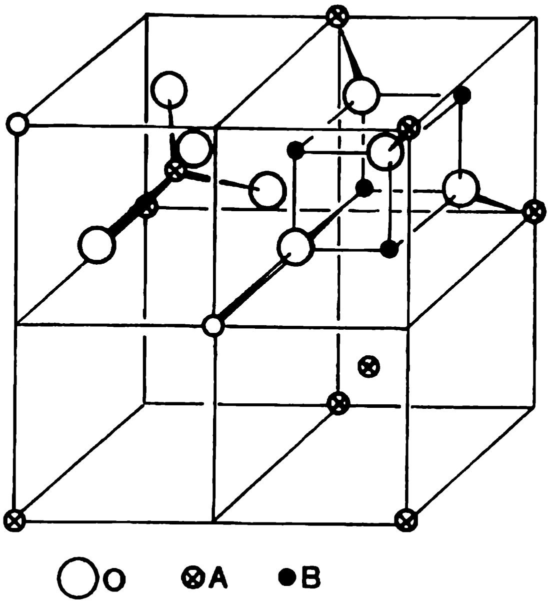
(Redrawn from Sposito, 1984) illustrates goethite surface hydroxyls and Lewis acid site. The dashed lines indicate hydrogen bonds.

Appendix 1.4. Structure of hausmannite.

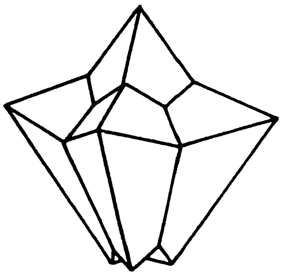


(Redrawn from Post, 1992) The Mn^{3+} occupy the octrahedral sites (lighter shading) and the Mn^{2+} are in the tetrahedral sites (darker shading).

Appendix 1.4. (continued) Structure of hausmannite.

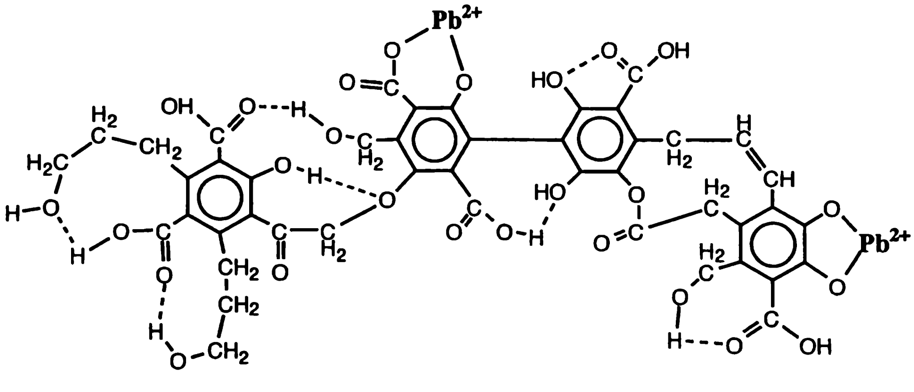


(Redrawn from Shriver et al., 1992) illustrates the spinel structure (AB_2O_4) unit cell.
A segment of the unit cell shawing the tetrahedral environment of A ions and the octahedral environment of B ions.



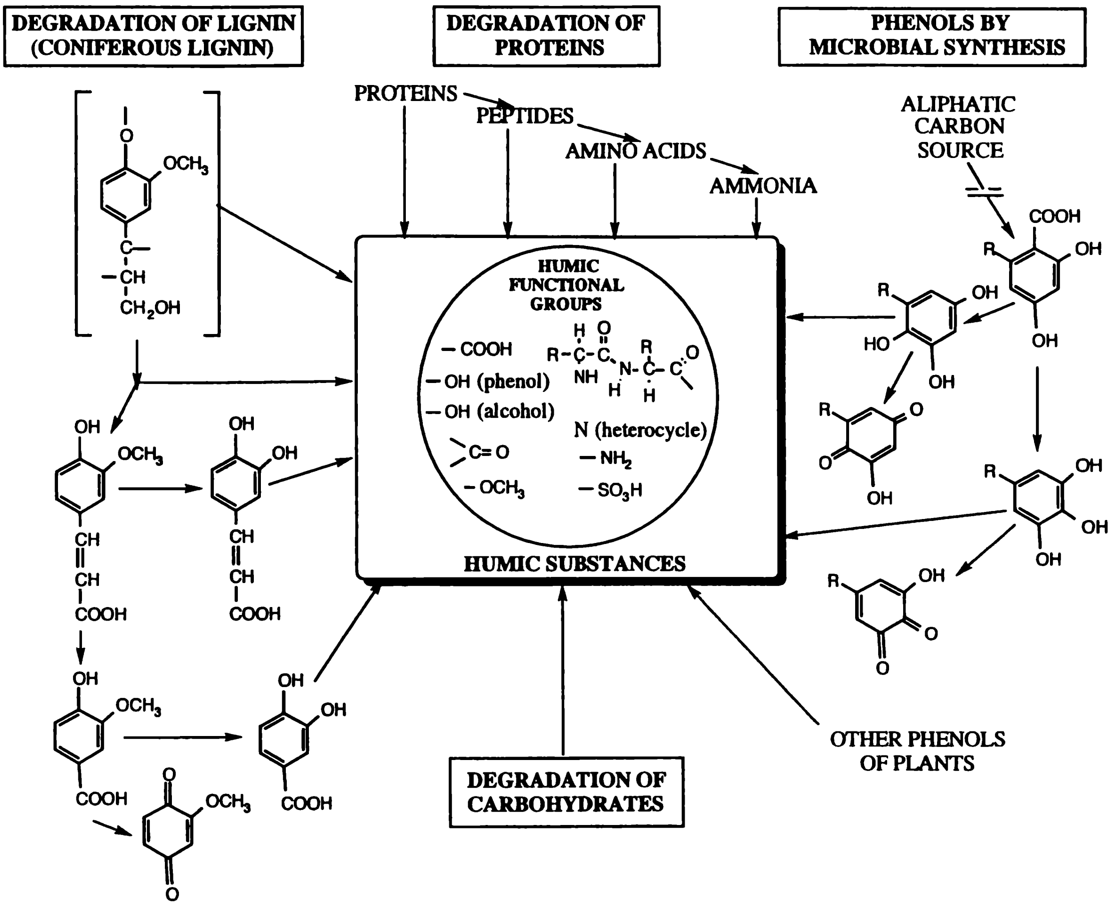
(Redrawn from Ford, 1932) illustrates an analogous twin of hausmannite.

Appendix 1.5. Complexation mechanism of lead by humic substance.



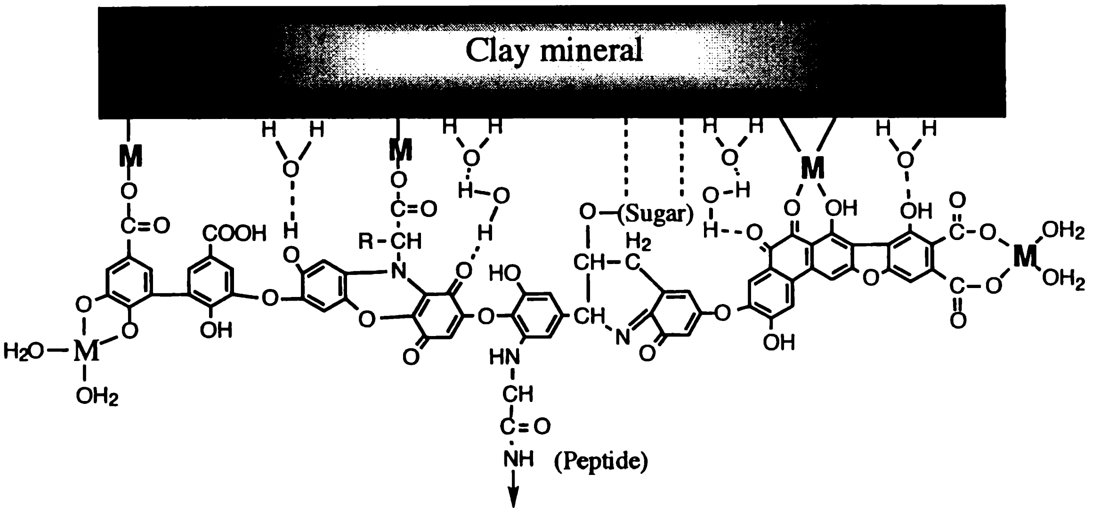
(Redrawn from Manceau et al., 1996)

Appendix 1.5. (continued) The structural precursors of humic substances in soils.



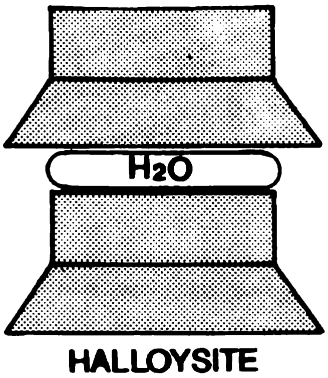
(Redrawn from Sposito, 1984)

Appendix 1.6. Schematic structure of the clay-humic acid complex.

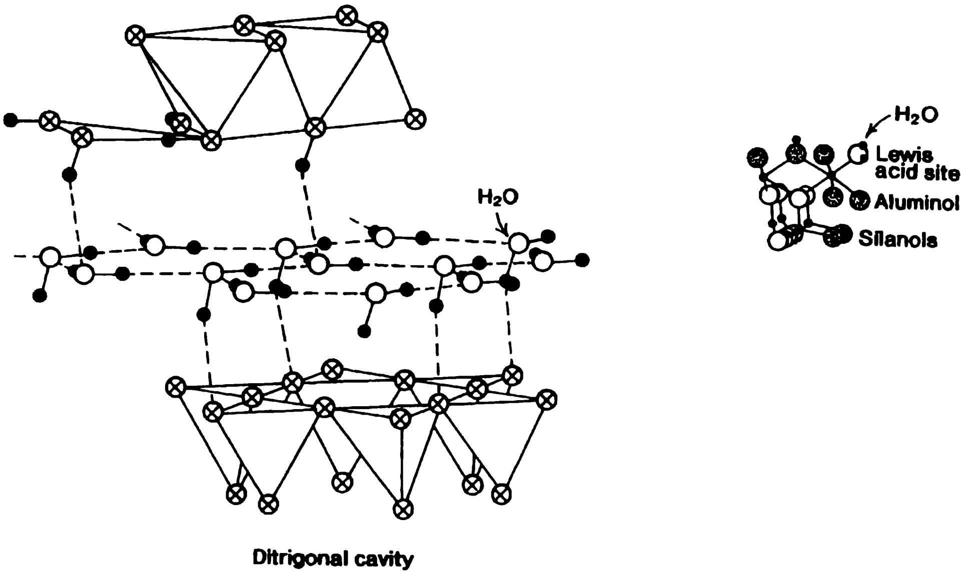


(Redrawn from Schindler, 1990)

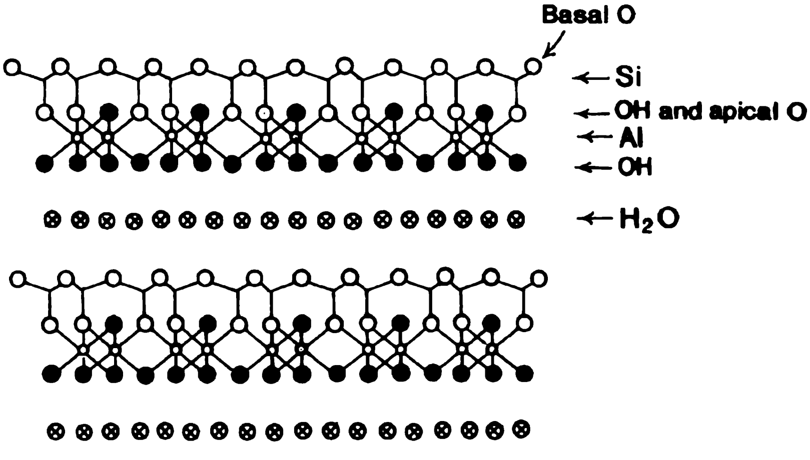
Appendix 1.7. Structure of halloysite.



(Redrawn from McBride, 1994) illustrates in terms of tetrahedral and octahedral sheets.

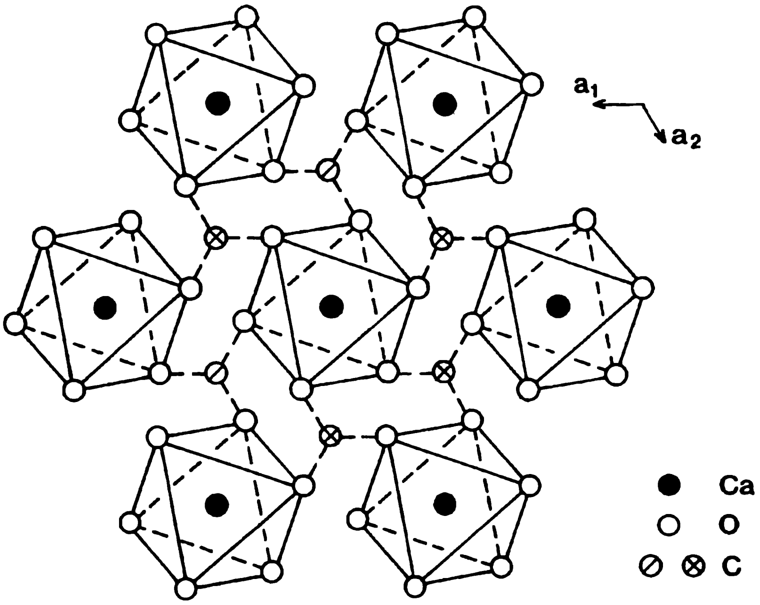


(Redrawn from Sposito, 1984) shows the ditrigonal cavity, structure of water in the interlayers of 10 Å halloysite, and the surface hydroxyl groups.



(Redrawn from Dixon, 1989) shows structure scheme based on octahedral and tetrahedral sheets.

Appendix 1.8. Structure of calcite.



(Redrawn from Dixon, 1989)

Appendix1.9. Examples of sequential extraction schemes in the literature: 1966 to 1993 compiled from Pickering, 1986; Calvet et al., 1990; Yong et al.,1993; Kersten & Forstner,1994; and Hall et al., 1996.
(step numbers refer to their respective positions in each extraction scheme)
Note: Schemes of Tessier et al. (1979) and BCR (1993) are presented in Table 2.5. Chapter 2.

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Nelson et al. (1966)			Dithionite	H_2O_2, bromoethanol			colloids in water
Chester & Hughes (1967)	1. NH_3OHCl + CH_3COOH	2. NH_3OHCl + CH_3COOH	3. $NH_2OH.HCl$ + CH_3COOH				pelagic sediments
Rose & Suhr (1971)		(adsorbed, carbonates) NaOAc, pH 5	(crystalline Fe oxides) DCB	(sulfides and organics) H_2O_2	(silicates) separated by size fraction		
Chao (1972)	1. $NH_2OH.HCl/$ HNO_3					2. hydroxylamine/ HNO_3	soil and sediments
Presley et al. (1972)				3. (bound to organics and sulfides) H_2O_2		1. (water soluble) H_2O_2 2. (easily reducible solids) $NH_2OH/$ HOAc	
McLaren & Crawford (1973)	1. $CaCl_2$	2. (specifically sorbed, carbonate bound) HOAc	4. (moderately reducible oxides) NH_4O_x/HO_x	3. (easily extractable organics) $K_4P_2O_7$	5. HF		soil

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Gupta & Chen (1975)	1. NH_4OAc	2. (specifically sorbed, carbonate bound) HOAc	4. (crystalline Fe-oxides) DCB (dithionite citrate buffer) 4. (moderately reducible oxides) $NH_2OH.HCl$/ HOAc	3. (oxidizable oxides + sulfides) H_2O_2	5. HNO_3/ HF/ $HClO_4$		
Patchineelam (1975)	1. $BaCl_2$, triethanylamine pH 8.1	4. (specifically sorbed carbonate bound) acidic cation exchanger		2. (bound to organics + sulfides) NaOH	(5. HNO_3/ $HClO_4$?)	3. (easily reduced substrates) NH_2OH/ HOAc	
Chao & Theobald (1976)			(Mn oxides) $NH_2OH.HCl$ in HNO_3 (amorphous Fe oxyhydroxides) $NH_2OH.HCl$ in HCl (crystalline Fe oxides) DCB	(sulfides and orgaics) $KClO_3$-HCl HNO_3	(silicates) HF-HNO_3		

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Stover et al. (1976)	KNO_3 + NaF		EDTA	$Na_4P_2O_7$	HNO_3		
Engler et al. (1977)	1. (exchangeable + adsorbed) NH_4OAc			3. H_2O_2/ HNO_3	4. $Na_2S_2O_4$/ HF/ HNO_3	2. (easily reducible substrate) $NH_2OH.HCl$, pH 2	marine sediments
Gatehouse et al. (1977)	1. NH_4OAc		3. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc 4. (crystallined Fe-oxides) $NH_2NH_2.HCl$		5. HF/HNO_3	2. (easily reducible substrate) $NH_2OH.HCl$/ NH_4OAc	
Gibbs (1977)	1. $MgCl_2$		2. (crystallined Fe-oxides) DCB	3. (easily extractable organics) NaOCl/ DCB	4. fusion		
Guy et al. (1978)	1. (exchangeable + adsorbed + organic) $CaCl_2$ + CH_3COOH + K-pyrophosphate	4. (carbonates + adsorbed + Fe-Mn nodules) $NH_2OH.HCl$ + CH_3COOH	2. (metal oxides + organic matter) H_2O_2 + dithionite + bromoethanol				synthetic sediments

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Filipek & Owen (1978)		1. (specifically sorbed, carbonate bound) HOAc	3. (moderately reducible oxides) $NH_2OH.HCl$/ HOAc 4. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc		5. HF/ HNO_3/ $HClO_4$	2. (easily reducible substrate) $NH_2OH.HCl$, pH 2	
Hoffman & Fletcher (1978)			2. (moderately reducible oxides) NH_4O_x/ HO_x 3. (easily reducible substrates) $NH_2OH.HCl$, pH 2 4. (crystalline Fe-oxides) DCB	1. (easily extractable organic) NaOCl	5. $HClO_4$/ HNO_3		
Forstner et al. (1979)	$BaCl_2$		NH_2OH, HNO_3 + CH_3COOH + HCl	H_2O_2 + NH_4OH	HF-$HClO_4$		
Shuman (1979)	1. $MgCl_2$			2. (bound to organics + sulfides) H_2O_2	HNO_3/ HCl/ HF	3. (moderately reducible solids) HO_x/ NH_4O_x (easily reduced substrates) H_2O_2 ?	
Schalscha et al. (1980)	KNO_3	NaF	EDTA	$Na_4P_2O_5$	HNO_3		

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Badri & Aston (1981)	1. NH_4OAc/ MgOAc		2. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc			3. (easily reducible substrate) NH_2OH. HCl, pH 2	
Bogle & Nichol (1981)			2. (moderately reducible oxides) NH_2OH.HCl/ HOAc	1. (easily extractable organics) NaOCl	4. HNO_3	3. (easily reducible substrate) NH_2OH. HCl, pH 2	
Boust & Saas (1981)	1. NH_4OAc 2. CuOAc 4. NaOAc		5. (crystalline Fe-oxides) HNO_3	3. (easily extractable organics) $Na_4P_2O_7$			
Filipek & Theobald (1981)	HOAc		(Mn oxides) NH_2OH.HCl in HNO_3 (amorphous Fe oxyhydroxides) NH_2OH.HCl in HOAc	(sulfides and organics) H_2O_2/ NH_4OAc in 6% HNO_3	(silicates) HF-HNO_3-HCl		
Forstner et al. (1981)	CH_3COONH_4		NH_2OH.HCl + HNO_3, pH 2 and $(COONH_4)_2$ + $(COOH)_2$, pH 3	H_2O_2, HNO_3, pH 2 @ 85 degree C extraction with CH_3COONH_4	HNO_3 at 180 degree C		

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Garcia-Miragaya (1981)	$CaCl_2$	CH_3COOH	EDTA	$Na_4P_2O_5$	HF		
Greffard et al. (1981)		resin-H^+	$(COONa)_2$ and $(COONa)_2$ + UV	H_2O_2 at 40 degree C			
Sondag (1981)	NH_4OAc at pH 4.5		(Mn oxides) $NH_2OH.HCl$, pH 4.5 (amorphous Fe oxyhydroxides) $(NH_4)_2C_2O_4$ in $H_2C_2O_4$ pH 3.3 (crystalline Fe oxides) $(NH_4)_2C_2O_4$ in $H_2C_2O_4$, under UV	(sulfides and organics) H_2O_2	HF-HCl		
Emmerich et al. (1982)	1. KNO_3	4. Na_2EDTA		3. NaOH	5. HNO_3	adsorbed fraction: 2. X-H_2O	soil
Schoer & Eggergluess (1982)	1. NH_4OAc			4. (bound to organics and sulfides) H_2O_2/ HNO_3	5. HNO_3	2. (easily reduced substrates) NH_2OH/ HNO_3 3. (moderately reducible solids) NH_4O_x/ HO_x	

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Dik & Allen (1983)	1. $MgCl_2$	2. (specifically sorbed, carbonate bound) NaOAc pH 5	4. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc 5. (moderately reducible oxides) NH_2OH. HCl/ HOAc			3. (easily reducible substrate) NH_2OH. HCl, pH 2	
Kuo et al. (1983)	$MgCl_2$		$(COONa)_2$ and citrate dithionite bicarbonate	$NaClO_4$ at degree C	HNO_3-$HClO_4$		
Meguelatti et al. (1983)	$BaCl_2$	CH_3COOH + CH_3COONa	NH_2OH + CH_3COOH	H_2O_2 + HNO_3 CH_3COONH_4	HF-HCl		
Shuman (1983)	1. $Mg(NO_3)_2$		4. (moderately reducible oxides) NH_4O_x/ HO_x	2. (easily extractable organics) NaOCl	5. HF/ HNO_3/ HCl	3. (easily reducible substrate) NH_2OH.HCl, pH 2	
Chang et al. (1984)	1. KNO_3	4. Na_2EDTA		3. NaOH	5. HNO_3 (70-80 degree C)	adsorbed fraction: 2. deionized water	soil

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Lee & Kittrick (1984)	1. $MgCl_2$	2. (specifically sorbed, carbonate bound) NaOAc pH 5	3. (moderately reducible oxides) NH_2OH. HCl/ HOAc 4. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc		5. HF/ $HClO_4$/ HCl		
Robinson (1984)	1 NH_4 citrate		4. (crystalline Fe-oxides) NH_2NH_2. HCl	3. (easily estractable organics) NaOCl/ HCl		2. (easily reducible substrate) NH_2OH.HCl, pH 2	
Salomons & Forstner (1984)	1. NH_4OAc	2. (specifically sorbed, carbonate bound) NaOAc pH 5	4. (moderately reducible oxides) NH_4O_x/ HO_x 5. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc		5. HNO_3	3. (easily reducible substrate) NH_2OH.HCl, pH 2	
Towner (1984)	1. $MgCl_2$	2. (specifically sorbed, carbonate bounds) NH_2OH.HCl/ NaOAc pH 5	4. (moderately reducible oxides) NH_2OH. HCl/ HOAc 5. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc	3. (easily extractable organics) $Na_4P_2O_7$			

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Hayes (1985)	1. NH_4OAc		3. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc		4. HF/ $HClO_4$	2. (easily reducible substrate) $NH_2OH.HCl$, pH 2	
Cardoso Fonseca & Martin (1986)	NH_4OAc at pH 4.5		(Mn oxides) $NH_2OH.HCl$, pH 2.5 (amorphous Fe oxyhydroxides) $(NH_4)_2C_2O_4$ in $H_2C_2O_4$, pH 3.3 in dark (crystalline Fe oxides) $(NH_4)_2C_2O_4$ in $H_2C_2O_4$ under UV		HF-HNO_3-HCl		
Gibson & Farmer (1986)	1. CH_3COONH_4, pH 7	2. CH_3COONa; pH 5	3, 4 Hydroxyl-ammonium + HNO_3/ CH_3COOH	5. H_2O_2 + HNO_3; 85 degree C	6. aqua regia + HF + boric acid		urban soil
Yanful et al. (1988)	1. $MgCl_2$ + Ag, thiourea	2. CH_3COONa + CH_3COOH	3. $NH_2OH.HCl$	4. + sulfides, H_2O_2 + HNO_3	5. HNO_3 + $HClO_4$ + HF		contaminated soil
Belzile et al. (1989)	1. $MgCl_2$	2. CH_3COONa/ $NH_2OH.HCl$/ HNO_3; room temperature	3. Mn oxide, $NH_2OH.HCl$/ HNO_3 NH_4OAc/ HNO_3	4. + sulfides, H_2O_2/ HNO_3, NH_4OAc/ HNO_3			sediments

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Zeien & Brummer (1989)	1. NH_4NO_3	2. (specifically sorbed, carbonate bound) NH_4OAc pH6	5. (moderately reducible oxides) NH_4O_x 6. (crystalline Fe-oxides) ascorbic acid/ NH_4O_x	4. (easily extractable organics) NH_4-EDTA	7. HF/ $HClO_4$/ HNO_3	3. (easily reducible substrates) NH_2OH. HCl/ NH_4OAc pH 6	
Clevenger (1990)	1. $MgCl_2$	2. NaOAc/ HOAc		3. HNO_3/ H_2O_2	4. HNO_3 (boiled)		mining wastes
Hirner (1992)	1. NH_4OAc		3. (moderately reducible oxides) HCl	2. (easily extractable organics) benzene/ methanol	4. HF/ $HClO_4$/ HNO_3		
Rule & Alden (1992)	1. NH_4OAc		3. (oxidizable oxides and sulfides) H_2O_2/ NH_4OAc 4. (crystalline Fe-oxides) Na-citrate		5. HNO_3/ H_2O_2	2. (easily reducible substrates) NH_2OH. HCl pH 2	
Yong et al. (1993)	1. KNO_3	2. NaOAc, pH 5	3. $NH_2OH.HCl$	4. H_2O_2 (3 steps)	5. HF/ $HClO_4$ + HCl		synthetic, natural, and contaminated soils

Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Campanella et al. (1995)	1. (ion exchange form and bound to carbonate) NH_4OAc		2. (reductive phase bound to Mn-Fe oxides) $NH_2OH.HCl$ + HOAc	3. + exchanging for acid-base effect at pH 1 HCl 4. NaOH then HNO_3 and HF (to solubilize silica bound to the struture of humic acid) 5. (bound as sulfides) HNO_3			marine and lukustrine sediment
Savvides et al. (1995)	1. NaOAc pH 8.2	2. NaOAc/ HOAc pH 5	3. (bound to Fe-Mn oxides) $NH_2OH.HCl$/ HOAc	4. H_2O_2/ HNO_3	5. HF/ HNO_3		contaminated sea sediment
Arunachalam et al. (1996)	1. NH_4OAc	2. CH_3COOH		4. (organic/ sulfidic fraction) H_2O_2	5. HNO_3	3. (reducible fraction) $NH_2OH.HCl$/ CH_3COOH	forest soil
Hall et al. (1996)	1. (adsorbed/ exhangeable/ carbonate) NaOAc pH 5		2. (amorphous Fe oxyhydroxides) $NH_2OH.HCl$/ HCl 60 degree C 3. (crystalline Fe oxides) $NH_2OH.HCl$/ HOAc 90 degree C	4. + sulfides $KClO_3$/ HCl	5. silicates HF-$HClO_4$-HNO_3		soils, tills, surficial sediments

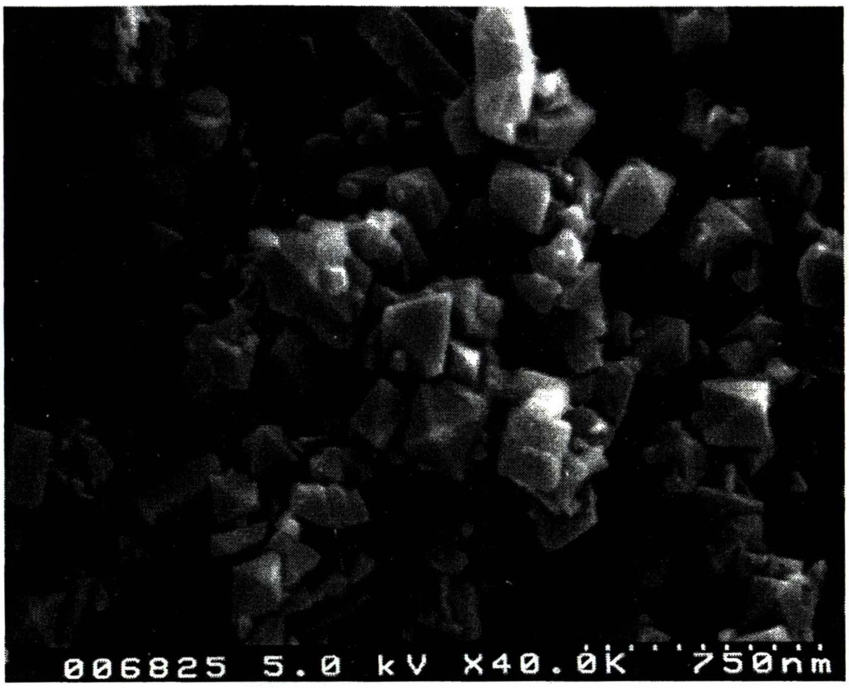
Appendix 1.9. (continued)

Authors	Exchangeable	Fraction associated with carbonates	Fraction associated with oxides	Fraction associated with organic matter	Total amount and/ or residual fraction	Other phases	Types of Materials
Tam & Wong (1996)	2. KNO_3		5. (Fe- and Mn-oxide bound) $Na_3C_6H_5O_7$, $NaHCO_3$, and $Na_2S_2O_4$	4. $Na_4P_2O_7$	6. HNO_3	1. (water soluble) H_2O 3. (inorganically bound) KF	mangrove soils
Zhang et al. (1997)	1. $Mg(NO_3)_2$		3. (crystalline Mn oxides or coprecipitated forms) $NH_2OH.HCl$ (amorphous forms) $(NH_4)_2C_2O_4.H_2O$ $H_2C_2O_4$ pH 3 4. (crystalline Fe oxide or coprecipitate forms) CBD, $Na_3C_6H_5O_7.2H_2O$, $NaHCO_3$, $Na_2S_2O_4$, 80 degree C	2. NaOCl (twice)			sandy citrus soils

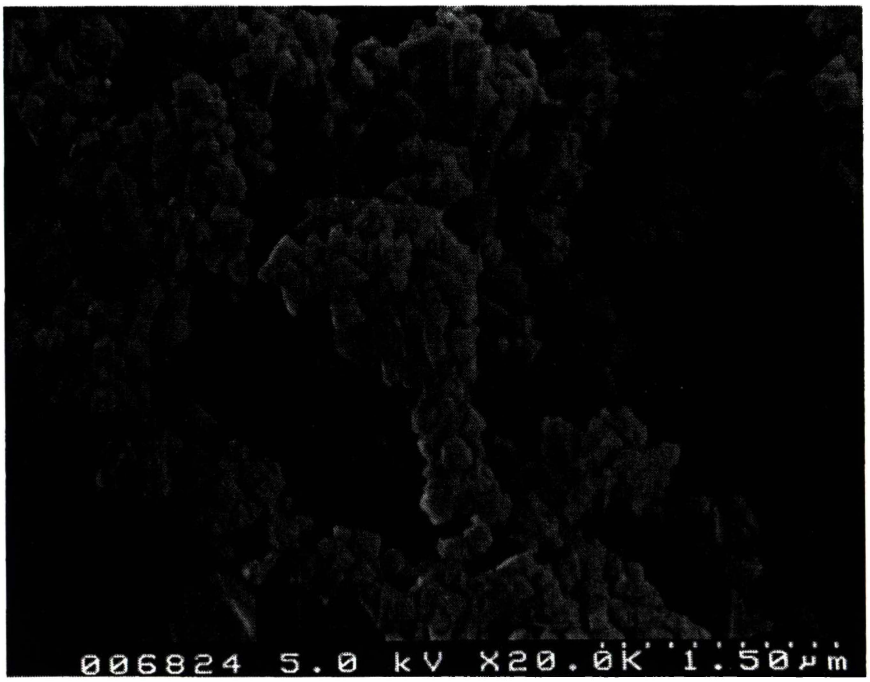
Appendix 2. Data relating to Chapter 2, and supplemental information

Appendix 2.1. Pictures of the solid phases from Scanning Electron Microscope.

hausmannite
(tetragonal octahedron)

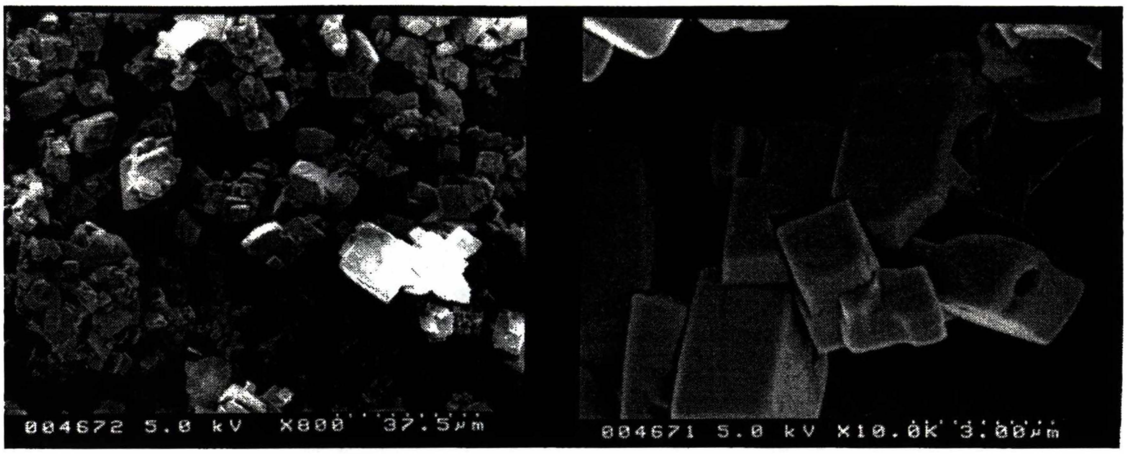


hausmannite



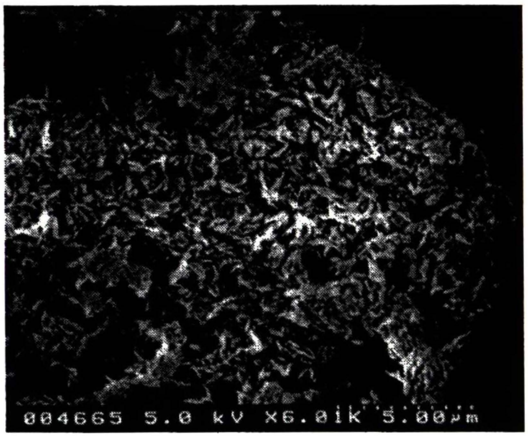
Appendix 2.1. (continued)

calcite
(rhombohedral structure)



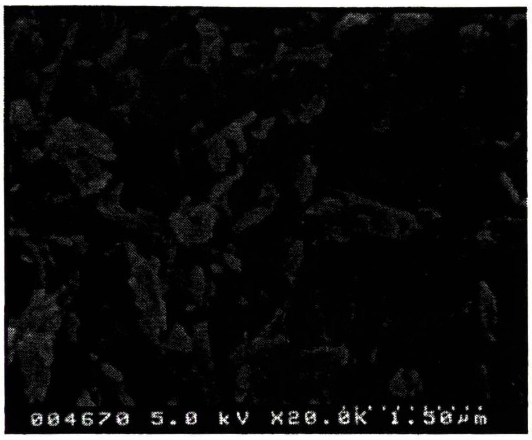
humic acid
(platy structure)

goethite
(needle like structure)



Appendix 2.1. (continued)

halloysite
(flat tubular structure)



Appendix 2.2. Comparison of d-spacing and relative intensity of X-ray diffraction results of the synthetic solid phases.

Solid phases		Calculated		Literature	
	2θ	d-spacing (Å)	intensity	d-spacing (Å)	intensity
goethite	20.9	4.250	53	4.183	100
(α FeOOH)	32.9	2.722	58	2.693	35
	34.3	2.614	74	2.583	12
	36.2	2.481	100	2.450	50
	52.9	1.731	89	1.719	20
halloysite	12.18	7.3	43	7.4 - 7.5	90
($Al_2Si_2O_5(OH)_4.2H_2O$ and	20.12	4.41	71	4.42	100
$Al_2Si_2O_5(OH)_4$)	26.68	3.34	100	3.34	90
	35.18	2.56	57	2.56	80
	38.28	2.35	63	2.36	60
	39.66	2.27	49	2.23	20
	54.88	1.673	51	1.678	80
	62.28	1.490	77	1.481	90
	73.84	1.277	49	1.283	70
calcite	29.28	3.050	100	3.035	100
($CaCO_3$)	31.38	2.851	3	2.845	3
	35.88	2.503	14	2.495	14
	39.28	2.294	82	2.285	18
	43.08	2.100	19	2.095	18
	47.06	1.931	10	1.927	5
	47.40	1.918	31	1.913	17
	48.44	1.879	27	1.875	17
	56.48	1.629	6	1.626	4
	57.28	1.608	14	1.604	8
hausmannite	28.8	3.0998	40	3.089	40
(Mn_3O_4)	32.0	2.7968	60	2.768	85
	35.9	2.5014	100	2.487	100
	37.8	2.3799	40	2.367	20
	58.3	1.5826	53	1.5762	25
	59.8	1.5465	80	1.5443	50

Appendix 2.3. Surface area measurement of the solid phases using adsorption of nitrogen (B.E.T. method).

Solid phases	Weight (g)	Temperature (degree C)	Outgassing time (hour)	Specific surface area ($m^2 g^{-1}$)	Mean specific surface area ($m^2 g^{-1}$)	95% confidence interval
halloysite	(1) 0.8856	120	2	24.1564	24.4	$24.4 < \mu < 24.6$
		120	6	24.1761		
		120	12	24.0818		
	(2) 0.8891	120	2	24.4501		
	(3) 0.8909	120	2	24.8359		
		200	1	24.3880		
			2	24.4501		

Note: without outgassing, the specific surface area (2 replicates) of halloysite = 21.6 and 23.6 $m^2 g^{-1}$

Solid phases	Weight (g)	Temperature (degree C)	Outgassing time (hour)	Specific surface area ($m^2 g^{-1}$)	Mean specific surface area ($m^2 g^{-1}$)	95% confidence interval
calcite	(1) 0.6622	120	2	0.6757	0.89	$0.70 < \mu < 1.08$
			6	0.7280		
			12	0.9057		
	(2) 0.6045	200	1	0.6578		
			2	1.1158		
	(3) 0.6526	120	2	1.2031		
	0.6464	120	2	0.9297		

Note: without outgassing the specific surface of calcite = 0.4746 $m^2 g^{-1}$

Appendix 2.3. (continued) Surface area measurement of the solid phases using adsorption of nitrogen (B.E.T. method).

Solid phases	Weight (g)	Temperature (degree C)	Outgassing time (hour)	Specific surface area (m^2 g^{-1})	Mean specific surface area (m^2 g^{-1})	95% confidence interval
goethite	(1) 0.6516	120	2	54.2906	54.9	$53.6 < \mu < 56.2$
			6	55.0589		
			12	55.3062		
		200 (a)	1	57.1525		
			2	61.3090		

Note: (a) At 200 degree C, the goethite was found to change from yellow to red; the corresponding specific surface areas were then excluded from the calculation of the mean value.
without outgassing the specific surface area = 52.004 m^2 g^{-1}

Solid phases	Weight(g)	Temperature (degree C)	Outgassing time (hour)	Specific surface area (m^2 g^{-1})
hausmannite	0.1844	120	6	12.3524 (b)
humic acid	0.2542	50	3	1.9226 (c)

Note: (b) without outgassing, the specific surface area of the hausmannite = 10.8629 m^2 g^{-1}.
(c) without outgassing, the specific surface are of the humic acid = 2.44093 m^2 g^{-1}.

In general, the surface area analysis was found to have good precision, there being no significant effect of temperature and outgassing time.

Appendix 2.4. Pb in "original", "clean", and spiked phases.

Solid phases	Sources ("Original")	Pb in the "original" phase [(a)] (microgram per gram)	Pb in the "clean" phase [(a)] (microgram per gram)	Pb in spiked phases (microgram per gram)
calcite	AR	Mean Pb = 0.13 n = 5 95% conf. int. $0.1 < \mu < 0.2$	-	Mean Pb = 1484 n = 6, %RSD = 6% 95% conf. int. $1412 < \mu < 1556$
		Mean Fe = 9 n = 4 95% conf. int. $6 < \mu < 12$	-	-
goethite	synthesized in this study	Mean Pb = 0.85 n = 3 95% conf. int. $0.4 < \mu < 1.4$	-	Mean Pb = 1822 n = 6, %RSD = 5% 95% conf. int. $1752 < \mu < 1892$
halloysite	NZ China Clay Ltd.	Mean Pb = 11 n = 5 95% conf. int. $10 < \mu < 12$	Mean Pb = 10 n = 3 95% conf. int. $8 < \mu < 10$	Mean Pb = 946 n = 6, %RSD = 1% 95% conf. int. $938 < \mu < 954$
		Mean Fe = 344 n = 4 95% conf. int. $334 < \mu < 354$	Mean Fe = 260 n = 3 95% conf. int. $231 < \mu < 289$	
hausmannite	synthesis	Mean Pb = 7 n = 4 95% conf. int. $0 < \mu < 19$		Mean Pb = 1843 n = 6, %RSD = 5% 95% conf. int. $1763 < \mu < 1923$
humic acid	Aldrich	Mean Pb = 9 n = 3 95% conf. int. $4 < \mu < 14$	Mean Pb = 8 n = 3 95% conf. int. $6 < \mu < 10$	Mean Pb = 1466 n = 3, %RSD = 2% 95% conf. int. $1441 < \mu < 1491$

Appendix 2.5. Pb, Mn, and Fe in natural samples of Te Rapa peat and Kainui soils.

Soils	Elements (migrogram per gram)		
	Pb	Mn	Fe
(1) Te Rapa	7	49	2830
(3 replicates)	8	50	2732
	6	48	2767
	Mean Pb = 7	Mean Mn = 49	Mean Fe = 2776
	% RSD = 14	%RSD = 2	% RSD = 2
(2) Kainui	26	1215	35780
(3 replicates)	23	1278	35765
	25	1269	36227
	Mean Pb = 25	Mean Mn = 1254	Mean Fe = 35924
	% RSD = 6	%RSD = 3	% RSD = 0.7

Appendix 2.6. Effect of the high temperature and acetic acid solution used in the reducing step (0.04 M $NH_4OH.HCl$) of the extraction protocol of Tessier et al. on sorptive capacity of humic acid.

Sample	Pb (microgram) retained on solid (gram) in the presence of acetic acid	Pb (microgram) retained on solid (gram) in the absence of acetic acid
humic acid @ room temperature	235 239	332 330
humic acid @ 96 degree C	98 94 101 (three replicates)	222 213

Appendix 2.7. Sources and preparations of the sequestering materials used in this study.

1. Sulfonate ion exchange membrane strips.

The sulfonate cation exchange membrane, supplied in a moist state in the form of 125 mm square sheets, was purchased from BDH Chemicals Ltd., England. The membrane is regarded as an ion exchange resin produced in sheets rather than in the conventional form of beads or granules with polystyrene cross-linked with divinylbenzene (BDH Product Information). Characteristics of the ion exchange membranes include high permselectivity, low electrical resistance, high mechanical strength, resistance to chemical attack, and high thermal resistance (BDH Product Information). After use, the membrane can be regenerated to its Na^+ form (Saggar et al., 1990). The regeneration procedure involves (1) washing the membrane thoroughly 2-3 times with clean water; (2) placing in a beaker containing 0.5 M NaCl and stirring occasionally for about 1 hour (repeating this step in fresh solution for another hour and followed by a couple of washings with clean water); and (3) keeping the membrane strips in clean water ready for use.

2. SiO_2 gel and wool functionalized with dithiocarbamate
(Silica-$Si(CH_2)_3$ $NHCS_2^-H^+$and wool-$NHCS_2^-H^+$).

These materials were supplied by Dr. W. Henderson (Chemistry Department, Waikato University, NZ). The preparation of the silica-immobilized ligand involved activation of the surface of silica gel (80 - 120 μm) by refluxing in concentrated HCl (Aue and Hastings, 1969; Khatib and Parish, 1989). The activated silica gel was then washed with distilled water until the washings were neutral, and dried at 300 °C. Reaction of the activated silica gel with excess 3-aminopropyl triethoxysilane, $(EtO)_3Si(CH_2)_3NH_2$, was then carried out in dry toluene at 100 °C. The product (Silica-$Si(CH_2)_3$ NH_2), was then reacted with excess CS_2 to form the dithiocarbamate. The derivatized silica gel was washed with distilled water and air-dried.

The functionalized wool was prepared by overnight soaking of clean white wool in a solution of toluene and CS_2. The dithiocarbamate-functionalized wool was then washed with methanol to remove CS_2 and allowed to dry in air.

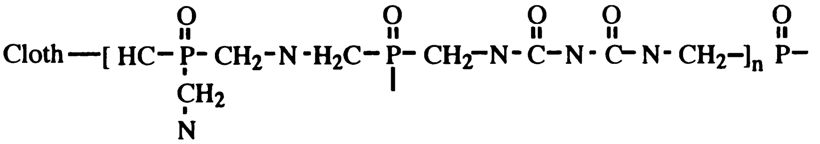
3. Thiol resin (RSH).

Duolite GT-73, supplied wet under distilled water, was purchased from Supelco Chromatography Products Ltd. This resin is characterized by the presence of thiol functional groups, a macroreticular matrix, a 16-50 mesh size (~ 300 μm to ~ 1200 μm), a maximum operating temperature of ~ 121 °C, and an effective pH range ~ 1- 13. Usual applications of the resin include removal of mercury, silver, lead, copper, and cadmium from waters and wastewaters.

4. SiO_2 gel functionalized with thiol groups
(Silica-$Si(CH_2)_3SCH_2CHOHCH_2SH$).

This material was supplied by Dr. W. Henderson (Chemistry Department, Waikato University, NZ). Activated silica gel (prepared as previously outlined for SiO_2 gel functionalized with dithiocarbamate) was reacted with 3-chloropropyl triethoxysilane, $Cl(CH_2)_3Si(OEt)_3$, in toluene at 100 °C. The product, silica-Si-$(CH_2)_3Cl$, was then reacted with excess $HSCH_2CH(OH)CH_2SH$ to form the thiol-functionalized silica.
The functionalized silica gel was then washed with water and allowed to dry.

5. Chemically-treated cotton fabric (Proban)



$$\text{Cloth}-[\,HC-\underset{\begin{subarray}{c}|\\CH_2\\|\\N\end{subarray}}{\overset{\overset{O}{\|}}{P}}-CH_2-N-H_2C-\underset{|}{\overset{\overset{O}{\|}}{P}}-CH_2-N-\overset{\overset{O}{\|}}{C}-N-\overset{\overset{O}{\|}}{C}-N-CH_2-]_n\,\overset{\overset{O}{\|}}{P}-$$

Proban is a trademark for a commercial flame-retardant cotton fabric, manufactured by Albright & Wilson, Ltd, UK. The material is a polymer formed from phosphonium salt ($P(CH_2OH)_4^+Cl^-$), urea, and ammonia (Henderson, 1996). Specific properties of flame retardants are discussed in the literature (Faroq et al., 1994; Hall et al, 1994). The chemistry of hydroxylmethyl phosphorus compounds, (particularly) in relation to their flame retardancy properties, is reviewed by Vail et al. (1982), Frank et al. (1982a, b), and Daigle and Frank (1982).

6. Phosphine-derivatized wool.
(wool-$\underset{|}{N}$-CH_2-$P(CH_2OH)_2$; wool-THP)

This material was supplied by Dr. W. Henderson (Chemistry Department, Waikato University, NZ). A solution of $P(CH_2OH)_3$ was prepared in aqueous solution by addition of 1 mole equivalent of NaOH to $P(CH_2OH)_4^+Cl^-$, THPC. White wool was soaked in the solution for about 2 minutes, and a small amount of methanol was then added to help wet the wool. The functionalized wool was then rinsed with water to remove excess $P(CH_2OH)_3$, washed with methanol and air-dried. The presence of phosphine groups on the wool is readily illustrated by the reaction with aqueous Ni^{2+} ions, which gives an orange colour due to the formation of square-planar nickel (II) phosphine species on the support (Henderson, 1996).

7. Aerophine® 3418A promoter.

Aerophine (sodium diisobutyl dithiophosphinate), supplied as 50% w/v aqueous solution, was purchased from American Cynamid Company, USA. Some relevant characteristics provided by the supplier include: alkaline pH, viscosity of 23 centipoise at 24 °C, and suitable to use with polyethylene.

Appendix 2.8.(a) Inter-Laboratory comparison of Pb in contaminated environmental samples to determine accuracy and overall precision.

Sample	This laboratory ($\mu g\ Pb\ g^{-1}$)	R.J.Hill ($\mu g\ Pb\ g^{-1}$)	Mean of replicate analyses ($\mu g\ Pb\ g^{-1}$)	Standard deviation of all the replicate analyses	Coefficient of variation (100 × SD/mean)	95% Confidence interval ($\mu g\ Pb\ g^{-1}$)
Dust	343	323	347	19	5	347 ± 24
(100 µm< dust < 1mm)	376	352				
		340				
Soil	78	82	81	2	2	81 ± 3
(< 1 mm)		80				
		82				

Note: Dust sample was collected from the first site at Steele park in April 1996. Soil sample was collected from the fifth sampling site at Mellville park April 1996. These samples were also used in the assessment of the potential usefulness of cryptand in inhibiting redistribution.

Appendix 2.8. (b) Partial characterization of contaminated soil and dust samples used in the assessment of the modified extraction scheme by cryptand.

Parameters ($\mu g\ g^{-1}$)*	Soil (soil fraction < 1 mm)	Dust (100 µm< dust fraction < 1 mm)
% Organic content	12.0 ± 0.00	12.0 ± 3.00
Ca	1710 ± 41.0	5620 ± 1170
Br	≤ 50.0	≤ 50.0
Fe	16600 ± 700	23400 ± 1940
Mn	1002 ± 31.4	368 ± 7.00
Al	26300 ± 2190	8210± 576
Cd	341 ± 79.6 ng g^{-1}	347 ± 142 ng g^{-1}
Cr	9.09 ± 0.704	21.6 ± 7.10
Cu	28.2 ± 7.70	61.9 ± 10.9
Ni	5.85 ± 2.42	13.8 ± 4.02
Pb	81.3 ± 2.67	338 ± 7.49
Zn	82.6 ± 1.93	204 ± 4.84

Note:

* for all metals except Cd.

Analyzed by RJ Hill Ltd.

The values reported are arithmetic means of three individual sample analyses ± 95% confidence error.

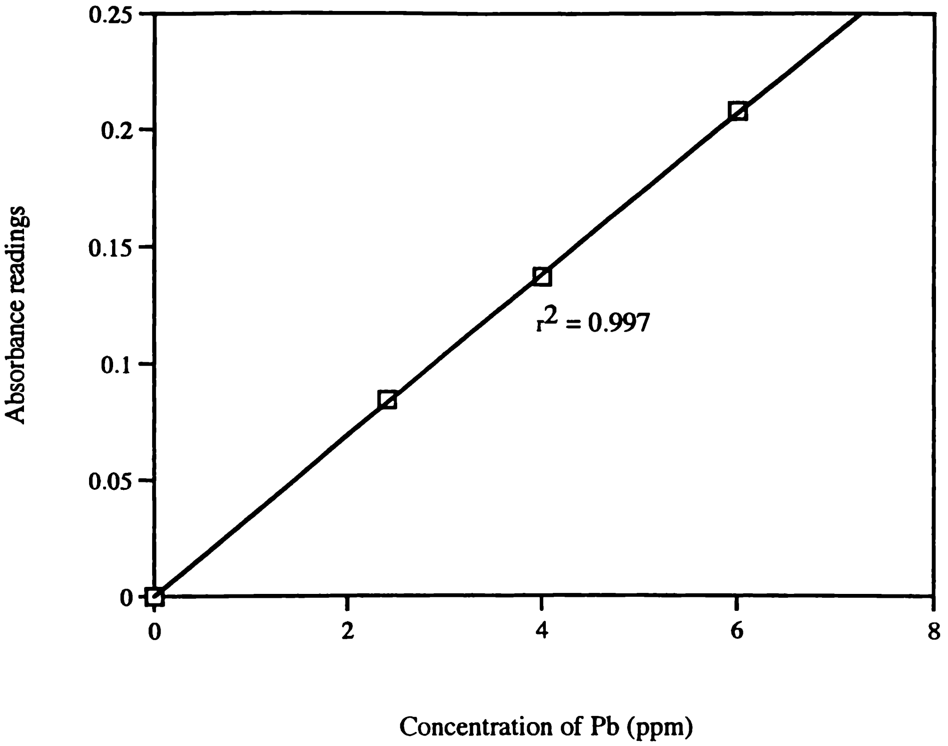
All except % organic content were analyzed by either ICP-MS or ICP-OES (R.J. Hill).

The analytical methods used and the detection limits are summarized in Appendix 2.8. (c).

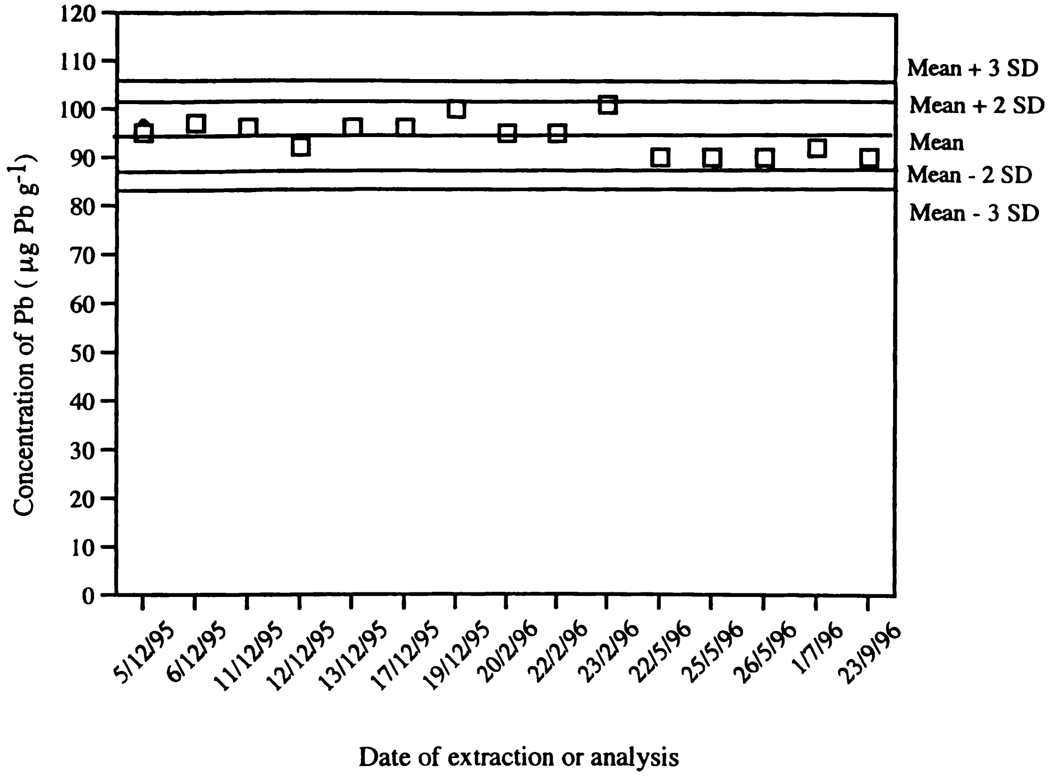
Percentage organic content was calculated by the difference of dry weight and weight after ignition.

Appendix 2.8. (c) Summary of methods and the detection limit used in characterization of contaminated soil and dust used in the assessment of the modified extraction scheme by cryptand.

Parameters	Methods used	Detection limits (in solution)
Ca	ICP-OES	0.02 $\mu g\ ml^{-1}$
Br	ICP-MS	0.005 $\mu g\ ml^{-1}$
Fe	ICP-OES	0.01 $\mu g\ ml^{-1}$
Mn	ICP-OES	0.005 $\mu g\ ml^{-1}$
Al	ICP-OES	0.02 $\mu g\ ml^{-1}$
Cd	ICP-MS	0.00005 $\mu g\ ml^{-1}$
Cr	ICP-MS	0.005 $\mu g\ ml^{-1}$
Cu	ICP-MS	0.005 $\mu g\ ml^{-1}$
Ni	ICP-MS	0.001 $\mu g\ ml^{-1}$
Pb	ICP-MS	0.0001 $\mu g\ ml^{-1}$
Zn	ICP-MS	0.001$\mu g\ ml^{-1}$



Appendix 2.9. (a) A typical calibration curve for Pb analysis during the investigation of sequential extraction.



Appendix 2.9. (b). Analysis of Pb in the reference soil material during the investigation of Pb in roadside soils and dust. (GBW 07401 reference soil material certified value: 98 ± 3 μg g^{-1})

Date of analysis	μg Pb g^{-1}
5/12/95	95 and 96 (2 sample replicates)
6/12/95	97
11/12/95	96
12/12/95	92
13/12/95	96
17/12/95	96
19/12/95	100
20/2/96	95
22/2/96	95
23/2/96	101
22/5/96	90
25/5/96	90
26/5/96	90
1/7/96	92
23/9/96	90

Note: arithmetic mean = 94; SD = 3.5; 2SD = 7.0; 3SD = 10.5; N =16.

Appendix 3. Data relating to Chapter 3

Appendix 3.1. Observed recovery of Pb from individually spiked humic acid as determined using step 1 followed by step 2 of Tessier et al.'s protocol, and observed recovery of Pb from individually spiked humic acid as determined using a single step 2 of the protocol.

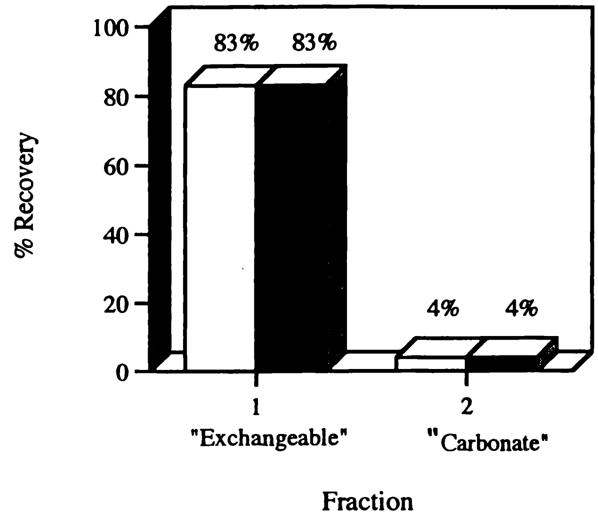


Fig. A. Observed recovery of Pb from individually spiked humic acid as determined using step 1 followed by step 2 of Tessier et al.' s protocol.

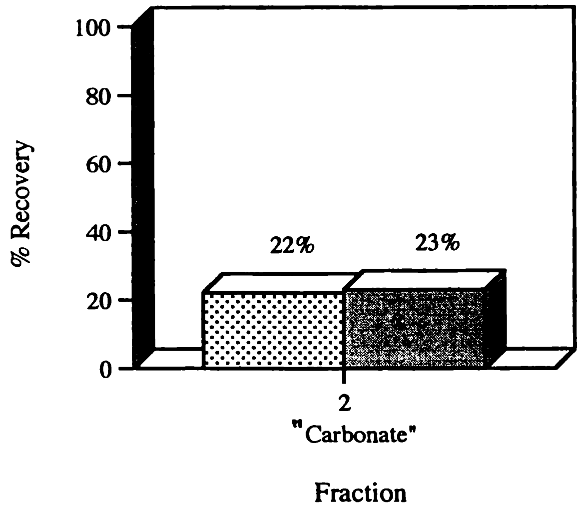


Fig. B. Observed recovery of Pb from individually spiked humic acid as determined using a single step 2 of Tessier et al.'s protocol.

Appendix 3.2. Percentage of Pb recovered from spiked natural soils using the BCR extraction.

	Pb (microgram) per g sample		Step 1 "Exchangeable and Carbonate bound" & "Water soluble"		Step2 "Reducible"		Step3 "Oxidizable"		Step4 "Residual"		Total % Recovery	
Spiked calcite + Te Rapa	302	302	7	7	15	15	74	75	8	8	104	105
Spiked calcite + Kainui	318	318	10	9	80	86	7	8	5	5	102	108
Spiked halloysite + Te Rapa	288	288	4	4	39	39	57	58	9	8	109	108
Spiked halloysite + Kainui	302	302	17	17	68	66	9	10	9	7	101	101

Appendix 4. Data relating to Chapter 4

Appendix 4.1. Percentage recoveries of Pb in aerophine extracts ("modified" first extraction step) collected from various systems.

Systems	total amount of Pb in the system (microgram)		without atom trap		Ti atom trap		quartz atom trap	
(i) 5 phase with 0.025 g spiked calcite (duplicate)	37	37	27	31	-		-	
(ii) (repeat) 5 phase with 0.025 g spiked calcite (duplicate)	37	37	63	67	-		-	
(iii) (repeat) 5 phase with 0.025 g spiked calcite	37	-	52 36$^{(1)}$	- -	73 66	- -	92 50	- -
(iv) 5 phase with 0.050 g spiked calcite (duplicate)	74	74	39 32$^{(1)}$	43 33$^{(1)}$	54 49	53 48	65 39	63 37
(v) individually spiked calcite (duplicate)	37	34	112 105	109 101	75 -	76 -	84 84	83 83

Note: The Pb recovery data in (i) and (ii) are illustrated in Fig. 4.1 subsection 4.2.1. The corresponding recovery of Pb at reducing, oxidizing, and acid digestion are: for (i) 24 and 34, 33 and 28, and none, respectively, with total recoveries of 93 and 84%; for (ii) 14 and 20, 21 and 24, and none, respectively, with total recoveries of 98 and 109%.

$^{(1)}$ indicates repeat FAAS analysis.

Appendix 4.2. Analysis of Pb in aerophine extracts (collected from a five-phase model soil with spiked calcite) by R J Hill Laboratories Ltd.

Sample name	Soluble Pb (1) ($g\ m^{-3}$)
Blank aerophine	< 0.001
Standard 2 ppm Pb aerophine	1.16
Aerophine sample 1	0.552
Aerophine sample 2	0.576

Note: (1) Method used (not Telarc Registered): filtered sample, ICP-MS, detection limit 0.001 $g\ m^{-3}$.

Analyst's comments: The results reported above were analyzed on 10 × dilutions. 100 × dilutions gave the following results: < 0.01, < 0.01, 0.09, 0.14 $g\ m^{-3}$ in the above sample order. Graphite furnance AA detected no lead in this matrix (< 0.2 $g\ m^{-3}$ for all samples)

Source: Laboratory report No: 95665.

Appendix 4.3. Percentages of Pb recovered from individually spiked calcite (0.025 g) in conventional 0.11 M acetic acid, at various extraction times (and total contact times).

Extraction time (not cumulative time)	Total contact time (Extraction time + centrifugation time)	% Recovery of Pb
15 min	25 min (a)	109
15 min	45 min (b)	117
1/2 h	1 h (b)	116
1 h	1.5 h (b)	117
16 h	16.5 h (b)	126

(a) The speed of centrifuation was 13 000 rpm.

(b) The speed of centrifugation was 10 000 or 12 000 rpm.

Appendix 4.4. Pb (0-4 ppm range) determined for palladium extracts from Experiments 4 & 5, obtained from two sets of standard solutions.

Standard solutions prepared with previous contact with MIBK (Calibration curve r^2 0.9954, max error 0.124 ppm)

Samples	Pb conc.(ppm)	Mean of at least 5 absorbance readings	% RSD
Blank	0	0.005	-
Standard 1	1	0.029	4.81
Standard 2	2	0.052	3.01
Standard 3	4	0.114	2.06
Sample from Expt. 4	2.579	0.071	7.49
Control sample from Expt. 5	0.103	0.003	high
Sample from Expt. 5	1.861	0.051	5.49

Standard solutions prepared without previous contact with MIBK (Calibration curve r^2 0.9976, max error 0.075 ppm)

Samples	Pb conc.(ppm)	Mean of 5 absorbance readings	% RSD
Blank	0	0.000	-
Standard 1	1	0.032	4.35
Standard 2	2	0.061	5.74
Standard 3	4	0.099	5.32
Sample from Expt. 4	2.629	0.074	4.70
Control sample from Expt. 5	0.017	0.001	high
Sample from Expt. 5	1.697	0.051	9.94

Appendix 4.5. Percentages of Pb and Zn recovered in aqueous extracts from Experiment 5 (Zn pyrrolidine dithiocarbamate trial). (values in parenthesis are those from repeated Experiment 8).

Elements	Total amount added in the system	Percentage recoveries in					
	(microgram)	acetic acid	palladium solution	NH_2OH HCl	ammonium acetate	aqua regia	Total % recovery
Pb	37	0 (0)	77 (82)	0 (0)	26 (41)	0 (0)	103 (123)
Zn	427	48 (62)	5 (0)	16 (18)	37 (36)	1 (2)	109 (118)

Appendix 4.6. Percentages of Pb and Zn recovered in aqueous extracts from Experiment 6 (Zn pyrrolidine dithiocarbamate trial).

Elements	Total amount added in the system	Percentage recoveries in					
	(microgram)	acetic acid	palladium solution	NH_2OH HCl	ammonium acetate	aqua regia	Total % recovery
Pb	37	0	0	0	90	20	110
Zn	427	55	0	18	43	3	119

Appendix 4.7. Percentages of Pb and Zn recovered in aqueous extracts from Experiment 7 (Zn pyrrolidine dithiocarbamate trial).

Elements	Total amount added in the system	Percentage recoveries in					
	(microgram)	acetic acid	palladium solution	NH_2OH HCl	ammonium acetate	aqua regia	Total % recovery
Pb	71	0	0	0	75	14	89
Zn	427	46	0	25	44	2	117

Appendix 4.8. Percentage recovery of Pb from the individually spiked halloysite (0.075 g) in conventional 0.11 M acetic acid, at various extraction times (and total contact times).

Extraction time (not cumulative time)	Total contact time (Extraction time + 1/2 h centrifugation time)	% Recovery of Pb
15 min	45 min	63
1/2 h	1 h	66
3 h	3.5 h	90
5 h	5.5 h	83
16 h	16.5 h	86

Appendix 4.9. Percentages of Pb and Zn recovered in aqueous extracts from Experiments 9 to 12 (Zn pyrrolidine dithiocarbamate trial).

Elements	Total amount added in the system (microgram)	Percentage recoveries in acetic acid	palladium solution	NH_2OH HCl	ammonium acetate	aqua regia	Total % recovery
Experiment 9 (5 h extraction time)							
Pb	37	0	0	0	91	21	112
Zn	427	41	0	22	45	1	109
Experiment 10 (1 h extraction time)							
Pb	37	0	0	0	88	15	103
Zn	427	56	0	17	42	1	116
Experiment 11 (15 min extraction time)							
Pb	37	0	82	0	42	0	124
Zn	427	52	20	11	30	1	114
Experiment 12 (45 min extraction time)							
Pb	37	0	46	0	64	17	127
Zn	427	62	0	15	36	1	114

Appendix 4.10. Percentages of Pb recovered in aqueous extracts from five-phase model soils containing spiked halloysite (Experiments 13 & 14) of Zn pyrrolidine dithiocarbamate trials, with different extraction times at the "modified" first extraction step.

Elements	Total amount added in the system (microgram)	Percentage recoveries in palladium solution		NH$_2$OH HCl	ammonium acetate	aqua regia	Total % recovery
Experiment 13							
Pb	72	25(a)	2(b)	0	60	11	98
Experiment 14							
Pb	72	51(c)	0(d)	0	42	6	99

Note: (a) and (b) refer to the recoveries of Pb at the first and second1/2 h extraction times, respectively (at the "modified" extraction step).
The recovery of 27% (~20 microgram Pb) is equivalent to about 40% of Pb released from the spiked halloysite within 1/2 h (48 microgram).
(c) and (d) refer to the recoveries of Pb at the first and second 15 min extraction times, respectively (at the "modified" extraction step).
The recovery of 51% (~ 37 microgram Pb) is equivalent to about 82% of Pb released from the spiked halloysite within 15 min (45 microgram).

Appendix 4.11. Percentage recoveries of Pb from 5-phase model soil containing spiked halloysite (Experiment 15), with successive modified extractions using $Zn(PDC)_2$.

Numbers of the successive extraction at the "modified" first step	Cumulative extraction time	Cumulative extraction time + centrifugation time	Pb (ppm) in palladium extracts			Mean Pb (ppm)	% Pb recovery (of total Pb in the system 73 microgram)	% Cumulative Pb recovery
			analyzed without atom trap		analyzed using quartz atom trap			
1st	15 min	25 min	3.082	-	2.837	2.960	54	54
2nd	30 min	50 min	1.002	-	0.943	0.973	4	58
3rd	45 min	1 h 15 min	0.453	-	0.451	0.452	4	62
4th	1 h	1 h 40 min	0.280	-	0.311	0.290	3	65
5th	1 h 15 min	2 h 5 min	0.197	0.168	0.278	0.214	3	68
6th	1 h 30 min	2 h 30 min	0.157	0.154	0.197	0.169	2	70
7th	1 h 45 min	2 h 55 min	0.156	-	0.142	0.149	2	72
8th	2 h	3 h 20 min	0.182	0.159	0.192	0.178	3	75
9th	2 h 15 min	3 h 45 min	0.179	0.155	0.157	0.164	2	77
10th	2 h 30 min	4 h 10 min	0.065	0.023	0.125	0.070	0	77
11th	2 h 45 min	4 h 35 min	0.047	-	0.173	0.087	0	77
12th	3 h	5 h	(-)0.029	-	0.135	0.068	0	77
13th	3 h 15 min	5 h 25 min	0.031	-	0.110	0.055	0	77

Extraction steps	% Recovery
Reducing step	0
Oxidizing step	10
Acid digestion step	3

Total recovery of Pb is in the range of 77 to 90%.

Appendix 4.12.(a). Percentage recoveries of Pb from Te Rapa soil containing spiked halloysite (Experiment 16), with successive modified extractions using $Zn(PDC)_2$.

Numbers of the successive extraction at the "modified" first step	Cumulative extraction time	Cumulative extraction time + centrifugation time	Pb (ppm) in palladium extracts		Pb (ppm)	% Pb recovery (of total Pb in the system 144 microgram)	% Cumulative Pb recovery
			analyzed without atom trap	analyzed using quartz atom trap			
1st	15 min	25 min	7.153	-	7.153	64	64
2nd	30 min	50 min	2.261	-	2.261	6	70
3rd	45 min	1 h 15 min	1.069	-	1.069	5	75
4th	1 h	1 h 40 min	0.643	-	0.643	4	79
5th	1 h 15 min	2 h 5 min	0.473	-	0.473	3	82
6th	1 h 30 min	2 h 30 min	0.328	-	0.328	2	84
7th	1 h 45 min	2 h 55 min	0.205	0.258	0.232	1	85
8th	2 h	3 h 20 min	0.125	0.237	0.181	1	86
9th	2 h 15 min	3 h 45 min	-	0.139	0.139	1	87
10th	2 h 30 min	4 h 10 min	-	0.098	0.098	0	87
11th	2 h 45 min	4 h 35 min	-	0.086	0.086	0	87
12th	3 h	5 h	-	0.051	0.051	0	87
13th	3 h 15 min	5 h 25 min	-	0.040	0.040	0	87

Extraction steps	% Recovery
Reducing step	0
Oxidizing step	6
Acid digestion step	3

Total recovery of Pb is in the range of 94 to 96%.

Appendix 4.12. (b) Pb (0-8 ppm range) determined for palladium extracts from Experiment 16 (Te Rapa soil with spiked halloysite), obtained from two sets of standard solutions.

Standard solutions prepared with previous contact with MIBK (Calibration curve r^2 0.9996, max error 0.061ppm)

Samples	Pb conc.(ppm)	Means of absorbance readings
Blank	0	0.002
Standard 1	2.4	0.128
Standard 2	4	0.207
Standard 3	6	0.311
Standard 4	8	0.401
1st extract from the successive extraction at the modified step	7.492	0.378
2nd extract	2.373	0.126

Standard solutions prepared without previous contact with MIBK (Calibration curve r^2 0.9992, max error 0.106 ppm)

Samples	Pb conc.(ppm)	Mean of 5 absorbance readings
Blank	0	0.000
Standard 1	2	0.116
Standard 2	4	0.233
Standard 3	6.4	0.348
Standard 4	8	0.429
1st extract from the successive extraction at the modified step	7.153	0.389
2nd extract from	2.261	0.131

Appendix 4.13. Percentage recoveries of Pb from Te Rapa soil containing spiked calcite (Experiment 17), with successive modified extractions using $Zn(PDC)_2$.

Numbers of the successive extraction at the "modified" first step	Cumulative extraction time	Cumulative extraction time + centrifugation time	Pb (ppm) in palladium extracts		Mean Pb (ppm)	% Pb recovery (of total Pb in the system 151 microgram)	% Cumulative Pb recovery
			Standard prepared without previous contact with MIBK	Standard prepared with previous contact with MIBK			
1st	15 min	25 min	11.664	11.674	11.669	99	99
2nd	30 min	50 min	2.829	2.775	2.802	2	101
3rd	45 min	1 h 15 min	0.866	0.887	0.877	2	103
4th	1 h	1 h 40 min	0.338	0.426	0.382	2	105
5th	1 h 15 min	2 h 5 min	0.155	-	0.155	0	105
6th	1 h 30 min	2 h 30 min	0	-	0	0	105
7th	1 h 45 min	2 h 55 min	0	-	0	0	105
8th	2 h	3 h 20 min	0	-	0	0	105
9th	2 h 15 min	3 h 45 min	0	-	0	0	105
10th	2 h 30 min	4 h 10 min	0	-	0	0	105
11th	2 h 45 min	4 h 35 min	0	-	0	0	105
12th	3 h	5 h	0	-	0	0	105
13th	3 h 15 min	5 h 25 min	0	-	0	0	105

Extraction steps	% Recovery
Reducing step	0
Oxidizing step	0
Acid digestion step	0

Total recovery of Pb is in the range of 99 to 105%.

Appendix 4.14. (a). Percentages of Pb recovered from five-phase soil models containing spiked calcite, a fixed composition of hausmannite of 10 %, but varying the percentage of humic acid, using 9×10^{-3} M cryptand in 0.11 M acetic acid (Fig. 4.8: Curve A).

Percentage of humic in the models	Step 1		Step 2: 0.1 M $NH_2OH.HCl$		Step 3: H_2O_2		Step 4: aqua regia		Total % recovery	
	(A) acetic acid	(B) cryptand/ acetic acid	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0	0	30	0 (a)	82	64 (a)	0	46 (a)	0	110	112
2	-	24	-	71	-	17	-	0	-	111
5	-	21	-	50	-	26	-	10	-	107
10	-	20	-	31	-	42	-	15	-	108
15	-	19	-	21	-	52	-	15	-	107
20	0	20	0	14	92	67	21	11	113	112

Note: (a) reason for this result unclear.

Appendix 4.14. (b) Percentages of Pb recovered from five-phase soil models containing spiked calcite, a fixed composition of humic acid of 20 %, but varying the percentage of hausmannite, using 9 ×10^{-3} M cryptand in 0.11 M acetic acid (Fig. 4.8: Curve B).

Percentage of hausmannite in the models	Step 1		Step 2: 0.1 M $NH_2OH.HCl$		Step 3: H_2O_2		Step 4: aqua regia		Total % recovery	
	(A) acetic acid	(B) cryptand/ acetic acid	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0	8	62	19	11	69	31	10	10	106	114
5	-	30	-	0	-	61	-	18	-	109
10	0	20	0	14	92	67	21	11	113	112

Appendix 4.14.(c) Percentages of Pb recovered from five-phase soil models containing spiked calcite, no hausmannite and varying the percentage of humic acid, using 9 ×10^{-3} M cryptand in 0.11 M acetic acid (Fig. 4.8: Curve C).

Percentage of humic in the models	Step 1		Step 2: 0.1 M $NH_2OH.HCl$		Step 3: H_2O_2		Step 4: aqua regia		Total % recovery	
	(A) acetic acid	(B) cryptand/ acetic acid	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0 (a)	41 (b)	102	65 (b)	12	0	0	0	0	106	112
2	30	97	54	12	18	0	0	0	102	109
5	20	90	41	12	42	11	0	0	103	113
10	11	77	29	11	63	23	0	0	103	111
15	4	72	20	8	75	34	0	0	99	111
20	8	62	19	8	69	40	10	0	106	116

Note: (a) In the absence of sand, Pb recovered 53%, 63%, 0%, and 0% at conventional first extraction step (0.11 M acetic acid with 25 min total contact time), reducing, oxidizing, and acid digestion steps, respectively.

(b) It is possible that in the absence of humic acid and hausmannite, Pb redistribution is influenced by goethite.

Appendix 4.14. (d) Percentages of Pb recovered from five-phase soil models containing spiked calcite, a fixed composition of humic acid of10 %, but varying the percentage of hausmannite, using 9×10^{-3} M cryptand in 0.11 M acetic acid (Fig. 4.8: Curve D).

Percentage of hausmannite in the models	Step 1		Step 2: 0.1 M $NH_2OH.HCl$		Step 3: H_2O_2		Step 4: aqua regia		Total % recovery	
	(A) acetic acid	(B) cryptand/ acetic acid	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0	11	77	29	11	63	23	0	0	103	111
1	13	71	29	15	53	18	0	0	95	104
2	10	61	18	7	64	30	0	0	92	98
4	7	48	0	0	73	44	15	10	95	102

Appendix 4.15.(a) Percentages of Pb recovered from five-phase model soils containing spiked calcite, a fixed compositon of hausmannite of 10 %, but varying the percentage of humic acid, using1×10^{-4} M NTA in 0.11 M acetic acid (Fig. 4.9: Curve E).

Percentage of humic acid in the model	Step 1		Step 2: 0.1M $NH_2OH.HCl$		Step3:H_2O_2		Step 4 : aqua regia		Total % Recovery	
	(A) acetic acid	(B) NTA/ acetic acid	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
0	0 (a)	17	0	7	64	67	46	19	110	110
2	-	13	-	0	-	65	-	26	-	104
5	-	12	-	6	-	67	-	20	-	105
10	-	9	-	0	-	77	-	18	-	104
15	-	8	-	0	-	85	-	14	-	107
20	0	0	0	0	92	86	21	16	113	102

Note: (a) data from Appendix 4.14 (Curve A).

Appendix 4.15.(b) Percentages of Pb recovered from five-phase model soils containing spiked calcite, a fixed composition of humic acid of 5%, but varying the percentage of hausmannite, using 1×10^{-4} M NTA in 0.11 M acetic acid (Fig. 4.9: Curve F).

Percentage of hausmannite in the model	Step 1		Step 2: 0.1M $NH_2OH.HCl$		Step3:H_2O_2		Step 4 : aqua regia		Total % Recovery	
	(A) acetic acid	(B) NTA/ acetic acid	(A)	(C)	(A)	(C)	(A)	(C)	(A)	(C)
0	32	87	52	17	32	11	0	0	116	115
1	22	66	56	25	36	24	0	0	114	115
2	17	58	46	24	42	27	8	0	113	109

Appendix 5. Data relating to Chapter 5

Appendix 5.1. Pb concentrations in top 2 cm soils (μg g^{-1}) vs distance (m) from kerbs of the four parks.

Milne Park

	Replicates (μg g^{-1})							
	#1	#2	#3	#4	#5	mean (μg g^{-1})	SD	mean ± 95% confidence interval
kerbside surface 0 - 2 cm	1309	1219	778	662	681	930	310	930 ± 385
10 m top 2 cm	90	92	127	191	211	142	56	142 ± 70
20 m top 2 cm	103	75	70	195	167	122	56	122 ± 70
50 m top 2 cm	39	35	38	57	67	47	14	47 ± 17

Melville

	Replicates (μg g^{-1})							
	#1	#2	#3	#4	#5	mean (μg g^{-1})	SD	mean ± 95% confidence interval
kerbside surface 0 - 2 cm	-	123	113	185	98	130	38	130 ± 60
kerbside 2 - 4 cm	81	59	60	-	-	67	12	67 ± 31
kerbside 4 - 6 cm	49	42	26	-	-	39	12	39 ± 29
25 m top 2 cm	34	30	36	25	24	30	5	30 ± 6
50 m top 2 cm	19	22	14	17	14	17	3	17 ± 5

Appendix 5.1. (continued) Pb concentrations in top 2 cm soils ($\mu g\ g^{-1}$) vs distance (m) from kerbs of the four parks.

University' s field on Knighton Road

	Replicates ($\mu g\ g^{-1}$)							
	#1	#2	#3	#4	#5	mean ($\mu g\ g^{-1}$)	SD	mean ± 95% confidence interval
kerbside surface 0-2 cm	786	703	731	691	580	698	75	698 ± 94
kerbside 2 - 4 cm depth	758	718	640	596	492	641	105	641 ± 130
10 m top 2 cm	69	90	62	74	-	74	12	74 ± 19
25 m top 2 cm	32	17	14	18	16	20	7	20 ± 9
50 m top 2 cm	19	23	16	-	-	19	3	19 ± 9

Steele Park

	Replicates ($\mu g\ g^{-1}$)							
	#1	#2	#3	#4	#5	mean ($\mu g\ g^{-1}$)	SD	mean ± 95% confidence interval
kerbside surface 0-2 cm	415	463	427	559	608	494	85	494 ± 105
6 m top 2 cm	126	206	224	211	157	185	42	185 ± 52
10 m top 2 cm	126	128	167	80	231	146	56	146 ± 70
20 top 2 cm	103	106	95	97	106	101	5	101± 6

Appendix 5.2. Sampling replicates and statistical analysis for Pb in top 2 cm soils and street dust of the four parks.

Milne Park

Date	Sample	μg Pb g^{-1} sample replicate									
		Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5	Mean	SD	95% Confidence Interval	Δ Mean soil (Nov 95 -$Mean_i$)	PoolRandomError @ 95% confidence level
Nov. 1995	top soil	1309	1219	778	662	681	930	310	930 ± 385		
	100 μm< dust < 1 mm	454	535	491	477	387	469	54	469 ± 67		
	dust< 100 μm	1111	1058	1455	-	-	1208	216	1208 ± 537		
Feb. 1996	top soil	1062	1018	548	646	560	767	253	767 ± 314	163	413
	100 μm< dust < 1 mm	508	321	398	657	768	530	183	530 ± 227		
	dust< 100 μm	1178	-	-	-	-	1178	-	-		
Apr.96	top soil	412	609	523	1024	1123	738	316	738 ± 392	192	457
	100 μm< dust < 1 mm	496	404	407	-	-	436	52	436 ± 129		
	dust< 100 μm	1166	1292	1257	-	-	1238	65	1238 ± 161		
Jun. 1996	top soil	-	-	-	-	-	-	-	-	-	-
	100 μm< dust < 1 mm	339	378	656	549	-	481	148	481 ± 235		
	dust< 100 μm	987	1281	971	-	-	1080	175	1080 ± 435		
Sept. 1996	top soil	918	819	382	570	327	603	261	603 ± 324	327	417
	100 μm< dust < 1 mm	278	302	269	278	-	282	14	282 ± 22		
	dust< 100 μm	619	628	650	643	-	635	14	635 ± 22		

Appendix 5.2 (continued) Sampling replicates and statistical analysis for Pb in top 2 cm soils and street dust of the four parks.

Melville Park

Date	Sample	µg Pb g^{-1} sample replicate									
		Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5	Mean	SD	95% Confidence Interval	Δ Mean (Nov 95 -Mean$_i$)	PoolRandomError 95% confidence level
Nov. 1995	top soil	123	113	185	98	-	130	38	130 ± 60		
	100 mm< dust < 1 mm	316	758	611	649	600	587	164	587 ± 204		
	dust< 100 mm	828	1150	919	935	1042	975	124	975 ± 154		
Feb. 1996	top soil	107	107	154	69	-	109	35	109 ± 55	21	64
	100 mm< dust < 1 mm	339	478	936	722	803	656	243	656 ± 302		
	dust< 100 mm	1966	2010	1519	-	-	1831	272	1831 ± 676		
Apr.96	top soil	91	124	94	88	78	95	17	95 ± 21	35	44
	100 mm< dust < 1 mm	522	573	481	559	-	534	41	534 ± 65		
	dust< 100 mm	973	922	1130	-	-	1008	108	1008 ± 268		
Jun. 1996	top soil	-	-	-	-	-	-	-	-	-	-
	100 mm< dust < 1 mm	387	250	314	398	-	335	67	335 ± 107		
	dust< 100 mm	625	556	506	-	-	562	60	562 ± 149		
Sept. 1996	top soil	56	75	88	59	110	78	22	78 ± 27	52	48
	100 mm< dust < 1 mm	305	370	812	743	-	558	257	558 ± 409		
	dust< 100 mm	498	463	820	804	-	646	192	646 ± 305		

Appendix 5.2 (continued) Sampling replicates and statistical analysis for Pb in top 2 cm soils and street dust of the four parks.

Knighton field

Date	Sample	μg Pb g^{-1} sample replicate									
		Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5	Mean	SD	95% Confidence Interval	Δ Mean (Nov 95 -Mean$_i$)	PoolRandomError 95% Confidence level
Nov. 1995	top soil	786	703	731	691	580	698	75	698 ± 94		
	100 mm< dust < 1 mm	1718	1718	1807	2038	2199	1896	214	1896 ± 226		
	dust< 100 mm	1903	1879	1876	1987	2033	1936	71	1936 ± 88		
Feb. 1996	top soil	752	612	700	645	618	665	60	665 ± 74	33	99
	100 mm< dust < 1 mm	2497	1704	1380	1740	3013	2067	669	2067 ± 669		
	dust< 100 mm	3431	3355	2669	2902	3801	3232	448	3232 ± 556		
Apr. 1996	top soil	688	661	703	581	538	634	71	634 ± 71	64	108
	100 mm< dust < 1 mm	2222	2544	2450	2214	-	2358	166	2358 ± 166		
	dust< 100 mm	3040	2993	3095	3090	-	3055	48	3055 ± 48		
Jun. 1996	top soil	-	-	-	-	-	-	-	-	-	-
	100 mm< dust < 1 mm	1363	1368	1236	1356	-	1330	63	1330 ± 63		
	dust< 100 mm	2320	2482	2359	2348	-	2377	72	2377 ± 72		
Sept. 1996	top soil	444	506	487	464	429	466	31	466 ± 31	232	85
	100 mm< dust < 1 mm	808	881	809	639	-	784	103	784 ± 103		
	dust< 100 mm	1018	945	1097	834	-	974	112	974 ± 112		

Appendix 5.2 (continued) Sampling replicates and statistical analysis for Pb in top 2 cm soils and street dust of the four parks.

Steele Park

Date	Sample	μg Pb g^{-1} sample replicate									
		Replicate #1	Replicate #2	Replicate #3	Replicate #4	Replicate #5	Mean	SD	95% Confidence Interval	Δ Mean (Nov 95 -Mean$_i$)	PoolRandomError 95% confidence level
Nov. 1995	top soil	415	463	427	559	608	494	85	494 ± 105		
	100 mm< dust < 1 mm	435	495	426	396	457	442	37	442 ± 37		
	dust< 100 mm	996	876	920	929	-	930	50	930 ± 80		
Feb. 1996	top soil	288	529	300	451	550	424	124	424 ± 154	70	155
	100 mm< dust < 1 mm	552	428	495	574	469	504	60	504 ± 60		
	dust< 100 mm	723	688	720	764	764	732	32	732 ± 32		
Apr. 1996	top soil	261	399	252	397	501	362	105	362 ± 130	132	139
	100 mm< dust < 1 mm	343	376	249	292	-	315	56	315 ± 89		
	dust< 100 mm	637	645	518	578	-	595	59	595 ± 94		
Jun. 1996	top soil	-	-	-	-	-	-	-	-	-	-
	100 mm< dust < 1 mm	446	355	410	295	-	356	65	356 ± 103		
	dust< 100 mm	1006	837	933	941	-	929	70	929 ± 111		
Sept. 1996	top soil	264	467	165	237	444	315	133	315 ± 165	179	163
	100 mm< dust < 1 mm	206	247	241	347	-	260	61	260 ± 97		
	dust< 100 mm	377	457	456	501	-	448	52	448 ± 83		

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