PERSISTENCE AND AVAILABILITY OF AGRICHEMICAL RESIDUES IN NEW ZEALAND HORTICULTURAL SOILS

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ABSTRACT

New Zealand has a long history of intensive horticulture and many of the greenfield sites designated for residential development have previously been extensively used for horticulture. Currently there is limited information on the potential levels and likely effects of agrichemical residues in horticultural soils available to regulatory authorities with a mandate to manage contaminants in soil. A series of investigations were undertaken to identify the key contaminants present in horticultural soils, to determine the availability and toxicity of contaminants to plants and earthworms, and to estimate likely human exposures to selected contaminants in residential settings.

Trace element and selected organochlorine pesticide concentrations were measured in soil samples collected from horticultural and grazing properties in three regions of New Zealand (Auckland, Tasman and Waikato). Elevated levels of arsenic (<2–58 mg kg^{-1}), cadmium (<0.1–1.5 mg kg^{-1}), copper (5–523 mg kg^{-1}), lead (5–243 mg kg^{-1}) and ΣDDT (<0.03–34.5 mg kg^{-1}) were detected in horticultural soils from all three regions. With the exception of cadmium and zinc, significantly higher levels of contaminants were generally detected in horticultural soils than in grazing soils ($p<0.05$). Concentrations of ΣDDT, arsenic, cadmium, copper, and lead in some soils and particularly orchard soils exceeded soil criteria for the protection of ecological receptors and/or human health. Additional analyses undertaken on the Auckland region samples infrequently detected organophosphorus and organonitrogen pesticides and at levels generally less than 1 mg kg^{-1} in horticultural soils. Acidic herbicides were not detected in the Auckland samples.

p,p′-DDE and *p,p′*-DDT were the predominant DDT residues measured in horticultural soils. The *p,p′*-DDE:*p,p′*-DDT ratios in the measured horticultural soils ranged from 0.4 to 9.7. Significant negative correlations were found between the *p,p′*-DDE:*p,p′*-DDT ratios and copper in the Auckland ($p<0.001$) and Waikato ($p<0.02$) orchard soils. These results suggest that copper may be a contributing factor to inhibited degradation of *p,p′*-DDT to *p,p′*-DDE in orchard soils and that the ratio of *p,p′*-DDE:*p,p′*-DDT in horticultural soils, especially orchard soils, should not be used as an indicator of recent use of *p,p′*-DDT.

A persulfate oxidation method was used to estimate the fraction of *p,p'*-DDT in orchard soils available for microbial degradation. The proportion of *p,p'*-DDT oxidised by the persulfate ranged from 4 to 37% indicating that a significant proportion of the *p,p'*-DDT in the orchard soils (up to 96% in some cases) may not be available for degradation by soil micro-organisms.

The availability and toxicity of aged ΣDDT and trace element residues in orchard and grazing soils to the endogenous earthworm *Aporrectodea caliginosa* (Lumbricidae) was assessed using a 28 day laboratory assay. The worms bioaccumulated the aged DDT residues by up to a factor of 3 with concentrations of ΣDDT in worm tissue increasing with increasing soil concentration ($p<0.001$). Worm tissue concentrations of ΣDDT correlated with the amount of ΣDDT desorbed from soil by two biomimetic extraction techniques, Tenax resin and C-18 disks, indicating that these methods may be suitable for determining the availability of aged ΣDDT residues to *A. caliginosa.* Concentrations of arsenic, copper and lead in worm tissue increased with increasing soil concentration of these trace elements ($p<0.01$). Cocoon production decreased with increasing soil and earthworm tissue copper concentrations ($p<0.05$).

A glasshouse study was undertaken to assess uptake of ΣDDT, arsenic, cadmium, copper and lead into lettuce (*Lactuca sativa*) and radish (*Raphanus sativus*) from 10 soils containing typical contaminant concentrations. ΣDDT concentrations in the assayed soils ranged from 0.02 to 12 mg kg^{-1}. The maximum plant tissue ΣDDT concentrations (DW) followed the order radish hypocotyl (190 μg kg^{-1}) >radish leaf (77 μg kg^{-1}) >lettuce (28 μg kg^{-1}) and there were significant correlations between all plant tissue types and the soil concentration of ΣDDT and *p,p'*-DDE ($p<0.01$).

Concentrations of cadmium, copper, lead and zinc in lettuce, copper in radish hypocotyls, and copper and zinc in radish leaves increased with increasing soil trace element concentration ($p<0.02$). Lettuce cadmium concentrations for plants grown on four out of ten assayed soils were equivalent to or exceeded the NZ food standard for leafy vegetables of 0.1 mg kg^{-1} FW. Lead concentrations in radish hypocotyls grown in three out of eight soils were equivalent to or exceeded half of the NZ food standard for lead in root vegetables of 0.1 mg kg^{-1} FW. Phytotoxicity was determined by measuring the dry mass yield of lettuce and radish, and by a five day seedling emergence and root elongation assay for lettuce and ryegrass (*Lolium perenne*). The

radish leaf yield and the root length of lettuce seedlings grown in orchard soils for five days decreased with increasing soil copper concentration (total and/or neutral salt extractable).

A simulated gastric extraction method was used to determine the bioaccessible fraction of arsenic, cadmium and lead in soil. The maximum percent bioaccessible fraction for the trace elements followed the order arsenic (45%)<lead (83%)<cadmium(100%). Likely human exposures to ΣDDT, arsenic, cadmium and lead in residential settings under two home grown produce consumption scenarios (10 and 50%) were estimated using methodology generally consistent with current NZ government policy.

Estimated daily intakes of ΣDDT, arsenic, cadmium and lead for lifetime exposures in residential settings did not exceed the WHO tolerable intakes under the 10% homegrown produce scenario. Similarly, the estimated ΣDDT and arsenic intakes for the 50% homegrown produce scenario did not exceed their respective WHO tolerable intakes. Estimated cadmium daily intakes for the 50% home grown produce consumption scenario exceeded the WHO tolerable intake for cadmium at soil concentrations greater than 0.75 mg kg^{-1} for a child and 1 mg kg^{-1} for the lifetime exposure. Estimated child lead intakes exceeded the WHO tolerable intake at soil concentrations greater than 450 mg kg^{-1}.

The results presented in this thesis have implications for on going applications of agrichemicals and soil amendments to horticultural land as well as residential subdivision of former horticultural land. Trace element concentrations on some properties have already reached concentrations where negative effects on terrestrial organisms have been demonstrated to occur. The results in this thesis suggest that a precautionary approach should be adopted to subdividing former horticultural sites. Horticultural land being subdivided in particular for lifestyle blocks should be assessed prior to subdivision to ensure that thresholds for acceptable human exposures are not exceeded.

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ABBREVIATIONS

AKL	Auckland
ANOVA	analysis of variance
ARC	Auckland Regional Council
ARA	Auckland Regional Authority
ASTDR	Agency for Toxic Substances and Disease Registry
ASTM	American Society for Testing and Materials
BAF	bioaccumulation factor
CCME	Canadian Council of Ministers for the Environment
CLEA	Contaminated Land Exposure Assessment (UK)
CEC	cation exchange capacity
CI	confidence interval
CRM	certified reference material
DDE	1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethylene
DDD	1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethane
DDT	1,1,1-trichloro-2,2-*bis*(*p*-chlorophenyl)ethane
ΣDDT	sum of *o,p´*and *p,p´* isomers of DDT, DDD and DDE
DEFRA	Department for Environment, Food Materials and Rural Affairs (UK)
DW	dry weight
EC_{50}	effective concentration 50
EQG	environmental quality guideline
FSANZ	Food Safety Australia New Zeland
FW	fresh weight
GC-ECD	gas chromatography with electron capture detection
GC-MS	gas chromatography mass spectrometry
GC-NPD	gas chromatography with nitrogen phosphorous detectors
GPC	gel permeation chromatography
HAIL	Hazardous Activities and Industries List
IARC	International Agency for Research on Cancer
IANZ	International Accreditation New Zealand
ICP-MS	inductively coupled plasma -mass spectrometry
ICP-OES	inductively coupled plasma –optical emission spectrometry
IRIS	Integrated Risk Management System (USEPA)
IVG	*in vitro* gastro intestinal

LC_{50}	lethal concentration 50
LOD	limit of detection
LOEC	lowest observed effect concentration
MAF	Ministry of Agriculture and Forestry
MRL	maximum residue level
MPR	maximum permissible residue
NCEH	National Council Environmental Health (US)
NEPC	National Environmental Protection Council
NRC	National Research Council (US)
NSW EPA	New South Wales Environmental Protection Agency
NZTTG	New Zealand Timber Treatment Guidelines
NZWWA	New Zealand Waste Water Association
OECD	Organization for Economic Co-operation and Development
PAH	polycyclic aromatic hydrocarbon
PBET	physiologically based extraction test
PCB	polychlorinated biphenyl
PHAC	Public Health Advisory Committee
POPs	persistent organic pollutants
PTWI	provisional tolerable weekly intake
RIVM	National Institute for Public Health and the Environment (Netherlands)
RSD	relative standard deviation
SBET	Simplified Bioaccessibility Extraction Test
SBRC	Solubility/Bioavailability Research Consortium
SMC	system monitoring compound
SPE	solid phase extraction
TDI	tolerable daily intake
TDC	Tasman District Council
TDS	total diet survey
TOC	total organic carbon
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
WHC	water holding capacity
WHO	World Health Organization
WKT	Waikato

1 INTRODUCTION AND THESIS OBJECTIVES

1.1 INTRODUCTION

Internationally, it is now widely accepted that the historic routine use of agrichemicals such as pesticides, fertilizers and soil amendments including lime and sewage sludge can result in undesirable levels of persistent organochlorine pesticides (dieldrin and ΣDDT) and trace elements (arsenic, cadmium, copper, mercury, lead and zinc) accumulating in some horticultural soils (Merwin *et al.,* 1994; Van Gaans *et al.,* 1995; Webber and Wang, 1995; Harris *et al.,* 2000). The persistence of organochlorine pesticides in soils is of significant concern due to their ability to bioaccumulate and impact on wildlife (Elliott *et al.,* 1994; Boul, 1995). Recently it has been demonstrated that aged organochlorine pesticide residues can be phytoavailable (Mattina *et al.,* 2000; White and Kottler, 2002).

Contamination of soil with elevated levels of trace elements can have adverse effects on soil invertebrates and micro-organisms and hence soil ecosystem function (e.g. Giller *et al.,* 1998; Cortet *et al.*, 1999; Merrington *et al.,* 2002). Elevated levels of trace elements in soils can have phytotoxic effects and result in trace element contamination of edible crops (Dudka and Miller, 1999; Kabata-Pendias and Pendias, 2001). Humans can be exposed to toxic trace elements and organochlorine pesticides through soil ingestion as well as by consuming food produced on contaminated land.

Until recently the focus for contaminated land issues in New Zealand (NZ) has been on individual sites contaminated through industrial activities and on grazing land. However, it has been recently recognised that horticultural properties are potentially contaminated sites and this has led to their inclusion on the Hazardous Activities and Industries List (HAIL) prepared by the Ministry for the Environment (Ministry for the Environment, 2004a). Prior to 2001, when this study commenced, there was limited information available to regulatory authorities with a mandate to manage

contaminants in soil on the categories and potential levels of agrichemical residues likely to be present in NZ horticultural soils.

Earlier investigations in NZ have identified the presence of elevated levels of ΣDDT in grazing soils (Roberts *et al.*, 1996), cadmium in market garden (Roberts *et al.*, 1994) and grazing soils (Roberts *et al.*, 1995; Taylor, 1997; Zanders *et al.*, 1999; Gray *et al.*, 1999a,b), and copper in orchard (Morgan and Bowden, 1993; Holland and Solomona, 1999) and vineyard (Taylor, 1999) soils. Hogg (2000) reported elevated levels of arsenic, copper, ΣDDT, dieldrin and Σendosulfan in storage shed and glasshouse soils on two horticultural properties in the Auckland region. These earlier reports indicated that residual levels of agrichemicals were likely to be present in NZ horticultural soils and that a more detailed assessment of the levels and types of contaminants present in horticultural soils was warranted. Since the investigations reported in this thesis were conducted (Gaw, 2002, 2003a,b; Gaw *et al.*, 2003a,b), surveys undertaken in Hawkes Bay (Macaskill, 2004; Proffitt and Macdonald, 2005) and the Bay of Plenty (SEM NZ, 2005) have confirmed the presence of elevated levels of ΣDDT and trace elements in long term horticultural soils.

Before aged agrichemical residues can be appropriately managed and soil guidelines developed, knowledge of the bioavailability and toxicity of key contaminants in horticultural soils is required. Currently, there is a paucity of information on the bioavailability and toxicity of trace elements and ΣDDT in NZ soils making it necessary to rely on information from overseas for risk assessments and the derivation of guidelines. Studies undertaken in NZ around the time of use showed that DDT was accumulated by earthworms from orchard soils (Collett and Harrison, 1968) and sheep from pasture soils (Harrison *et al.*, 1969; 1970), was toxic to insect-eating birds (Collett and Harrison, 1968; Wilson, 1980), had limited toxicity to soil invertebrates and soil micro-organisms (Tate, 1974; Martin, 1976, 1978) and no effect on pasture plants (Martin, 1974). However, approximately 30 years after last being applied, low concentrations of DDT residues are still being measured in NZ animal products (Cressey *et al.*, 2000) indicating that DDT residues in soil remain available for uptake.

With the possible exception of cadmium, there is also limited information on the bioavailability and toxicity of trace elements in NZ soils (McLaughlin *et al.*, 2000a) and in particular from field contaminated soils. Only a handful of previous studies have investigated trace element uptake by edible plants from NZ soils. Field and pot trials have demonstrated that cadmium present in NZ grazing and market garden soils is phytoavailable (Roberts *et al.* 1995; Andrewes *et al.*, 1996; Gray *et al.*, 1999a). Similarly Rooney *et al.* (1999) measured lead uptake by a range of vegetable and herbage plants from lead shot contaminated pasture. Bolan *et al.* (2003a) measured copper uptake from spiked soil by *Brassica juncea* L. An earlier pot trial measured trace element uptake by plants from sewage sludge amended soils (Whitton and Wells, 1978).

Laboratory assays utilising grazing soils spiked with copper salts reported phytotoxic effects and toxicity to soil invertebrates at copper and arsenic concentrations comparable to those measured in some horticultural soils (O'Halloran and Booth as cited in Markich *et al.,* 2002; Bolan *et al.*, 2003a). Yeates *et al.* (1994) and Bardgett *et al.* (1994) reported trace element uptake by earthworms and deleterious effects on herbage, soil invertebrates and soil microbial properties for copper-chrome-arsenic contaminated pasture soil. This NZ specific data indicated that trace elements in horticultural soils were likely to be bioavailable and toxic to plants and earthworms.

Currently bioavailability data from overseas is relied on for risk assessments of contaminated soils in NZ. NZ soils tend to be younger and have higher organic matter contents (Burney *et al.*, 1975), lower pH and lower levels of carbonates than soils in other regions of the world (Hewitt, 1997; Lowe *et al.,* 2000). Contributing factors to the uniqueness of NZ soils include a nutrient conservative flora, few fires in the indigenous evergreen forest and the absence of native soil casting fauna (Hewitt, 1997). All of these factors can influence soil development and in several areas of NZ tephra-fall deposits are the main source of soil forming materials, hence top down soil formation processes can dominate (Lowe *et al.,* 2000). Variable charge minerals are more dominant in NZ soils than those from the Northern Hemisphere where permanent charge minerals are more dominant (McLaughlin *et al.,* 2000a).

These differences in soil characteristics mean that data from overseas on the fate and bioavailability of contaminants (trace elements and synthetic organic contaminants) may not be directly applicable under NZ conditions. For example, studies of pesticide fate and degradation undertaken in NZ have indicated that pesticides may behave differently in NZ soils (Sarmah *et al.*, 2004). The lower soil pH levels may have implications for the bioavailability of trace elements in NZ soils as pH is a key variable determining the availability of trace elements in soil (Adriano, 2001; Kabata-Pendias and Pendias, 2001).

1.2 AGRICHEMICAL USE IN NEW ZEALAND HORTICULTURE

In this section, the focus is on agrichemicals for which residual levels were found to be an issue in NZ soils as a result of the investigations reported in this thesis. Current pesticide use in NZ has been recently reviewed by Manktelow *et al.* (2005).

A variety of agrichemicals with persistent active ingredients have been extensively used on horticultural properties throughout NZ over the last 100 years. The New Zealand Department of Agriculture was established in 1892 and in 1893 two 'Pomologists' were appointed to provide information on the chemical treatment of disease in orchards. By 1903 the majority of fruit tree growers were using chemical sprays and in 1903 the Orchard and Garden Pests Act was passed which made it an offence to allow certain specified diseases to be present in an orchard (Cunningham, 1925). The three main compounds in use at this time were Bordeaux mixture (copper), lime-salt-sulfur and Paris Green (copper and arsenic based pesticide). The passing of the Agricultural Chemicals Act 1959 made the use of pesticides subject to compulsory regulatory control and established the Agricultural Chemicals Board (Buckland *et al.*, 1998).

1.2.1 PERSISTENT ORGANOCHLORINE PESTICIDES

Persistent organochlorine pesticides which have been registered for use in NZ include DDT, DDD, lindane, dieldrin, heptachlor, kepone, methoxychlor, endrin, heptachlor, hexachlorobenzene, thiodan, telodrin, aldrin, chlordane and toxaphene (Slade, 1964; Buckland *et al.*, 1998). From 1964 onwards the use of organochlorine pesticides (OCs) was controlled through the Agricultural Chemicals (Insecticides) Regulations. These regulations were introduced to prevent unacceptable residues of OCs accumulating in meat and dairy products. Organochlorine pesticides could only be used by horticulturalists under permit (Slade, 1964) and permits were only issued for horticultural use where non-organochlorine compounds were ineffective (Osborne, 1976). Organochlorine pesticides including DDT were subsequently replaced by carbamates and organophosphorus compounds. All products containing persistent organochlorine pesticides were deregistered for use in NZ in 1989 (Buckland *et al.*, 1998).

1.2.1.1 DDT AND DDD

1,1,1-Trichloro-2,2-*bis*(*p*-chlorophenyl)ethane (*p,p'*-DDT) was the active ingredient in a wide range of products used internationally to control insect pests from the late 1940s until the 1970s (ATSDR, 2002; Boul, 1995). In NZ *p,p'*-DDT was widely used to control grass grub (*Costelytra zelandia*) in grazing soils, and was extensively used on horticultural properties until the mid 1970s to control insect pests including codlin moth (*Cydia pomonella*) and bronze beetle (*Eucolaspis brunnea*) (Osborne, 1976). *p,p'*-DDT containing products were also available to home gardeners (Yates, 1963) and were used to control pests in houses including ants (Hymenoptera: Formicidae), cockroaches (Blattodea: Blattidae), carpet beetles (Coleoptera: Dermestidae), bed bugs (*Cimex lectularius*) and fleas (Siphonaptera) (Ferro, 1976).

DDT was mainly used for horticultural activities either as a wettable powder or as an emulsion. (Atkinson *et al.*, 1956). Prills containing *p,p'*-DDT were also frequently

mixed with fertiliser or lime and applied to agricultural pasture, market gardens and parkland (Orchard *et al.*, 1991; Buckland *et al.*, 1998).

1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethane (DDD) is a degradation product of DDT and was also widely used as an insecticide to control chewing insects on a range of crops including vegetables, fruit and grapes (Moran, 1958; Slade, 1964). It was available as a wettable powder, dust or emulsion and was used at higher concentrations compared to DDT to control codling moth (Atkinson *et al.*, 1956).

1.2.1.2 ALDRIN AND DIELDRIN

Aldrin and dieldrin were introduced as stock remedies in 1954 and were also used on horticultural crops. Dieldrin is both a degradation product of the pesticide aldrin and a pesticide itself. Aldrin was more widely used than dieldrin, and was used to control horticultural pests such as wireworm (Elateridae), soldier fly *(Inopus rubiceps)* and black vine weevil (*Otiorhynchus sulcatus*) (Slade, 1964; Buckland *et al.*, 1998). Dieldrin was recommended by the NZ Horticulture Division for use on strawberries and root crops (Slade, 1964) and was also used to control carrot rust fly (*Psilia rosae*), crickets (Orthoptera: Gryllidae), armyworm (Lepidoptera: Noctuidae), thrips (Thysanoptera) and grass grub (Buckland *et al.*, 1998; Atkinson *et al.*, 1956).

From 1964 onwards the use of dieldrin was controlled through the NZ Agricultural Chemicals (Insecticides) Regulations. Dieldrin was banned for use in sheep dips as a veterinary insecticide in the 1960s (Osborne, 1976) and could only be used by horticulturalists under permit (Slade, 1964). In 1975 the Agricultural Chemicals Board recommended that the issuing of permits for any use of dieldrin cease (Buckland *et al.*, 1998). However, dieldrin was still registered for specific use by authorised applicators in NZ in 1983 (Pesticides Board, 1983).

1.2.2 TRACE ELEMENTS

1.2.2.1 LEAD ARSENATE AND OTHER ARSENICALS

Arsenic based compounds including lead arsenate, calcium arsenate and copper arsenate were among the first persistent pesticides used both in NZ and internationally to control chewing insects on fruit, vegetables and ornamental crops (Cunningham and Cottier, 1933). Lead arsenate was widely used in NZ orchards to control codling moth between the early 1900s and the late 1960s (Atkinson *et al.*, 1956). It was also registered for use in home gardens (Yates, 1963). Sodium arsenite; *ortho*-arsenite (Na_3AsO_3) and *meta*-arsenite ($NaAsO_2$) were used as herbicides, however due to their toxicity to humans these products were withdrawn from use in NZ during the early 1970s (Matthews, 1960, 1975). Arsenic based insecticides are no longer registered for use in NZ, however one arsenic based herbicide (MSMA) is still registered.

1.2.2.2 COPPER

Products containing copper were historically and are currently used in NZ as fungicides. These products include Bordeaux mixture (copper sulfate and hydrated lime) (Cunningham, 1925; Atkinson *et al.*, 1956), Burgundy mixture (copper sulfate, sodium carbonate and water) (Cunningham, 1925) and copper oxychloride. Copper sulfate may also have been used as an herbicide on some properties (Smith, 1982). Copper is still widely used in NZ horticulture as a fungicide on particular crops; 35 specific copper-based fungicide products are currently registered for use in NZ (Kim *pers comm.*, 2005). Yearly loading rates for crops that receive copper vary from 0.6 kg ha^{-1} yr^{-1} for potatoes up to 17 kg ha^{-1} yr^{-1} for avocadoes (Mills *et al.*, 2004).

1.2.2.3 MERCURY

Mercury compounds have been widely used in horticultural formulations for their antifungal and antibacterial properties. For example, phenylmercuryl chloride and phenylmercuryl ammonium lactate were active ingredients in sprays used to control black spot (*Venturia inaequalisin*) in apples (The New Zealand Fruitgrowers Federation, 1967). Organomercury compounds were also used as fungicides in vineyards (Barzi *et al.*, 1996). Mercuric chloride was used in market gardening to control potato scab (*Spongospora subterranean*), clubroot (*Plasmodiophora brassicae*) in brassicas and against some soil insects (Atkinson *et al.*, 1956).

1.2.2.4 OTHER TRACE ELEMENTS

A range of other trace elements have also been associated with agrichemical applications in NZ. Zinc is a constituent of some fungicides including Propineb® and Mancozeb®, both commonly used dithiocarbamates. Increased cadmium and zinc levels in NZ soils have been associated with fertiliser use (Taylor and Percival, 2001). Historically NZ has sourced phosphate rock used to make superphosphate fertiliser from Nauru and Christmas Island, both of which generally contain higher levels of cadmium than other sources of phosphate rock (Bramley, 1990).

Essential trace elements including manganese, cobalt, copper, boron, molybdenum, nickel and zinc were added to some fertilizers, as some NZ soils are known to be deficient in these trace elements (e.g. Bollard, 1955; Smith *et al.*, 1976). Organic tin compounds were used as acaricides (e.g. fenbutatin-oxide and cyhexatin), have been registered for use as fungicides (Long, 1983), and the tin-based compounds azocyclotin and fenbutatin oxide are still registered for use in NZ as miticides.

1.3 BIOAVAILABILITY OF CONTAMINANTS FROM SOIL

The toxicity to and accumulation of soil-borne contaminants by terrestrial organisms is determined by their bioavailability (Janssen *et al.*, 1997a; NRC, 2003; Peijnenburg and Jager, 2003). There are a number of definitions and interpretations of the term bioavailability which are often scientific discipline specific (Adriano, 2001; NRC, 2003). In their review of the bioavailability of contaminants from soil and sediments, the National Research Council (2003) focused on bioavailability processes rather than clarifying definitions (NRC, 2003). They summarised the bioavailability processes which occur in soil as including: binding and release of a contaminant from soil; transport of the released contaminant to a target organism's membrane; direct contact of an organism with bound contaminants, uptake of the contaminant of interest through a physiological membrane and circulation of the contaminant within the organism leading to either accumulation or a toxic effect.

Juhasz *et al.* (2003) proposed that the following three criteria needed to be met before a contaminant could be considered bioavailable; the organism is exposed to the matrix containing the contaminant, a proportion of the contaminant is available and the organism is able to take up the contaminant of interest. The bioavailability of contaminants in soil has been reported to be contaminant, soil and organism specific (Kelsey *et al.*, 1997; Cortet *et al.*, 1999; Alexander, 2000; Reid *et al.*, 2000; Kabata-Pendias and Pendias, 2001; Peijnenburg, 2002; Lanno *et al.*, 2004).

Soil chemical and physical characteristics can determine the bioavailability of contaminants to terrestrial organisms and in particular organisms which are exposed to contaminants through soil pore water (Van Gestel and Ma, 1988; Plette *et al.*, 1999; Peijnenburg, 2002). The amount and type of soil organic matter are key variables which have been shown to influence the bioavailability of organic contaminants including ΣDDT in soil (Luthy *et al.*, 1997; Tang *et al.*, 1999; Sijm *et al.*, 2000; Cornelissen *et al.*, 2005). Mineral phases including soil clay content may also determine the availability of organic contaminants (Kookana *et al.*, 1998; Oliver and Naidu, 2003). Soil properties which have been shown to influence the

bioavailability of trace elements in soil include pH, cation exchange capacity, soil organic matter content, iron and aluminium oxides, texture, aeration and moisture content (Van Gestel *et al.*, 1995; Dudka and Miller, 1999; Adriano, 2001; Kabata-Pendias and Pendias 2001). These soil properties in combination with the physico-chemical properties of the contaminant of interest determine the rate of release of the contaminant from the solid phase, the partitioning of the contaminant between the soil pore water and the solid phase, and hence the availability of the contaminant for uptake (Murphy and Zachara, 1995; Plette *et al.*, 1999; Reid *et al.*, 2000; Sauvé *et al.*, 2000; Allen, 2002).

Chemical speciation in both the solid phase and the soil pore water also determines the extent to which contaminants are bioavailable (Nolan *et al.*, 2003; Sauvé *et al.*, 1998; NRC, 2003; Peakall and Burger, 2003). For example, the presence of competing ions or complexing ligands in soil solution can determine bioavailability of trace elements (Krishnamurti *et al.*, 1997; Plette *et al.*, 1999; Sauvé *et al.*, 2000; Nolan *et al.*, 2003; Inaba and Takenaka, 2005). The amount and type of dissolved organic matter can enhance the desorption of organic compounds and trace elements in solution from the solid phase to the soil solution and can determine the availability of contaminants for uptake from the soil solution (Chiou *et al.*, 1986; Adriano, 2001; Inaba and Takenaka, 2005; Strobel *et al.*, 2005).

Studies have shown that the bioavailability and toxicity of trace elements and organic contaminants can be greater from soils which have been freshly spiked with contaminants compared to field contaminated soils (Merry *et al.*, 1986a; Hatzinger and Alexander, 1995; Robertson and Alexander, 1998; Tang *et al.*, 1999; Scott-Fordsman *et al.*, 2000; Peijnenburg, 2002; Davies *et al.*, 2003; Basta *et al.*, 2005). This decrease in availability and toxicity has been attributed to time dependent sorption and entrapment processes which sequester the contaminants in less available forms. This process is often referred to as aging and is both contaminant and soil dependent (Chung and Alexander, 1998; NRC, 2003). The bioavailability of organic contaminants can be reduced through sorption to soil minerals and organic matter, and entrapment in soil micropores and soil organic matter from which the rate of release is very slow (Pignatello and Xing, 1996; Luthy *et al.*, 1997). Trace elements

can become less available through the formation of insoluble precipitates, chemisorption processes, diffusion into the mineral matrix and occlusion caused by the deposition of layers of organic and inorganic matter (McBride, 1994; McLaughlin *et al.*, 1998; NRC, 2003).

1.3.1 BIOAVAILABILITY AND TOXICITY OF CONTAMINANTS TO EARTHWORMS AND PLANTS

1.3.1.1 EARTHWORMS

Internationally, earthworms are commonly used as indicators of the bioavailability of contaminants in soil and the potential for these contaminants to enter the terrestrial foodchain (Spurgeon *et al.*, 2003). Reasons why earthworms are considered to be suitable test organisms for the bioavailability of contaminants in soil include:

- earthworms live in the soil and hence are in contact with soil;
- earthworm species which ingest soil represent a dietary route for uptake of contaminants;
- field validation of laboratory assays is possible;
- earthworms can take up contaminants directly from the soil as their exterior epidermal surface is vascularised with no cuticle;
- earthworms have a low level of mixed-function oxidase (MFO) which reduces metabolism of organic compounds enabling higher accumulation of organic compounds than in other invertebrate species;
- the ecology and physiology of earthworms is well understood.
- a range of standardised protocols (e.g. OECD and ASTM) have been developed for measuring effects on earthworms at the sub-organism, organism and population level (Lanno *et al.*, 2004).

As well as being useful indicators of soil contamination, earthworms play a key role in the degradation of organic matter in soils (McLaren and Cameron, 1996) and in determining physical and chemical properties of soil. Earthworms physically mix

soil components through burrowing (Langdon *et al.,* 2003), contribute to the structure, aeration and drainage of soil (Edwards, 1983; McLaren and Cameron, 1996) and decrease the bulk density of soil (Francis and Fraser, 1998).

Earthworms can be exposed to contaminants in soil through dermal contact with the soil pore water and by direct ingestion of soil. Toxic effects of contaminants on earthworms which have been measured in bioassays include mortality, decreased growth and development, reduced cocoon production, behavioural changes and changes in biomarkers (Spurgeon *et al.*, 2003). Contaminants can reduce biomass and alter earthworm species diversity in the field (Spurgeon and Hopkin, 1999; Nahmani *et al.*, 2003).

1.3.1.2 PLANTS

Uptake of contaminants into edible plants is one of the exposure pathways considered by regulatory agencies when deriving guidelines for contaminants in soil for the protection of human health. The predominant pathway for trace element uptake by plants is passive and active absorption through plant roots (Kabata-Pendias and Pendias, 2001) across the plasma membrane of the root cells, the so called "soil-plant barrier" (Vangronsveld and Clijsters, 1994) followed by translocation into other plant organs. Root uptake and translocation into plant tissue has been recently demonstrated for a range of persistent organic pollutants including ΣDDT (Lunney *et al.*, 2004), *p,p'*-DDE (White and Kottler, 2002; White *et al.,* 2003a) and chlordane (Mattina *et al.,* 2000; Mattina *et al.,* 2004). Plant roots can absorb organic compounds from the soil solution via passive diffusive processes as well as from the vapour phase (Collins *et al.*, 2006).

Other exposure routes for plants include adherence or incorporation of fine soil particles into plant tissue (Dudka *et al.,* 1996) and some plants may be able to absorb contaminants from both dry and wet deposition through their leaves (Mehra and Farago, 1994; Collins *et al.*, 2006). Plants can also take up organic contaminants from the vapour phase (Barber *et al.*, 2002).

Soil contamination can inhibit seed germination and plant growth thus reducing crop yields (Dennis and Edwards 1964; Mitra and Raghu, 1989; Kabata-Pendias and Pendias, 2001). DDT is generally assumed to have low toxicity to plants as it was used to control insects on crops. Whilst many of the trace elements (e.g. copper and zinc) are essential nutrients, they can become toxic above plant and/or trace element dependent thresholds (Kabata-Pendias and Pendias, 2001). Mechanisms of trace element toxicity include altering the permeability of cellular plasma membranes causing loss of cellular components, inhibition of the action of enzymes and hence enzymatic processes such as photosynthesis and competition for binding sites and increased enzyme activity which places stress on the plant (Vangronsveld and Clijsters, 1994; Kabata-Pendias and Pendias, 2001).

1.3.2 CHEMICAL TOOLS TO ASSESS BIOAVAILABILITY OF CONTAMINANTS IN SOIL

There is a growing body of evidence to suggest that the amount of contaminant measured in soil using "total" acid digestions for trace elements or exhaustive extractions with organic solvents for organic contaminants may not accurately predict the fraction of the contaminants that is bioavailable (Alexander, 2000; Nolan *et al.*, 2003; Peijnenburg and Jager, 2003). Many environmental scientists advocate that bioavailability should be incorporated into risk assessments and the derivation of soil quality guidelines (Alexander, 1995; McLaughlin *et al.*, 2000b; Allen, 2002; Sauvé, 2002; Meers *et al.*, 2005; Tandy *et al.*, 2005). However, before bioavailability can be routinely considered in risk assessments, robust tools which target the appropriate risk pathways and can accurately predict availability are required (McLaughlin *et al.*, 2000b; NRC, 2003).

Several different extraction techniques have been suggested as a means to measure or estimate point in time bioavailability of contaminants to terrestrial organisms and to provide surrogates for bioassays which can be both expensive and time consuming (Basta and Gradwohl, 2000; McLaughlin *et al.*, 2000b). These chemical methods are operationally defined and target the soluble and readily available fractions of

contaminants in soil (NRC, 2003). For trace elements, these include extractions with neutral salts and complexing extractants, ion exchange resins and diffusive gradients in thin films (DGT). The relative merits and applications of these techniques have been reviewed by McLaughlin *et al.* (2000b) and NRC (2003).

Extraction methods which have been used to measure availability of organic contaminants include extractions with mild solvents (butanol, methanol, *n*-propanol and ethyl acetate), solutions containing cyclodextrins and supercritical fluid as well as biomimetic techniques (Tang *et al.*, 1999; Reid *et al.*, 2000; NRC, 2003). Biomimetic techniques use membranes and solid phase adsorbents to simulate partitioning of an organic contaminant between an organism and pore water (Sijm *et al.*, 2000) and are discussed further in Chapter Six. Many of the extraction techniques for both trace elements and organic contaminants have not been validated against concurrent bioassays (NRC, 2003).

Chemical methods have also been developed to assess the oral bioaccessibility of trace elements from contaminated soil and hence the potential for human exposure from soil ingestion (Ruby *et al.*, 1996; Rodriguez *et al.*, 1999; Kelley *et al.*, 2002; Oomen *et al.*, 2003). These methods simulate conditions in the human gastric tract and provide an estimate of the amount of trace element which would be desorbed in the stomach (Kelley *et al.*, 2002; Oomen *et al.*, 2002).

1.4 THESIS OUTLINE AND OBJECTIVES

A series of investigations were undertaken to identify the key contaminants likely to be present in NZ horticultural soils. The key contaminants of concern based on comparison with soil quality criteria for the protection of terrestrial organisms and human health were arsenic, cadmium, copper, lead, zinc and ΣDDT.

Plant and earthworm assays were undertaken to measure the bioavailability of these key contaminants from orchard soils. Earthworms and plants were selected as the test organisms for two reasons: - 1) the accumulation of contaminants by earthworms and

plants are pathways for the movement of contaminants through terrestrial food chains (Collins *et al.*, 2006; Duarte-Davidson and Jones, 1996; Dudka and Miller, 1999; Kabata-Pendias and Pendias, 2001; Spurgeon *et al.*, 2003) and 2) to enable direct comparison with overseas data.

Aporrectodea caliginosa (Lumbricidae) was selected as the test species for the work reported in this thesis, as it is the most common earthworm in NZ (Springett, 1992) and it plays a key role in mixing topsoil (McLaren and Cameron, 1996). It has been suggested that *A. caliginosa* are a more ecologically relevant test species than the commonly used *Eisenia fetida* (Lumbricidae) (Kula and Larink, 1998). This is because *A. caliginosa* are endogenous earthworms which live in the soil and feed on decomposed organic matter in the soil whereas the more commonly used test species *E. fetida* are litter dwelling species which feed on soil surface litter deposits.

Lettuce were selected for the plant assays because they are regularly grown in home vegetable gardens and were identified as one of the most commonly eaten vegetables in the 1997 NZ national nutrition survey (Ministry of Health, 1999). It is also one of the plant species used in international tests determining contaminant phytoavailability e.g. OECD (Peijnenburg *et al.*, 2000). Radish was selected as it is a fast growing root vegetable which is also commonly grown in home gardens. Ryegrass (*Lolium perenne*) was chosen for the seedling emergence and root elongation assay as it is monocotyledonous plant and an important species in NZ pasture (Waghorn and Clark, 2004).

Potential human exposures in residential settings to ΣDDT, arsenic, cadmium and lead were estimated using default exposure scenarios consistent with current NZ policy. Data from the plant assay were used to estimate potential exposures from consumption of homegrown produce and a simulated gastric extraction procedure was used to determine the bioaccessible fraction of trace elements from soil.

The objectives of this thesis were to:

i. Identify the agrichemical residues likely to be of concern in NZ horticultural soils.
ii. Investigate the bioavailability of key contaminants (trace elements and DDT residues) to selected plants and earthworms using laboratory-based assays.
iii. Measure the toxicity of aged agrichemical residues (trace elements and DDT residues) to plants and earthworms using bioassays.
iv. Compare chemical methods to predict bioavailability of contaminants in soil to the results of the bioassays.
v. Estimate likely human exposure to selected trace elements (arsenic, cadmium and lead) and ΣDDT from horticultural soils in residential settings.

These objectives are reported in detail in the following chapters of this thesis:

Chapter Three:	Agrichemical residues in Auckland horticultural soils.
Chapter Four:	Comparison of agrichemical residues in horticultural soils from three regions.
Chapter Five:	Persistence of DDT, DDE and DDD in NZ horticultural soils.
Chapter Six:	Bioavailability and ecotoxicity of aged DDT residues in horticultural soils.
Chapter Seven:	Bioavailability and ecotoxicity of trace elements in horticultural soils.
Chapter Eight:	Human exposure to ΣDDT and selected trace elements.

The methodology used in this thesis is described in Chapter Two. The main findings of the experiments reported in each chapter are summarised and discussed in the final chapter. Chapter Nine also identifies areas recommended for further investigation.

2 MATERIALS AND METHODS

2.1 INTRODUCTION

This chapter presents an outline of the methodology used to generate the data presented in this thesis.

2.2 SAMPLE COLLECTION AND SAMPLE PREPARATION

2.2.1 REGIONAL SURVEYS

2.2.1.1 SAMPLE COLLECTION

Soil samples from horticultural, agricultural and background sites were collected from Auckland region between April and August 2001, the Waikato region between May and October 2002 and Tasman district in September 2002 (Figure 2.1). The aim of the sampling was to assess broad-field contamination over wide areas, and care was taken to avoid potential hotspots (e.g. spray sheds and farm dumps). The following criteria were used to select suitable sampling sites:

- Consent had been given by the landowner (conditional on maintenance of anonymity).
- The site had not undergone significant earthworks (apart from what would be normal for the specified land use).
- The site had not been regularly flooded (with the exception of some tobacco land).
- The site had not been used as a landfill or a cleanfill.
- The horticultural activity was typical of horticultural activities occurring within the region.

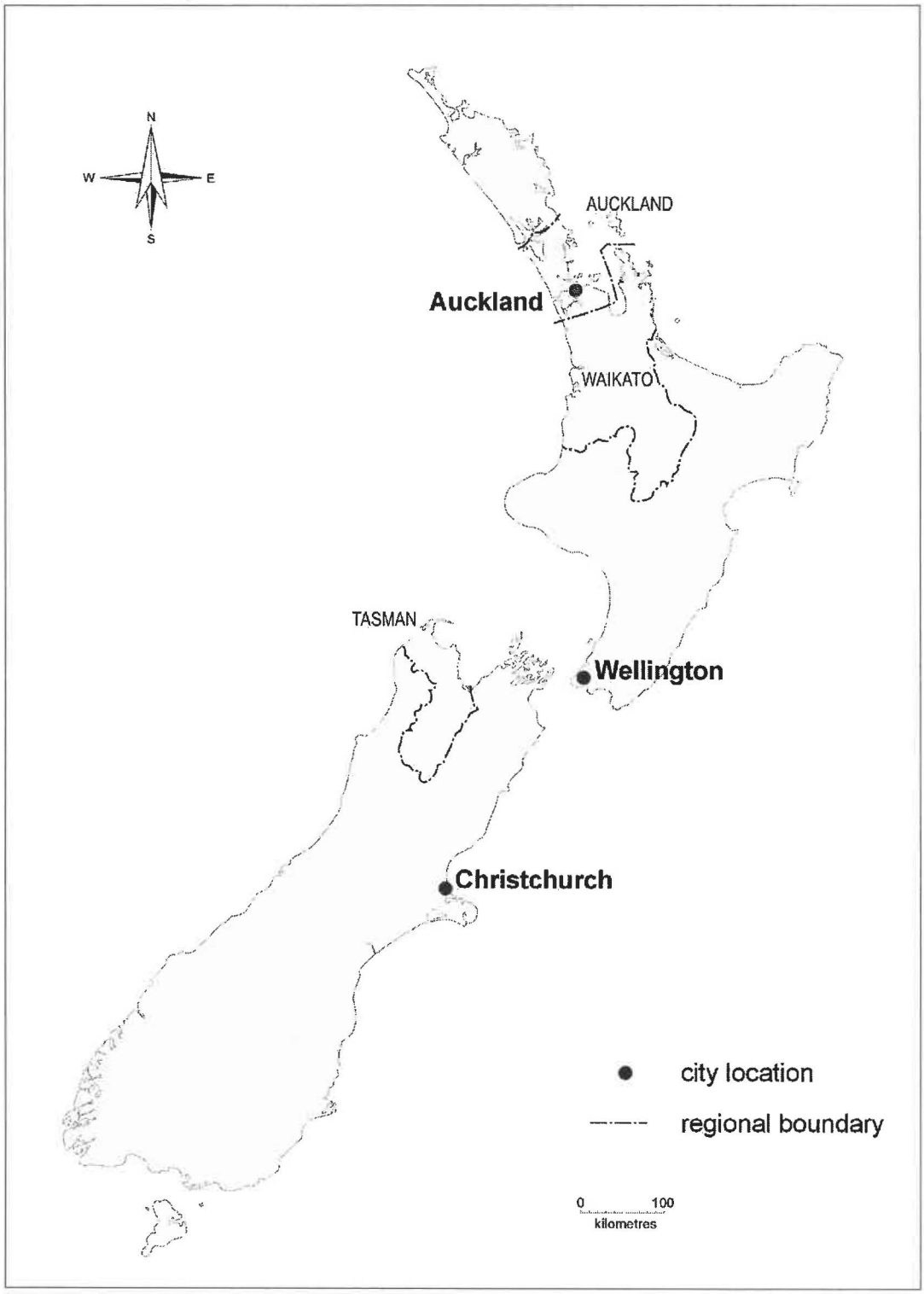


Figure 2.1: Map showing the location of the regions sampled.

Representative samples from the Auckland region were obtained by collecting 10 soil cores from within a hectare using a "Z" sampling pattern. Up to four hectares were sampled on each property from cropping areas with the same spray history and soil characteristics and the bulk soil samples collected from each hectare were aggregated into a single composite sample which was prepared according to the Australian Standard for sampling contaminated soils (AS 4482.1, 1997).

Representative samples from the Waikato and Tasman sites were obtained by taking 10 soil cores collected using a "Z" sampling pattern from a representative one hectare area on each property (Figure 2.2). This sampling procedure ensured a representative sample of sufficient mass was obtained for combined analysis; between 330 g and 520 g of soil was collected from each hectare. On glasshouse properties, each glasshouse was sampled separately using the "Z" sampling pattern.

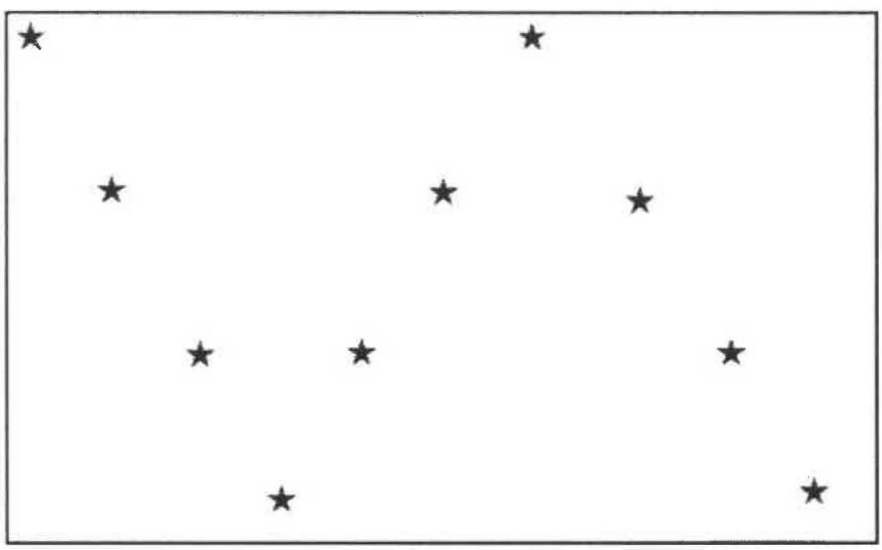


Figure 2.2: The sampling pattern used on cropping areas. Each bulk soil sample contained 10 soil cores collected from an area ≤ one hectare.

Grass and decomposing organic matter were removed from the surface of each sampling location before soil samples were collected. Samples were taken to a nominal depth of 7.5 cm using a stainless steel corer (diameter 2.5 cm). The sampling depth of 7.5 cm was chosen as this depth represents the immediate surface

layer that a future user (e.g. a child) of the site would be exposed to as well as the material that could potentially enter an adjacent waterway through runoff or erosion of soils (Nortcliff, 2001). This sampling depth is also consistent with the sampling depth of 5 to 10 cm recommended by the New Zealand Public Health Commission (Graham and Bates, 1996) for preliminary sampling on contaminated sites.

2.2.1.2 SOIL PREPARATION AND STORAGE

Samples were transported on ice to a laboratory at the University of Waikato. Upon arrival at the lab, the soil cores for each one hectare area were fully homogenised. For the Auckland samples only, composite samples were prepared by homogenising equal proportions of the bulk soil sample collected from each hectare. The composite samples were prepared from bulk soil samples collected from cropping areas with the same spray history and soil characteristics. A representative subsample of each sample was air dried at 30 °C for 5 days and sieved to <2 mm prior to being submitted to Hill Laboratories (Hamilton, New Zealand) (a commercial analytical laboratory) for trace element analysis. For multi-residue pesticide and acidic herbicide analyses, samples were submitted in a field-moist condition. Waikato and Tasman samples submitted to Hill Laboratories for both trace element and organochlorine pesticide analyses were air-dried (<2 mm).

2.2.1.3 DEPTH PROFILES

Three 1 m deep cores were collected from two orchards; one long-term site currently planted with apple trees (one core) and one historic site now used to graze cattle (two cores). The cores were collected using a custom built stainless steel piston corer (50 mm diameter). The cores were divided into subsections based on the soil horizons. The subsections were submitted to Hill Laboratories (Hamilton) field moist where the samples were air dried, ground to <2 mm and analysed for ΣDDT (Section 2.5.1.3) and trace elements (refer section 2.6.1.1).

2.2.2 BIOASSAY SOILS

2.2.2.1 WORM ASSAY SOILS

For the worm assay, soil was collected from six active or former orchards and four control sites in the Auckland and Waikato regions in July 2003. Where possible, a control or unsprayed area (usually an adjoining pasture) was identified for each property. Soil was collected from the A horizon (nominal depth ~15 cm) using a stainless steel spade. Turf sods were cut, turned over and the soil from underneath collected. The soil was collected from within a one hectare block on each site using the "Z" sampling pattern to gain a representative composite sample from within this area. Approximately 10 kg of soil was collected from each sampling location. Soils were collected over 3 days and stored at <5 °C prior to use.

2.2.2.2 PLANT ASSAY SOILS

The plant trial soils were collected from the Auckland region over the time period 10 March to 12 March 2002. Bulk soil samples were collected from four long-term horticultural properties (three pipfruit orchards and one vineyard) and four control sites (two bushblocks and two grazing paddocks). It was not possible to locate a suitable background/baseline site for each orchard property. Approximately 20 kg of soil was collected from each sampling location using the sampling methodology described in section 2.2.2.1. The plant trial soils were stored in bags at ambient temperature for a maximum of seven days before the start of the plant trial.

Soil used in the seedling emergence and root elongation toxicity tests was taken from the bulk soil samples collected for the worm assay, described above in Section 2.2.2.1.

2.3 BIOASSAYS

2.3.1 WORM ASSAY

The biovailability of contaminants to earthworms was assessed using a modification of the 28 day sublethal toxicity test for *A. caliginosa* developed by Kula and Larink (1998). Field harvested *A. caliginosa* supplied by Rangimarie Worm Farm, Motueka were harvested from the same area and provided in two batches. Batch one was used in the bioassay and batch two was used to determine baseline levels of contaminants and check the accuracy of the field identification of *A. caliginosa.* Upon receipt at the University of Waikato, the worms were maintained at 15 °C in a temperature control unit at AgResearch Ruakura for seven days prior to the start of the experiment. A representative subsample of the worms was culled and classified according to the identification key developed by Sims and Gerard (1985). Two worm species were identified – *A. caliginosa* (90%) and *Aporrectodea rosea* (10%).

The toxicity and earthworm accumulation of aged contaminants from soil was tested using eight soils (five orchard and three grazing soils). Four replicates were prepared for each soil by weighing 1 kg (DW equivalent) of field-moist soil (<4 mm) into 4 L plastic containers (Stowers Containment Solutions) and adjusting to 60% water holding capacity (WHC) with deionised water. The soils were equilibrated overnight before twelve individually weighed mature (clitellate) earthworms (*A. caliginosa)* were added to each replicate. The top of each container was covered with fine nylon mesh to prevent the worms from escaping. Soil moisture contents were maintained at 60% WHC by the addition of deionised water every two days. Throughout the trial, the containers were maintained at 15 °C in a temperature control unit at AgResearch, Ruakura under a light:dark regime of 16:8 h. The containers were placed on benches in the temperature control unit in a randomised pattern and the containers were re-randomised twice during the bioassay.

After 28 days, the worms were recovered from each pot by hand sorting, rinsed in deionised water and individually weighed to assess changes in bodymass. The

recovered worms were depurated for 72 h on moist filter paper (Advantec 5B); which was replaced daily. After depuration the worms were thoroughly rinsed in ultra pure deionised water, frozen at -20 °C and freeze dried (Dynavac FD12) before being ground in a modified spice grinder. In order to obtain sufficient tissue for analysis the worms from all replicates within each treatment were composited. The number of cocoons produced by the worms in each container was estimated by wet sieving half of the soil within each test container.

2.3.2 PLANT ASSAYS

2.3.2.1 PHYTOAVAILABILITY OF AGED CONTAMINANTS IN SOIL

A pot trial experiment was conducted at the Biological Sciences glasshouse complex at the University of Waikato to assess the phytoavailability of aged contaminants from horticultural soils, collected as described in Section 2.2.2.2. To provide additional contaminant concentrations within the tested range, two further bulk soil samples were prepared by blending soil from an orchard with soil from the adjacent bush block. Two species of edible plants were used to assess contaminant uptake from each soil; lettuce (*Lactuca sativa* var Buttercrunch) and radish (*Raphanus sativus* var Salad Crunch).

The method for the plant trial was adapted from Gray *et al.* (1999a). Four replicates were prepared for each plant species and each soil. For each replicate, field-moist soil (equivalent to 500 g DW) was weighed into a polyethylene-lined 15 cm diameter pot. The polyethylene liner was used to prevent moisture loss and contact of the soils with the pots (Moustakas *et al.*, 2001). The lettuce seedlings were grown from commercial seed (Yates) in plugs of potting mix before planting as 13-day-old seedlings. The radish seeds (Yates) were initially oversown at 9 seeds per pot and thinned to a maximum of 5 per pot at 10 days old.

The pots were placed in rows on benches and the pot positions were randomized every 7 days. The pots were maintained at 75% WHC with deionised water. The

plants were initially watered daily but towards the end of the trial the lettuce plants required watering twice daily. Supplementary lighting was not used and the temperature was maintained between 10 and 25 °C for the duration of the trial. The average minimum temperature was 14 °C and the average max temp 24 °C. A nutrient solution, prepared from analytical grade reagents (Table 2.1), was added to all treatment pots twice during the trial. The first addition of nutrient solution (25 mL diluted to 50 mL with distilled water per pot) was added 2 days after planting with a second addition after 40 days. The lettuces were harvested 47 days after transplanting and the radishes after 35 days; both plant species were grown to maturity.

Table 2.1: Fertiliser regime used for the pot trial (after Gray *et al.*, 1999a).

Nutrient	Salt	kg ha^{-1}	Per pot (mg)	In 25 mL (mg L^{-1})
N	NH_4NO_3	100	180	7200
P	$Ca(H_2PO_4)_2.H_2O$	40	72	2880
K	K_2HPO_4	60	108	4320
S	K_2SO_4	17	31	1240
Mg	$MgSO_4.7H_2O$	10	18	720

Thirty-five out of the 36 lettuce plants were harvested as one lettuce plant was damaged during transplant and subsequently died. The above ground parts of the lettuce plants were cut at approximately 0.5 cm above ground level using a stainless steel blade. The roots and surrounding soil were stored at 5 °C for a maximum of 15 days before the roots were recovered by washing. The radishes were recovered from each pot by washing the soil under running water to remove adhering soil particles. The radish plants were separated into leaves, hypocotyls and roots using a stainless steel blade. The dry mass yields were measured for all plant parts.

Adhering soil particles were removed from all plant parts by washing under running water followed by rinsing in distilled water, followed by a final rinse in either doubly distilled or deionised water. The plant material was frozen at -20 °C in zip lock plastic bags, freeze dried (Dynavac Freeze Drier Model FD12), and the dry weights recorded. Prior to grinding, the freeze-dried plant material was dried in an oven at 30

°C for 24 h to remove any residual moisture from the freezer. The lettuce leaves, and the radish hypocotyls and leaves were ground using a Tecator Knifetec 1095 Sample mill.

2.3.2.2 SEEDLING EMERGENCE AND ROOT ELONGATION

Seedling emergence and root elongation toxicity tests were carried out on 10 soils containing varying levels of aged contaminants (6 orchards and 4 grazing soils). One species of monocotyledon, ryegrass (*Lolium perenne* var Bronsyn LN 4786A), and one species of dicotyledon, lettuce (*La. sativa* var Buttercrunch) were used. The seeds were commercially sourced and the germination rate confirmed beforehand (>90%). The methodology of Chang *et al.* (1997) and Cook *et al.* (2002) was adapted for this assay and each soil was tested in triplicate. The seed germination and root elongation test were conducted in the same petri dish. For each soil, 25 g of soil (DW equivalent) was weighed into 8.5 cm polycarbonate petri dishes. The soils were moistened with deionised water to 75% WHC and the soils left to equilibrate overnight. Ten seeds were placed on the top of the soil in each dish and covered with 22.5 g of fine sand. The petri dishes were placed in zip lock polyethylene bags and incubated at 25 °C under a light:dark (16:8 h) regime for 5 days in a controlled environment room (AgResearch, Ruakura). After 5 days the upper sand layer was removed before the number of germinated seeds was counted and the total root and shoot lengths measured using digital calipers.

2.4 CHARACTERISATION OF SOILS: PHYSICAL AND CHEMICAL PROPERTIES

The total organic carbon content (%TOC), pH, Olsen P content and cation exchange capacity (CEC) of the soil samples were determined using methods developed by the NZ Soil Bureau (Blakemore *et al.*, 1987).

2.4.1 TOTAL ORGANIC CARBON (% TOC)

One g of finely ground and sieved (<250 μm) air-dried (30 °C) soil was weighed into a conical flask. Calibration standards of a known mass of organic carbon were prepared from sucrose (BDH, general reagent grade). Twelve mL of conc. H_2SO_4 was added to the samples and standards and the resulting slurries were left to stand for 10 min with occasional swirling by hand. Six mL of 3 *M* chromium trioxide was then added and the solutions mixed by swirling and left to stand for exactly 10 min before dilution to almost 200 mL with deionised water. The diluted solutions were left to stand overnight and then made up to a final weight of 200 g. An aliquot of this solution was centrifuged for 10 min at 2000 rpm and the absorption of the supernatants read at 600 nm using 10 mL cuvettes and a Meter-tek SP-830 spectrophotometer. An in-house soil standard (<250 μm, air dried 30 °C) was included in each batch of samples. The method detection level calculated from data for the in-house soil standard was 0.8% TOC and the %RSD for replicate measurements was 5.4% (n = 21).

2.4.2 SOIL PH

Ten grams of air dried (<2 mm) soil was weighed out and 25 mL of distilled water added. The samples were homogenised using a high speed stirrer and left to stand overnight. Soil pH measurements were determined using a Mettler Toledo MP 220 pH meter calibrated with pH 4 and pH 7 buffers. An in-house soil standard was included in each batch of samples, and the %RSD for repeat measurements of this was 4% (n = 10). The worm trial soils were analysed in triplicate and the %RSD for replicates was in the range 0.2 to 1.2%.

2.4.3 CATION EXCHANGE CAPACITY

For determination of cation exchange capacity, 0.5 g of soil (dried at 30 °C, <2 mm) was weighed into a 50 mL polypropylene centrifuge tube. Forty mL of 0.01 *M* AgTU was added and the tubes mixed end over end (50 rpm) for 16 h. The 0.01 *M* AgTU solution was prepared by dissolving 30 g of thiourea and 17 g of $AgNO_3$ in 2 L of distilled water. The solutions were centrifuged at 2000 rpm for 10 min and a 25 mL aliquot filtered (Whatman 42) into a 30 mL polypropylene vial. Standards were prepared by diluting the 0.01 *M* AgTU solution with a 0.2 *M* thiourea solution. Samples and standards were diluted 100 times with a 1000 $\mu g\ mL^{-1}$ solution of Cs as an ionisation buffer. The resulting solutions were measured for silver by atomic absorption spectroscopy (GBC Avanta) at 328.1 nm using an air-acetylene flame. The mean %RSD for duplicate samples was 12, 11 and 4% for the Auckland, Tasman and Waikato samples respectively. The %RSD for repeat analyses (n = 9) of an in-house QC soil with a low CEC (7 mmol/100 g) was 18%.

2.4.4 OLSEN P

Two g of air dried soil was extracted with 40 mL of 0.5 *M* $NaHCO_3$ in a 50 mL polycarbonate centrifuge tube. The centrifuge tube was placed on an end over end shaker (50 rpm) for 30 min. A 10 mL aliquot of the extract was filtered through Whatman 42 filter papers into a 100 mL volumetric flask. Three mL of 0.5 *M* H_2SO_4 was added and the flask swirled until the solution stopped producing gas bubbles. Approximately 70 mL of distilled water was added to each flask. Murphy and Riley reagent B was prepared by adding 1.056 g of ascorbic acid per 100 mL of a 1.2% solution of ammonium molybdate (Murphy and Riley reagent A). Eight mL of Murphy and Riley reagent B was added to each flask. The solutions were made up to 100 mL and left standing to allow the resulting molybdenum blue complex to develop. After 20 min the absorbance of each solution was read at 880 nm using 10 mL cuvettes and a Meter-tek SP-830 spectrophotometer.

Seven replicates of a low level soil sample (9 mg kg^{-1}) were similarly analysed and an MDL of 8 mg kg^{-1} calculated using the USEPA recommended method (Title 40: Protection of the Environment Part 136, Appendix B Electronic Code of Federal Regulations, 2005). A sample with a low Olsen P value (11 mg kg^{-1}) was used as an in-house control soil and the %RSD for repeat analyses (n = 14) was 24%. The worm trial soils were analysed in duplicate and the %RSD for samples with Olsen P values ranging from 12 to 69 mg kg^{-1} varied from 1.4 to 3.4%.

2.4.5 PARTICLE SIZE

Field moist soil samples were prepared for particle size analysis using the method of Knoert and Vandenberghe (1997). Soil organic matter was removed by adding 10 mL of 10% H_2O_2 to 1 g of field-moist soil in a wide mouthed 50 mL glass jar and leaving to stand overnight. The H_2O_2 was removed by heating gently on a hotplate to almost dryness and the treated soils were re-suspended in 10 mL of 10% Calgon. The samples were left to stand overnight and then sonicated (Astrason) for 5 min. Particle size was determined by laser diffraction analysis using a Malvern Instruments Mastersizer.

2.5 PESTICIDE RESIDUES

2.5.1 REGIONAL INVESTIGATIONS

The samples collected during the regional investigations were analysed by Hill Laboratories, Hamilton.

2.5.1.1 MULTI-PESTICIDE (ORGANOCHLORINE, ORGANONITROGEN AND ORGANOPHOSPHORUS COMPOUNDS) RESIDUES IN SOIL

Auckland samples were analysed for a suite of organochlorine, organonitrogen and organophosphorus pesticides (Figure 2.3). Field-moist soil samples (8.5 g) were mixed 1:1 with sodium sulphate and extracted with ethyl acetate (20 mL) using sonication (Sonorex digital 10P), followed by shaking. Samples were cleaned up by gel permeation chromatography (GPC). The GPC system comprised a Gilson 307 pump, and a Gilson 232 Bio auto sampler with a 401 diluter, a pre-column packed with S-X_3 Biobeads and two Phenomenex Phenogel columns (300 x 7.8 mm, packed with 10 micron beads with a 100 Angstrom pore size), coupled in series. The mobile phase was 1:1 ethylacetate:cyclohexane. Samples were spiked with 0.5 mg kg^{-1} equivalent of triphenylphosphate (TPP) as a system monitoring compound. One sample in each batch was matrix-spiked with selected compounds. A procedural blank was included with each batch of 18 samples. Three field moist blind duplicates were included amongst samples submitted for multi-pesticide residue screening.

The purified extracts were analysed by gas chromatography (GC) using an Agilent 6890 plus GC with micro electron capture (ECD) and nitrogen phosphorous detectors (NPD detector) using internal standard calibration with GC-MS (Agilent 6890 plus with 5973 MS) confirmation of detected pesticides.

For GC-ECD/NPD analyses, 2 x 5 µL aliquots of the GPC cleaned extracts were injected using an Agilent PTV injector in large volume mode. The initial temperature of the injector was held at 20 °C for 0.4 min and increased at 320 °C/min to 340 °C and held for 5 min, then increased at 200 °C/min ramp to 350 °C and held for 2 min. Analytes were chromatographically separated using an HP ultra-2 GC column (0.2 mm ID x 0.33 µm film thickness x 25 m column length). The initial column temperature was held at 40 °C for 4 min and increased at 30 °C/min to 120 °C, then increased at 11 °C/min to 320 °C where it was held for 4 min.

For the GC-MS confirmation analyses, 2 x 10 μL aliquots of the sample were injected. The initial temperature of the injector was held at 20 °C for 1.5 min, increased by 300 °C/min to 320 °C and held for 2.5 min, then increased by 320 °C/min to 340 °C and held for 3 min. A DB-XLB GC column (0.25 mm ID x 0.25 μm film x 30 m) was used to chromatographically separate target compounds. The initial column temperature was held at 40 °C for 4 min, then increased by 30 °C/min to 120 °C, then increased by 11 °C/min to 320 °C where it was held for 4 min.

The method detection limits for target compounds in the multi pesticide residues screen were typically in the range of 0.005 to 0.05 mg kg^{-1} (Figure 2.3) and were 0.005 mg kg^{-1} for the *o,p'*- and *p,p'*- isomers of DDT, DDE and DDD. Concentrations of target analytes in all procedural blanks were found to be less than their detection limits. The mean percentage difference for pesticides measured in duplicate samples was 19%. The 95% confidence interval for the mean recovery of the internal standard TPP was 89 ± 3%. The 95% confidence interval for mean recovery of matrix-spiked DDT, DDE and DDD was 84 ± 13% and the 95% confidence interval for mean recovery of all matrix-spiked compounds was 76 ± 4% (range 51 to 124%, n = 80).

Multiresidue GC screen (lab code - FCGC)

Acephate	0.02	Chordane -cis	0.005	Endrin	0.005	Leptophos	0.01	Propazine	0.01
Acetochlor	0.01	Chordane -trans	0.005	Endrin Ketone	0.005	Lindane (gamma-BHC)	0.005	Propetamphos	0.01
Alachlor	0.01	Clomazone	0.02	EPN	0.01	Linuron	0.05	Propham	0.01
Aldrin	0.005	Coumaphos	0.02	EPTC*		Malathion	0.01	Propiconazole	0.01
Atrazine	0.01	Cyanazine	0.01	Esfenvalerate	0.01	Metalaxyl	0.02	Prothiofos	0.01
Atrazine-desethyl	0.01	Cyfluthrin	0.01	Ethion	0.01	Methacrifos	0.01	Pyrazophos	0.01
Atrazine-desisopropyl	0.03	Cyhalothrin	0.01	Etrimphos	0.01	Methamidophos	0.02	Pyrethrin	0.03
Azaconazole	0.02	Cypermethrin	0.01	Famphur	0.01	Methidathion	0.02	Pyrifenox	0.01
Azinphos methyl	0.02	Cyproconazole	0.01	Fenamiphos	0.01	Methiocarb	0.02	Pyrimethanil	0.01
Azoxystrobin	0.02	Cyprodinil	0.02	Fenarimol	0.01	Methoxychlor	0.005	Quintozene	0.01
Benalaxyl	0.01	DDD (2,4')	0.005	Fenitrothion	0.01	Metolachlor	0.01	Quizalofop-ethyl	0.01
Bendiocarb	0.01	DDD (4,4')	0.005	Fenpropathrin	0.01	Metribuzin	0.01	Simazine	0.01
Benodanil	0.01	DDE (2,4')	0.005	Fenpropimorph	0.01	Mevinphos	0.01	Sulfotep	0.01
BHC (alpha)	0.005	DDE (4,4')	0.005	Fensulfothion	0.01	Myclobutanil	0.01	Tebufenpyrad	0.01
BHC (beta)	0.005	DDT (2,4')	0.005	Fenthion	0.02	Nitrofen	0.01	Terbacil	0.01
BHC (delta)	0.005	DDT (4,4')	0.005	Fenvalerate	0.01	Nitrothal-isopropyl	0.01	Terbuconazole	0.01
Bifenthrin	0.01	Deltamethrin	0.01	Fluadioxynil	0.02	Norflurazon	0.01	Terbufos	0.01
Bitertanol	0.01	Demeton-s-methyl	0.03	Fluazifop-butyl	0.01	Omethoate	0.03	Terbumeton	0.01
Bromacil	0.01	Diazinon	0.01	Fluometuron	0.01	Oxadiazon	0.01	Terbuthylazine	0.01
Bromophos ethyl	0.01	Dichlobenil	0.01	Fluralaxyl	0.01	Oxadixyl*		Terbuthylazine desethyl	0.01
Bromopropylate	0.01	Dichlofenthion	0.01	Flusilazole	0.02	Oxychlordane	0.005	Terbutryn	0.02
Bromoxynil*		Dichlofluanid	0.01	Fluvalinate	0.01	Oxyfluorfen	0.01	Tetrachlorvinphos	0.01
Bupirimate	0.01	Dichloran	0.01	Folpet	0.01	Paclobutrazol	0.01	Thiometon	0.02
Buprofezin	0.01	Dichlorvos	0.03	Haloxyfop-methyl	0.01	Parathion ethyl	0.01	Tolyfluanid	0.01
Captafol	0.01	Dicofol	0.05	HCB	0.005	Parathion methyl	0.01	Triadimefon	0.01
Captan	0.01	Dicrotophos	0.01	Heptachlor	0.005	Penconazole	0.01	Tri-allate	0.02
Carbaryl	0.02	Dieldrin	0.005	Heptachlor Epoxide	0.005	Pendamethalin	0.01	Triazophos	0.01
Carbofuran	0.01	Difenoconazole	0.01	Hexaconazole	0.01	Permethrin	0.01	Trifloxystrobin	0.03
Carbophenothion	0.01	Dicofol	0.05	Hexazinone	0.01	Phorate	0.02	Triflurallin	0.01
Carboxin	0.01	Dimethoate	0.02	Hexythiazox	0.03	Phosmet	0.01	Vinclozolin	0.02
Chlorfenvinphos	0.01	Dinocap	0.05	Imazalil	0.03	Phosphamidon	0.01		
Chlorfluazuron	0.01	Diphenylamine	0.02	Indoxacarb	0.01	Pirimicarb	0.01		
Chlorotoluron	0.01	Disulfoton	0.05	Iodofenphos	0.01	Pirimiphos methyl	0.01		
Chlorpropham	0.01	Diuron	0.02	Iprodione	0.01	Prochloraz	0.01		
Chlorpyrifos	0.01	Endosulfan I	0.005	Isazophos	0.01	Procymidone	0.01		
Chlorpyrifos methyl	0.01	Endosulfan II	0.005	Isofenphos	0.01	Prometryne	0.01		
Chlozolinate	0.01	Endosulfan sulphate	0.005	Kresoxim methyl	0.01	Propachlor	0.02		

Enter lab code – Multires in GC multires box for inclusion of Chlorothalonil, endrin aldehyde, HCB, Naled and Sulfentrazone

Figure 2.3: Scan of document outlining detection limits (mg kg^{-1} DW) for multi-residue pesticide screen carried out by Hill Laboratories.

2.5.1.2 ACIDIC HERBICIDES

Acidic herbicides were extracted from field-moist soil samples (50 g) which were acidified with 5 mL of 20% orthophosphoric acid and ground with 50 g of anhydrous sodium sulphate. A 6 g subsample was extracted by accelerated solvent extraction (Dionex ASE 200 Accelerated Solvent Extractor) using a binary solvent mixture of dichloromethane and acetone (1:1). The crude extracts were back extracted with acidified sodium sulphate; cleaned up using GPC (Gilson Autosampler and GPC) and methylated with diazomethane before GC-MS analysis. Samples were spiked to a

level equivalent to 0.05 mg kg^{-1} 2,4,6-tribromophenol (2,4,6-TBP) and/or 2,3,6-trichlorophenylacetic acid (2,3,6-T) as system monitoring compounds. One sample in each batch was matrix spiked with a suite of acidic herbicides at 0.05 mg kg^{-1} equivalent. A procedural blank was included with each batch of samples (n = 18). Three field-moist duplicates were submitted to the laboratory for the acidic herbicide analyses.

The extracts were analysed by GC-MS (Agilent 6890 plus with 5973 MS) in selected ion monitoring mode using internal standard calibration. For the GC-MS analysis of acidic herbicides, 2 μL aliquots of the sample were injected using the Agilent PTV injector in split/splitless mode. The initial temperature of the injector was held at 20 °C for 1.5 min, increased by 300 °C/min to 320 °C and held for 2.5 min, then increased by 320 °C/min to 340 °C and held for 3 min. A DB-XLB GC column (0.25 mm ID x 0.25 μm film x 30 m) was used to chromatographically separate target compounds. The initial GC-MS column temperature was as held at 40 °C for 4 min, increased by 30 °C/min to 160 °C, increased by 5 °C/min to 210 °C, then increased by 30 °C/min to 320 °C where it was held for 2 min.

The method detection limit for the target analytes was 0.01 mg kg^{-1}. Concentrations of target compounds in all procedural blanks were found to be less than their detection limits (Table 2.2). Acidic herbicides were not detected in any of the cropping area samples or field duplicates. The 95% confidence intervals for the mean recoveries of 2,4,6-TBP and 2,3,6-T were 74 ± 3% and 76 ± 3% respectively. The 95% confidence interval for the mean recovery for the matrix spikes (excluding picloram) was 84 ± 5% (range: 60 to 129 %). Low recoveries were obtained for picloram (≤10%), and therefore data for picloram should be considered qualitative. Picloram was not detected in any sample analysed as part of this study, however as no other acidic herbicides were detected it is unlikely that picloram was present in detectable concentrations.

Table 2.2: Hill Laboratories' detection limits for acidic herbicides (mg kg^{-1} DW).

Acidic herbicide	Detection limit (mg kg^{-1})	Acidic herbicide	Detection limit (mg kg^{-1})
2,4-D	0.01	Haloxyfop	0.01
2,4,5-T	0.01	MCPA	0.01
Bentazone	0.01	MCPB	0.01
Bromoxynil	0.01	Mecoprop	0.01
Clopyralid	0.01	Picloram	0.01
Dicamba	0.01	Quizalofop	0.01
Dichlorprop	0.01	Silvex	0.01
Fluazifop	0.01	Triclopyr	0.01
Fluroxypyr	0.01		

2.5.1.3 ORGANOCHLORINE PESTICIDE ANALYSES: WAIKATO AND TASMAN SURVEYS

Samples from the Waikato and Tasman surveys were analysed for a suite of organochlorine pesticides (Table 2.3). Dried (30 °C) and ground (<2 mm) soil (2.00 ± 0.05 g) was moistened with orthophosphoric acid (1 mL). The samples were extracted with 10 mL of hexane:acetone (1:1) using sonication extraction (90 min) (Sonorex digital 10P Sonicator). Extracts were cleaned up using florisil columns. An internal QC sample, consisting of a fully characterised bulk homogenous field contaminated sample, was analysed with each batch of samples (n = 25). Individual samples were spiked with pentabromobiphenyl (0.2 mg kg^{-1} equivalent) as a system monitoring compound (SMC). One sample per batch was employed as a matrix spike sample and spiked with 0.05 mg kg^{-1} of the full suite of organochlorine pesticides being analysed. A procedural blank was also included with each batch of samples. One blind duplicate sample per 10 soil samples was submitted for analysis. For the Waikato survey only, one replicate of an in-house control soil was submitted for analysis.

The purified extracts were analysed by GC-ECD (Agilent 6890N with dual micro-ECD) with internal standard calibration. A 2 µL aliquot was injected using a 7683 automatic liquid sampler and the Agilent 6850 PTV in cold splitless and large volume injection mode. An SGE BPX50 GC column (30 m x 0.25 mm ID x 0.25 µm film thickness) was used to chromatographically separate analytes and an SGE BPX5

column (30 m x 0.25 mm ID x 0.25 μm film thickness) was utilised for confirmation. The initial column temperature was 120 °C, increased by 60 °C/min to 220 °C, then increased by 5 °C/min to 250 °C and then increased by 30 °C/min to 300 °C and held for 1 min.

The method detection limits for the organochlorine pesticides were typically in the range 0.005 to 0.02 mg kg^{-1} and were 0.005 mg kg^{-1} for the *o,p'*- and *p,p'*- isomers of DDT, DDE and DDD (Table 2.3). The concentration of target analytes in all procedural blanks was below the corresponding detection limit. The 95% confidence intervals for the mean recovery of the SMC were 107 ± 4% and 99 ± 5% for Tasman and Waikato soil samples respectively. The percent difference for measured pesticides in submitted blind duplicate samples was ≤20%. The 95% confidence interval for the recoveries of DDT, DDE and DDD from the matrix-spiked samples was 102 ± 23% (68 to 153%).

Table 2.3: Hill Laboratories' detection limits (mg kg^{-1} DW) for organochlorine pesticides.

Organochlorine	Detection limit (mg kg^{-1})	Organochlorine	Detection limit (mg kg^{-1})
Aldrin	0.005	*o,p'*-DDT	0.005
Alpha-BHC	0.005	*p,p'*-DDT	0.005
Beta-BHC	0.005	Dieldrin	0.005
Gamma-BHC	0.005	Endosulfan I	0.005
Total Chlordane	0.02	Endosulfan II	0.005
cis-Chlordane	0.005	Endosulfan sulfate	0.005
trans-Chlordane	0.005	Endrin	0.005
o,p'-DDE	0.005	Endrin aldehyde	0.005
p,p'-DDE	0.005	Heptachlor	0.005
o,p'-DDD	0.005	Heptachlor epoxide	0.005
p,p'-DDD	0.005	Methoxychlor	0.005

The 95% confidence intervals for mean recoveries of spiked organochlorine pesticides were 91 ± 13% and 115 ± 9% for the Tasman and Waikato soil samples respectively. Recoveries of organochlorine pesticides from a spiked Tasman sample ranged between 66 and 104% with the exception of methoxychlor (191%) and endrin aldehyde (52%). Methoxychlor was not detected in any sample collected in the Tasman District. For the Waikato survey, recoveries of organochlorine pesticides

from a spiked soil sample ranged from 83 to 120% with the exception of methoxychlor (165%) and *p,p'*-DDD (153%). The elevated recovery for *p,p'*-DDD is most likely due to the *p,p'*-DDD concentration of the sample (0.100 mg kg^{-1}). Methoxychlor was not detected in any soil sample collected from the Waikato region.

2.5.2 DETERMINATION OF DDT RESIDUES IN BIOASSAY SOILS

DDT determinations for the bioassay soils were undertaken at HortResearch, Ruakura, by the following methodology.

2.5.2.1 ACETONE:HEXANE EXTRACTION

Field-moist soil samples (10 g DW equivalent) were weighed into 200 mL Schott bottles with Teflon lined screw caps. Oven dried samples (plant trial soils, QA/QC soils) were remoistened by the addition of 1 mL of distilled water. One mL of concentrated phosphoric acid was added to all samples which were mixed by hand and left to equilibrate for 15 min. Sufficient Na_2SO_4 (10–20 g) to disperse sample aggregates was added and the thoroughly mixed by hand. All soil samples were spiked with aldrin (50–250 µL of an aldrin standard prepared in *iso*-octane) as an internal recovery standard. The aldrin spike level was based on the expected DDT residue concentrations (samples had previously been collected from the same sites). The aldrin spike concentrations used for the worm and plant assay soils were equivalent to 0.1 mg kg^{-1}, 5 mg kg^{-1}, and 25 mg kg^{-1} dry weight of soil. A separate sub-sample of soil was weighed and dried at 105 °C for moisture determination.

The soil samples were extracted with 50 mL of 2:3 (v/v) acetone:hexane using sonication (30 min) followed by shaking on a rotary shaking table (300 rpm for 60 min). Extra Na_2SO_4 was added to some samples to prevent samples from "clumping" during shaking. After the extraction step, 75 mL of Milli-Q water was added to each Schott bottle to partition hexane and centrifuged (10 min at 2000 rpm) to aid phase

separation. A 0.5 mL aliquot of the washed extract was purified using silica-gel mini adsorption chromatography (Davisil, activated overnight at 130 °C) and the analytes were eluted with 2.5 mL 20% ethyl-acetate in hexane. The purified extract was concentrated using gentle heat and N_2, exchanged into *iso*-octane and further diluted as needed for analysis. An aliquot of the final extract in *iso*-octane was transferred to an autosample vial for GC analysis.

Each batch of samples (max 24 samples) included a solvent blank, solvent spike, control soil blank and control soil spike. All QA/QC samples were spiked with 250 μL of a 10 μg mL^{-1} aldrin standard prepared in *iso*-octane. The solvent spike and the control soil spike were spiked with 250 μL of a 10 μg mL^{-1} mixed organochlorine pesticide standard prepared in *iso*-octane to provide a soil concentration equivalent to 0.25 mg kg^{-1}. In-house QC soil samples were also analysed with each batch of samples. For the plant trial soils, one duplicate sample was analysed for every 10 samples.

The 95% confidence intervals for the mean recoveries of individual isomers of DDT, DDE and DDD were excellent (Table 2.4). DDT compound concentrations in the solvent blank were typically less than the detection concentrations.

The 95% confidence interval for the mean recovery of aldrin was 93 ± 4% for the plant trial soils and 99 ± 5% for the worm trial. Similar 95% confidence intervals for the internal aldrin standard recoveries were obtained for each spike level (Table 2.5) demonstrating the robustness of the analytical method. While the recovery of aldrin for the 25 mg kg^{-1} spike was lower than at other concentrations, it should be noted that these samples were diluted ten-fold in order to quantitate aldrin within the optimal linear range of the ECD whereas the DDT compound data were obtained from the corresponding undiluted sample extracts.

Table 2.4: 95% confidence intervals for mean % recoveries of DDT compounds from the solvent spikes (n = 7) and control soil spikes (n = 7). The QC samples were spiked to provide a soil concentration equivalent to 0.25 mg kg^{-1}.

Compound	Solvent spikes	Control soil spikes
Aldrin	100 ± 17	102 ± 12
o,p'- DDE	107 ± 8	108 ± 8
p,p'-DDE	103 ± 18	107 ± 10
o,p'-DDD	103 ± 8	105 ± 11
p,p'-DDD	102 ± 11	107 ± 7
o,p'-DDT	104 ± 11	106 ± 5
p,p'-DDT	108 ± 14	104 ± 9

Table 2.5: 95% confidence intervals for mean % recoveries of the internal standard aldrin according to spike level.

Spike level (mg kg^{-1})	n	95% Confidence interval
0.1	34	99 ± 4
5	19	102 ± 5
10	7	102 ± 7
25	9	78 ± 4

The mean %RSD for analysis of ΣDDT in duplicate samples was 15% for the plant trial soils. The worm soils were analysed in triplicate and the mean %RSD for ΣDDT was 8.9%. Good agreement was obtained for analysis of the in-house QC samples between HortResearch and Hill Laboratories using comparable analytical methods, (refer Section 2.5.1.3) (Table 2.6). The %RSD for replicate analyses of the in-house QC soils using the HortResearch method was ≤23%.

Table 2.6: Interlaboratory comparison for DDT analyses, where Hills denotes Hill Laboratories. Results (mg kg^{-1} DW) are presented as means with the %RSD in brackets.

Compound	Sample A			Sample B			Sample C		
	Author		Hills	Author		Hills	Author		Hills
o,p'- DDE	<0.01		<0.005	<0.01		<0.005	0.04	(6)	<0.005
p,p'-DDE	0.161	(11)	0.171	0.933	(16)	0.986	7.74	(10)	6.36
o,p'-DDD	<0.01		<0.005	<0.01		<0.005	0.220	(4)	0.20
p,p'-DDD	0.015	(11)	0.016	0.042	(23)	0.048	0.523	(8)	0.74
o,p'-DDT	<0.01		0.007	<0.01		0.011	0.379	(5)	0.41
p,p'-DDT	0.056	(10)	0.076	0.160	(6)	0.165	6.21	(1)	7.59
ΣDDT	0.23	(10)	0.27	1.14	(16)	1.21	15.1	(5)	15.3

2.5.2.2 ETHYL ACETATE EXTRACTION

Duplicate soil samples from the worm trial (10g DW equivalent) were weighed into 200 mL Schott bottles, spiked with aldrin as an internal standard and extracted with 50 mL of ethyl-acetate by sonicating for 30 min followed by shaking at 300 rpm for 60 min. The extracts were allowed to settle and a 20 mL aliquot was transferred to a glass scintillation vial (25 mL) containing 3 g Na_2SO_4 as a drying agent. One mL of the ethyl-acetate extract was exchanged into hexane using gentle heat and evaporation with N_2 gas and purified for analysis as described in Section 2.5.2.1.

The same QA/QC samples as employed for the acetone:hexane extractions (Section 2.5.2.1) were included. Three levels of internal standard aldrin spikes were employed; equivalent to 0.1 mg kg^{-1}, 5 mg kg^{-1}, and 25 mg kg^{-1}.

Target analytes in the solvent blank were present at levels lower than detection concentrations and the 95% confidence interval for recoveries of DDT compounds was 95 ± 3% and 90 ± 3% respectively for the solvent spike and control soil spike. The 95% confidence intervals for recovery of aldrin were 92 ± 4%, 91 ± 5% and 95 ± 3% for spike levels of 0.1 mg kg^{-1}, 5 mg kg^{-1}, and 25 mg kg^{-1} respectively. The %RSD for duplicate samples was <21% for the individual DDT isomers and the mean %RSD for duplicate analyses of ΣDDT was 7%.

2.5.3 PERSULFATE OXIDATION

Persulfate oxidation was performed using a method adapted from Cuypers *et al.* (2000). Field-moist soil (5 g DW equivalent) was mixed with $K_2S_2O_8$ and milli-Q water in 100 mL glass Schott bottles to provide a persulfate ($S_2O_8^{2-}$):organic matter ratio of 12 g/g and a final solution persulfate concentration of 0.0357 g mL^{-1}. The capped sample bottles were placed in an incubator and heated at 80 °C for 3 h with regular hand swirling. After cooling, the soil was recovered from the extraction bottles by filtering through GFA filters under vacuum. The soils and filters were

extracted with 50 mL 2:3 acetone:hexane using the method described in Section 2.5.2.1. Persulphate blanks were extracted by adding with 30 mL of hexane to the Schott bottles and shaking (300 rpm) for 60 min. A 1 mL aliquot of hexane was removed and exchanged into 1 mL *iso*-octane using gentle heat and N_2 for analysis.

Experiments were undertaken to determine if the persulphate oxidation procedure was able to degrade DDT compounds. Duplicates of two soils with %TOC concentrations of 2.4% (soil A) and 4.6% (soil B) as well as blank persulfate solutions were spiked with two levels of DDT compounds equivalent to final soil concentrations of 0.3 and 1.30 mg kg^{-1}. The soil was recovered by filtration as described above and the persulphate solution filtrate retained. The soil and filters were extracted with 2:3 (v/v) acetone:hexane as described in Section 2.5.2.1. The persulfate solution blanks and the filtrates were extracted with 30 mL of hexane (60 minute shake at 300 rpm). For both soil and filtrate, a 1 mL aliquot of the hexane extract was purified as previously described (Section 2.5.2.1). The cleaned-up extract was concentrated using gentle heat and N_2, exchanged into *iso*-octane, and diluted as required for analysis.

A procedural solvent blank, control soil blank and control soil and solvent spikes were also extracted with 2:3 (v/v) acetone:hexane (Section 2.5.2.1). Aldrin was used as the internal recovery standard for the extraction of both the soil and filtrate. The persulfate treated soil was spiked with 100 μL of 10 μg mL^{-1} aldrin standard (prepared in *iso*-octane) to an equivalent concentration of 100 μg kg^{-1}. The filtrate was spiked with 50 μL of 10 μg mL^{-1} aldrin standard (prepared in *iso*-octane). The 95% confidence intervals for the mean recovery of DDT compounds were 110 ± 15% and 116 ± 18% for the QA/QC solvent and soil spikes respectively. The 95% confidence interval for the mean recovery of aldrin, the internal recovery standard was 111 ± 6% for the persulfate solution and 96 ± 5% for soil indicating that recovery of DDT compounds from the acetone:hexane extractions was excellent.

The results from the soil spiking experiments indicated that the persulfate oxidation procedure was able to oxidize DDT, DDE and DDD. The amount of spiked DDT compound degraded in the presence of soil ranged from 68 to 95% (Table 2.7).

Table 2.7: Percent of DDT compounds degraded by persulfate oxidation for two soils spiked with two concentrations of DDT compounds. Results are presented as mean of duplicates.

	0.3 mg kg^{-1}			1.3 mg kg^{-1}		
	Solution	**Soil A**	**Soil B**	**Solution**	**Soil A**	**Soil B**
o,p'-DDE	>98	89	92	97	81	77
p,p'-DDE	>98	88	76	97	79	72
o,p'-DDD	>98	89	93	>98	81	82
p,p'-DDD	>98	94	95	>98	88	84
o,p'-DDT	>98	77	85	96	68	69
p,p'-DDT	>98	81	86	96	71	69

2.5.4 SEQUENTIAL EXTRACTION OF DDT RESIDUES IN SOIL

A three step sequential extraction scheme was employed in an attempt to determine the presence of bound DDT residues in soil. During the first extraction step, the soil was extracted with 2:3 (v/v) acetone:hexane and the retained soil was then extracted with dichloromethane. In the final stage the soil organic matter was saponified with methanolic KOH to release bound DDT residues.

2.5.4.1 ACETONE:HEXANE EXTRACTION

Field-moist soil samples (5 g DW equivalent) were initially extracted in duplicate using the 2:3 acetone:hexane method described in Section 2.5.2.1. The samples were not spiked with aldrin to avoid possible interferences in the base saponification step. The extracted soil residue was recovered by vacuum filtration through GFA filters and the retained soil cake rinsed with 2:3 (v/v) acetone:hexane to remove any previously extracted DDT remaining in residual solvent. The filter and soil residues were retained for dichloromethane Soxhlet extraction. A second batch of samples

was extracted with and without the addition of phosphoric acid to determine whether this step affected the release of "bound' residues.

2.5.4.2 DICHLOROMETHANE EXTRACTION

The previously extracted GFC filters and soil were placed into 30 x 100 mm Whatman cellulose thimbles (pre-extracted with dichloromethane) and Soxhlet extracted for 16 h with 180 mL of dichloromethane (Mallinckrodt Chromar). After Soxhlet extraction, the soil samples were recovered and retained for base saponification extraction. The dichloromethane extracts were reduced in volume and exchanged into hexane by rotary evaporation. The extracts were passed through a column containing Na_2SO_4 and cotton wool to remove light particulates and colloids. The extract (ca 1 mL) was purified for analysis using silica-gel mini adsorption chromatography as described in section 2.5.2.1. Control samples included solvent blanks and solvent spiked with 100 µL aliquots of both a 1.0 µg mL^{-1} aldrin and a 1.0 µg mL^{-1} mixed organochlorine standard (prepared in *iso*-octane). The 95% confidence interval for the mean recovery of spiked DDT compounds was 86 ± 8%.

2.5.4.3 BASE SAPONIFICATION

A base saponification method adapted from Northcott and Jones (2003) was employed to determine whether this procedure released bound residues remaining non-extractable in the soil. The soil recovered from the dichloromethane extraction was placed into a 200 mL Schott bottle with a Teflon lined screw cap lid. 50 mL of methanolic KOH (pH 12) (prepared by mixing 700 mL of methanol and 50 mL of 2M KOH) was added and the tube and contents were incubated at 95 °C for 5 h. The content of the tubes were mixed every hour by gently swirling by hand. The initial incubation was carried out in a water bath and subsequent extractions in an incubator. After incubation the tubes were cooled to room temperature and weighed to determine if any solution was lost during incubation. A 25 mL aliquot of the lye was

transferred to a 35 mL glass centrifuge tube (Kimax, Oakridge style) and extracted with three separate 5 mL aliquots of hexane. The hexane extracts for each sample were combined and evaporated to 1 mL using gentle heat and N_2 gas. A 0.5 mL portion of the extract was purified on silica gel using the method described in Section 2.5.2.1. The final volume was adjusted to 1 mL in *iso*-octane and sample extracts were further diluted as required for GC-ECD analysis

Concentrations of target analytes were less than detection limits in procedural blanks. The recovery of DDT compounds was determined using methanolic KOH blanks spiked with 100 μL and 500 μL of 50 μg mL^{-1} DDT compound standard prepared in *iso*-octane to equivalent concentrations of 0.1 μg mL^{-1} and 0.5 μg mL^{-1}. DDT compounds were not recovered from the 0.1 μg mL^{-1} spike (Table 2.8). The low recoveries of *o,p'* and *p,p'* DDT obtained from the 0.5 μg mL^{-1} spike in combination with the elevated recoveries for *o,p'* and *p,p'* DDE indicate that DDT is degraded by the base saponification process. The samples were analysed in two batches. For batch 2, the hexane extracts were spiked with 100 μL of 1.0 μg mL^{-1} aldrin as an internal recovery standard and the 95% confidence interval for the mean recovery of aldrin from soil extracts was 88 ± 6%.

Table 2.8: Percent recovery of DDT compounds from spiked methanolic KOH solutions.

	% Compound recovered	
spike level	**0.1 μg mL^{-1}**	**0.5 μg mL^{-1}**
o,p'-DDE	0	126
p,p'-DDE	0	144
o,p'-DDD	0	0
p,p'-DDD	0	0
o,p'-DDT	0	25
p,p'-DDT	0	0

2.5.5 PLANT AND WORM TISSUE DDT RESIDUES

2.5.5.1 WORM TISSUE

Samples of freeze-dried worm tissue (0.5 g) were weighed into glass centrifuge tubes (50 mL Kimax Oakridge) with Teflon lined screw caps and 0.1 g celite was added as a dispersal agent. Samples were extracted with 20 mL 2:3 (v/v) acetone:hexane using sonication (10 min) and rotary shaking (60 min at 300 rpm; 30 mL of water was added and the samples centrifuged (5 min at 1800 rpm) to aid phase separation of hexane. The upper hexane layer was transferred to a glass scintillation vial. Six mL of hexane was added to the centrifuge tube which was shaken for a further 30 min before the hexane was recovered and combined with the first hexane extract; this step was repeated. The combined hexane extract was passed through a column of Na_2SO_4 to remove any residual water carried over from phase partitioning. Twenty μL of *n*-dodecane was added to the dried hexane extract which was blown down to dryness using gentle heat and N_2. The dried sample extract was reconstituted in 2 mL of dichloromethane.

1.2 mL of the DCM extract was filtered through an acrodisc 0.45 mm PVDF membrane filter into a tapered autosampler vial for GPC cleanup to remove lipids and other high molecular weight material co-extracted from the worm matrix.

GPC was carried out using a Shimadzu LC-10AT HPLC system connected to a Shimadzu SPD-10A UV detector and FRC-10A fraction collector. One mL of filtered DCM extract was injected onto two GPC columns (44 cm x 1 cm dia. columns packed with Bio-beads SX-8) connected in series and eluted with DCM at a flow rate of 1.4 mL/min. The eluting sample was collected in two separate fractions. Fraction one, containing the co-extracted lipids was collected in a pre-weighed 25 mL glass vial, and the fraction containing the DDT compounds was collected in a second glass vial. The two GPC extract fractions were blown to dryness using gentle heat and N_2. The glass vial containing worm lipids (fraction one) was dried to constant weight at 50 °C to gravimetrically determine the amount of lipid extracted from each worm sample. Fraction two was dissolved in 1 mL hexane and 0.5 mL transferred to a

florosil column for clean-up and eluted with 3.5 mL hexane and 4 mL 5% ethyl acetate in hexane. The combined eluates were blown down using gentle heat and N_2, exchanged into *iso*-octane and diluted as necessary for analysis by GC-ECD.

Each batch of samples included procedural blanks and solvent and control worm sample spikes. The solvent and control worm tissue were spiked with 0.1 mL of 1.0 $\mu g\ mL^{-1}$ mixed organochlorine standard (prepared in *iso*-octane) to a level equivalent to 200 $\mu g\ kg^{-1}$. Aldrin was used as the internal recovery standard at three concentrations; equivalent to 100 $\mu g\ kg^{-1}$, 200 $\mu g\ kg^{-1}$ and 2000 $\mu g\ kg^{-1}$. The worm tissue samples were extracted and analysed in two batches.

For batch one, the 95% confidence interval for the mean recovery of DDT compounds from the solvent and control tissue spikes was 71 ± 2% and 106 ± 38% respectively. The worm tissue used for determining spike recoveries had elevated concentrations of *p,p'*-DDE (0.42 mg kg^{-1}) and DDT (0.08 mg kg^{-1}) and the 95% confidence interval for mean recovery of DDT compounds was 83 ± 5% if these two isomers were excluded. In batch 2, a different composite worm sample was used as the control spike (ΣDDT concentration of 0.128 mg kg^{-1}) and the 95% confidence intervals for the mean recovery of DDT compounds from the control tissue and solvent spike were 86 ± 5% and 80 ± 2% respectively.

Levels of target analytes in the procedural blanks were below the detection limit. The 95% confidence intervals for mean aldrin recoveries were comparable between the two batches and between the three spike levels demonstrating the robustness of the method (Table 2.9). The results for DDT compound concentrations in worm tissue are reported as the mean of replicates ($n \geq 2$) and the mean %RSD value for ΣDDT measured in duplicate analyses was 10%.

Table 2.9: 95% Confidence intervals for mean percent recoveries of aldrin from worm tissue.

Spike level (μg kg^{-1})	Batch 1	Batch 2
100	78 ± 7	
200		77 ± 5
2000	74 ± 2	107 ± 7
All samples	76 ± 4	88 ± 8

2.5.5.2 DDT RESIDUES IN PLANT TISSUE

Freeze-dried plant samples (0.5 g) were extracted with 15 mL of 2:3 (v/v) acetone:hexane. The extraction and subsequent cleanup steps are the same as those employed for the worm tissue and are detailed in Section 2.5.5.1. A 20 μL aliquot of *n*-dodecane was added as keeper solvent to later batches of samples to improve recovery of DDT compounds and aldrin. The final extract volume was adjusted to 0.25 mL in a tear-drop GC vial to provide improved analyte concentration and method detection limits.

A procedural solvent blank and solvent and control plant tissue spikes were included as quality control samples. One sample duplicate was included for every 10 samples. The solvent and control plant tissue were initially spiked with 100 μL of a 1.0 μg mL^{-1} mixed organochlorine standard and 100 μL of a 1.0 μg mL^{-1} aldrin standard prepared in *iso*-octane (spike concentrations equivalent to 200 μg kg^{-1}). The plant tissue samples (lettuce and radish hypocotyl) were initially spiked with 100 μL of a 1.0 μg mL^{-1} aldrin standard prepared in *iso*-octane to give a concentration equivalent to 200 μg kg^{-1}. For later batches of samples, the aldrin and organochlorine spike levels were reduced to give a concentration equivalent to 100 μg kg^{-1}.

Target analytes in all solvent blanks were lower than detectable amounts. The mean %RSD for ΣDDT from duplicate analyses was 15%, 8% and 8.5% for lettuce leaves, radish hypocotyls and radish leaves respectively. The 95% confidence intervals for mean recoveries of DDT compounds and aldrin from plant tissue are presented in Table 2.10.

Table 2.10: 95% confidence intervals for mean percent recoveries of DDT compounds and aldrin from plant tissue. One control sample was spiked per sample batch.

	Spike level ($\mu g\ kg^{-1}$ DW)	95 % Confidence interval	
		DDT compounds	Aldrin
lettuce			
batch 1	200	a	101 ± 5
batch 2	200	a	103 ± 5
batch 3	100	79 ± 7	86 ± 4
radish hypocotyl			
batch 1	200	76 ± 4	64 ± 7
batch 2	100	84 ± 5	82 ± 5
radish leaf			
batch 1	100	83 ± 4	41 ± 10
batch 2	100	135 ± 11[b]	104 ± 6

[a]Samples spiked to a level exceeding the calibration range. [b]95% confidence interval for recovery of DDT compounds from the solvent spike was 91 ± 5%.

The solvent spike and the control plant tissue spike for the lettuce samples were inadvertently overspiked with 100 µL of 10 $\mu g\ mL^{-1}$ to a level outside the calibration range. To check the recovery of DDT compounds during the extraction and analysis of lettuce, a control lettuce sample and solvent blank were spiked with the correct amount of 100 µL of a 1.0 $\mu g\ mL^{-1}$ mixed organochlorine standard and the resulting 95% confidence interval for mean recovery of DDT compounds from lettuce tissue was 81 ± 4%. Three of the samples were re-analysed in subsequent batches and the %RSD was ≤18% for ΣDDT.

The lower aldrin recoveries for batch one of the radish leaves and the solvent spikes are most probably due to loss of aldrin during the drying step employed to exchange solvents from hexane to DCM. However,the 95% confidence interval for the mean recovery of DDT compounds from the spiked control radish leaf in the same analysis batch was 83 ± 4% indicating that DDT compounds were not lost during drying of this sample. Two samples in the same batch were analysed in duplicate; despite varying aldrin recoveries (%RSD ≤ 40%), the %RSD was less than 3% for ΣDDT concentrations for both samples. Two radish leaf samples were reanalysed in subsequent batches and the %RSD was ≤ 23% for ∑DDT.

Subsequently, two measures were undertaken to ensure the robustness of the extraction method; mirex was added as a second internal standard and 20 μL of *n*-dodecane was added as a keeper solvent to reduce compound loss during drying steps. Samples were spiked with 50 μL of a 1.0 μg mL^{-1} mirex standard in addition to aldrin. The 95% confidence intervals for mean mirex recoveries for radish leaves (batch 2), radish hypocotyls (batch 2) and lettuce (batch 3) were 107 ± 5%, 87 ± 4%, and 66 ± 6% respectively.

2.5.6 CHEMICAL ASSESSMENTS OF THE BIOAVAILABILITY OF DDT RESIDUES IN SOIL

2.5.6.1 TENAX –TA RESIN

The methodology for the Tenax equilibration was adapted from Macrae and Hall (1998) and Morrison *et al.* (2000). Duplicates of field moist soil equivalent to 1 g of soil (DW) were weighed into 50 mL glass centrifuge tubes (Kimax, Oakridge) and 0.5 g of Tenax TA absorbent resin added to each tube. Each centrifuge tube was filled to the top with aqueous 0.005 *M* $CaCl_2$/0.01 *M* NaN_3 and sealed with a Teflon lined screw cap. The centrifuge tubes were placed on a rotary shaker (48 rpm) for 24 h. The Tenax resin was separated from the soil-water slurry by centrifugation (5 min at 1800 rpm) and recovered by vacuum extraction. The recovered resin was extracted by shaking with three individual 5 mL volumes of 2:3 (v/v) acetone:hexane. The acetone:hexane extracts were combined in a 35 mL glass centrifuge tube (Kimax, Oakridge), partitioned with water and the hexane layer removed. The washed hexane extract was blown down to approximately 0.5 mL using gentle heat and N_2 and transferred to a silica column for clean-up as described in Section 2.5.2.1. The final sample volume was 1 mL in *iso*-octane and samples were further diluted with *iso*-octane as required for analysis. Two procedural blanks were included with each batch of samples.

The Tenax adsorption experiment was repeated at a later date to determine the variability between extractions. For the second batch of samples, the amount of Tenax adsorbent was reduced to 0.25 g while the mass of soil was unchanged. The aqueous solution used for equilibration was prepared without the addition of NaN_3 to test whether the presence of sodium in solution promoted the release of DDT from soil as demonstrated by Kantachote *et al.* (2004). There were no significant differences ($p<0.05$, paired t-test) in the amount of ΣDDT concentrations released from the soils with and without NaN_3 indicating that at the levels used in the desorption experiment NaN_3 was not enhancing the release of DDT.

Concentrations of DDT compounds in procedural blanks were below detection limits. The mean %RSD for ΣDDT from duplicate extractions within the same batch was 9.0% for batch one and 4.2% for batch two.

2.5.6.2 C-18 DISKS

The methodology for the C-18 disk equilibration experiment was adapted from Krauss and Wilcke (2001). For each soil, duplicates of field-moist soil equivalent to 10 grams of dry soil were weighed into a 200 mL Schott bottle and 200 mL of an aqueous 0.005 *M* $CaCl_2$/0.01M NaN_3 solution was added. A solvent rinsed and conditioned 47 mm glass fibre impregnated C-18 SPEC disk was placed into each bottle which was sealed with Teflon lined screw caps. The C-18 disks were rinsed under vacuum with acetone (3 x 10 mL), and preconditioned by passing through 20 mL methanol (2 x 10 mL) followed by Milli-Q water (2 x 10 mL). The conditioned filters were temporarily stored in a beaker of Milli-Q water until they were transferred to extraction bottles. The slurries were incubated at 40 °C for 15 days and were gently stirred by hand each day to ensure released DDT compounds were homogeneously distributed between the soil and C-18 filter discs. One procedural blank was included. After 15 days, the filters were recovered and adhering soil particles were removed by rinsing with distilled water and gentle sonication.

The filters were extracted by gently shaking overnight with 20 mL 2:3 (v/v) acetone:hexane. The acetone:hexane solution was recovered and the extraction step was repeated. The acetone:hexane solutions were combined and partitioned against water to recover the hexane layer. The recovered hexane extract was dried by passing through a small column of anhydrous sodium sulphate. The dried hexane extracts were evaporated under N_2 to reduce the volume to 0.5 mL for clean-up on mini silica columns as described in section 2.6.2.1. The purified extract volume was adjusted to 1 mL (in *iso*-octane) and subsequently diluted ten fold for analysis by GC-ECD. DDT compounds were not detected in the procedural blank. The mean %RSD for ΣDDT compounds extracted from duplicate samples was 15%.

2.5.7 EXTRACT ANALYSIS AND DATA ACQUISITION

All samples were analysed by gas chromatography with electron capture detection (Varian 3600 CX), Varian 1078 split/splitless injector, and Varian 8200 CX autosampler. An Agilent HP-5 glass capillary column, 30 m x 0.25 mm ID glass capillary column coated with 0.25 μm 1% phenyl-dimethylsiloxane phase was used to chromatographically separate the target compounds. The initial column temperature was held at 80 °C, for 1 min, increased at 15 °C/min to 180 °C and held for 4 min, increased, at 1.5 °C/min to 220 °C and then increased at 50 °C/min to 320 °C where it was held for 10 min. The injector and detector temperatures were held at 250 °C and 320 °C respectively. A 1 μL injection aliquot was injected in purged-splitless mode with a splitless time of 45 seconds. Helium was used as carrier gas at a flow rate of 1.2 mL/min.

Millenium acquisition software (Waters Corporation) was used to acquire and analyse the data. External standard calibration was used to quantify the DDT compounds and the internal recovery compound, aldrin. Calibration standards ranging from 2.5 to 260 μg L^{-1} and prepared in *iso*-octane were used to prepare calibration curves and quantify target compounds. A liner test mix was analysed at the beginning and end of each GC run to check for degradation of DDT compounds during analysis of sample

batches. Each set of 20 samples was bracketed with a solvent blank and a 5 and 50 μg L^{-1} standard to assess calibration stability and instrument drift. The quantified results were not been corrected for the recovery of the internal recovery standard (aldrin) and residue concentrations are reported on a dry weight basis.

Detection limits were determined from replicate analyses of spiked samples as recommended by the USEPA (Title 40: Protection of the Environment Part 136, Appendix B (Electronic Code of Federal Regulations, 2005)). Seven replicates each of soil and plant material were spiked at a level equivalent to 5 μg L^{-1} in solution. The calculated detection limit for the *o,p'*- and *p,p-'* isomers of DDT, DDE and DDD was 2 μg kg^{-1} in plant tissue and 10 μg kg^{-1} in soil. The detection limits for the plant material were applied to the worm samples. Solution concentrations of target analytes less than 1 μg L^{-1} were not quantified.

2.6 TRACE ELEMENTS

2.6.1 SOILS

2.6.1.1 REGIONAL SURVEY SOILS

Trace elements (15) were determined using US-EPA Method 200.2 (Total Recoverable Metals in Soils/Sediments/Sludges) (USEPA, 1991). Oven-dried (30 °C, <2 mm, 1 g) samples were weighed into 50 mL polycarbonate vials and digested with 4 mL 50% HNO_3 + 10 mL 20% HCl at 85 °C for 30 min. The digests were cooled, diluted to 100 mL, and the extracted trace elements determined by ICP-MS (Elan 6000) at Hill Laboratories. A laboratory procedural blank, internal QC sample (certified reference material AGAL 10, Australian Government Analytical Laboratories, Sydney, Australia), and blind duplicate samples were included in each batch of samples. A certified reference material (GBW07401 Soil, National Research Centre for CRMs) and blind duplicates (one per 10 samples) were submitted to the laboratory with each batch of samples.

Concentrations of target trace elements in procedural blanks were less than their respective method detection limits. The recoveries for arsenic, cadmium, copper, lead, mercury and zinc from the certified reference material were between 86 and 107%. Blind duplicate results were typically within 20% (except for trace element concentrations close to the detection limit). Method detection limits (mg kg^{-1} DW) in soil were antimony (0.4), arsenic (2), boron (20), cadmium (0.1), chromium (2), cobalt (0.4), copper (2), iron (40), lead (0.4), manganese (1), mercury (0.1), molybdenum (0.4), nickel (2), tin (1) and zinc (4).

2.6.1.2 BIOASSAY SOILS

The samples (1 g of <2 mm dried soil) were weighed into 50 mL acid washed polycarbonate centrifuge tubes at the University of Waikato. The sample digestion step was undertaken at Hill Laboratories. Samples were digested in the polycarbonate centrifuge tubes using the method described in Section 2.6.1.1 and made up to a final volume of 20 mL with deionised water. The digests were initially analysed at The University of Waikato by ICP-OES using a 3-fold dilution. The ICP-OES operating procedures are described in Section 2.5.3 and the practical quantitation limits are listed in Table 2.9. A procedural blank, replicates of a CRM soil and a previously analysed in-house QC soil, and one duplicate sample were analysed with each set of 10 samples.

WORM TRIAL SOILS

The worm trial soil digests were analysed for copper, iron, lead and manganese by ICP-OES at the University of Waikato and for arsenic, zinc and cadmium by ICP-MS at Hill Laboratories. Each sample was digested in triplicate using the method detailed in section 2.6.1.1 and the %RSD for triplicate ICP-OES analyses were <12%, <20%, <12% and <10% for copper, lead, manganese and iron respectively. The detection

limits were 0.2, 0.01 and 4 mg kg^{-1} for the ICP-MS analyses of arsenic, cadmium and zinc respectively.

PLANT TRIAL SOILS

Iron, manganese, copper and lead concentrations in the acid digests were determined by ICP-OES at the University of Waikato (refer Section 2.6.4). A soil sample from each pot was analysed for lead and copper and the mean %RSD for analysis of each treatment soil (n = 8) was 9% and 5% for copper and lead respectively. Iron and manganese concentrations were determined for the bulk soil samples only. Two soil samples from each treatment were analysed for cadmium, arsenic and zinc by ICP-MS at Hill Laboratories as the cadmium and arsenic levels in the extracts were below the practical quantitation limits (Table 2.18, Section 2.6.3) which could be achieved at the University of Waikato. Ongoing renovations in the Chemistry Department made zinc measurements at the time potentially unreliable. A subset of the soil samples were analysed for arsenic, copper and lead in both laboratories and good agreement was obtained between results from both laboratories (Table 2.11).

Table 2.11: Inter-laboratory comparison for soil trace element analyses. Samples analysed by Hill Laboratories were analysed by ICP-MS and samples analysed at the University of Waikato were analysed by ICP-OES. Units are mg kg^{-1} DW.

Sample Code	Arsenic		Copper		Lead	
	Hills	Uni	Hills	Uni	Hills	Uni
A	0.4	<9	3	3	4	<4
B	1.7	<9	20	17	8	8
C	2.3	<9	21	17	34	34
D	1.7	<9	14	12	19	19
E	5.6	<9	80	71	83	75
F	2.1	<9	137	110	57	54
G	35.6	35	345	315	127	127
H	15.2	15	410	383	65	62
I	33.3	33	306	306	118	116
J	18.3	17	168	165	70	67
K	28.0	28	262	248	99	99
L	1.2	<9	84	78	3	<4

2.6.1.3 SUMMARY OF RESULTS FOR QUALITY ASSURANCE SAMPLES

Two soil samples CRM GBW07401 (National Research Centre for CRMs) and the in-house QC soil were used to ensure the accuracy and precision of the soil analyses. As well as including a replicate of the CRM in each batch of samples, four replicates of the CRM were analysed at the beginning of all the soil analyses (initial QA/QC check) to check the method and five replicates were analysed towards the end of the soil analyses (final QA/QC check). The overall summary for analyses of the certified reference material is presented in Table 2.12 and for the in-house reference standard in Table 2.13. Elevated zinc recoveries were occasionally obtained for the CRM and this may be a result of the dilutions required. Zinc analyses can be sensitive to differences in acid concentration between diluted samples and standards (G Robinson *pers comm*, 2004). The recovery for the in-house QC soil was used to assess the reliability of the zinc results.

Table 2.12: Summary of trace element analyses of the certified reference material CRM GBW07401. Results reported as mean with the standard deviation in brackets (mg kg^{-1}).

	N[a]	Lab	As	Cd	Cu	Fe	Pb	Mn	Zn
Certified value			34 (5)	4.3 (0.6)	21 (2)	5.19[b] (0.13)	98 (8)	1760 (98)	680 (39)
Plant trial	4	Uni	32 (1)	na[c]	18 (2)	32948	86 (4)	1777 (51)	na
	1	Hill Labs	35	5.0	21	na	94	na	786
Initial QA/QC check	4	Uni	37 (2)	3.7 (0.03)	19 (3)	25172	84 (3)	2058	640 (72)
Worm trial	1	Uni	na	na	18	30525	94	1836	na
	1	Hill Labs	29	4.5	na	na	na	na	625
Final QA/QC check	5	Uni	28 (1)	4.8 (0.1)	17 (0.2)	28543 (2071)	94 (2)	1785 (85)	709 (50)
Gastric	1	Hill Labs	36	5.4	19	31500	103	na	737

[a]Number of replicates. [b]% TFe_2O_3, [c]not analysed.

Table 2.13: Summary of analyses for the in-house QC soil for trace elements. Results reported as meanswith the standard deviation in brackets (mg kg^{-1}).

	N	Lab	As	Cd	Cu	Fe	Pb	Mn	Zn
Hill Labs[a]	1	Hill Labs	6	0.2	78	5400	68	93	17
Plant trial	5	Uni	na	na[b]	71 (3)	na	59 (1)	na	na
Initial QA/QC check	1	Uni	<9	<0.6	72	5667	60	na	14
Worm trial	1	Uni	na	na	75	6132	67	81	na

[a]One replicate of this sample was analysed by Hill Laboratories during the regional survey work. [b]Not analysed.

Overall replicate measurements of the external and in-house reference samples (Tables 2.12 and 2.13), and interlaboratory comparisons (Table 2.11) showed that the analytical protocols employed were achieving acceptable levels of accuracy and precision.

2.6.2 WORM AND PLANT TISSUE

2.6.2.1 WORM TISSUE

Portions of freeze-dried and ground worm tissue samples (0.2 g) were weighed into 30 mL polycarbonate vials at the University of Waikato and submitted to Hill

Laboratories for digestion and analysis. The worm samples were digested using conc. nitric (1 mL) and hydrochloric (0.2 mL) acids in capped polycarbonate vials at 85 °C for 1 h. The digests were made up to 20 mL with deionised water and analysed by ICP-MS (Elan 6000). Method detection limits for arsenic, cadmium, copper, iron, lead and zinc were 0.1, 0.002, 0.05, 2, 0.01 and 0.1 mg kg^{-1} (DW) respectively. Trace element concentrations in the procedural blank were below the MDL with the exception of lead. The blank value for lead was 0.01 µg and samples have been corrected. Two duplicates of a certified reference material NIST Standard Reference Material 1577b Bovine Liver were analysed with the worm tissue samples and the mean recoveries for cadmium, copper, iron, lead and zinc were 98, 96, 94, 97 and 95% respectively. The certified value for arsenic was less than the detection limit. The percent difference for duplicate samples of the CRM and worm tissue ranged from 0 to 9% with a mean of 2%.

2.6.2.2 PLANT TISSUE

Freeze dried and ground plant samples (0.5 g) were weighed into 50 mL polycarbonate centrifuge tubes at the University of Waikato. Sample digestion was completed at Hill Laboratories using a modification of the method of Hamon *et al.* (1997). Five mL of conc. nitric acid was added to the polycarbonate tubes and the samples were pre-digested overnight. The samples were digested at 100 °C in a digestion block (custom made) for 1 h followed by 1 h at 120 °C. The plant digests were made to 20 mL with deionised water. A procedural blank, one replicate of CRM GBW 7603 (Bush Branches and Leaves) and one duplicate per 10 samples was included in each batch of 40 samples.

The plant digests were initially analysed at the University of Waikato using ICP-OES. With the exception of copper, zinc and iron, the trace element levels in edible plant parts were generally below or close to the achievable practical quantitation limits (Section 2.6.3, Table 2.18). The edible parts of the plants were subsequently analysed by ICP-MS at Hill Laboratories which provided detection limits for As, Cd, Cu, Pb and Zn of 0.4, 0.02, 0.2, 0.04 and 0.4 mg kg^{-1} DW respectively. The results

reported for iron and titanium in plant tissue, and for copper and zinc concentrations in radish leaves were obtained using the ICP-OES at the University of Waikato. A subset of the radish leaf digests (n = 14) were analysed by ICP-MS at Hill Laboratories and the percent difference for samples analysed by both laboratories was less than 9% for iron, copper and zinc (Table 2.14).

Table 2.14: Interlaboratory comparison for trace element analysis of radish leaves (mg kg^{-1} DW).

	Cadmium		Copper		Zinc		Iron	
Sample Code	**Hills**	**Uni**	**Hills**	**Uni**	**Hills**	**Uni**	**Hills**	**Uni**
Bushblock2 A	0.48	<0.8	5	4	157	152	105	103
Bushblock2 B	0.31	<0.8	6	4	194	183	84	83
Bushblock2 C	0.38	<0.8	5	4	136	144	94	94
Bushblock2 D	0.32	<0.8	6	4	144	143	106	105
Orchard2 A	1.03	1.0	39	40	68	71	51	48
Orchard2 B	1.17	1.2	39	39	69	67	50	48
Orchard2 C	1.08	0.9	44	46	71	69	66	65
Orchard2 D	1.15	1.1	35	35	65	63	67	61
Orchard1 A	0.80	<0.8	35	36	100	103	78	79
Orchard1 B	0.76	<0.8	36	37	105	113	63	63
Orchard1 C	0.88	0.9	31	33	102	107	58	59
Orchard1 D	0.78	<0.8	30	29	95	99	67	67
Orchard1 D	0.79	<0.8	30	31	96	95	66	64

The recoveries for trace elements (excluding cadmium) for the CRM (GBW 7603 Bush Branches and Leaves) ranged from 76 to 104% for plant samples analysed by ICP-OES at the University of Waikato and from 73 to 111% for samples analysed by ICP-MS at Hill Laboratories (Table 2.15). Six replicate acid digests of a second CRM (GBW07604 Poplar Leaves) were analysed by ICP-OES at the University of Waikato providing 95% confidence intervals 101 ± 1%, 100 ± 17% and 113 ± 10% for the recovery of copper, iron and zinc respectively.

Table 2.15: Results for replicate trace element analyses of CRM GBW 7603 (Bush Branches and Leaves) (mg kg^{-1}). Results are reported as mean with standard deviation in brackets.

Trace Element	Certified or Proposed Value	Hill Laboratories (n = 6)	University
Arsenic	1.25 (0.1)	1.2 (0.8)	na
Cadmium	0.32[a]	0.84 (0.03)	0.88 (0.12, n = 6)
Copper	6.6 (0.4)	6.2 (0.3)	5.0 (0.4, n = 8)
Iron	1070 (40)	781 (37, n = 4)	810 (22, n = 8)
Lead	47 (2)	50 (2)	46 (0.1, n = 2)
Zinc	55 (2)	61 (3)	57 (4, n = 3)

[a]Proposed value.

The mean recovery of cadmium for the CRM GBW 7603 Bush Branches and Leaves was greater than 260% for digests analysed by both ICP-MS and ICP-OES (Table 2.15), with similar results from the two laboratories. For this reason it was suspected that the proposed value provided for cadmium in the CRM is incorrect. The recovery for analyses of the soil CRM (GBW 7401 Soil) were within the certified range (Table 2.12) and Hill Laboratories' internal checking procedures had not found any problems with cadmium analyses in the plant material. Three replicates of three certified reference materials GBW 07604 (Poplar Leaves), GBW 07603 (Bush Branches and Leaves) and NIST (Apple Leaves 1515) were digested and analysed in the same batch. The cadmium concentrations for GBW 07604 (Poplar Leaves) and NIST (Apple Leaves 1515) were in agreement with the certified ranges whereas the cadmium concentration for GBW 07603 was twice the proposed value (Table 2.16) indicating that the proposed value supplied by the manufacturer is likely to be incorrect.

Table 2.16: Certified values and measured cadmium concentration (mg kg^{-1} DW) in certified reference materials.

Certified Reference Material	Certified value	Hills Value
GBW 07604 Poplar Leaves	0.32 ± 0.05[a]	0.38 ± 0.1
GBW 07603 Bush Branches and Leaves	0.32[b]	0.76 ± 0
NIST Apple Leaves 1515	0.013 ± 0.002[c]	0.02 ± 0.01

[a]Mean ± one standard deviation. [b]Proposed value only, no certified value supplied. [c]95% confidence limit plus an allowance for the uncertainty.

2.6.3 ICP-OES ANALYSES AT THE UNIVERSITY OF WAIKATO

Acid digests were analysed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a GBC Integra XL ICP Spectrometer coupled with a GDC SDS-270 autosampler. The operating parameters for the ICP-OES are listed in Table 2.17. The optical path was purged with nitrogen for arsenic analyses to remove spectral interferences due to oxygen.

The samples were diluted for analysis and the standards were prepared in either 5 or 10% nitric acid (BDH Analar) to match the acid strength of the sample extract solution. Fresh standards (0.01, 0.05, 0.10, 0.50, 1.0, 5.0 and 10.0 mg L^{-1}) were prepared by volumetric dilution of a 100 mg L^{-1} mixed trace element stock standard (Fe, Mn, As, Cd, Pb, Cu, Zn) with Ultrapure water and Analar grade acid. The mixed stock standard was prepared by volumetric dilution of individual 1000 mg L^{-1} standards (BDH Spectrosol). Selected standards and blanks were re-run every 20 samples to check for instrument drift and sample carry over.

Table 2.17: Operating parameters for the ICP-OES at The University of Waikato.

	As	Cd	Cu	Fe	Pb	Mn	Zn
Wavelength (nm)	188.979	228.802	324.754	239.924	220.353	293.306	213.856
Plasma power	1200	1200	1200	1200	1200	1200	1200
Nebuliser gas flow (L min^{-1})	0.42	0.42	0.42	0.42	0.42	0.42	0.42
Plasma gas flow (L min^{-1})	10	10	10	10	10	10	10
Auxiliary gas flow (L min^{-1})	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Viewing height (mm)	6	6	6	6	6	6	6
PMT volts	750	800	700	600	780	600	700

Instrument detection limits (Table 2.18) were determined using the USEPA recommended method (Title 40: Protection of the Environment Part 136, Appendix B (Electronic Code of Federal Regulations, 2005)). However, these (statistically derived) detection limits were lower than the practical solution concentrations which could be routinely achieved for all elements except lead and zinc, and higher practical quantitation limits were applied (Table 2.18).

Table 2.18: Detection and quantitation limits for ICP-OES trace element analyses at The University of Waikato.

Trace Element	Typical ICP-OES detection limits[a] (mg L^{-1})	Calculated ICP-OES detection limits[b] (mg L^{-1})	Estimated and applied practical quantitation limit (mg L^{-1})	Effective quantitation limit for soils (mg kg^{-1})	Effective quantitation limit for plant material (mg kg^{-1})
Arsenic	0.1	0.050	0.150	9	12
Cadmium	0.005	0.003	0.010	0.6	0.8
Copper	0.005	0.020	0.050	3	4
Iron		0.024	0.075	5	6
Lead	0.03	0.065	0.065	4	5
Manganese		0.017	0.060	4	5
Zinc	0.005	0.050	0.050	3	4

[a]Hill Laboratories typical detection limits for the same model of ICP-OES. [b]Determined using the USEPA recommended method (Title 40: Protection of the Environment Part 136, Appendix B (Electronic Code of Federal Regulations, 2005).

2.6.4 CHEMICAL ASSESSMENTS OF THE BIOAVAILABILITY OF TRACE ELEMENTS

2.6.4.1 NEUTRAL SALT EXTRACTIONS

Two neutral salt extractions ammonium nitrate and calcium chloride were used to assess the bioavailable fraction of trace elements in archived soils (dried at 30 °C and sieved <2 mm) from the plant and worm trials. The soil samples were weighed into 50 mL polycarbonate centrifuge tubes at The University of Waikato and the samples submitted to Hill Laboratories for extraction and analysis. The instrument detection limits for the extractions were 0.01, 0.0005, 0.005, 0.2, 0.001 and 0.01 mg L^{-1} for arsenic, cadmium, copper, iron, lead and zinc respectively.

AMMONIUM NITRATE (1 *M* NH_4NO_3)

The method for the 1 *M* NH_4NO_3 extractions was adapted from Nagel *et al.* (2003). Duplicate samples (10 g of dried < 2mm soil) were weighed into 50 mL centrifuge tubes and 25 mL of 1 *M* NH_4NO_3 was added to each sample, followed by shaking for 2 h (Heidolph Unimax 2010 shaker) and then centrifuging at 2000 rpm. An aliquot of

the supernatant was filtered through 0.45 μm filters (Mini-sart) and the samples acidified with 0.5 mL conc. HNO_3. The acidified extracts were diluted ten-fold with 1% HNO_3 for ICP-MS analysis. Two procedural blanks were extracted and analysed; trace element levels in the procedural blanks were below the instrument detection limit with the exception of zinc (0.01 mg L^{-1}) and iron (0.3 mg L^{-1}) for the 1 *M* NH_4NO_3 blanks. The zinc and iron results for 1 *M* NH_4NO_3 extractions have been blank corrected. The mean %RSD for duplicate analyses was 4, 4, 17, 6 and 4% for cadmium, copper, iron, lead and zinc respectively.

CALCIUM CHLORIDE (0.01 *M* $CaCl_2$)

The method for the 0.01 *M* $CaCl_2$ extraction was adapted from Gray *et al.* (1999a). Duplicate samples (5 g of dried <2mm soil) were weighed into 50 mL centrifuge tubes and 25 mL of 0.01 *M* $CaCl_2$ was added to each sample and then samples were shaken for 16 h on an orbital shaker (Heidolph Unimax 2010 shaker) followed by centrifuging at 2000 rpm. An aliquot of the supernatant was filtered through 0.45 μm filters (Mini-sart) and the samples acidified with 0.5 mL conc. HNO_3. The acidified extracts were diluted ten-fold with 1% HNO_3 for ICP-MS analysis. Two procedural blanks were extracted and analysed; trace element levels in the procedural blanks were below the instrument detection limits. The mean % RSD for duplicate analyses was ≤ 5% for cadmium, copper, lead and zinc.

2.6.4.2 SIMULATED GASTRIC EXTRACTIONS

The oral bioavailability of arsenic, cadmium and lead from orchard soils was assessed using a modified version of the Solubility/Bioavailability Research Consortium *in vitro* method (Kelley *et al.*, 2002). Ten soils, previously analysed for trace elements using the USEPA method 200.2 (total recoverable metals) (USEPA, 1991) and providing a range of trace element concentrations were selected for gastric extraction analysis from archived sample material The gastric extractions were undertaken by Hill Laboratories. Subsamples of the archived soils were sieved to <250 μm using

stainless steel sieves. The <250 μm soil fractions together with one replicate of certified reference material GBW 07401, were digested and analysed using the method described in Section 2.6.1.1. The detection limits were 1, 0.05 and 0.2 mg kg^{-1} for arsenic, cadmium and lead respectively. The recoveries for the CRM were acceptable (Table 2.11).

For the gastric extraction, 1 g of <250 μm soil was weighed into a 500 mL LDPE container and 100 mL of simulated gastric fluid composed of 0.4 *M* glycine adjusted to pH 1.5 with concentrated hydrochloric acid added. The resulting soil-gastric solution slurries were shaken on an orbital mixing incubator (Ratek RATOM11) for 1 h at 37 °C. The extracts were filtered through <0.45 μm filters (Mini-Sart), diluted ten fold with 1% HNO_3 and analysed by ICP-MS. Procedural blanks were included in each batch and concentrations of target analytes were below instrument detection limits. Two samples were analysed in triplicate across two separate extraction batches and the mean %RSDs for triplicate analyses of the same sample were 2, 5, and 2% for arsenic, cadmium, and lead respectively.

2.7 CLEANING PROCEDURES FOR LABORATORY AND FIELD EQUIPMENT

2.7.1 FIELD EQUIPMENT

Sampling equipment was cleaned at the beginning of the day's sampling, between properties, prior to collecting any hotspot samples, and if more than one cropping area was sampled on a property. The soil corer and trowel were cleaned by employing a three bucket system. The first bucket was used for scrubbing with a solution containing Decon 90™, the second for rinsing with tap water and the final for triple rinsing with distilled water. Once cleaned, the sampling equipment was placed in new plastic bags for transport. Before commencing sampling, the cleaned stainless

steel soil corer and steel spade used to collect the soils were "conditioned" by collecting a minimum of six soil cores or samples which were discarded.

2.7.2 SOIL PHYSICAL AND CHEMICAL CHARACTERISTICS

For general soil chemical and physical soil property determinations, glassware was rinsed, soaked overnight in a Decon 90™ solution and then triple rinsed with distilled water. Non volumetric glassware was oven dried (40 °C) in trays lined with paper and volumetric glassware was dried upside down at ambient temperature.

2.7.3 TRACE ELEMENT ANALYSES

Glassware was initially rinsed, soaked in a detergent solution and then thoroughly rinsed with tapwater. The glassware was then soaked for at least 4 h and preferably overnight in 10% nitric acid (distilled water). The glassware was then soaked in distilled water for 1 hour and then triple rinsed with ultrapure deionised water. Non volumetric glassware was oven dried in trays lined with paper. Pipettes were stored in a 10% nitric acid solution and were similarly rinsed before use.

2.7.4 CLEANING OF GLASSWARE FOR ORGANIC ANALYSES

Adhering solids were removed from glassware by scrubbing before triple rinsing with drum grade ethanol and soaking overnight in a dilute Decon 90 solution. After soaking in Decon the glassware was scrubbed, washed with multiple rinses of hot tap water and dried. Non volumetric glassware was oven dried and volumetric glassware and plastic lids were dried at ambient temperature. Prior to use, all glassware was triple rinsed with the appropriate solvent.

3 AGRICHEMICAL RESIDUES IN AUCKLAND HORTICULTURAL SOILS

3.1 INTRODUCTION

Throughout New Zealand intensively cropped soils on the peri-urban fringe are coming under increasing pressure for residential development. Many of the greenfields sites designated for development in the Auckland region through the Auckland Regional Growth Strategy (Regional Growth Forum, 1999) either have been used, or are currently being used for intensive horticulture. International experience (e.g. NSW EPA 1995; Van Gaans *et al.*, 1995; Webber and Wang, 1995; Harris *et al.*, 2001) indicated that agrichemical residues (both synthetic organic compounds and trace elements) may also be an issue for New Zealand horticultural soils. Prior to the investigations reported here there was limited information available on the levels of synthetic organic compounds and trace elements likely to be present in horticultural soils as a result of the routine use of agricultural chemicals. This lack of information made it difficult to identify the hazards and level of risk associated with changing landuse.

The purpose of this investigation was to determine the extent to which organochlorine, organonitrogen and organophosphorous pesticides as well as acidic herbicides and trace elements had accumulated in Auckland cropping soils.

In this investigation 47 soil samples from 42 sites were screened for a suite of 213 target analytes (synthetic organics and trace elements) in order to determine the range and levels of agrichemical residues likely to be present in horticultural soils.

3.1.1 HORTICULTURE IN THE AUCKLAND REGION

The Auckland region has a long history of horticulture. The first recorded market gardens were established in the 1840s. In 1965 there were 5782 hectares of horticultural land in the Auckland region and by 1979 the land area had increased to 8488 hectares or approximately 3% of the region's farmland. A comparison of the land under each horticultural use (excluding cut flowers) in 1965 and 1979 is provided in Table 3.1. By June 2000 the area of land cultivated for horticultural crops had increased further to 11605 hectares with outdoor vegetables contributing the largest proportion (Statistics NZ, 2001).

Table 3.1: Total area (ha) in horticulture in the Auckland region in 1965 and 1979. Data from ARA (1981).

	1965	1979
Pipfruit	526	563
Stonefruit	267	288
Citrus	97	165
Subtropicals	24	105
Grapes	236	783
Strawberries	34	108
Vegetables	4386	6206
Glasshouses	40	59
Nurseries	172	211
Total	5782	8488

The first orchards in the Auckland region were planted in Birkenhead in 1838. Most of the early orchards were small and catered for the grower's own needs with occasional surpluses sold in local markets. Codling moth and blackspot virtually eliminated orcharding between 1870 and 1900. Legislation requiring disease control, along with more effective sprays was introduced after 1903 and this led to the re-establishment of orcharding in the Auckland region (Fielding, 1957).

In 1945 there were 477 hectares (2133 acres) of orchards in the Auckland region (Winn, 1968) and this had increased to approximately 850 hectares by 1960 (ARA, 1981). In 1978 there was an estimated 501 hectares of pipfruit, 267 of stone fruit, 115 of citrus and 56 of subtropicals planted in the Auckland region (ARA, 1981).

Many of the earlier horticultural holdings produced a variety of crops and it has only been since the 1960s that there has been increasing specialisation (ARA, 1981). In comparison to other New Zealand fruit growing regions, the Auckland region was a mixed fruit region (Nottage, 1950; Fielding, 1957; ARA, 1981). Grapevines were a common feature on west Auckland holdings (Henley, 1950; Moran, 1958; Garelja, 1975). Market gardening also occurred in conjunction with orcharding and viticulture (Hunt, 1956).

3.1.2 OBJECTIVES

The principle objectives of the investigation undertaken in the Auckland region were to identify the:

- Levels of agrichemical residues likely to be of concern in horticultural soils in the Auckland region and

- Horticultural landuse(s) most likely to contain elevated levels of agrichemical residues.

3.2 METHODS SUMMARY

3.2.1 SAMPLE COLLECTION

Suitable sampling sites were identified using the following methods: assistance from territorial authorities (environmental health officers, dangerous goods officers and park staff), Auckland Regional Council staff and Auckland Regional Public Health Service staff, local knowledge of the researcher, aerial photographs, and listings in the Auckland telephone directory. Finding enough suitable sites and contacting property owners took approximately one month. Site owners were provided with a letter explaining the purpose of the study and guaranteeing confidentiality.

Precise details of site locations are not provided in this thesis because an undertaking of confidentiality was made to the site owners. For the purposes of the investigations reported in this thesis, the ability to obtain cooperative access to a full range of sites from across the landuse categories was seen as being of prime importance.

The sampling sites were selected according to a set of criteria related to landuse and activities which had occurred on the property (Section 2.2.1, Chapter Two). A total of 47 samples were collected from within the cropping areas of 42 properties. The landuse categories sampled were glasshouses, market gardens, multi-use, orchards, and vineyards. Multi-use sites were sites that had been used for more than one horticultural activity; for example, an orchard that had been converted into a market garden.

Generally, an aggregate sample containing ten subsamples was collected for each hectare from broad cropping areas, and the aggregate samples for up to 4 hectares combined to form a composite according to the methodology outlined in Chapter Two, Section 2.2.1. The number of samples collected and analysed per landuse and age category is listed in Tables 3.2 and 3.3. On three glasshouse properties and one orchard more than one sample was collected as different cropping histories and/or soil characteristics precluded compositing of samples. Additional samples were collected from three background sites with no known previous history of horticultural or grazing use (forest remnants) and three long-term grazing sites. The samples were collected between April and August 2001.

Table 3.2: Number of samples collected according to landuse. More than one sample was collected from one orchard property and 3 glasshouse properties.

Landuse	Properties (n)	Samples (n)
Background	3	3
Grazing	3	3
Glasshouses	8	12
Market gardens	8	8
Multi-use	4	4
Orchards	12	13
Vineyards	10	10

Table 3.3: Number of properties sampled according to category and age groupings.

Landuse	Properties	<1975[a]	>1975[b]
Glasshouses	8	8	0
Market gardens	8	8	0
Multi-use	4	2	2
Orchards	12	11	1
Vineyards	10	5	5
Total	42	34	8

[a]Property was developed for horticultural use prior to 1975. [b]Property was developed after 1975.

In addition, a one hectare block on an historic orchard site was re-sampled six times to determine the sampling variability using the standard "z" sampling pattern in different orientations. For four properties (two orchards, one vineyard and a market garden), the aggregate samples that comprised the composite were analysed to determine the spatial variability of the contaminants from hectare to hectare within a cropping area on a property.

The site category was based on the current landuse and the best available knowledge. It is possible that because of limitations in available information a site was included in an incorrect category. Several of the long-term orchards had other cropping activities such as market gardening occurring concurrently some time during their history. These sites were still classified as orchards as it is assumed that the dominant landuse was orcharding and that the spray schedules were selected according to the variety of fruit trees grown. There may have been outdoor cropping on some glasshouse sites prior to the establishment of glasshouses.

The properties included in this survey are considered to be representative of the types of horticultural activities that have occurred or are currently occurring in the Auckland region. Efforts were made to ensure that sites from across the Auckland region were included for each landuse category, however this was not always possible. It is probable that some landuse types were over-represented in the survey and others have not been included. Due to the relatively small sample size within each landuse category the results can be seen as being indicative of the scale of the problem in the Auckland region, rather than definitive.

3.2.1.1 SAMPLING PROTOCOL

A "Z" sampling pattern, as described in Chapter Two, was used to collect one aggregate sample per hectare from the cropping area. Each aggregate sample comprised 10 soil cores *i.e.* a sample from one hectare contained 10 soil cores. Up to four hectares were sampled on each property and in most cases the samples for each hectare were combined to form a composite sample. The composite samples were prepared according to Australian standards for sampling contaminated soils (AS 4482.1, 1997). The sampling depth was 7.5 cm.

Composite samples were only prepared if the aggregate samples came from areas that had the same cropping and spray history, and if the soil material had similar characteristics. All aggregate samples used to prepare a composite sample were collected from the same nominal depth. On several of the properties (usually glasshouse sites), aggregate samples were not composited due to differences in soil characteristics and cropping history.

3.2.1.2 VALIDATION OF SAMPLING STRATEGY

A one hectare block on an historic orchard was sampled 6 times to determine the overall variability of sampling and analysis. The soil samples were analysed for trace elements, ΣDDT (organochlorine analysis method), %TOC and pH (Table 3.4) and the relative standard deviation (%RSD) calculated for each parameter. The %RSDs calculated for soil pH, %TOC and iron and manganese indicate that the soil within the one hectare block is relatively homogenous. The %RSDs for the contaminants of interest are consistent with those expected for analysis and imply that ΣDDT, copper, lead and arsenic are also relatively evenly distributed within the section of cropping area sampled.

Table 3.4: Analytical results and %RSD for six replicate samples collected from the same one hectare block. Units are mg kg^{-1} dry weight except where specified.

Sample	ΣDDT	As	Cd	Cu	Pb	Fe	Mn	%TOC	pH
A	1.53	9	0.2	76	59	7830	113	3.8	5.66
B	1.96	6	0.2	78	68	5400	93	3.9	5.61
C	2.80	7	0.2	79	81	8160	106	4.1	5.63
D	1.61	8	0.2	63	58	7650	107	3.7	5.66
E	1.54	5	0.2	65	61	6160	86	3.8	5.69
F	1.92	6	0.3	69	57	8680	105	3.7	5.71
%RSD	26	21	19	10	14	17	10	4	0.7

The 95% confidence error for repeated sampling and analysis of ΣDDT at this site is within 25% of the mean value (confidence interval 1.47–2.31 mg kg^{-1}). This result suggests that the ΣDDT distribution over the site was quite uniform and that the sampling regime was appropriate for generating reliable average values for ΣDDT levels at each site.

3.2.1.3 DEPTH PROFILES

Three 1 m deep cores were collected from two orchards, one long-term site currently planted with apple trees (one core) and one historic site now used to graze cattle (two cores). The cores were collected using a stainless steel piston corer. The cores were divided into subsections based on the soil horizons. The subsections were submitted to Hill Laboratories (Hamilton) field moist. The samples were air dried and ground to <2 mm and then analysed for trace elements (15) and ΣDDT (organochlorine analysis method).

3.2.2 ANALYSIS OF SAMPLES

The soil samples were analysed by Hill Laboratories using IANZ registered methods. The soil samples were analysed for a multi pesticide and herbicide-residue screen (comprising 181 compounds), and for 15 trace elements and 17 acidic herbicides. The analytical methodology, list of analytes and their detection limits is provided in

Chapter Two. The Auckland soil samples were submitted for organic pesticide residue analysis field-moist and the determined levels are reported on an oven-dried basis. A subsample was air dried and sieved (<2 mm) at The University of Waikato for trace element and soil characteristic analyses.

3.2.3 DATA REPORTING

The soil samples were analysed for acidic herbicides (17), multi pesticide residues (181) and trace elements (15). Where values were less than the detection limit, half of the detection limit was assigned for statistical purposes. The value of statistical analysis is limited when the data is segregated into landuse categories due to the smaller data sets; however, results can still be seen to be indicative of typical concentration ranges.

The data for the cropping areas has been further subdivided into properties in existence pre and post 1975. This subdivision has been based on the history of pesticide usage. DDT, DDD and dieldrin could only be used by horticulturists under permit after 1964 and the use of lead arsenate was phased out during the 1970s. It has been assumed that it is unlikely that organochlorines and lead arsenate would have been used in significant quantities on properties developed after 1975. To avoid repetition, a comparative analysis and detailed discussion of the pre 1975 Auckland results are presented in Chapter Four along with the results for the subsequent studies undertaken in the Waikato Region and Tasman District.

3.3 RESULTS AND DISCUSSION

3.3.1 ACIDIC HERBICIDES

The soil samples were analysed for a suite of 17 acidic herbicides. Acidic herbicides were not detected in any samples from cropping areas, possibly due to their relatively short half lives. For example, Bolan and Baskaran (1996) measured half lives of 17.5 to 38.3 days for 2,4-D in New Zealand North Island pasture soils. Webber and Wang (1995) detected acidic herbicides in Canadian agricultural soils at maximum levels of 0.06 mg kg^{-1} and concluded that heavy use of phenoxy acid herbicides is unlikely to result in elevated residues in soils.

3.3.2 MULTI-RESIDUE PESTICIDE SCREEN

Full results for the compounds detected in the multi-residue organochlorine, organonitrogen and organophosphorus screen are presented in Appendix A. Where not detected, detection limits are as specified in Figure 2.3 (Chapter Two). Only 39 out of the 181 pesticides assayed for in the multi-residue pesticide screen were detected in the Auckland cropping soils examined in this investigation. The frequency of detection is shown in Table 3.5; insecticides (14) and fungicides (14) were detected most frequently followed by herbicides (9) and then miticides (2). The most commonly detected synthetic organic pesticides were ΣDDT and related breakdown products, dieldrin, procymidone, endosulfan and/or related degradation products and dicofol. Procymidone is a fungicide, dicofol is an organochlorine miticide and endosulfan is an organochlorine insecticide used to control a wide range of chewing and sucking insects. The structures of the most commonly encountered pesticides are presented in Figure 3.1. Pesticide residues were detected in 42 of the 47 cropping area samples. The greatest number of pesticide residues detected in a sample collected from a cropping area was 20. Pesticide residues were not detected in any of the samples collected from the background sites.

On almost all occasions, organonitrogen and organophosphorus pesticides were detected in cropping area soils at levels of less than 1 mg kg^{-1}. Similar values (<0.1–2.4 mg kg^{-1}) of organophosphorus and organonitrogen pesticides have been reported by Hogg (2000) for soil samples collected from 2 glasshouse sites in the Auckland region. A limited number of samples (6/47) contained these pesticides at levels greater than 2 mg kg^{-1}: for example, oxadiazon (7.8 mg kg^{-1}), pirimiphos methyl (2.9 mg kg^{-1}), and prothiofos (4.2 mg kg^{-1}). All of these exceptions were in soil samples collected from glasshouses with current crops. Hence, it seems likely these residues are from recent spray applications. Unfortunately full spray diaries were not available for these properties.

Szeto and Price (1991) detected 14 organophosphorus and nitrogen containing pesticides on 12 vegetable farms in British Columbia and with only one exception at levels less than 2 mg kg^{-1}. Also in agreement with the results presented in this chapter, no organophosphorus or organonitrogen pesticide was consistently detected and the authors concluded that the residues detected were due to applications during the previous growing season (Szeto and Price, 1991). In comparison, organophosphorus pesticides were not detected in soil samples from NSW market gardens and orchards (NSW EPA, 1995) although detection limits for this study were not reported. Only one organophosphorus pesticide, fonofos (<0.025–0.100 mg kg^{-1}) was detected in a survey of Canadian agricultural soils (Webber and Wang, 1995). The results of the current investigation together with those of other workers provide a consistent picture that common acidic herbicides, organonitrogen and organophosphorus pesticides do not tend to leave long term residues in horticultural soils due to their relatively short environmental half-lives.

Table 3.5: Minimum and maximum levels (mg kg^{-1} DW) of organochlorine, organonitrogen and organophosphorus pesticides detected in Auckland horticultural cropping soils.

Pesticide	Chemical class[a]	Half-life[b] (days)	No. of times detected	Min	Max
Fungicides					
Azoxystrobin	strobilurin	7	1	<0.02	0.24
Bitertanol	triazole		1	<0.02	0.21
Bupirimiate	pyrimidinol		1	<0.01	0.02
Cyprodanil	anilipyrimidine		2	<0.02	0.56
Fenamirol	pyrimidine		2	<0.01	0.04
Fludioxanil	phenylpyrrole		1	<0.02	0.29
Fluvalinate	pyrethroid		1	<0.01	0.05
Iprodione	dicarboximide	50	4	<0.02	0.05
Metalaxyl	phenylamide	40	3	<0.03	0.09
Myclobutanil	triazole		5	<0.01	0.13
Nitrothal-isopropyl	nc		2	<0.01	0.04
Procymidone	dicarboximide	15	8	<0.01	0.52
Penconazole	triazole		1	<0.01	0.03
Terbucanazole	triazole	120	1	<0.01	0.2
Insecticides					
Bifenthrin	pyrethroid	95	2	<0.01	0.15
Buprofezin	thiadiazine		1	<0.01	0.05
Chlorpyrifos	organophosphorus		1	<0.01	0.40
ΣDDT[c]	organochlorine	7300	32	<0.012	289
Dichlorvos	organophosphorus	1	1	<0.01	0.01
Dieldrin	organochlorine	1825	13	<0.002	0.56
ΣEndosulfan	cyclodiene organochlorine	27	8	<0.006	2.97
Lindane	organochlorine	456	1	<0.002	0.035
Oxychlordane			2	<0.005	0.015
Oxyfluorfen	diphenyl ether	291	1	<0.01	0.013
Permethrin	pyrethroid	30	2	<0.01	0.7
Pirimiphos-methyl	organophosphorus	24	3	<0.01	2.9
Prothiofos	organophosphorus		2	<0.01	4.2
Tebufenpyrad	pyrazole		1	<0.01	0.1
Herbicides					
Alachlor	chloroacetamide	21	2	<0.02	1.70
Dichlobenil	benzonitrile		1	<0.01	0.04
Diuron	urea	372	3	<0.02	0.26
Linuron	urea	81	1	<0.05	0.14
Oxadiazon	oxadiazole		2	<0.01	7.8
Pendamethalin	dinitroaniline	130	4	<0.01	0.14
Simazine	1,3,5 triazine	91	3	<0.01	0.24
Terbuthylazine	1,3,5 triazine	50	2	<0.01	1.3
Terbuthylazine-desethyl	1,3,5 triazine (degradation product)		1	<0.01	0.03
Miticides					
Bromopropylate	benzilate		2	<0.01	1.40
Dicofol	organochlorine	60	11	<0.05	11.0

[a]Chemical class identified using *The Pesticide Manual* 12th Edition (British Crop Protection Council, 2000). [b]Half-lives taken from Green and Clothier (2002). These figures are not exact and can vary depending on soil and climate, but provide and indication of a compound's relative environmental persistence. [c]Sum of both the *o,p'*- and *p,p'*- isomers of DDT and degradation products DDE and DDD.

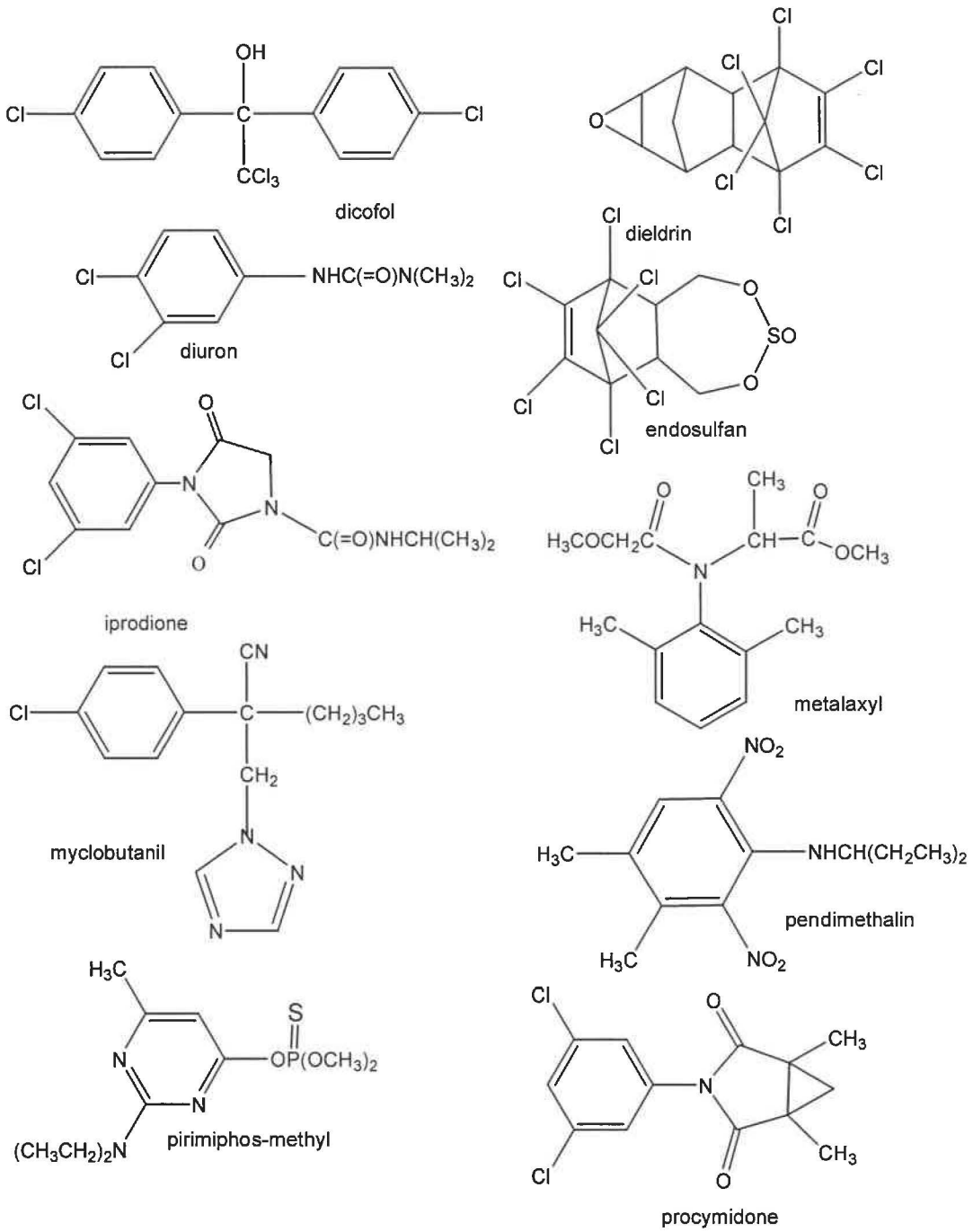


Figure 3.1: Structures of the pesticides most frequently detected in Auckland horticultural soils (Structures for DDT and DDE are presented in Chapter Five).

3.3.3 ORGANOCHLORINE PESTICIDES

The analysis suite included 25 persistent organochlorine pesticides (and their degradation products) of which only four were detected in soil samples. ΣDDT and dieldrin were the two organochlorine pesticides most frequently detected in this survey. Lindane was detected once at trace levels (0.035 mg kg^{-1}) in a glasshouse soil sample, and oxychlordane (0.015 mg kg^{-1}) was detected in two samples collected from the same orchard. These findings are in agreement with the results of Buckland *et al.'s* (1998) assessment of organochlorine residues in New Zealand background soils which found that HCB, ΣDDT and dieldrin were the most frequently detected organochlorine pesticides. ΣDDT and dieldrin residues were only detected on Auckland horticultural properties developed prior to 1975. This is consistent with the registration and use of DDT and dieldrin in New Zealand, because persistent organochlorine compounds were phased out during the 1970s (e.g. Buckland *et al.*, 1998).

3.3.3.1 ΣDDT

The values for both isomers of DDT (i.e. *o,p'*- and *p,p'*-) and their breakdown products (DDE and DDD) are reported as a combined figure ΣDDT in Table 3.6. DDT isomers and/or breakdown products were detected in 33 out of 47 soil samples collected from cropping areas on horticultural properties in the Auckland region. ΣDDT residues were detected in all 8 market garden samples, 9 out of 13 orchard samples, 9 out of 12 glasshouse, 5 out of 10 vineyard and 1 out of 4 multi-use samples. The median value of ΣDDT (0.2 mg kg^{-1}) measured in cropping areas in this survey exceeds the background level of 0.025 mg kg^{-1} reported by Buckland *et al.* (1998) for Auckland urban soils. The ΣDDT results reflect these compounds persistence and are further discussed in Chapters Four and Five.

Table 3.6: Summary statistics for ΣDDT residues (mg kg^{-1} DW) in cropping area samples collected from horticultural properties in the Auckland region.

Landuse	No. of samples	No. of positives	Min	Max	Mean	Median
Glasshouses	12	9	<0.03	289	25.2	0.75
Market gardens	8	8	0.08	0.91	0.311	0.19
Multi-use	4	1	<0.03	0.09	0.04	0.04
Orchards	13	9	<0.03	24.41	4.35	1.17
Vineyards	10	5	<0.03	2.84	0.69	0.14
Overall	47	32	<0.03	289	7.68	0.20

3.3.3.2 DICOFOL

Dicofol was detected in 11 out of 47 Auckland horticultural soil samples at levels ranging from 0.01 to 11 mg kg^{-1} and was present in samples from all landuse categories with the exception of multi-use sites. Dicofol is an organochlorine pesticide still registered for use in New Zealand and is also a minor metabolite of DDT (Kiigemagi and Terriere, 1972). In New Zealand it is currently used to control mites on a wide variety of crops (Fussell and Walton, 2001). Dicofol was detected predominantly in association with ΣDDT residues. Only one sample containing dicofol did not also contain ΣDDT residues. Although it has a reported half-life of 60 days (Green and Clothier, 2002), dicofol was detected (0.41 mg kg^{-1}) in one sample which had reportedly not been sprayed for 6 years at the time of sampling. There is limited recent information published on dicofol residues in horticultural soils. Frank *et al.* (1976) measured dicofol levels ranging from not detected to 0.32 mg kg^{-1} (DW) in Southern Ontario orchard soils.

3.3.3.3 DIELDRIN

Dieldrin (<0.005–0.56 mg kg^{-1}) was detected in 13 of 47 soil samples collected from horticultural properties and most frequently on market garden properties (6 out of 8). Dieldrin was not detected in any of the samples collected from horticultural properties developed after 1975.

3.3.3.4 ENDOSULFAN

Endosulfan and its degradation products (endosulfan II and endosulfan sulphate) were detected in 8 out of 47 Auckland horticultural soil samples. ΣEndosulfan residues were mainly detected in market garden (4/8) and glasshouse (4/12) soils at concentrations ranging from <0.006 to 2.97 mg kg^{-1}.

3.3.4 CORRELATION BETWEEN FREQUENCY OF DETECTION AND HALF LIFE FOR PESTCIDES

Green and Clothier (2002) compiled a database of physico-chemical properties for pesticides available for use in New Zealand which is mainly based on overseas sources. For pesticides detected in Auckland cropping soils, where a half life was available (n = 23), linear regression was carried out to determine whether any relationship existed between half-life and the frequency of detection (both variables log normalized). Although a weak relationship existed between the log of the two variables ($R = 0.449$, $p < 0.05$), this relationship no longer existed when two persistent pesticides (∑DDT and dieldrin) were removed from the data set. These pesticides were assumed to have half-lives of 20 years and 5 years, respectively. No relationship was found between detection frequency and half-life for the modern pesticides, which had half-lives ranging from one day (dichlorvos) to one year (diuron). The implication of these findings is that the likelihood of detection for modern pesticides with short half-lives is primarily influenced by the pattern and frequency of use in the days and weeks before sampling.

The results presented in Table 3.5 indicate that there is little or no accumulation of the widely used modern synthetic organic pesticides assayed for in cropping soils in the Auckland region. There are some caveats to this statement. Firstly, it relates to broad cropping soils only and not to hot-spots. Secondly, some specific classes of modern pesticides, including bipyridyls (paraquat and diquat), dithiocarbamates (mancozeb, maneb, metiram, propineb, thiram and ziram), and phosphonyls

(glyphosphate, glufosinate-ammonium) were not included in this investigation as cost-effective IANZ registered laboratory analytical methods for their measurement were not readily available.

Potential soil accumulation issues exist for bipyridyls, some dithiocarbamates, and some tin-based compounds. Recent modelling studies indicate that the bipyridyls (e.g. paraquat and diquat) may accumulate in horticultural soils where they have been routinely used (Green and Clothier, 2002), hence it would be appropriate to include them in future investigations of the type reported here (when IANZ registered analytical methods are available). However, relative risks from soil residues of bipyridyls are thought to be limited because of their capacity to bind strongly to soil (Kookana and Aylmore, 1993). Correspondingly, soil guidelines for these compounds are relatively high. For example, the USEPA Region 9's preliminary remediation goal values for diquat and paraquat are 130 mg kg^{-1} and 270 mg kg^{-1}, respectively. This suggests that accumulation of the bipyridyls might only become an issue in extreme cases or around hot spots.

Although dithiocarbamates degrade rapidly in soil (e.g. mancozeb has a half-life of 43 days (Green and Clothier, 2002), some of these compounds (e.g. products containing propineb and mancozeb) are applied as complexes containing zinc and manganese. While the parent compound may have a short half-life there is the potential for these trace elements to accumulate in horticultural soils on which dithiocarbamate pesticides have been extensively used. Other synthetic organic pesticides which may also contribute to the trace element loading in horticultural soils include azocyclotin and fenbutatin-oxide, both of which contain tin.

3.3.5 TRACE ELEMENTS

Soil samples were analysed for a suite of 15 trace elements (Table 3.7). All of the trace elements except boron were detected in soil samples collected from cropping areas on horticultural properties in the Auckland region. This is not unexpected because all of the trace elements assayed occur naturally in soil, in contrast to the

situation with synthetic organic compounds. The maximum, minimum and median values for all trace element levels in cropping areas are listed in Table 3.7.

The trace elements of concern were identified by comparing the survey results with previously collected background information for the Auckland region (ARC, 2001). The median values for arsenic, cadmium, copper, lead, tin and zinc exceeded the median values for these trace elements in baseline non-volcanic soils (Table 3.7). The majority of cropping areas sampled in this survey were on non-volcanic soils. The trace element results will be discussed in further detail in Chapter Four.

Table 3.7: Concentrations of trace elements (mg kg^{-1} DW) measured in cropping areas on horticultural properties in the Auckland region compared to previously published median values for baseline concentrations in non-volcanic soil (ARC, 2001).

Trace element	Minimum	Maximum	Median	Median for Auckland (ARC)[a]
Antimony	<0.4	1.7	<0.4	na[b]
Arsenic	<2	34	7	4.7
Boron	<20	<20	<20	15.8
Cadmium	0.1	1.1	0.4	0.05
Chromium	3	108	13	10.9
Cobalt	0.5	46.1	2	5.4
Copper	7	490	57	9.8
Iron	1600	65500	15600	na
Lead	3	1250	32	12.7
Manganese	18	4570	213	284
Mercury	<0.1	0.4	0.1	0.107
Molybdenum	<0.4	3.4	0.8	na
Nickel	<2	83	4	7.1
Tin	<1	8	1	<0.7
Zinc	9	510	53	52.1

[a]Non-volcanic soils ARC (2001). [b]na = not analysed.

The maximum values of arsenic, cadmium and copper were measured in orchard soils (Table 3.8) and these elevated levels are most likely the result of long-term use of agrichemicals. In comparison, the maximum levels of lead (1250 mg kg^{-1}) and zinc (510 mg kg^{-1}) were measured in a glasshouse soil sample. As the soil sample contained paint flakes, it is highly probable that the lead and zinc were from paint pigments, and the galvanised materials used to construct the glasshouse may have

been a further source of zinc. This maximum lead level associated with this glasshouse was approximately three times the Ministry of Health guideline for lead in high contact soils of 400 mg kg^{-1}. Soil contamination associated with lead based paint on buildings has been reported elsewhere in New Zealand. For example Reeves *et al.* (1982) reported geometric mean lead levels of 842 mg kg^{-1} in soil and 3.6% in paint from a housing area in Auckland where lead based paint was known to have been widely used. A composite soil sample collected from beneath a Waikato galvanised iron (and lead painted) woolshed at Walton in late 2004 contained 1120 mg kg^{-1} zinc and 335 mg kg^{-1} lead (Kim *pers comm*, 2005). Mielke *et al.* (2001) reported median zinc levels of 31 000 mg kg^{-1} in paint samples collected from houses in New Orleans.

When comparing the datasets (glasshouses excluded) for the sites developed after 1975 with the sites developed prior to 1975 using log t-tests, the mean values for arsenic and lead were significantly higher ($p<0.001$) in the pre 1975 sites. This is consistent with the known use of lead-arsenate pesticides in New Zealand. Copper and zinc concentrations were also significantly higher ($p<0.05$) as would be expected for properties which had been in use for the greatest length of time

Table 3.8: Summary statistics for trace element concentrations (mg kg^{-1} DW) in Auckland horticultural soils.

Landuse	N	Min	Max	Mean	Median	SD	Geo mean
Arsenic							
Glasshouses	12	<2	21	9	8	6	6
Market gardens	8	4	11	6	6	2	6
Multi-use	4	<2	14	6	4	6	4
Orchards	13	2	34	15	11	11	11
Vineyards	10	<2	14	5	4	4	4
Overall	47	<2	34	9	7	8	6
Cadmium							
Glasshouses	12	0.1	1.0	0.5	0.6	0.3	0.4
Market gardens	8	0.4	1.0	0.7	0.6	0.3	0.6
Multi-use	4	0.1	0.7	0.4	0.4	0.3	0.3
Orchards	13	0.1	1.1	0.4	0.3	0.3	0.3
Vineyards	10	0.2	0.7	0.4	0.3	0.2	0.3
Overall	47	0.1	1.1	0.5	0.4	0.3	0.4
Copper							
Glasshouses	12	7	253	69	32	83	39
Market gardens	8	21	137	51	38	39	42
Multi-use	4	14	105	48	37	41	36
Orchards	13	21	490	209	173	180	122
Vineyards	10	16	152	80	78	49	62
Overall	47	7	490	105	57	123	60
Lead							
Glasshouses	12	6	1250	150	32	352	41
Market gardens	8	14	46	24	21	10	23
Multi-use	4	7	37	16	10	14	13
Orchards	13	11	178	72	53	54	54
Vineyards	10	3	88	42	37	32	26
Overall	47	3	1250	72	32	182	33
Tin							
Glasshouses	12	<1	8	2	2	2	1
Market gardens	8	1	3	2	3	1	2
Multi-use	4	<1	3	<1	<1	1	1
Orchards	13	<1	4	2	1	1	1
Vineyards	10	<1	3	1	1	0.8	1
Overall	47	<1	8	2	1	1	1
Zinc							
Glasshouses	12	9	510	125	102	132	79
Market gardens	8	31	109	62	52	26	58
Multi-use	4	12	83	38	29	31	30
Orchards	13	22	236	62	44	56	49
Vineyards	10	14	152	54	49	40	43
Overall	47	9	510	75	53	80	53

3.3.6 SPATIAL DISTRIBUTION OF CONTAMINANTS

The spatial heterogeneity of residual contaminants was investigated for four properties. Each of the individual aggregate samples used to prepare the composite sample for the cropping area was analysed for ΣDDT, trace elements, %TOC and pH. The percentage relative standard deviations (%RSD) for the aggregate samples from each property were calculated (Table 3.9) and these were compared to the %RSD for multiple analyses of the same sample and the %RSD for determined levels in 6 replicate samples collected from the same one hectare block (Table 3.4).

The %RSDs calculated for iron, manganese, %TOC and pH are comparable to those obtained for analysis only and indicate that the soil composition within the cropping area on each property was reasonably homogenous. The spatial variability observed for the target contaminants (ΣDDT, arsenic and lead) was greater than the variability due to sampling and analysis, this was particularly the case for the two orchard sites. These results indicate that compositing samples collected from different blocks within a horticultural property may not be appropriate.

This increased variability may be due to the history before the current ownership, including land lying fallow. The majority of Auckland orchards were mixed fruit orchards (Fielding, 1957; Garelja, 1975) and it is possible that different parts of the orchard had different spray schedules. For example the 1956 spray schedule for pipfruit included DDT whereas the schedule for stone fruit did not (Atkinson *et al.*, 1956). Henley (1950) stated that *"the spraying programme is generally similar for the different species in the orchard but the early spring fruiting of the citrus demands greater attention over the winter months."* Many of the orchardists grew market garden crops in between the rows. It is also possible that different areas of the property had different replanting histories depending on the types of fruit trees being replaced.

Table 3.9: % Relative standard deviations (with concentration ranges in brackets; mg kg^{-1}) for selected parameters between aggregate samples from cropping areas. Up to four aggregate samples (1 per hectare) were collected from each cropping area.

Landuse	n	ΣDDT	As	Cd	Cu	Pb	Fe	Mn	%TOC	pH
Market garden	4	12 (0.52–0.67)	12 (4–5)	13 (0.4–0.5)	11 (60–76)	4 (12–13)	10 (49000–58900)	3 (1660–1790)	4 (2.1–2.3)	2 (6.64–6.92)
Orchard A	4	41 (9.5–28.6)	14 (37–52)	10 (0.5–0.6)	8 (297–354)	35 (27–67)	13 (15000–20200)	24 (186–274)	7 (4.0–4.7)	2 (5.59–5.90)
Orchard B	4	63 (0.17–2.23)	17 (5–7)	22 (0.2–0.3)	5 (56–62)	35 (27–67)	24 (6350–10700)	43 (75–179)	6 (3.2–3.7)	3 (5.66–6.04)
Vineyard	2	18 (0.35–0.45)	0 (4)	28 (0.2–0.3)	6 (85–93)	14 (35–43)	25 (6300–8990)	30 (79–121)	7 (3.7–4.1)	0.1 (5.8–5.94)
Sampling and analytical variability	6	26	21	19	10	14	17	10	4	0.7
Analytical variability	≥3	16	8	7	7	8	7	6	5	4

3.3.7 CONTAMINANT DEPTH PROFILES IN ORCHARDS

Elevated concentrations of trace elements and ΣDDT were measured in horticultural soils and generally orchards contained the highest levels. To better understand the vertical distribution of contamination, further investigations into the depth profiles of contaminants in orchard soils were undertaken. As described in Section 2.2.1.3 (Chapter Two), three soil cores to an approximate depth of one metre were collected from two orchards, one long-term site currently planted with apple trees (one core) and one historic site now used to graze cattle (two cores). The cores were divided into subsections based on the soil horizons. The results for the top 40 cm of the soil cores are presented here in Table 3.10. The entire length of the cores were analysed for ΣDDT and trace elements were only determined for the top 40 cm.

Across the three recovered cores, copper levels were highest at the surface and tended to decrease with depth, and to large extent copper levels on both properties were associated with the top 20 cm. Comparable results were obtained by Merry *et al.* (1983) in soil cores from Australian orchards and Jorgensen *et al.* (2005) in a former glasshouse soil in Denmark. Besnard *et al.* (2001) investigated the vertical distribution of copper in soil on a vineyard and found that the copper was mainly located in the 0-10 cm horizon after which copper levels decreased significantly, although the vineyard in the study had not been ploughed since replanting. In orchard one, there was a significant correlation ($p<0.01$) between copper and %TOC.

Arsenic levels in the three soil cores tended to increase to a depth of approximately 15 to 17 cm and then decrease. The maximum arsenic levels occurred at between 5 and 30 cm for six Washington orchard soils (Peryea and Creger, 1994). Similar trends were also observed by Merry *et al.* (1983) in soil cores from Australian orchards in that the highest arsenic concentrations were not at the surface. They attributed this to leaching of the arsenic through the soil profile. In contrast, arsenic concentrations have been reported to decrease with depth in orchard soils in Hawkes Bay (NZ) (Proffitt and Macdonald, 2005). Washington State (Yokel and Delistraty, 2003) and Ontario (Elfving *et al.*, 1994). Arsenic also decreased with depth in NSW bananalands (NSW EPA, 1997).

Table 3.10: Vertical distribution of contaminants (mg kg^{-1} DW) and soil characteristics in orchard soils. Horizontal lines in the tables mark the soil boundaries.

Orchard one (long-term):

Depth (cm)	As	Cd	Cu	Pb	ΣDDT	Fe	Mn	%TOC	Olsen P
0-8	37	1.0	840	255	39.10	14200	250	10	82
8-14.5	85	0.4	305	320	13.76	17000	326	2.4	120
14.5-21	69	0.2	136	219	3.07	17900	149	1.7	93
21-29	10	<0.1	29	28	0.41	15800	36	1.2	40
29-37	3	<0.1	9	8	0.08	23800	17	0.9	7

Orchard two Core A (historic):

Depth (cm)	As	Cd	Cu	Pb	ΣDDT	Fe	Mn	%TOC	Olsen P
0-8	4	0.3	87	77	2.97	1900	65	4.7	53
8-12.5	8	0.2	108	89	2.36	1840	35	3.6	66
12.5-17	19	0.1	124	73	0.64	1550	20	1.9	85
17-21.5	16	<0.1	74	37	0.23	1130	13	2.4	63
21.5-26.5	14	<0.1	58	37	0.42	1080	13	2.2	55
26.5-31.5	10	<0.1	37	16	0.09	794	9	2.4	32
31.5-36.5	7	<0.1	24	8	0.04	905	6	2.4	18
36.5-40.5	25	<0.1	63	26	0.177	1050	11	2.4	43

Orchard two Core B (historic):

Depth (cm)	As	Cd	Cu	Pb	ΣDDT	Fe	Mn	%TOC	Olsen P
0-5	5	0.2	50	42	0.687	2100	63	4.1	49
5-10	6	0.1	50	42	0.665	2010	33	3.1	48
10-17	10	<0.1	51	34	0.949	1870	18	2.0	37
17-22.5	4	<0.1	24	10	0.128	1210	8	1.4	15
22.5-28	<2	<0.1	11	4	0.031	855	4	1.8	10
28-33	3	<0.1	20	11	0.267	1240	9	1.7	13
33-38	<2	<0.1	8	5	0.141	1010	6	1.2	14

A possible factor contributing to enhanced leaching of arsenic in orchard soil is the use of phosphate containing fertilisers. Peryea and Kammereck (1997) demonstrated that PO_4^{3-} ions can enhance arsenic leaching in soils. In orchard one, there was a highly significant relationship between Olsen P and arsenic (log values).

Lead levels on both properties tended to increase slightly below the surface layer and then decrease in a similar pattern to that reported by Peryea and Creger (1994). There was no evidence of lead accumulation below the top 20 cm on both properties. Lead levels in soil cores from Australian (Merry *et al.*, 1983), Washington (Peryea and Creger, 1994; Yokel and Delistraty, 2003) and Ontario (Elfving *et al.*, 1994) orchard soils also decreased with depth.

The ΣDDT levels in the three soil cores tend to decrease with depth with the greater part of the residues in the top 15 cm. This result is in agreement with that of Cooke and Stringer (1982) who investigated the vertical distribution of DDT in an English orchard. They found that the greater part of all ΣDDT residues were in the top 10 cm of soil in an undisturbed orchard. Orchard *et al.* (1991) found that ΣDDT residues in two Canterbury (NZ) agricultural soils decreased with depth particularly below 20 cm, with ΣDDT still being detected on both of these properties at 30 cm. In the current study, ΣDDT was detected to a depth of approximately 40 cm on both properties.

The results presented in Table 3.10 indicate that there has been some downwards migration of contaminants in the orchard soils. Several mechanisms have been suggested for transport of contaminants down the soil profile including leaching, bioturbation by soil invertebrates (Boul, 1995), soil cultivation (Merry *et al.*, 1983), transport on clay mineral and organic colloids (Kookana *et al.*, 1998; Karathanasis *et al.*, 2005; Jorgensen *et al.*, 2005) application of other agrichemicals (Beck *et al.*, 1993) and facilitated transport by organic acids (Jorgensen *et al.*, 2005).

While cultivation with a crawler tractor was common practice in NZ orchards (Winn, 1968; Henley, 1950) and both landowners reported cultivating the soil, cultivation is unlikely to be the only mechanism for transport of contaminants within the soil profile. The soil boundary layers observed in the soil cores indicate that on these properties, the cultivation depth was approximately 10 cm whereas ΣDDT was measured to depths of 40cm. The practice of soil cultivation to control weeds on orchards was discontinued during the 1960s. Interpretation of these depth profile results is problematic as copper, cadmium and manganese continued to be added to orchard soils for decades after the use of pesticides containing *p,p'*-DDT and lead arsenate ceased.

The apparent downwards migration of copper, lead and ΣDDT particularly in orchard one may be due to transport on colloidal material. Drying cracks were visible in the soil core collected from orchard one and these may have acted as a pathway for the

downwards migration of ΣDDT and trace elements associated with colloids through the soil profile (Boul, 1995). In addition, leaf litter from the deciduous fruit trees will have continued to be added to the soil surface effectively burying earlier contamination.

3.4 CONCLUSIONS

DDT and its degradation products DDE and DDD were the pesticide residues most frequently detected in Auckland cropping area soils. ΣDDT and dieldrin were not detected on sites developed for horticultural use after 1975 and this is consistent with their recorded use in NZ. Acidic herbicides were not detected in cropping area soils and organophosphorus and organonitrogen pesticides were detected infrequently and generally at levels less than 1 mg kg^{-1}.

Arsenic, cadmium, copper and lead were the trace elements detected at the highest levels in cropping soils and this is consistent with the agrichemicals known to have been used in the Auckland region. The median values for tin and zinc in cropping soils exceeded the median baseline values for the Auckland region indicating that these trace elements may also be accumulating in some cropping area soils. The mean values for arsenic, copper, lead and zinc were significantly higher ($p<0.05$) for sites developed for horticultural use prior to 1975 than on sites developed after 1975. In the cores collected from two orchard sites elevated concentrations of ΣDDT, arsenic, cadmium, copper and lead were measured in the top 20 cm. Concentrations of copper and ΣDDT decreased with depth whereas arsenic tended to initially increase to a depth of 15 cm and then decreased.

4 COMPARISON OF AGRICHEMICAL RESIDUES IN HORTICULTURAL SOILS FROM THREE REGIONS

4.1 INTRODUCTION

Results presented in Chapter Three for the Auckland region indicated that elevated levels of selected agrichemical residues (arsenic, cadmium, copper, lead, zinc and ΣDDT) were likely to be present in soil on long-term horticultural properties. Sampling was subsequently undertaken in two further horticultural regions (Waikato and Tasman), with the focus on these specific contaminants only, to determine whether this was likely to be an issue in other parts of NZ. As there are differences between the Auckland, Waikato and Tasman regions in terms of climate, historical horticultural crops and dominant soil types it was probable that there may also have been differences in plant diseases and pests. These regional differences may have resulted in different spray regimes and hence different levels and types of residual agrichemicals in soil. Campbell (1936) stated that *"orchardists' spraying programmes vary to some extent to meet the different temperature and humidity conditions obtained in different parts of the country"*. For example, in 1957 commercial orchards in the Auckland region were acknowledged as requiring frequent spraying due to bacterial and insect pests (Fielding, 1957). Market requirements may also have influenced the spray regimes employed within a region. Unlike the Auckland region and the Tasman District, prior to the early 1980s horticulture in the Waikato region generally supplied the local rather than the export market (MAF, 1972).

The purpose of the investigations reported in this Chapter were to determine the extent to which organochlorine pesticides and trace elements had accumulated in cropping soils of two further regions, Tasman and Waikato, and to compare the concentrations of contaminants with available soil criteria for the protection of ecological receptors and human health.

4.1.1 HISTORIC HORTICULTURE IN THE TASMAN DISTRICT

Crops historically grown in the Tasman District included pipfruit, tobacco, vegetables, berries and hops. The total area in horticulture in the Nelson region (including Nelson City Council) in 1981 was 4296 hectares (Hadfield, 1982). In 1965 there were 4000 acres (1620 ha) of pipfruit planted in the Waimea County. Two-thirds of the orchards were located in the coastal belt of the Moutere Gravels from Mariri to Mapua with smaller areas of production located on alluvial soils around Riwaka, Richmond, Brightwater and Wakefield (Owens, 1965). Berries, mainly raspberries and boysenberries, were produced in the Tadmor-Tapawera-Motupiko districts with scattered holdings in the Wai-iti and Moutere Valleys (Owens, 1965). This region was the only region in NZ to produce tobacco and hops on a commercial scale (Hadfield, 1982) and in 1972 there were 4681 acres (1895 ha) of tobacco (James, 1975). Tobacco is no longer grown in the Tasman District; current uses for land historically used to grow tobacco include grazing and kiwifruit. Vegetables were mainly produced on the Waimea Plain around Hope, Appleby and Stoke; around Motueka and Riwaka and in scattered areas in the Moutere Valley (Owens, 1965).

4.1.2 HISTORICAL HORTICULTURE IN THE WAIKATO REGION

Only a limited amount of information has been recorded on horticultural activities in the Waikato region prior to the early 1980s. Traditionally, pastoral farming (sheep and dairying) dominated the Hamilton Basin's landuse (Bird and Lohrey, 1985). Small-scale cropping and horticulture has occurred in the Waikato region since the late 1880s. Wheatfields were established at Te Awamutu and Rangiaohia during the mid 1800s (Barber, 1987). Prior to the late 1970s the majority of horticultural activities were geared towards the local rather than export markets (Bird and Lohrey, 1985). A growth period was experienced by the NZ horticultural industry between 1978 and 1982 (Bird and Lohrey, 1985) and by 1980 there were 1549 hectares in fruit and vegetable production in the Waikato region (Bollard, 1981). The horticultural

landuses in the Waikato region included berryfruit, glasshouses, market gardens, vineyards and orchards.

The first fruit trees in the Waikato region were planted by missionaries (Campbell, 1936). During the 1870s and 1880s orchards were planted in the vicinity of Hamilton and Cambridge. As in the Auckland region, early attempts at orcharding in the Waikato were wiped out by the introduction of orchard pests and diseases including codlin moth. Many of these early orchards were removed under the 1903 Orchard and Garden Diseases Act (Campbell, 1936 and Barber, 1987). According to Fielding (1957) there were an estimated 45 orchards totalling 150 acres (61 ha) in Hamilton in 1956 with the majority of orchards planted in pip and stonefruit. There were no significant plantings of citrus in the Waikato (Nobbs, 1963).

Market gardening in Franklin District began in the late 1880s and early 1900s. There were few commercial market gardens in the Hamilton Basin prior to the late 1970s and those in existence supplied the local market (Bird and Lohrey, 1985). Discovery of the potato cyst nematode at Pukekohe Hill in 1972 forced several growers to relocate to Pukekawa, Onewhero and Te Kohanga in the early 1970s (Wai Shing, 1977). Less than 40 ha of market gardens existed in the Pukekawa-Onewhero area prior to the 1970s (Maggs, 1987), however by 1977 there was 1021 ha of market gardening in Pukekawa, Onewhero and Te Kohanga (Wai Shing, 1977).

The majority of vineyards have historically been located in the Te Kauwhata area (Moran, 1958) where the Te Kauwhata Viticultural Research Station was established in 1895 (Barber, 1987). Both table and wine grapes were planted in this area during the 1920s (Moran, 1958). In 1976 there were 17–19 vineyards, each approximately 3 acres in size; totalling 81 acres (32 ha) or 8% of the national total (Townsend, 1976).

Glasshouses were scattered throughout the Waikato region; and tomatoes and cucumbers were the main crops. Many of the glasshouses that were in existence prior to 1975 have since been removed and the land redeveloped for housing. A wide range of berryfruit is and has historically been grown in the Waikato region. Most of

the berryfruit produced in the Waikato region was consumed locally, however there was also a limited amount exported to Australia (MAF, 1972).

Horticultural activities occurring in the Auckland region were described in Section 3.1.1.

4.1.3 OBJECTIVES

The principal objectives of the work reported in this Chapter were to:

- Determine the extent to which residual historic pesticide contamination is also likely to be a problem for horticultural soils in a further two NZ regions; the Waikato Region and the Tasman District.
- Identify any regional differences in levels and types of contaminants.
- Identify the landuse category with the highest residues.
- Investigate possible relationships between contaminant (ΣDDT and selected trace elements) concentrations and soil characteristics.

4.2 METHODS SUMMARY

4.2.1 SAMPLE SITE SELECTION

As was the case with the Auckland investigation, horticultural sites from within Tasman and Waikato regions were selected according to landuse. The results for the 3 regions have been combined and the Waikato and Tasman data compared with that from the Auckland region. Results for a total of 108 composite samples are reported: 38, 45 and 25 composite samples were collected from the Auckland, Waikato and

Tasman regions respectively (Table 4.1). All samples were collected on condition of anonymity, hence site locations and soil type data, which could enable identification of specific sites when combined with the landuse, are not reported.

The landuse types reported in this chapter for the Auckland region included grazing, glasshouses, market gardens, orchards and vineyards. Grazing, berryfruit, market-gardens, orchards and former tobacco properties were the landuse types sampled in the Tasman region. Waikato region samples were collected from background (under indigenous vegetation), grazing, berryfruit, market-garden, orchard and vineyard sites. Auckland samples were collected between April and August 2001, Waikato samples were collected between May and October 2002 and Tasman samples were collected in September 2002.

Table 4.1: Summary of samples collected from the Waikato, Tasman and Auckland regions.

Landuse	Waikato	Tasman	Auckland[a]
Berryfruit[b]	7	5	0
Glasshouses	3	0	10
Market Gardens	7	5	8
Orchards	7	5	12
Tobacco[c]	0	5	0
Vineyards	7	0	5
Grazing sites	7	5	3
Indigenous vegetation	7	0	0
Total	45	25	38

[a]Only samples collected from properties developed before 1975 have been included in this summary, [b]Some Waikato and Tasman berryfruit properties may have been developed after 1975, [c]Tobacco was only grown in the Tasman District.

The year 1975 was selected as the cutoff point for inclusion of properties in the Tasman and Waikato surveys as the main contaminants of interest (with the exception of copper and zinc) were generally discontinued for use in NZ after this time. In the Auckland survey, there were significant differences ($p<0.05$) for levels of arsenic, copper, lead, and zinc between properties developed prior to and after 1975 (Section 3.3.5, Chapter Three). Organochlorine pesticides were not detected on properties developed for horticultural use after 1975. With regard to copper and zinc, properties

in production for the longest time period are expected to contain the highest soil contaminant levels. The cutoff point for Waikato berryfruit properties was extended to 1980 as discussions with growers suggested that dieldrin was being applied to control mites until the mid 1980s.

Waikato and Tasman data were determined for composite soil samples (comprising 10 soil cores collected using a "Z" sampling pattern) collected from a representative one hectare area on each property. The size of the area sampled was reduced to one hectare following a review of spatial variability data for the Auckland region as described in Chapter Three (Section 3.3.6). Quality control procedures included the analysis of blind duplicate samples (one per ten samples), and the inclusion of a certified reference material (trace elements only) and in-house QC samples for organochlorine pesticides.

4.2.2 ANALYTICAL METHODOLOGY

All samples were analysed in a laboratory accredited by International Accreditation NZ (IANZ, previously TELARC) using registered methodologies. Two methodologies were used to determine organochlorine pesticide levels. The Auckland samples were analysed for a suite of organochlorine, organonitrogen and organophosphorous pesticides using a multi-pesticide residue screen method (Chapter Two, Section 2.5.1.1). The purpose of the initial Auckland work was to identify the agrichemical residues likely to be present in cropping soils at elevated levels. The samples collected in subsequent Tasman and Waikato samples were analysed for organochlorine pesticides using a specific organochlorine pesticide analysis method (Chapter Two, Section 2.5.1.3).

4.2.3 DATA REPORTING CONDITIONS

Statistical analyses were carried out using customized Microsoft Excel worksheets and Data Desk 6.0 (Data Description Inc., New York). Where values were less than

the detection limit, half of the detection limit was assigned for statistical purposes. Significant relationships between soil characteristics and key contaminants (arsenic, cadmium, copper, lead, zinc and ΣDDT) were determined on log-normalized data (excluding pH) using Pearson's correlation coefficients. Significant differences between regions and landuses were calculated using analysis of variance (ANOVA) on ranked data. When significant differences occurred, differences between specific landuses and/or regions were determined by Tukey's multiple comparison test ($p<0.05$). Tobacco sites were excluded from the dataset as they are an historical landuse. Full statistical analysis was not undertaken for berryfruit sites as some of these sites were developed after 1975. Glasshouse sites were also excluded due to limited numbers of samples.

4.2.4 SELECTION OF SOIL GUIDELINES FOR COMPARATIVE PURPOSES

For each contaminant, an assessment of the significance of the residual contamination was made by comparing the data with the target and intervention values of the Dutch soil criteria (Ministry of Housing, Spatial Planning and the Environment, 2000), Canadian Environmental Quality Guidelines (CCME, 1999) and NZ ecotoxicity data and soil guidelines (copper and arsenic), where available (Table 4.2).

It was necessary to use some international guidelines as NZ has not yet developed a comprehensive set of its own risk-based soil guidelines for many common contaminants. Work is underway to develop such guidelines (or standards). In the interim, NZ's Ministry for the Environment have provided a preferred hierarchy for selecting soil guidelines when no NZ figure is available (Ministry for the Environment, 2003). Under this system, risk-based guidelines from the United Kingdom, the Netherlands and Canada are generally preferred because the approaches adopted when estimating risk in these jurisdictions are comparable to those favoured in NZ (Ministry for the Environment, 2003).

This assessment utilised the 10% produce ingestion guideline for copper and arsenic jointly promulgated by the NZ Ministry for the Environment and Ministry of Health (1997). These guidelines consider phytotoxicity and multiple exposure pathways including produce ingestion, soil ingestion and dermal contact. The 50% produce ingestion guideline for copper was not used as Cavanagh (2004) identified algebraic errors in the methodology used to calculate plant uptake and hence human exposure to copper through eating produce grown on–site may have been overestimated.

The Dutch target values are derived from ecotoxicological data for soil species and are protective of soil quality whereas exceedance of the intervention values indicates serious risk to plant and animal life or human health (Ministry of Housing, Spatial Planning and the Environment, 2000). The Canadian EQGs are generic guidelines designed to protect human and key ecological receptors. Soil quality guidelines are developed for both human health and ecological receptors and the most protective guideline is chosen as the recommended soil quality guideline. The following exposure routes were considered as part of the derivation of the agricultural landuse soil guideline: soil contact (crops/plants, invertebrates, nutrient cycling processes, livestock/wildlife), soil and food ingestion (livestock/wildlife) and human health (multi media exposure, child) (CCME, 1999).

4.2.4.1 DETERMINING WHEN A GUIDELINE HAS BEEN EXCEEDED

The usual approach of regulatory agencies in NZ in determining whether a guideline has been exceeded at a site is a simple comparison of the analytical numbers obtained with appropriate guideline values. This approach is robust in cases where the measured concentration is well above or below the guideline. However, from a scientific perspective, it is less robust when the analytically determined concentration is close to (marginally above or below) a guideline value. In such cases, it is appropriate to more explicitly consider how representative the sample might be of the site, variation between samples, and random analytical error. This approach leads to three categories. A sample result can be above guideline, below guideline, or indistinguishable from the guideline.

An estimate of combined sampling and analytical error for cropping areas was obtained by analysing replicate samples collected from one site (Chapter Three, Section 3.3.2). The Student's t-test 95% error was calculated as a percentage and the value subtracted from each guideline in accordance with Ministry for the Environment protocols (Ministry for the Environment, 2004b). For the purposes of the comparison presented in this thesis the trigger level has been set at the concentration which is indistinguishable from the guideline (Table 4.2).

Two relevant data sets covering replicate sampling and analysis are available: one where the contaminant concentrations were at low levels (previous paragraph), and the other where contaminant concentrations were generally above soil guideline values. The second data set was replicate samples collected during 2003 from residential properties that had been built on an old orchard in Hamilton. This work was carried out by Hamilton City Council and Environment Waikato in response to information that came to light during the Waikato horticultural soils survey described in this chapter. Data for the replicate samplings has been provided in *Contaminated Land Management Guidelines No 5: Site Investigation and Analysis of Soils* (Ministry for the Environment, 2004b). These samples were collected using the same sampling protocol and analysed by Hill Laboratories using the same analytical methods as the work presented in this chapter.

The Student's t-test 95% errors calculated from the first data set (Table 4.2) would represent a worst case scenario for this work as the site that was repeatedly sampled had low concentrations of contaminants. Precision of analytical methods are generally poorer at concentrations closer to the detection limits and hence there were larger errors calculated than may have been the case if a site with higher contaminant concentrations had been repeatedly sampled. In comparison, the Student's t-test 95% errors calculated for the second data set, with higher concentrations of contaminants (Appendix A), were less than 6% (data supplied by Environment Waikato). For the purposes of this comparison to soil guideline criteria, the Student's t-test 95% error for the higher level samples was used and the errors for cadmium, tin and zinc were estimated to be 10.4% (equivalent to the error for arsenic) following discussion with

Hill Laboratories regarding the expected analytical variability. This is seen as valid because the soil guideline values are themselves at moderately high concentrations. It is therefore likely that the relative (percent) precision will be better when soil contaminant concentrations are near their guideline values, than when they are closer to background.

Table 4.2: Guidelines for contaminants in soil (mg kg^{-1}) used for comparative purposes.

Contaminant	95% error calculated at low contaminant concentrations (%)	95% error for moderate contaminant concentrations (adopted in this work) (%)	Guideline (mg kg^{-1})	Trigger value[a] (mg kg^{-1})
Arsenic	22.6	5.5	30[c]	28
			29[d]	27
			55[e]	52
Cadmium	19.8	10.4	0.8[d]	0.7
			1.0[f]	0.9
			1.4[g]	1.3
Copper	10.1	3.6	130[c]	125
			370[h]	357
			63[g]	61
Lead	14.7	4.1	70[g]	67
			85[d]	82
			530[e]	508
Mercury	nc[b]	10.4	6.6[g]	5.9
			10[e]	9
Tin	nc	10.4	5[g]	4.5
Zinc	10.4	10.4	140[d]	132
			200[g]	189
ΣDDT	9.4	9.4	0.7[g]	0.6
			4[e]	3.6

[a]Trigger values used in this study for comparative purposes. The guideline has been adjusted to take analytical and sampling variability into account and the trigger level is the value at which the concentration is indistinguishable from the guideline when variability is considered.
[b]Student's t-test 95% error not calculable for tin and mercury as these trace elements were not detected on the property sampled. Typical errors for analysis of duplicate samples at the relevant soil guideline were supplied by Hill Laboratories (G Robinson *pers comm*, 2004).
[c]New Zealand Timber Treatment Guidelines 10% produce ingestion (Ministry for the Environment and Ministry of Health, 1997).
[d]Dutch target value (Ministry of Housing, Spatial Planning and the Environment, 2000).
[e]Dutch intervention value (Ministry of Housing, Spatial Planning and the Environment, 2000).
[f]NZ Biosolids guidelines (NZWWA, 2003).
[g]Canadian CCME EQG for agriculture (CCME, 1999).
[h]New Zealand Timber Treatment Guidelines, soil ingestion only (Ministry for the Environment and Ministry of Health, 1997).

4.3 RESULTS AND DISCUSSION

The results for selected trace elements and organochlorine pesticides from the Waikato and Tasman regions are compared with those for Auckland properties developed prior to 1975. The summary data for ΣDDT are presented in Table 4.4 and summary statistics for arsenic, cadmium, copper, lead, mercury, tin and zinc in Tables 4.6 to 4.12. The full dataset for all other trace elements is presented in Appendix A.

4.3.1 ORGANOCHLORINE PESTICIDES

In agreement with data obtained for horticultural soils in the Auckland region, ΣDDT was the most commonly detected organochlorine pesticide followed by dieldrin and Σendosulfan. In Waikato samples, endrin was detected in one glasshouse (0.233 mg kg^{-1}) and endrin aldehyde was detected twice; once in a glasshouse (0.01 mg kg^{-1}) and once on a market garden property (0.068 mg kg^{-1}). Low levels of lindane (0.005–0.017 mg kg^{-1}) were detected in three Waikato orchard samples and chlordane residues (cis, trans and total isomers = 0.04 mg kg^{-1}) were detected in one grazing sample collected in the Tasman District.

4.3.1.1 ΣDDT

The values obtained for the *o,p'*- and *p,p'*- isomers DDT, DDE and DDD have been combined and reported in this chapter as a single figure, ΣDDT. Data for individual residues is presented in Chapter Five. Two IANZ registered analytical methodologies were used to determine ΣDDT levels in soil. The Auckland samples were extracted using a multi-residue analysis method that encompassed 181 pesticides in order to determine the full range of pesticides likely to be present in horticultural soils. Organochlorine pesticides were identified as the predominant residues and the subsequent samples collected from the Waikato and Tasman regions were analysed using an optimized method for a suite of organochlorine pesticides. Full details for both methods are provided in Chapter Two. Briefly for the multi-residue method,

samples were extracted with ethyl acetate followed by gel permeation chromatography and for the organochlorine extraction method, samples were extracted with hexane:acetone and cleaned up using florosil.

Six samples were analysed by both methods (Table 4.3). In general the recoveries for the multi-residue and organochlorine analyses were comparable for samples containing elevated residue concentrations but deviated significantly for samples containing lower residue concentrations. On some occasions, the extraction recoveries at lower concentrations of residual ΣDDT obtained by the multi-residue analysis method were approximately 50% of those obtained by the specific organochlorine pesticide analysis method (Table 4.3). Thus, it is likely that the multi-residue analysis methodology (while capable of detecting a wider range of pesticides) underestimates the concentration of ΣDDT residues present in soil. Accordingly, for low level samples, the ΣDDT levels determined using the optimized organochlorine pesticide analysis method are considered more robust than those determined using the multi-residue pesticide methodology.

The ΣDDT concentrations measured in horticultural (<0.03–289 mg kg^{-1}) and grazing soils (<0.03–1.30 mg kg^{-1}) in all three regions (Table 4.4) exceed those previously reported as background levels (maximum background levels of 0.034 to 2.70 μg kg^{-1} for *p,p´*-DDT and 0.048 to 2.69 μg kg^{-1} for *p,p´*-DDE) in NZ indigenous forest soils by the Ministry for the Environment (Buckland *et al.,* 1998).

ΣDDT was detected in 31 of the 35 Auckland, 29 of the 31 Waikato, and all of the Tasman horticultural samples. The levels of ΣDDT measured in the NZ horticultural soils (<0.03–34.5 mg kg^{-1}, one glasshouse outlier of 289 mg kg^{-1}) (Table 4.4) are in agreement with ranges previously reported for NZ. Typical ΣDDT levels of 0.11 and 6.2 mg kg^{-1} were reported for two glasshouse properties in the Auckland region (Hogg, 2000), levels in the range <0.01 to 28.2 mg kg^{-1} for Hawkes Bay Orchards (note samples collected 1966 to 1969) (Wilson, 1980) and <0.01 to 20.1 mg kg^{-1} in a representative survey of 233 residential properties located on former orchards in Hamilton, NZ (Kim *pers comm.,* 2005). Macaskill (2004) measured comparable

ΣDDT levels in the range <0.01 to 15.3 mg kg^{-1} in a survey of Hawkes Bay horticultural soils.

The geometric mean of ΣDDT levels in soils in all 3 regions generally followed in the order: orchards>market gardens>grazing>background (Table 4.4). Overall, higher levels of ΣDDT were detected in Waikato orchard and market-garden soils than in corresponding landuses in the Tasman region. ΣDDT levels in Waikato and Tasman orchards were significantly higher than in market garden soils. This ranking is agreement with the results of Wan *et al.* (1989) who reported higher levels of ΣDDT in Australian orchard soils than in vegetable cropping soils. Canadian data (Ripley, 2003; Harris *et al.*, 1977) also ranks orchards as the horticultural landuse with the highest ΣDDT residues.

Table 4.3: Comparison of concentrations (mg kg^{-1}) of DDT residues measured using two extraction methodologies.

Analyte	Organochlorine	Multi-residue	Analyte	Organochlorine	Multi-residue
o,p'-DDD	0.009	<0.005	*o,p'*-DDD	0.096	0.074
o,p'-DDE	<0.005	<0.005	*o,p'*-DDE	0.007	0.015
o,p'-DDT	0.016	0.014	*o,p'*-DDT	0.167	0.009
p,p'-DDD	0.016	<0.005	*p,p'*-DDD	0.247	0.12
p,p'-DDE	0.117	0.05	*p,p'*-DDE	1.82	1.10
p,p'-DDT	0.121	0.087	*p,p'*-DDT	1.40	0.55
ΣDDT[a]	0.282	0.16	ΣDDT	3.74	1.87
o,p'-DDD	<0.005	<0.005	*o,p'*-DDD	0.652	0.43
o,p'-DDE	<0.005	<0.005	*o,p'*-DDE	0.021	0.084
o,p'-DDT	<0.005	<0.005	*o,p'*-DDT	1.90	1.10
p,p'-DDD	<0.005	<0.005	*p,p'*-DDD	2.78	1.10
p,p'-DDE	0.018	0.009	*p,p'*-DDE	6.50	6.70
p,p'-DDT	0.008	<0.005	*p,p'*-DDT	10	15
ΣDDT	0.038	0.024	ΣDDT	21.9	24.4
o,p'-DDD	0.075	0.09	*o,p'*-DDD	0.01	<0.005
o,p'-DDE	0.006	<0.005	*o,p'*-DDE	<0.005	<0.005
o,p'-DDT	0.382	0.23	*o,p'*-DDT	0.031	0.006
p,p'-DDD	0.255	0.10	*p,p'*-DDD	0.032	0.05
p,p'-DDE	0.614	0.40	*p,p'*-DDE	0.293	0.137
p,p'-DDT	2.72	1.70	*p,p'*-DDT	0.232	0.199
ΣDDT	4.05	2.52	ΣDDT	0.601	0.398

[a]Sum of of *o,p'* and *p,p'*-DDT, DDE and DDD (values <0.005 included as half of LOD).

These elevated levels of ΣDDT (Table 4.4) in horticultural soils result from historical use of *p,p'*-DDT as an insecticide. It is unlikely that the ΣDDT levels determined for horticultural soils arise from recent widespread use of DDT since DDT products were deregistered for use in NZ in 1989 (Buckland *et al.*, 1998) and from the mid 1960s could only be used under permit (Slade, 1964). DDT isomers can be impurities in dicofol (currently registered in NZ as an acaricide) and hence it is possible that there may have been small inputs to ΣDDT levels on properties where dicofol has been applied. The maximum allowable level of ΣDDT in dicofol for NZ is 0.1% (Australian Pesticides and Veterinary Medicines Authority, 2004) and, at the recommended application rate, cumulative recent inputs would be low.

There are several factors which may partially or in combination explain the higher ΣDDT levels found in orchard soils compared to other landuses including rate of application, farming practices and exposure to sunlight. In NZ, orchards received the highest application rates for DDT (Harrison 1973). Market gardens tended to produce a range of vegetable crops in rotation and DDT was not recommended for all vegetable crops (e.g. Atkinson *et al.*, 1956). The higher levels of DDT found in orchard and vineyard soils compared to market garden soils may be partly due to lack of tillage of the soil in recent years. Soil cultivation may enhance loss of ΣDDT through volatilisation and erosion (Bailey *et al.*, 1974 cited in Harris *et al.*, 2000) and DDT has been reported to be less persistent in cultivated plots (Lichenstein *et al.*, 1971). However, it should be noted that prior to the 1960s it was common practice in NZ to cultivate the soil on orchard properties.

DDT has been reported to be degraded photochemically (Taschenberg *et al.*, 1961) and lower levels of DDT have been measured in soils without vegetation than in those with vegetative cover (Talekar *et al.*, 1983). All of the orchards sampled had a constant grass cover. This grass cover in orchards may inhibit exposure of the soil to sunlight preventing significant photochemical degradation, whereas in market gardens the soil is frequently exposed to sunlight through cultivation.

Table 4.4: ΣDDT concentrations (mg kg^{-1} DW) measured in Auckland, Tasman and Waikato soils. The values obtained for the *o,p'*- and *p,p'*-isomers DDT, DDE and DDD have been combined and reported as a single figure, ΣDDT.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Detected	9	5	7		Detected		5	6
	Range	<0.03–24.4	1.49–7.14	0.37–34.5		Range		0.05–5.46	<0.03–0.88
	Mean	4.71	3.66	8.39		Mean		1.35	0.40
	S.D.	7.01	2.18	12.12		S.D.		2.32	0.33
	Geo mean	0.68	3.19	3.20		Geo mean		0.37	0.24
	Median	2.23	3.09	3.22		Median		0.32	0.31
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Detected	8		3		Detected		5	
	Range	<0.03–289		0.23–0.96		Range		0.24–6.38	
	Mean	30.22		0.59		Mean		2.89	
	S.D.	91.01		0.37		S.D.		2.77	
	Geo mean	0.77		0.51		Geo mean		1.63	
	Median	1.38		0.58		Median		1.74	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Detected	7	5	7		Detected	1	4	4
	Range	0.09–0.91	0.07–1.16	0.04–1.68		Range	<0.03	<0.03–1.30	<0.03–0.75
	Mean	0.32	0.32	0.63		Mean	<0.03	0.49	0.23
	S.D.	0.28	0.47	0.70		S.D.	0	0.61	0.28
	Geo mean	0.24	0.17	0.32		Geo mean	<0.03	0.16	0.09
	Median	0.19	0.12	0.39		Median	<0.03	0.11	0.08
Vineyards	N	5	0	7	Background[d]	N	0	0	7
	Detected	5		6		Detected			1
	Range	0.25–2.84		<0.03–1.26		Range			<0.03–0.05
	Mean	1.37		0.23		Mean			<0.03
	S.D.	1.04		0.46		S.D.			0.01
	Geo mean	1.01		0.08		Geo mean			<0.03
	Median	1.10		0.06		Median			<0.03

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

Irrigation on market garden soils may have also increased the loss of DDT through volatilisation, as the rate of volatilisation is influenced by soil moisture content (Dimond and Owen, 1996). Irrigation has been shown to influence ΣDDT levels elsewhere in NZ; ΣDDT levels were lower on irrigated grazing plots in mid Canterbury (Boul *et al.*, 1994).

In all three sampling locations, ΣDDT levels were significantly higher in horticultural cropping soils than in grazing soils. This is most likely due to the frequency of application of DDT on horticultural properties. DDT was typically applied once every three years on NZ grazing properties (Roberts *et al.*, 1996) whereas it was applied several times per year on horticultural properties (Atkinson *et al.*, 1956).

The ΣDDT levels measured in cropping areas on horticultural (mainly orchard) properties (Table 4.4) are in agreement with those reported in the international literature. ΣDDT levels in NSW market garden and orchard soils ranged from not detected to 2.95 mg kg^{-1} (NSW EPA, 1995). Aigner *et al.* (1998) measured ΣDDT concentrations in 38 USA agricultural soils and the maximum value measured was 11.8 mg kg^{-1}. The ΣDDT concentrations measured in NZ orchards agree with those from three Canadian fruit growing regions which had mean ΣDDT levels of 1.9, 7.1 and 14.4 mg kg^{-1} 20 years after the last application (Harris *et al.*, 2000). Similarly, ΣDDT levels of 0.2 to 7.2 mg kg^{-1} have been reported for market garden soils in British Columbia (Szeto and Price, 1991), which is comparable to the range reported here for market gardens.

The ΣDDT levels reported in Table 4.4 for grazing sites are comparable with those reported for grazing properties elsewhere in NZ. For example, Orchard *et al.* (1991) carried out experiments on the degradation of DDT in NZ soils using three agricultural soils with ΣDDT levels (top 5 cm) of 2.6, 1.3 and 0.004 mg kg^{-1}. Roberts *et al.* (1996) reported a mean value for ΣDDT residues in paddocks on Canterbury farms of 0.27 mg kg^{-1}; 7% of these had ΣDDT levels greater than 1.0 mg kg^{-1}. Holland (1996) commented that while DDT levels on NZ farms were low (<0.1 mg kg^{-1}), levels in the range 1 to 5 mg kg^{-1} were not uncommon for Canterbury farms.

More recently Macaskill (2004) reported ΣDDT concentrations in the range 0.01 to 0.2 mg kg^{-1} for Hawkes Bay pasture and the median concentration of ΣDDT in NZ pastoral soils has been estimated to be 0.24 mg kg^{-1} (Kim *pers comm.*, 2004).

ΣDDT concentrations in 47% of the horticultural samples were either indistinguishable from, or exceeded, the Canadian soil guideline of 0.7 mg kg^{-1} and 17% exceeded the Dutch intervention value of 4 mg kg^{-1}. The current soil screening level of ΣDDT permitted for conversion to dairying is 0.2 mg kg^{-1} (Mashlan, 2001) and is based on an industry-specified extraction method which extracts approximately 50% of the ΣDDT extracted by the methods used in this work (P Robinson *pers comm.*, 2005). Allowing for the differences in extraction, an estimated 60%, 50%, and 60% of the Auckland, Waikato and Tasman horticultural soils (glasshouse samples excluded) respectively would not be suitable for dairying. Two of the Tasman and one of the Waikato grazing samples also exceeded 0.4 mg kg^{-1}. Agriculture Australia (Ambrose, 2000) recommends that concentrations of DDT in soil should not exceed 0.1 mg kg^{-1} for grazing and should be less than 0.01 mg kg^{-1} for raising poultry. These recommendations were made to ensure that no animal products sold in Western Australia exceed 50% of the maximum residue level for DDT.

4.3.1.2 DIELDRIN

Dieldrin levels in horticultural soils ranged from <0.005 to 0.56 mg kg^{-1} (Table 4.5) Dieldrin was detected in soil samples from seven Waikato horticultural properties (<0.005–0.052 mg kg^{-1}), but at lower levels than in Auckland horticultural soils (<0.005–0.56 mg kg^{-1}) and was most frequently detected in samples collected from market gardens (4 out of 7 samples). Dieldrin was also detected in one Waikato background soil sample (0.011 mg kg^{-1}); this site had been previously grazed. Comparable concentrations of dieldrin were detected on tobacco properties (0.006 to 0.095 mg kg^{-1}) and on one grazing property (0.005 mg kg^{-1}) in the Tasman District. The dieldrin levels measured in cropping areas on several horticultural properties

exceeded the maximum background level of 0.042 mg kg^{-1} reported by Buckland *et al.* (1998) for NZ soils and Hogg (2000) reported dieldrin concentrations up to 0.35 mg kg^{-1} in glasshouse soils which is considerably higher than the maximum level found in glasshouse soils in this study (0.078 mg kg^{-1}).

Table 4.5: Dieldrin levels (mg kg^{-1} DW) measured in horticultural and grazing soils from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	Auckland	Tasman	Waikato
Orchards	N	12	5	7
	Detected	0	0	2
	Range	<0.005	<0.005	<0.005–0.019
Glasshouses	N	10	0	3
	Detected	4		1
	Range	<0.005–0.072		<0.005-0.012
Market gardens	N	8	5	7
	Detected	6	0	4
	Range	<0.005–0.56	<0.005	<0.005–0.052
Vineyards	N	5	0	7
	Detected	2		0
	Range	<0.005–0.009		<0.005
Berryfruit	N	0	5	7
	Detected		0	0
	Range		<0.005	<0.005
Tobacco	N	0	5	0
	Detected		5	
	Range		0.006–0.095	
Grazing	N	3	5	7
	Detected	0	1	0
	Range	<0.005	<0.005–0.005	<0.005
Background	N	0	0	7
	Detected			1
	Range			<0.005–0.011

The dieldrin levels measured in NZ horticultural soils are comparable to those reported in the international literature. Several studies have reported dieldrin concentrations in cropping soils in Canada; Szeto and Price (1991) measured concentrations in the range 0.1 to 1.3 mg kg^{-1} on four market garden properties in the Lower Fraser Valley, British Columbia and Wan *et al.* (2005) reported a maximum concentration of 2.31 mg kg^{-1} for a more recent survey of cropping soils within the same general area. In comparison, Webber and Wang (1995) reported a maximum

dieldrin level of 0.01 mg kg^{-1} for Canadian agricultural soils. The NSW EPA (1995) measured levels ranging from not detected to 0.49 mg kg^{-1} in soil from nine market garden properties; despite dieldrin not being detected in an earlier survey of soils used for vegetable and tropical fruit production in NSW (Wan *et al.*, 1989).

4.3.1.3 ENDOSULFAN

Endosulfan and its degradation products (endosulfan II and endosulfan sulphate) have been combined and reported as a single figure. Endosulfan and/or its degradation products were detected on seven Waikato horticultural properties (0.005–0.417 mg kg^{-1}) and most frequently on berryfruit properties (4/7). ΣEndosulfan was only detected once (0.30 mg kg^{-1}), also on a berryfruit property, in the Tasman survey. In comparison, Σendosulfan was detected in 8 out of 35 soil samples collected from pre 1975 horticultural properties in the Auckland region and at higher levels (<0.02–2.97 mg kg^{-1}) (Section 3.3.3.4) than in the Tasman and Waikato samples.

Endosulfan is still registered for use in NZ under the tradename Thiodan (Fussell and Walton, 2001) and is used as an insecticide on vegetable, berryfruit and ornamental crops. Since endosulfan has a reported half-life of 30 to 70 days (Fussell and Walton, 2001), the detected residues may be due to recent use.

Szeto and Price (1991) have reported Σendosulfan levels of 0.01 to 14.9 mg kg^{-1} on 12 market garden properties in British Columbia. Webber and Wang (1995) measured total endosulfan concentrations up to 0.08 mg kg^{-1} in three samples from intensively cropped soils in Canada and concluded that these levels were the result of using Thiodan during the growing season in which the samples were collected. More recently Wan *et al.* (2005) reported Σendosulfan concentrations of <0.02 to 5.60 mg kg^{-1} for cropping soils in the Lower Fraser Valley, British Columbia.

4.3.2 TRACE ELEMENTS

4.3.2.1 ARSENIC

Arsenic levels in horticultural soils ranged from <2 to 58 mg kg^{-1} (Table 4.6); in comparison Longhurst *et al.* (2004) measured median arsenic concentrations in NZ agricultural soils ranging from 2.3 to 9.5 mg kg^{-1} depending on soil type.

Overall arsenic levels in orchards were consistently higher than in the other horticultural landuses surveyed. Based on a Tukey's multiple comparison test of ranked data, differences in arsenic concentrations between orchard and grazing sites were significant in the Auckland and Tasman regions with orchards having higher levels. Arsenic levels in Tasman orchards were also significantly higher than those measured in tobacco and grazing sites.

In this study, the elevated arsenic levels detected in the orchard soil samples may be attributed to the historic use of lead arsenate as a pesticide to control chewing insects such as codling moth. The Pb:As ratios on orchard sites with elevated arsenic and lead levels ranged from 3.4 to 6.6 (mg kg^{-1} basis) and are comparable to the range (3.49 ± 0.98) reported for four contaminated orchard soils in central Washington (Wagner *et al.*, 2003). Wagner *et al.* (2003) attributed the difference from 2.77 (weight:weight basis) calculated for $PbHAsO_4$ to leaching of arsenic to the subsoil. $PbHAsO_4$ was the main form of lead arsenate used in NZ orchards (Cunningham and Cottier, 1933). Other studies (e.g. Merry *et al.*, 1983) have also concluded that elevated levels of arsenic in orchard soils have resulted from the use of arsenic based insecticides.

Table 4.6: Arsenic concentrations (mg kg^{-1}) measured in soil samples collected from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	2–34	3–48	4–58		Range		<2–4	7–25
	Mean	15	30	18		Mean		2	13
	S.D.	12	19	22		S.D.		1	7
	Geo mean	11	21	10		Geo mean		2	12
	Median	11	33	6		Median		2	11
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Range	<2–20		8–25	(historic)	Range		<2–3	
	Mean	9		16		Mean		2	
	S.D.	6		9		S.D.		1	
	Geo mean	6		14		Geo mean		2	
	Median	9		15		Median		<2	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	4–11	2–21	6–11		Range	<2–3	<2–7	3–9
	Mean	6	10	9		Mean	2	3	6
	S.D.	2	7	2		S.D.	1	3	2
	Geo mean	6	7	9		Geo mean	2	2	5
	Median	6	10	9		Median	3	<2	5
Vineyards	N	5	0	7	Background[d]	N	58	0	7
	Range	2–14		6–15		Range	1–12		3–8
	Mean	7		10		Mean	5		6
	S.D.	4		3		S.D.	3		2
	Geo mean	6		9		Geo mean	4		5
	Median	7		8		Median	5		6

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

Elevated arsenic levels (e.g. >15 mg kg^{-1}) were also measured in samples collected from Auckland glasshouses (2) and Waikato berryfruit (2) and glasshouse (2) sites. On these sites, leaching of arsenic from copper-chrome-arsenic (CCA) treated timber (benches and posts) is the most likely source. Internationally CCA treated timber is increasingly being recognised as a source of arsenic contamination in soil (e.g. Khan *et al.*, 2005). A recent study by Robinson *et al.* (2004) measured elevated arsenic levels in soil adjacent to CCA-treated posts in Marlborough vineyards indicating that arsenic leaches from CCA-treated timber under NZ conditions.

Lead arsenate was still being recommended for use on orchards in the Tasman District in 1967 as some insect pests had developed resistance to DDD (The New Zealand Fruitgrowers Federation, 1967). However, despite a longer period of use of lead arsenate in the Tasman District, there were no significant differences in arsenic levels in orchards between the three regions.

The arsenic levels in cropping areas measured in all three regions are consistent with the range reported in old orchard soils in New York State (1.6–141 mg kg^{-1}) (Merwin *et al.*, 1994), and in the cropping area of an old orchard converted to a residential subdivision in North Carolina (arsenic 3.1–114 mg kg^{-1}) (USEPA, 2001a). Lower levels of arsenic (not detected–9.0 mg kg^{-1}) were reported for a survey of orchard and market garden properties in NSW, Australia (NSW EPA, 1995). Soil arsenic levels between 11 and 78 mg kg^{-1} (mean 40 mg kg^{-1}) were recorded in a 2003 survey of residential properties on a former orchard site in Hamilton, NZ (Kim *pers comm.*, 2004).

In this work, arsenic levels in 29% of the orchard samples were indistinguishable from, or exceeded, both the NZ arsenic guidelines of 30 mg kg^{-1} and the Dutch target value of 29 mg kg^{-1}. Only one sample from a Waikato orchard exceeded the Dutch soil intervention value of 55 mg kg^{-1}. Levels of arsenic in some orchard soils were comparable with levels shown to impact on terrestrial organisms in NZ soils. For example O'Halloran and Booth (as cited in Markich *et al.*, 2002) reported a LOEC for arsenic of 50 mg kg^{-1} for decreased shoot weight growth in *La. sativa* seedlings and an EC_{50} of 45 mg kg^{-1} for a 28 day growth test for adult *A. caliginosa.*

4.3.2.2 CADMIUM

Cadmium levels (<0.1–1.5 mg kg^{-1}) reported in Table 4.7 are comparable with those measured by Roberts *et al.* (1994) on 312 pastoral properties and 86 non-agricultural sites throughout NZ (average level 0.44 mg kg^{-1}, maximum value of 1.53 mg kg^{-1} for pastoral sites and average background level for non-agricultural sites of 0.20 mg kg^{-1}). The elevated cadmium levels in several of the samples collected from the Auckland, Tasman and Waikato regions are most likely due to the use of phosphate fertilisers which have been associated with elevated cadmium levels elsewhere in NZ (Taylor, 1997; Taylor and Percival, 2001).

There was no significant difference in cadmium levels between grazing and horticultural sites and this is because fertiliser is also heavily used on grazing land to improve production. In this investigation, the highest cadmium levels were measured in Waikato region soils. This may be partly due to soil characteristics since allophanic (aquand) soils (a common soil order in the Waikato region) have high phosphate retention capacities, requiring higher rates of fertilizer application (McLaren and Cameron, 1996).

The cadmium levels reported here (Table 4.7) for soils from three NZ regions are comparable with the range (<0.5–1.7 mg kg^{-1}) reported for rural soils in the Dutch province of Zeeland (Van Gaans *et al.,* 1995) and in 3045 agricultural soils from the USA (<0.01–2.0 mg kg^{-1}) (Holmgren *et al.,* 1993). The presence of elevated cadmium can have greater significance in NZ (and Australia) compared with a number of other countries, due to the lower soil pH values which tend to increase plant uptake of this element (McBride, 2002). The average horticultural soil pH was 6.2 for Tasman, 6.1 for Waikato and 6.0 for Auckland. However, lower pH values are common; for example 83 recently sampled pastoral, horticultural, arable, forest and background sites of the Waikato region of NZ showed an average pH of 5.47 (range 3.95–6.49), and most of these sites already receive lime (Kim *pers comm.*, 2005).

Table 4.7: Cadmium concentrations (mg kg^{-1}) measured in soil samples collected from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	0.1–1.1	0.3–1.0	0.8–1.5		Range		0.2–0.6	0.6–1.2
	Mean	0.4	0.5	1.1		Mean		0.3	0.8
	S.D.	0.3	0.3	0.2		S.D.		0.2	0.2
	Geo mean	0.3	0.5	1.1		Geo mean		0.3	0.8
	Median	0.3	0.4	1.0		Median		0.2	0.9
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Range	<0.1–1.0		0.3–0.5		Range		0.2–0.7	
	Mean	0.5		0.4		Mean		0.3	
	S.D.	0.4		0.1		S.D.		0.2	
	Geo mean	0.4		0.4		Geo mean		0.3	
	Median	0.6		0.4		Median		0.3	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	0.4–1.0	0.1–0.4	0.3–0.6		Range	0.4–0.5	<0.1–0.9	0.5–1.5
	Mean	0.7	0.2	0.5		Mean	0.4	0.4	0.7
	S.D.	0.3	0.1	0.1		S.D.	0.1	0.4	0.3
	Geo mean	0.6	0.2	0.5		Geo mean	0.4	0.2	0.7
	Median	0.6	0.2	0.5		Median	0.4	0.2	0.6
Vineyards	N	5	0	7	Background[d]	N	58	0	7
	Range	0.2–0.7		0.2–0.7		Range	0.05–0.46		<0.1–0.3
	Mean	0.4		0.3		Mean	0.12		0.1
	S.D.	0.2		0.2		S.D.	0.09		0.1
	Geo mean	0.4		0.3		Geo mean	0.09		0.1
	Median	0.4		0.3		Median	0.05		0.1

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

Internationally, cadmium levels in cropping soils are of concern as cadmium is readily taken up by plants from soil and plant tissue levels can exceed food standards before phytotoxic effects occur. The NZ food standard for cadmium levels in leafy and root vegetables has been lowered from 1.0 mg kg^{-1} FW to 0.1 mg kg^{-1} FW (FSANZ, 2005). Fiftieth-percentile cadmium intakes (excluding oysters) in the most recent total dietary survey for NZ ranged from 13% of the provisional tolerable weekly intake (PTWI) for a female to 37% of the PTWI for a 5–6 year child (Vannoort and Thomson, 2005).

The recommended soil limit for cadmium in agricultural soil proposed under the Guidelines for the Safe Application of Biosolids to Land in NZ, is 1.0 mg kg^{-1} (NZWWA, 2003). This is also the limit recommended by the UK for residential soils with soil pH 6 (DEFRA and Environment Agency, 2002a). This value is similar to the CCME EQG guide for cadmium of 1.4 mg kg^{-1} (CCME, 1999).

Cadmium levels in 5%, 32% and 20% of Tasman, Waikato and Auckland horticultural soil samples, and two grazing soils (Waikato and Tasman) were indistinguishable from, or exceeded, the Biosolids guideline of 1.0 mg kg^{-1} (NZWWA, 2003). Two Waikato samples (an orchard and a grazing site) exceeded or were indistinguishable from the CCME EQG of 1.4 mg kg^{-1}.

Cadmium levels in NZ horticultural and agricultural soils are likely to increase due to continued use of phosphate fertilizers and other agrichemicals; current estimated loading rates for the Waikato region range from 1.9 g ha^{-1} yr^{-1} (asparagus) to 37.2 g ha^{-1} yr^{-1} (potatoes) (Mills *et al.*, 2004). In 1997, the NZ fertilizer industry introduced a voluntary code reducing cadmium levels in phosphatic fertilizers to 280 mg kg^{-1} P, or approximately 24 mg kg^{-1} as superphosphate (Furness, 2003). This has resulted in a modest reduction in the accumulation rate of cadmium in NZ agricultural soils, with the reduction in cadmium content being partly countered by an increase in sales of superphosphate fertiliser. The current estimated accumulation rate for pastoral soils is still 77% of the previous value (Kim, 2005). It has been estimated that preventing further accumulation in soils would require an 80% reduction in the cadmium content of NZ superphosphate fertilisers (Ballance Agri-Nurients, 2005).

4.3.2.3 COPPER

The copper levels measured in soils generally followed the order orchard>vineyard>market-gardening (Table 4.8) and in the Auckland and Waikato regions, vineyard and orchard copper concentrations were significantly higher than those for grazing soils. A comparison of datasets using a log t-test showed that soil from horticultural properties contained significantly higher levels of copper than grazing soils ($p<0.001$). Such differences may be due to the widespread and prolonged use of copper-based fungicides on horticultural properties. Holland and Solomona (1999) also proposed that elevated soil copper levels in NZ orchard soils arise from the long-term use of copper-based fungicides.

Ranges of copper concentrations detected in horticultural soils were similar in the Waikato and Auckland regions (22–523 mg kg^{-1} and 21–490 mg kg^{-1} respectively). However, statistically ($p<0.05$) lower levels (6–123 mg kg^{-1}) were detected in horticultural soils in the Tasman District, possibly as a result of variations in spray regimes due to differences in local climate. In addition some soils in the Tasman District are known to be copper deficient (Chittenden *et al.*, 1966). Auckland and Waikato orchards had significantly higher copper concentrations than Tasman orchards.

The concentrations of copper reported in Table 4.8 are consistent with those previously reported for horticultural properties in NZ. These include mean copper levels of 126 and 87 mg kg^{-1} in soils on two Central Otago apricot orchards (Morgan and Bowden, 1993) and 60 to 480 mg kg^{-1} in 19 NZ orchard soils (Holland and Solomona, 1999). The range of copper levels for vineyards in the Auckland (70–152 mg kg^{-1}) and Waikato (22–115 mg kg^{-1}) regions is in keeping with the range (25–105 mg kg^{-1}) reported by Taylor (1999) for five vineyards in the Waikato region. Hogg (2000) measured copper levels of 15.2 and 353 mg kg^{-1} in glasshouse soils from the Auckland region.

Table 4.8: Copper concentrations (mg kg^{-1}) measured in soil samples collected from the Auckland, Tasman and Waikato.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	21–490	10–123	242–523		Range		15–111	22–161
	Mean	224	58	344		Mean		41	86
	S.D.	179	43	109		S.D.		40	45
	Geo mean	137	43	330		Geo mean		31	75
	Median	207	60	303		Median		20	80
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Range	7–253		31–76	(historic)	Range		7–40	
	Mean	78		47		Mean		27	
	S.D.	90		25		S.D.		13	
	Geo mean	42		43		Geo mean		23	
	Median	46		33		Median		30	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	21–137	6–67	26–112		Range	8–45	5–55	12–33
	Mean	51	40	60		Mean	22	19	20
	S.D.	39	23	31		S.D.	20	21	7
	Geo mean	42	31	54		Geo mean	17	12	19
	Median	38	37	44		Median	13	8	18
Vineyards	N	5	0	7	Background[d]	N	58	0	7
	Range	70–152		22–115		Range	1–45		8–30
	Mean	107		71		Mean	13		18
	S.D.	37		32		S.D.	10		8
	Geo mean	102		64		Geo mean	9		16
	Median	99		81		Median	10		20

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

A wide range of copper values for horticultural soils have been reported in the international literature. Copper levels in Tasmanian and South Australian orchards were in the range of 11 to 320 mg kg^{-1} (Merry *et al.*, 1983); in the range of 100 to 1500 mg kg^{-1} in Champagne vineyards (Besnard *et al.*, 2001); and up to a maximum level of 945 mg kg^{-1} in Italian vineyard soils (Deluisa *et al.*,1996). Pietrzak and McPhail (2004) reported mean copper concentrations in the range 9 to 229 mg kg^{-1} for the top 1 cm of Victorian vineyards. In comparison, the maximum copper level measured in a vineyard in this survey was 152 mg kg^{-1}. Copper values on some horticultural properties in the surveyed NZ regions exceeded those in rural soils in the Dutch province of Zeeland (<5–65 mg kg^{-1}) (Van Gaans *et al.*, 1995). Copper values in 3045 agricultural soils from the USA ranged from <0.6 to 495 mg kg^{-1} with a geometric mean of 18 mg kg^{-1} (Holmgren *et al.*, 1993). Market garden copper values are comparable with those reported for vegetable cropping fields in British Columbia (13–120 mg kg^{-1}) (De Pieri *et al.*, 1996).

Copper levels on 48% of the horticultural sites sampled exceeded or were indistinguishable from the CCME copper guideline value of 63 mg kg^{-1} and 17% of horticultural samples exceeded the Dutch intervention value of 190 mg kg^{-1}. Six orchard samples exceeded the NZ value of 370 mg kg^{-1} which is based on soil ingestion only. The elevated levels of copper measured on some properties have implications for the ongoing use of copper containing formulations in NZ as they are comparable with levels demonstrated to have negative effects in ecotoxicity tests. For example O'Halloran and Booth (as cited in Markich *et al.*, 2002) calculated an EC_{50} of 500 mg kg^{-1} for decreased shoot weight in a 14 day seedling growth test and an EC_{50} of 114 mg kg^{-1} for a 28 day adult growth test with *A. caliginosa*. As part of this work, Gaw *et al.* (2003b) reported negative impacts of increasing copper concentration on soil microbial properties for the Auckland orchard soils.

4.3.2.4 LEAD

Lead levels in Auckland, Tasman and Waikato horticultural soils (glasshouse sites excluded) generally followed the order orchards>vineyards>market-gardens and were

significantly higher in horticultural soils (8–243 mg kg^{-1}) than in grazing soils (6–43 mg kg^{-1}) (Table 4.9). In Auckland and Tasman regions, orchard soils had significantly ($p<0.05$) greater lead levels than market garden soils. The elevated lead levels in orchard samples are most likely due to the use of lead arsenate for the control of chewing insects as across all three regions, there was a highly significant correlation ($p<0.001$) between log lead and log arsenic concentrations in orchard soils. Yokel and Delistraty (2003) also reported a positive and significant correlation between lead and arsenic in former orchard soils in Washington.

Although, higher lead levels were generally found in Tasman orchard soils (geometric mean 108 mg kg^{-1}), there were no significant differences ($p<0.05$) in orchard soil lead levels between the three regions. The results reported here for background sites and grazing sites agree with the range for median lead values (6–16 mg kg^{-1}) reported by Longhurst *et al.* (2004) for NZ agricultural soils.

The range of lead levels reported in Table 4.9 for NZ orchards (overall 11–251 mg kg^{-1}) is lower than that reported for old orchard soils in New York State (1.48–720 mg kg^{-1} (Merwin *et al.*, 1994) and comparable to the mean of 170 mg kg^{-1} reported for orchard soils in Tasmania and South Australia (Merry *et al.*, 1983). Lead levels in some NZ horticultural soils, particularly orchards, exceed those found in rural soils in the Dutch province of Zeeland (<5–104 mg kg^{-1}) (Van Gaans *et al.*, 1995) and agricultural soils in the USA (<1.0–135 mg kg^{-1}) (Holmgren *et al.*, 1993).

The lead levels measured on NZ market garden properties (8–48 mg kg^{-1}) are comparable with those (5–26 mg kg^{-1}) reported for vegetable properties in British Columbia (De Pieri *et al.*, 1997). The range of lead levels measured in Auckland and Waikato glasshouse soils is similar to that measured (15–405 mg kg^{-1}) for glasshouse soils in Almería, Spain (Gil *et al.*, 2004). As discussed in Chapter Three, the extreme lead value of 1250 mg kg^{-1} measured in an Auckland glasshouse is most probably due to lead-based paint flakes in the sample.

Table 4.9: Lead concentrations (mg kg^{-1} DW) measured in soil samples collected from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	11–178	15–243	14–251		Range		8–14	17–46
	Mean	76	149	77		Mean		11	28
	S.D.	54	85	102		S.D.		2	10
	Geo mean	59	108	36		Geo mean		10	27
	Median	59	165	18		Median		10	29
Glasshouses	N	10		3	Tobacco	N	0	5	0
	Range	6–1250	0	21–68	(historic)	Range		5–16	
	Mean	175		38		Mean		10	
	S.D.	384		26		S.D.		5	
	Geo mean	45		33		Geo mean		9	
	Median	34		26		Median		8	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	14–46	8–21	21–48		Range	16–21	6–11	12–43
	Mean	24	13	33		Mean	18	9	24
	S.D.	10	5	9		S.D.	3	2	13
	Geo mean	23	13	32		Geo mean	18	8	21
	Median	21	12	35		Median	18	8	18
Vineyards	N	5	0	7	Background[d]	N	58	0	7
	Range	31–88		22–51		Range	<1.5–56		11–56
	Mean	62		35		Mean	16		29
	S.D.	25		10		S.D.	12		18
	Geo mean	57		34		Geo mean	12		24
	Median	62		37		Median	13		24

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

Lead levels on 20% of horticultural properties including 11 orchards, three glasshouses (Auckland) and two vineyards (Auckland) were indistinguishable from, or exceeded, the CCME EQG guideline value of 70 mg kg^{-1} and nine orchard samples also exceeded the Dutch target value of 85 mg kg^{-1}. No orchard exceeded the intervention value of 530 mg kg^{-1}. One Auckland glasshouse sample containing 1250 mg kg^{-1} lead was twice the Dutch intervention value.

Lead inputs to NZ soils are expected to be much lower now than previously, as lead based agrichemicals are no longer registered for use and lead additives were withdrawn from petrol in 1996. The results of the NZ total dietary surveys since 1982 show a continuing reduction in lead levels in food which has been partially attributed to the removal of leaded petrol (Vannoort *et al.,* 2000). Current residual inputs would include lead as a contaminant of certain fertilisers and sewage sludges.

4.3.2.5 MERCURY

Overall mercury levels measured in horticultural soils (<0.1–1.1 mg kg^{-1}) were low relative to guideline values. The highest mercury levels were measured in orchard soils from the Tasman and Waikato regions (Table 4.10) and at 1.1 mg kg^{-1} were approximately five times the average background level for soil mercury in NZ soils. Mercury containing pesticides were used in orchards in NZ (The New Zealand Fruitgrowers Federation, 1967). However, in the Auckland region, mercury levels in orchard soils were similar to those in market garden soils and the mercury levels for all landuses are within the range reported for background soils in the Auckland region (<0.03–0.42 mg kg^{-1}) (ARC, 2001).

Table 4.10: Mercury concentrations (mg kg^{-1}) measured in soil samples collected from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	<0.1–0.3	<0.1–0.5	<0.1–1.1		Range		<0.1	0.2
	Mean	0.1	0.2	0.4		Mean		<0.1	0.2
	S.D.	0.1	0.2	0.4		S.D.		0	0
	Geo mean	0.1	0.1	0.3		Geo mean		<0.1	0.2
	Median	<0.1	<0.1	0.3		Median		<0.1	0.2
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Range	<0.1–0.3		<0.1–0.1		Range		<0.1	
	Mean	0.1		<0.1		Mean		<0.1	
	S.D.	0.1		0.03		S.D.		0	
	Geo mean	0.1		<0.1		Geo mean		<0.1	
	Median	0.1		<0.1		Median		<0.1	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	0.1–0.4	<0.1	<0.1–0.4		Range	<0.1	<0.1	<0.1–0.3
	Mean	0.2	<0.1	0.3		Mean	<0.1	<0.1	0.1
	S.D.	0.1	0	0.1		S.D.	0	0	0.1
	Geo mean	0.2	<0.1	0.2		Geo mean	<0.1	<0.1	0.1
	Median	0.2	<0.1	0.3		Median	<0.1	<0.1	0.1
Vineyards	N	5	0	7	Background[d]	N	58	5	7
	Range	<0.1–0.2		<0.1–0.2		Range	<0.03–0.42		<0.1–0.4
	Mean	0.2		0.1		Mean	0.13		0.2
	S.D.	0.1		0.1		S.D.	0.10		0.1
	Geo mean	0.2		0.1		Geo mean	0.10		0.2
	Median	0.2		0.1		Median	0.11		0.2

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

The mercury levels (<0.1–1.1 mg kg^{-1}) measured in horticultural soils in the three NZ regions sampled are comparable with those measured in soil samples from 13 orchards in New York State (0.01–0.55 mg kg^{-1}) by Merwin *et al.,* (1994), and in rural soils in the Dutch province of Zeeland (<0.2–0.7 mg kg^{-1}) by Van Gaans *et al.,* (1995). Mercury levels in cropping soils did not exceed either the CCME guideline value of 6.6 mg kg^{-1} or the Dutch intervention value of 10 mg kg^{-1} and are unlikely to increase significantly, as industrial sources of mercury to the NZ atmosphere are limited, and mercury containing pesticides are no longer in use.

4.3.2.6 TIN

Tin levels measured in horticultural soils were in the range <1 to 7 mg kg^{-1} (Table 4.11). Organotin compounds were registered in NZ for use as fungicides and acaricides (Long, 1983) and are a probable source of the elevated tin levels measured in some soils. In the Tasman district, tin was only detected in orchard soils (1–4 mg kg^{-1}), in the Waikato region the highest levels were measured in orchard soils (3–7 mg kg^{-1}), while in the Auckland region similar concentrations of tin were detected in market garden (1–3 mg kg^{-1}), and orchard soils (<1–4 mg kg^{-1}).

The similarity of these levels may be a result of soil type rather than spray regime. None of the soil samples collected in the Auckland region exceeded the background levels reported for tin (0.4–3.9 mg kg^{-1}) (ARC, 2001). Tin levels on five Waikato orchard sites and one Auckland glasshouse were indistinguishable from, or exceeded, the CCME EQG for tin (5 mg kg^{-1}) and it is possible that tin levels may increase on some properties as tin based formulations (e.g. fenbutatin oxide and azocyclotin) are still registered for use in NZ.

Table 4.11: Tin concentrations (mg kg^{-1}).measured in soil samples collected from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	<1–4	1–4	3–7		Range		<1	1–4
	Mean	2	3	5		Mean		<1	2
	S.D.	1	1	2		S.D.		0	1
	Geo mean	1	2	5		Geo mean		<1	2
	Median	1	3	5		Median		<1	2
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Range	<1–8		1–2		Range		<1	
	Mean	2		2		Mean		<1	
	S.D.	2		0.6		S.D.		0	
	Geo mean	2		2		Geo mean		<1	
	Median	1		2		Median		<1	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	1–3	<1	2–3		Range	<1	<1	<1–3
	Mean	2	<1	3		Mean	<1	<1	1
	S.D.	1	0	0.5		S.D.	0	0	1
	Geo mean	2	<1	3		Geo mean	<1	<1	1
	Median	3	<1	3		Median	<1	<1	1
Vineyards	N	5	0	7	Background[d]	N	58	0	7
	Range	<1–3		<1–4		Range	0.4–3.9		<1–2
	Mean	2		2		Mean	0.9		1
	S.D.	1		1		S.D.	0.9		0.6
	Geo mean	1		2		Geo mean	0.7		1
	Median	1		2		Median	0.4		1

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

4.3.2.7 ZINC

Zinc levels in horticultural soils ranged from 9 to 236 mg kg^{-1} (Table 4.12) with one extreme value of 510 mg kg^{-1} measured in an Auckland glasshouse soil. There were no consistent differences in zinc levels among horticultural landuse category and region across the three regions. Overall zinc levels on horticultural sites were not significantly different from grazing sites. The geometric means for soil zinc residues for surveyed landuses in the Waikato region (64–108 mg kg^{-1}) exceeded the geometric mean for background soils (44 mg kg^{-1}), whereas the geometric means obtained for zinc levels in the Auckland region were comparable to reported background levels in non volcanic soils of this region (geometric mean of 45 mg kg^{-1}, range: 9–179 mg kg^{-1}) (ARC, 2001). Longhurst *et al.* (2004) reported that median zinc in NZ agricultural soils ranged from 42 to 91 mg kg^{-1} depending on soil type. The moderately elevated zinc levels on some properties may have several possible sources. For example, fertilizer use has been implicated in elevated zinc levels in NZ soils (Taylor and Percival, 2001) and zinc is an ingredient in some fungicides such as Zineb (Long, 1983).

The highest zinc value (510 mg kg^{-1}) measured in a cropping area was collected from an Auckland glasshouse. This sample contained paint flakes and had an elevated lead level of 1250 mg kg^{-1}, hence it is possible that in this case the elevated zinc is derived from a pigment in the paint. Mielke *et al.* (2001) reported median zinc levels of 31000 mg kg^{-1} in paint samples collected from houses in New Orleans. Galvanised materials used to construct the glasshouse may be a further source of zinc.

Few of the investigations of horticultural soils reported in the literature include zinc data. Zinc levels within the range 7 to 95 mg kg^{-1} have been reported for rural soils in the Netherlands (Van Gaans *et al.,* 1995), levels from 25 to 260 mg kg^{-1} have been reported for nine market garden properties in NSW, Australia (NSW EPA, 1995), levels of <3.0 to 264 mg kg^{-1} have been found in American agricultural soils (Holmgren *et al.,*1993) and mean levels ranging from 43 to 107 mg kg^{-1} have been measured in some British Columbian vegetable cropping soils (De Pieri *et al.,* 1996).

Table 4.12: Zinc concentrations (mg kg^{-1}) measured in soil samples collected from the Auckland, Tasman and Waikato regions.

Landuse	Parameter	AKL[a]	TDC[b]	WKT[c]	Landuse	Parameter	AKL	TDC	WKT
Orchards	N	12	5	7	Berryfruit	N	0	5	7
	Range	22–236	33–97	35–197		Range		11–77	90–158
	Mean	62	70	119		Mean		46	121
	S.D.	59	27	48		S.D.		24	28
	Geo mean	48	65	108		Geo mean		39	118
	Median	41	78	121		Median		45	119
Glasshouses	N	10	0	3	Tobacco	N	0	5	0
	Range	9–510		83–111		Range		34–77	
	Mean	133		93		Mean		63	
	S.D.	144		16		S.D.		17	
	Geo mean	78		92		Geo mean		61	
	Median	114		85		Median		67	
Market gardens	N	8	5	7	Grazing	N	3	5	7
	Range	31–109	32–138	65–100		Range	21–80	24–133	40–99
	Mean	62	90	78		Mean	42	59	67
	S.D.	26	40	13		S.D.	33	46	23
	Geo mean	58	81	77		Geo mean	34	47	64
	Median	52	84	72		Median	24	38	58
Vineyards	N	5	0	7	Background[d]	N	58	0	7
	Range	32–152		35–149		Range	9–179		29–74
	Mean	77		89		Mean	59		46
	S.D.	45		39		S.D.	39		17
	Geo mean	68		81		Geo mean	45		44
	Median	66		91		Median	52		43

[a]Auckland, [b]Tasman, [c]Waikato, [d]Background trace element data for non volcanic soils in the Auckland region (ARC, 2001).

Zinc levels in one Auckland orchard and one Auckland glasshouse soil sample exceeded the CCME agricultural EQG of 200 mg kg^{-1} and in the case of the glasshouse, paint flakes were the most probable source of zinc. However, 12 horticultural and one grazing samples either exceed or are indistinguishable from the Dutch target value for zinc of 140 mg kg^{-1}. As several zinc-based fungicides and fertilizers are still widely used in NZ, zinc levels in productive soils are likely to increase. Recent NZ estimates suggests that under a typical spray regime, potatoes, grapes and onions receive substantial loadings of zinc from zinc-containing pesticides, estimated at 7.5 kg ha^{-1} yr^{-1} (potatoes), 4.5 kg ha^{-1} yr^{-1} (grapes), and 2.4 kg ha^{-1} yr^{-1} (onions) (Mills *et al.*, 2004).

4.3.3 CORRELATION ANALYSES

The dataset was analysed for possible relationships between contaminants, and contaminants and key soils properties using Pearson's correlation coefficients on log-normalised data (except pH). The dataset was broken down into several sub datasets defined by both region and landuse to determine whether there were any region specific or landuse specific relationships. The subsets of data used to calculate each correlation matrix are listed in Table 4.13. Each landuse was also analysed by region, e.g. Tasman market gardens. Berryfruit sites were not included as some of these sites were developed after 1975 and tobacco sites from the Tasman District were also excluded from the dataset as they are an historical landuse and these sites have been converted to a variety of other landuses. Each correlation matrix was calculated twice; once for trace elements and once for ΣDDT. The ΣDDT data for the three regions were not combined as two extraction methodologies were used to analyse the samples. All samples were included for trace elements and samples in which ΣDDT was not detected were excluded from the dataset when determining the correlation coefficients between ΣDDT, and trace elements and soil characteristics. Possible relationships between ΣDDT and associated degradation products, and trace elements and soil properties are explored separately in Chapter Five. A selection of the correlation matrices for each region are presented in Appendix A.

Table 4.13: Description of datasets used to calculate the correlation matrices of Pearson's correlation coefficients.

	Auckland				Tasman			Waikato			
	M	**O**	**V**	**G**	**M**	**O**	**G**	**M**	**O**	**V**	**G**
All horticulture	X	X	X		X	X		X	X	X	
AKL horticulture	X	X	X								
TDC horticulture					X	X					
WKT horticulture								X	X	X	
Glasshouses				X							
Market gardens	X				X			X			
Orchards		X				X			X		
Vineyards			X							X	
Grazing				X			X				X

M=Market garden, O=Orchard, V=Vineyard, G=Grazing.

Correlation analysis is a measure of numerical association and can be a useful tool to explore datasets. The presence of a significant correlation only means that the two variables are related in some way and does not mean that there is a cause and effect relationship between the variables (French and Lindley, 2000).

4.3.3.1 CORRELATIONS BETWEEN CONTAMINANTS

Across all regions (Table 4.14), there were highly significant relationships ($p<0.001$) between the log copper levels and both log lead and log arsenic levels in horticultural soils. These significant relationships can be explained by the long-term concurrent use of copper-based fungicides and lead-arsenate pesticides. Similar, significant relationships ($p<0.05$) between copper and arsenic and lead (log values) were also observed within each region for orchard samples and in Auckland glasshouse samples Strong correlations between arsenic, copper and lead have also been reported for Australian (Merry *et al.*, 1983) and Japanese apple orchard soils (Aoyoma and Nagumo, 1997).

Elevated levels of cadmium and zinc in NZ soils have been linked to applications of superphosphate fertilisers (e.g. Taylor and Percival, 2001). In a national survey of NZ agricultural topsoils, Longhurst *et al.* (2004) reported that the cadmium content of pastoral topsoils was highly correlated with total P concentrations. This relationship

has also been reported in several other studies of cadmium in NZ pastoral soils (Roberts *et al.,* 1994; Taylor, 1997; Gray *et al.*, 2000). However, this relationship may not always extend to the plant available P pool in horticultural soils, measured as Olsen P. In this work, significant correlations between cadmium and Olsen P concentrations (log values) were found only for market gardens ($p<0.05$) and Auckland glasshouses ($p<0.001$). Olsen P correlated with copper ($p<0.05$) and zinc ($p<0.02$) in the Tasman samples ($p<0.01$), with arsenic in orchard ($p<0.01$), vineyard ($p<0.01$), and market garden samples ($p<0.01$), with copper and lead ($p<0.05$) in Auckland vineyard samples, and with copper in Auckland orchard ($p<0.01$) and market garden ($p<0.02$) samples. Arsenic levels in orchards and market gardens and Auckland glasshouses (log values) were significantly ($p<0.01$) correlated with soil Olsen P concentrations.

Table 4.14: Pearson's correlation coefficients for log values of trace elements and selected soil characteristics for the combined three regions horticultural soils dataset (n = 56). Significant correlations are presented in bold.

	Fe	Mn	As	Cd	Cu	Pb	Zn	%TOC	pH	CEC	OlsenP
Fe	1										
Mn	**0.784*** **	1									
As	0.007	-0.004	1								
Cd	0.024	**0.286***	0.161	1							
Cu	0.006	0.129	**0.492*** **	**0.39** **	1						
Pb	-0.219	-0.182	**0.778*** **	0.199	**0.498*** **	1					
Zn	**0.41** **	**0.46*** **	**0.308***	**0.322***	**0.415** **	0.148	1				
%TOC	**-0.454*** **	**-0.338** **	-0.138	0.242	0.266	-0.011	-0.015	1			
pH	0.067	0.082	0.156	0.224	-0.014	-0.03	0.277*	-0.295*	1		
CEC	-0.098	-0.09	0.078	0.217	**0.447*** **	0.108	0.231	**0.638*** **	-0.059	1	
OlsenP	**0.301***	0.211	**0.418** **	0.064	0.131	0.209	0.193	**-0.568*** **	**0.277***	-0.219	1

*p<0.05, ** p<0.01, ***p<0.001

There was a significant correlation ($p<0.02$) between log cadmium and log zinc across the horticultural soil samples. Zinc and cadmium concentrations (log values) were also correlated in Auckland glasshouse soils. Jinadasa *et al.* (1997) reported a significant correlation between log Zn and log Cd levels in vegetable soils from Greater Sydney. Some degree of correlation between zinc and cadmium may be expected because these trace elements are geochemically associated (Bewers *et al.*, 1987). As a result of this association, agrichemicals containing zinc are likely to be a further source of cadmium since zinc ores can also contain cadmium (Kim, 2005). Similar, but highly significant relationships ($p<0.001$), were also observed between log cadmium and log copper concentrations in the datasets for horticultural soils from all three regions, the Waikato region, and Auckland vineyards and a quite significant correlation in Auckland glasshouses ($p<0.02$).

Several correlations were found for log values of copper and zinc; across the data for the 3 regions combined ($p<0.01$), in orchard soils ($p<0.02$), in market garden soils ($p<0.01$) and in Auckland glasshouse soils ($p<0.01$). A similar correlation between copper and zinc has been reported for Italian orchards and vineyards (Paoletti *et al.*, 1998).

Overall, inter-correlations between lead, arsenic and copper are likely to be due mainly to routine historical use of lead arsenate insecticide and copper fungicides on these soils, rather than natural associations. This is because concentrations of these elements tend to be elevated above their background values more often than not, and therefore the correlations observed can be ascribed to anthropogenic input.

Log values of ΣDDT correlated with several of the trace elements of concern. Again, the correlations observed are most likely due to concurrent use of agrichemicals rather than causative relationships. In the Auckland region, ΣDDT levels in horticultural soils correlated with arsenic ($p<0.01$), copper ($p<0.001$) and lead ($p<0.001$); with arsenic ($p<0.05$), cadmium ($p<0.02$), copper ($p<0.01$) and lead ($p<0.01$) in orchards; and with zinc ($p<0.05$) in vineyards. In the Waikato horticultural soils dataset ΣDDT correlated with cadmium ($p<0.01$) and copper ($p<0.001$); and with copper ($p<0.02$) and lead ($p<0.05$) in Waikato orchards. ΣDDT

was correlated with arsenic ($p<0.02$), cadmium ($p<0.05$) and lead ($p<0.001$) in Tasman horticultural soils and with lead in Tasman market gardens ($p<0.02$).

4.3.3.2 CORRELATIONS BETWEEN SOIL CHARACTERISTICS AND CONTAMINANT LEVELS

The organic matter content (%TOC), the cation exchange capacity (CEC), textural class, and pH along with iron and manganese oxides have been identified as important parameters controlling the fate and behaviour of contaminants in soils. The dataset was explored to see whether variability in contaminant levels could be explained by soil characteristics. Key soil characteristics for soil samples collected in the Auckland and Waikato regions and Tasman District are presented in Tables 4.15 to 4.17. Significant relationships between key soil characteristics and contaminant levels (ΣDDT, arsenic, cadmium, copper, lead and zinc) were determined on log normalised data (excluding pH) using Pearson's correlation coefficients.

ΣDDT

Pearson's correlation coefficient analysis was used to explore possible relationships between ΣDDT and key soil properties. Soil organic matter can be an important adsorption phase for organic compounds including ΣDDT. However, in agreement with the results of Harner *et al.* (1999) and Kannan *et al.* (2003) no correlation was found between %TOC and ΣDDT concentration. This contrasts with the results of Aigner *et al.* (1998) and Szeto and Price (1991) who reported that ΣDDT levels were highest in soils with high organic matter content. However, both of these studies included muck soils which have organic carbon contents (~ 30 to 60%) much greater than those measured in the current study. No other relationships were observed between soil characteristics and ΣDDT in the current study. This finding indicates that the ΣDDT concentrations measured in the soils (Table 4.4) are predominantly the result of the application history rather than soil characteristics.

Table 4.15: Soil characteristics for Auckland samples collected from properties developed after 1975. Units are mg kg^{-1} for Fe, Mn and Olsen P, and mmoles/100 g for CEC.

Landuse	Parameter	Fe	Mn	%TOC	pH	CEC	Olsen P
Glasshouses	Range	4870–41100	18–2410	0.5–6.8	4.71–6.45	1–32	6–223
n = 10	Mean	20100	844	3.8	5.73	23	130
	S.D.	13000	919	1.9	0.48	9	80
	Geo mean	15800	312	3.1	5.71	18	85
	Median	17600	343	3.7	5.85	25	151
Market garden	Range	6610–65500	133–4570	1.6–10.8	5.95–6.33	8–30	75–212
n = 8	Mean	35600	1650	4.2	6.13	21	110
	S.D.	20500	1550	3.6	0.15	7	47
	Geo mean	27600	849	3.1	6.13	20	103
	Median	39600	1650	2.6	6.11	22	88
Orchard	Range	6930–36100	88–1600	3.4–15.9	5.28–6.39	17–36	14–174
n =12	Mean	15200	400	5.9	5.82	25	82
	S.D.	8740	537	3.4	0.44	6	47
	Geo mean	13000	225	5.3	5.80	24	67
	Median	14100	176	4.8	5.82	24	82
Vineyards	Range	7260–19600	125–328	3.8–7.2	5.92–6.34	22–26	27–154
n = 5	Mean	13100	204	5.3	6.10	24	70
	S.D.	5190	76	1.3	0.18	2	54
	Geo mean	12300	194	5.2	6.09	24	56
	Median	11400	187	5.5	6.02	24	38
Grazing	Range	6800–34000	107–1850	3.7–5.1	5.41–5.78	6–27	18–48
n = 3	Mean	18300	1212	4.6	5.63	14	31
	S.D.	14100	961	0.8	0.20	11	16
	Geo mean	14800	693	4.5	5.63	12	28
	Median	14000	1680	4.9	5.71	10	27

Table 4.16: Soil characteristics for Tasman samples (n = 5 for each landuse). Units are mg kg^{-1} for Fe, Mn and Olsen P, and mmoles/100 g for CEC.

Landuse	Parameter	Fe	Mn	%TOC	pH	CEC	Olsen P	%clay	%silt	%sand
Berryfruit	Range	2940–28400	90–671	1.3–3.6	5.60–6.32	11–23	27–101	12–24	49–65	14–38
	Mean	14900	326	2.4	5.85	15	60	17	57	26
	S.D.	9280	214	0.9	0.29	5	33	5	6	10
	Geo mean	11900	270	2.3	5.85	15	52	16	57	24
	Median	13900	299	2.2	5.72	14	49	16	57	29
Market garden	Range	12200–44200	294–1250	1.5–5.4	5.33–6.46	15–26	15–240	22–32	47–59	13–30
	Mean	36700	928	3.3	6.00	19	117	26	53	21
	S.D.	13800	375	1.5	0.46	4	98	4	4	7
	Geo mean	33300	832	3.0	5.99	18	79	26	53	20
	Median	43200	1040	3.0	5.95	17	65	25	52	22
Orchard	Range	5020–26300	76–340	1.7–2.7	6.17–6.63	13–19	82–107	8–20	54–63	19–38
	Mean	11400	177	2.2	6.35	16	95	16	58	26
	S.D.	8500	103	0.38	0.17	2	11	5	4	8
	Geo mean	9610	155	2.2	6.35	16	95	16	58	25
	Median	8480	170	2.1	6.31	16	97	19	57	23
Tobacco (historic)	Range	10500–24800	240–559	1.6–2.5	5.76–6.30	6–16	54–93	7–30	36–65	5–52
	Mean	18100	408	2.1	6.14	10	83	17	50	33
	S.D.	5700	132	0.4	0.22	5	17	8	12	19
	Geo mean	17300	390	2.1	6.13	9	82	15	49	26
	Median	19900	388	2.3	6.23	8	90	17	52	30
Grazing	Range	6260–37400	93–978	1.9–5.7	5.55–6.24	15–33	7–52	13–29	42–67	8–45
	Mean	20700	456	4.1	5.96	22	37	21	57	23
	S.D.	14500	422	1.5	0.28	7	18	7	9	15
	Geo mean	16500	289	3.8	5.95	21	31	20	56	18
	Median	14300	274	3.8	5.96	21	45	21	57	21

Table 4.17: Soil characteristics for Waikato soil samples. Units are mg kg^{-1} for Fe, Mn and Olsen P, and mmoles/100g for CEC.

Landuse	N	Parameter	Fe	Mn	%TOC	pH	CEC	Olsen P	%clay	%silt	%sand
Berryfruit	7	Range	16300–34400	864–3190	3.7–7.3	5.56–6.11	8–25	37–103	8–13	67–79	13–22
		Mean	22400	1920	5.9	5.96	14	56	9	74	17
		S.D.	5940	888	1.2	0.25	7	22	2	5	4
		Geo mean	21800	1730	5.8	5.96	13	53	9	74	16
		Median	21500	1760	5.7	6.05	11	52	9	75	17
Glasshouses	3	Range	10200–18400	494–1310	3.3–5.5	5.02–5.88	6–20	55–114	11–19	60–67	14–25
		Mean	14900	932	4.8	5.41	15	84	15	64	21
		S.D.	4220	411	1.2	0.44	8	30	4	4	6
		Geo mean	14400	863	4.6	5.40	13	80	15	64	20
		Median	16000	993	5.4	5.33	19	82	15	66	24
Market garden	7	Range	18100–56100	2230–6090	1.6–2.9	6.04–6.46	13–21	90–180	12–32	64–74	4–18
		Mean	40400	4080	2.1	6.19	16	135	23	69	8
		S.D.	13790	1403	0.5	0.15	3	34	7	4	6
		Geo mean	38022	3870	2.1	6.19	16	131	22	69	7
		Median	44100	3720	1.9	6.13	17	138	23	70	5
Orchard	7	Range	12700–34000	682–6140	3.9–8.4	5.81–6.26	19–27	24–126	6–17	61–77	12–26
		Mean	18800	2110	6.7	6.04	25	55	11	70	19
		S.D.	7170	1990	1.7	0.18	3	33	4	5	5
		Geo mean	17900	1530	6.5	6.04	25	49	10	70	18
		Median	17900	1240	6.9	5.97	26	44	12	71	18
Vineyard	7	Range	22000–33500	329–1900	2.4–5.9	6.02–6.30	14–34	25–123	9–21	52–76	11–35
		Mean	25500	992	3.9	6.15	24	74	16	65	19
		S.D.	3810	594	1.3	0.09	7	37	4	9	9
		Geo mean	25300	840	3.7	6.15	23	65	15	65	18
		Median	24300	795	3.6	6.16	24	72	15	67	15

Table 4.17: Continued.

Landuse	N	Parameter	Fe	Mn	%TOC	pH	CEC	Olsen P	%clay	%silt	%sand
Grazing	7	Range	11600–45200	487–1740	4.0–9.4	5.50–6.02	14–24	10–70	7–17	45–79	9–45
		Mean	19700	1020	6.0	5.80	18	41	12	65	23
		S.D.	11400	461	2.0	0.18	3	18	4	11	11
		Geo mean	17900	938	5.7	5.79	18	36	11	64	21
		Median	16200	863	5.4	5.86	18	45	11	66	21
Background	7	Range	6350–40600	461–2100	2.5–13.8	4.64–5.96	12–25	6–45	6–18	60–75	9–23
		Mean	20600	1120	6.5	5.40	20	20	14	71	16
		S.D.	12700	648	4.7	0.44	5	14	5	7	6
		Geo mean	17200	980	5.2	5.38	20	16	13	70	15
		Median	19300	843	3.9	5.45	22	14	17	71	15

TRACE ELEMENTS

Iron and Manganese content

Iron and manganese hydroxides can be important sorption phases for trace elements in soils due to their reactivity and high surface area (Adriano, 2001; Kabata-Pendias and Pendias, 2001). Log values of manganese and iron were highly ($p<0.001$) correlated with each other in the following datasets; all orchards, Tasman horticultural soil samples, all Auckland samples (glasshouses excluded), all market garden soils and all vineyard soils ($p<0.01$). This consistent iron-manganese correlation is likely to reflect the natural geochemical association between these two elements (Kabata-Pendias and Pendias, 2001), although the possible presence of contaminant iron and manganese in these soils is not ruled out. Ferrous sulphate is registered for use in NZ as an herbicide and fungicide, and manganese is present in a commonly-used dithiocarbamate fungicide (Mancozeb).

In recent sampling of 30 non-horticultural sites (predominantly pastoral soils with some forest soils, sampled to 10 cm depth), Environment Waikato reported geometric means and ranges of 12500 mg kg^{-1} (1020–56900 mg kg^{-1}) for iron and 560 mg kg^{-1} (24–4700 mg kg^{-1}) for manganese (Kim *pers comm.*, 2005). The fact that market gardens and orchards in this work (Tables 4.15 to 4.17) show manganese above the upper end of the range typical for pastoral or forest soils suggests that a component of manganese in market garden and orchard soils is likely to be anthropogenic. This is supported by the highly significant relationship between zinc and manganese (Table 4.14). The only manganese containing fungicide (Mancozeb, for which 18 separate products are licensed) also contains zinc.

Copper ($p<0.02$) and zinc ($p<0.05$) in orchard soils are moderately correlated with iron and similar relationships were observed for copper and zinc in market garden soils ($p<0.02$) (all log values). Iron levels in Waikato market garden soils correlated with cadmium ($p<0.02$), arsenic ($p<0.001$) and lead ($p<0.05$). Zinc and iron levels were correlated in both the Tasman ($p<0.05$) and Auckland ($p<0.02$) datasets. However, when the data for the three regions were combined there was no correlation

between any trace element contaminant and iron. Generally significant relationships between iron or manganese and trace elements were only observed when trace element concentrations were low indicating that (under these circumstances) the dominant source of the trace elements may be the soil parent material rather than anthropogenic.

There were only a limited number of significant correlations between manganese and other trace elements. These included; very significant correlations ($p<0.01$) with log values of cadmium, copper and zinc in orchard soils, and cadmium in Waikato vineyards. When the data for the three regions were combined, manganese was significantly correlated with cadmium ($p<0.05$) and zinc ($p<0.001$) (all log values). As noted above, the highly significant manganese-zinc correlation may be a result of the use of dithiocarbamates. The correlation with cadmium may be, at least partially due to cadmium being an impurity in zinc products. Zinc-containing sprays have been cited as a possible secondary source of cadmium (after superphosphate fertiliser) on some horticultural soils, and may contain Zn:Cd at a 500:1 ratio (Kim, 2005). The manganese-copper correlation is likely to be due to concurrent or sequential use of manganese-based and copper-based fungicides over the same soil.

Cation exchange capacity

The CEC of a soil is proportional to the surface area of the soil components and is influenced by the organic matter content, the type and amount of clay as well as iron, manganese and aluminium oxides (Adriano, 2001). Across the data for the three regions combined there was a highly significant correlation ($p<0.001$) between the CEC and the copper level (log values). The soil copper concentrations in vegetable cropping fields in the Lower Fraser Valley, British Columbia were also significantly correlated with CEC (De Pieri *et al.*, 1996) and Akinnifesi *et al.* (2005) measured higher CECs in cocoa orchard soils which had received copper based fungicides. Cadmium and CEC were significantly correlated in both Auckland ($p<0.02$) and Waikato ($p<0.05$) orchard soils. Similarly, cadmium levels in British Columbian

vegetable fields increased with increasing CEC although the relationship was "*not strictly linear*" (De Pieri *et al.,* 1997).

Soil organic carbon

Soil organic matter can be an important sorption phase for trace elements and many trace elements have a high affinity for soil organic matter (Adriano, 2001). For example, Soon and Abboud (1990) measured trace element content and key soil properties in north western Alberta soils and concluded that soil organic matter was an important variable which affected the levels and distribution of trace elements.

There was no consistent relationship between trace elements and %TOC. The %TOC and soil copper concentrations were negatively correlated for market gardens ($p<0.05$) but positively correlated in vineyard soils ($p<0.01$). No other relationships were found between %TOC and soil trace element concentration. Similarly, no correlation was observed between trace element concentration and soil organic matter content in a comparison of urban and agricultural Argentinian soils (Lavado *et al.*, 1998). However, copper levels in vegetable soils from the Lower Fraser Valley, British Columbia correlated with soil carbon content (loss on ignition) and cadmium and lead levels tended to increase with organic matter content (De Pieri *et al.*, 1996, 1997). Lead levels in Spanish glasshouse soils also correlated with soil organic matter (Gil *et al.,* 2004).

When the data for the three regions was combined, there was a highly significant relationship between CEC and %TOC ($p<0.001$). This relationship between CEC and %TOC is expected as the soil organic matter is a contributing factor to the CEC (Kabata-Pendias, 2004). A similar relationship was observed between the organic matter content and CEC in vegetable cropping soils in the Lower Fraser Valley, British Columbia (De Pieri *et al.*, 1996). As discussed previously, there were significant relationships between soil copper concentration and the CEC. It is possible that the copper levels are inhibiting the degradation of organic matter and hence increasing the CEC. Trace element contamination can inhibit the microbial

decomposer community in soil causing organic matter to accumulate (Doelman *et al.*, 1994; Sauvé *et al.*, 1997).

Soil pH

Soil pH is a key parameter controlling the solubility and mobility of trace elements in soil (Kabata-Pendias and Pendias, 2001). However, the pH levels in horticultural soils are altered to ensure that they are within the optimum range for the current crop. The pH ranges for horticultural soils within each region were; Auckland (5.3–6.6), Waikato (5.8–6.5) and Tasman (5.3–6.6) and are within the optimum ranges for fruit and vegetable crops under NZ conditions which vary from 4.8 to 7.5 depending on the crop (McLaren and Cameron,1996).

Log zinc concentration positively correlated with pH in the horticultural soils ($p<0.05$) when orchard, market garden and vineyard data for the three regions was combined, whereas there was a negative correlation between log zinc and pH in Auckland market garden soils ($p<0.02$). Soil pH levels also positively correlated with log cadmium and log copper in vineyard ($p<0.02$) and with log cadmium, and log copper ($p<0.05$) in market garden soils. Lime is used to raise the pH in horticultural soils to improve productivity; however an increased soil pH increases cation adsorption, and reduces mobilisation and leaching. In comparison, no relationships between trace element concentration and pH were found in a survey of Argentinian urban and agricultural soils (Lavado *et al.*, 1998). The marginal relationships for these NZ surface soils suggest that under NZ's more acidic average soil conditions there may be some loss of cationic contaminants through leaching.

Soil particle size

The soil particle size distribution was determined for the Waikato and Tasman soils. Log values of arsenic, cadmium and copper positively correlated with the %clay ($p<0.02$) in Waikato market garden soils, but there was a negative correlation

between copper content and %clay in Waikato vineyard soils ($p<0.05$). Similarly there was a negative correlation ($p<0.02$) between lead concentration and %clay in Tasman horticultural soils. Contrasting relationships between trace elements and soil particle size have also been reported for other studies. For example, there was no correlation between textural class and lead content in Michigan orchard soils (Francek, 1997). In comparison, Holmgren *et al.* (1993) measured cadmium, lead, zinc, copper and nickel levels in agricultural soils of the United States of America and reported that trace element levels tended to increase with increasing clay content. Similarly lead levels in Spanish glasshouse soils correlated with the clay fraction (Gil *et al.*, 2004).

Influence of soil management on residual contaminant levels

A contributing factor to the limited number of correlations observed between contaminants concentrations and soil properties may be that horticultural soils are continually altered. For example, the pH is often adjusted by applying lime and other soil amendments including organic matter (e.g. composts and manures) are also added to cropping soils. Roberts *et al.* (1995) found that the pH levels of South Auckland market garden soils were higher and that the organic matter content lower relative to soils under native vegetation. It was common practice to cultivate soils on NZ horticultural properties to control weeds and this may be a further contributing factor to the overall lack of strong and consistent correlations between soil properties and trace element levels. Cultivating or tilling the soil regularly would mix the topsoil and the underlying soil (Soon and Abboud, 1990) and on some Tasman orchards caused severe erosion of the topsoil (Leighs, 1977). In addition some properties were deep ripped (ploughed to greater depths) to improve drainage. The small size of the datasets may have masked significant correlations between soil characteristics and contaminant levels.

4.3.4 SOURCE OF CONTAMINANTS

It is probable that the main source of the contaminants reported here for NZ horticultural soils is the historical use of agrichemicals and soil amendments including fertilizers. Across the three regions combined, ΣDDT, copper, lead and arsenic levels in horticultural soils were significantly higher ($p<0.05$) than in grazing soils which receive limited inputs of pesticides and generally lower applications of fertilisers and lime. In addition, across the three regions sampled there were significant correlations ($p<0.02$) between log ΣDDT and the log values of arsenic, cadmium, copper and lead indicating a common source of contamination. The significant correlations observed between Olsen P and trace elements also indicate that the residual trace element levels are a result of the use of agrichemicals.

The data presented in Section 4.3.3.2 for the three regions indicates that factors controlling the levels and types of contaminants found in soil on a horticultural property include the length of time a property was in use, the types of agrichemicals used and their application rates rather than soil characteristics. Although it was not possible to obtain a full site history for all properties; residual contaminant levels tended to be higher on properties particularly orchards which had been in use for the longest time periods. For the Auckland samples, the mean values arsenic, copper, lead and zinc were significantly higher in the pre-1975 sites than for those horticultural sites developed after 1975 (Section 3.3.5). ΣDDT was not detected on horticultural sites developed after 1975. Similar trends have been observed in Ontario apple orchards where arsenic, copper and lead levels increased with age of the orchard (Frank *et al.,* 1976) and in Tanzanian coffee orchards where soil copper concentrations increased with age of coffee trees (Loland and Singh, 2004). The NSW EPA (1995) identified varying disposal practices as a further contributing factor to the variability in residual contamination levels found among properties.

Other potential contributing sources of trace elements include discharges from heavy industry and vehicle emissions although current air-borne inputs into rural NZ soils are known to be low. As NZ has few high temperature industrial processes, Gray *et*

al. (2003) concluded that the most likely atmospheric sources of metal inputs into rural NZ soils was from dry deposition of wind-blown fine soil and dust. Recent air-borne ΣDDT inputs are unlikely to be significant as the ΣDDT levels in NZ air do not exceed 50 pg m^{-3} (Ministry for the Environment, 1998). Currently biosolids, another potential source of contaminants, are not routinely used as soil amendments in NZ; however, this may change in the future (Ministry for the Environment, 2002).

4.3.5 REGULATORY IMPLICATIONS

Around the world, and in NZ, there is intense interest in residual pesticides on horticultural land driven, at least in part, by an increased demand for conversion into residential properties. In recent years, human health guideline values for contaminants in residential soils have been developed, and many of these have been adopted by environmental protection agencies and local authorities as regulatory tools. In the context of a subdivision, such guideline values are used to assess the suitability of the land being subdivided for its designated purpose. Guideline values are generally designed to protect against chronic exposure and are derived on the basis of exposure to residents by all potential routes, including adventitious ingestion of soil and dust, uptake of contaminants in home-grown produce, inhalation, and dermal absorption.

Of the contaminants detected in this work the concentrations of arsenic and ΣDDT were most problematic in terms of their potential to exceed residential soil guideline values for human health on some properties. In NZ, the guideline value for arsenic for protection of human health in residential soil is 30 mg kg^{-1} (Ministry for the Environment and Ministry of Health, 1997). In this study, 7 of the 24 (or 29%) orchard soils tested had arsenic levels indistinguishable from, or exceeding, 30 mg kg^{-1}, making them potentially unsuitable for residential subdivision without remedial action (adjusted for 95% error). There is currently no national NZ guideline value for ΣDDT in residential soil and where a value needs to be employed to assess the suitability of land for subdivision, this is selected by the territorial authority. The results presented here also have implications for managing land which is remaining in horticultural use. Levels of cadmium, copper, tin and zinc on some properties already exceed soil quality criteria, which are ecotoxicity-based indicating that continuing

inputs of these trace elements will need to be managed in order to protect the soil resource.

4.4 CONCLUSIONS

The levels of ΣDDT, arsenic, lead, cadmium, copper, tin and zinc measured in Waikato and Tasman horticultural soils were comparable to those measured in Auckland horticultural soils and confirm that the routine historical use of agrichemicals may result in residual contamination in NZ horticultural soils. The results for the Tasman and Waikato regions confirm that DDT and its degradation products DDE and DDD are the predominant persistent organochlorine pesticide residues likely to be detected in NZ horticultural soils.

Across the three regions, arsenic, copper, lead, and ΣDDT concentrations were significantly greater ($p<0.05$) in horticultural soils than in grazing soils whereas for cadmium and zinc there was no significant difference between concentrations measured in horticultural and grazing soils. Generally orchard soils contained the highest concentrations of arsenic, copper, lead, and ΣDDT.

Levels of ΣDDT, arsenic, lead, cadmium, copper, tin and zinc frequently exceeded soil quality criteria and hence have implications for future use and management of horticultural land. These results have implications for the on-going use of agrichemicals as concentrations of cadmium, copper, tin and zinc in some samples exceeded ecotoxicity based soil criteria. However, there are currently limited soil ecotoxicity data available for NZ.

The limited number of correlations between soil characteristics and contaminant concentrations indicates that the frequency of application of agrichemicals and the time period that a property was active, are the main factors which determine levels of residual contamination.

5 PERSISTENCE OF DDT, DDE AND DDD IN NZ HORTICULTURAL SOILS

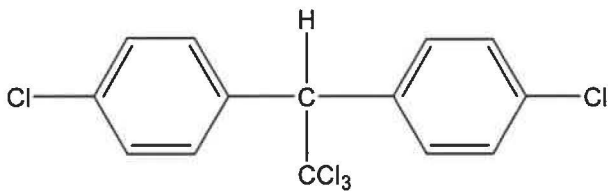
5.1 INTRODUCTION

Elevated ΣDDT concentrations were detected in soils from horticultural properties in the Auckland, Tasman and Waikato regions (Chapter Four). A preliminary evaluation of the results for the Auckland region revealed abnormally low *p,p'*-DDE: *p,p'*-DDT ratios (0.03–5.6) for some sites compared to those previously reported for historic pastoral applications of DDT in NZ (Boul, 1996). The ratios suggested either inhibited degradation of *p,p'*-DDE to *p,p'*-DDT or recent use of DDT and prompted a more detailed assessment of the predominant residues of DDT present in New Zealand horticultural soils and the factors which may influence their persistence. It was also of interest to determine if bound residues of ΣDDT were present in NZ horticultural soils.

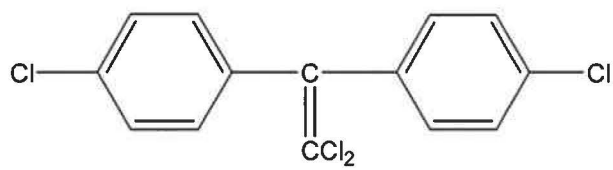
Technical grade DDT was applied in a variety of formulations typically containing *p,p'*-DDT (77.1%), *o,p'*-DDT (14.9 %), *p,p'*-DDD (0.3 %), *o,p'*-DDD (0.1 %), *p,p'*-DDE(4 %), *o,p'*-DDE (0.1 %) and unidentified components (3.5%) (WHO, 1989). The structures of the *p,p'* isomers of DDT, DDE and DDD are shown in Figure 5.1. Once deposited into the soil environment, hydrophobic organic contaminants such as ΣDDT can become bound to and/or sequestered within the soil matrix (Luthy *et al.*, 1997; Semple *et al.*, 2003) making them less available for both microbial and abiotic degradation. Additionally ΣDDT residues may be lost from soil through a variety of mechanisms including volatilisation, erosion and runoff, as well as through biotic and abiotic degradation (Boul, 1995).

The predominant degradation products of DDT in soil are reportedly DDD (1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethane) and DDE (1,1-dichloro-2,2-*bis*(*p*-chlorophenyl)ethylene) with DDE being formed in aerobic environments through dehydrochlorination and DDD being formed in anaerobic environments by reductive

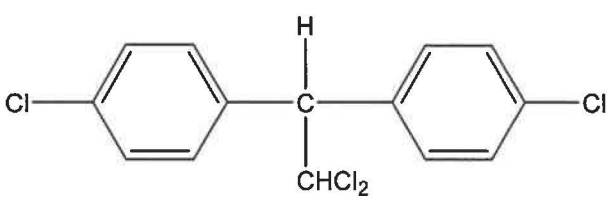
dechlorination (Aislabie *et al.*, 1997). A range of half-lives have been proposed for DDT in soil including 20 to 30 years in Maine forest soils (Dimond and Owen, 1996), 15 to 50 years in Australian soils (Ambrose, 2000) and 10 years in Canterbury (NZ) soils (Boul *et al.*, 1994).



p,p'-DDT



p,p'-DDE



p,p'-DDD

Figure 5.1: Structures of the *p,p'*-isomers of DDT, DDE and DDD.

Possible mechanisms of abiotic degradation of DDT in soil have been reviewed by Boul (1995). Mechanisms which were identified in laboratory trials to degrade DDT and its metabolites include degradation catalysed by metallic ions (e.g. iron), dehydrochlorination by high temperatures and photochemical degradation (Boul, 1995). Organic matter, moisture, clay content and pH were also found to play a role in the abiotic degradation of DDT residues in soil. However, Boul (1995) stated that some of the conditions needed to facilitate these abiotic processes may not be

common in NZ soils. DDT has been reported to be more persistent under acidic conditions (Wolfe *et al.*, 1977; Andréa *et al.*, 1994).

The microbial degradation of DDT in soils has been extensively reviewed by Aislabie *et al.* (1997) and Foght *et al.* (2001). Bacteria and fungi have been reported to degrade DDT and DDD in pure cultures and in soil, but only a few organisms capable of degrading DDE have been identified (Foght *et al.*, 2001). The biodegradation of DDT and its degradation products is thought to be co-metabolic, meaning that the micro-organisms involved do not gain any nutrients or energy for growth from the process and require an alternate carbon source as a growth substrate. Micro-organisms which can degrade DDT are either able to dechlorinate DDT or produce enzymes which can degrade chlorinated organics. Factors which may enhance the persistence of DDT in soils include its low water solubility as well as the presence of chlorine substituents (Foght *et al.*, 2001).

Organic compounds including pesticides can form non-extractable or bound residues in soil. Bound residues have been defined as follows: –

> "*Bound residues represent compounds in soil, plant or animal which persist in the matrix in the form of the parent substance or its metabolite(s) after extractions. The extraction method must not substantially change the compounds themselves or the structure of the matrix...*" (Fuhr *et al.*, 1998).

These bound residues can result from entrapment in the mineral and organic fractions of the soil matrix as well as from the formation of chemical bonds to the soil matrix. Further details on the formation of bound organic residues are available from Gevao *et al.* (2000), Northcott and Jones (2000) and Barraclough *et al.* (2005). The environmental significance of bound residues is not well understood (Barraclough *et al.*, 2005). There are concerns that bound residues may in the future become available for release as a consequence of changes to the soil matrix by for example, degradation of organic matter (Gevao *et al.*, 2000; Northcott and Jones, 2000) or through biological activity (Verma and Pillai, 1991). Additionally if these bound residues are bioavailable to terrestrial organisms, exposure and uptake could potentially be underestimated by conventional solvent extraction techniques.

Several studies have suggested that DDT and its metabolites DDE and DDD can form bound or non-extractable residues in soil to a limited extent (e.g. Lichtenstein *et al.*, 1977; Agarwal *et al.*, 1994, Andréa *et al.*, 1994; Boul, 1996). These findings may not be applicable to horticultural soils as the majority of reported studies used single applications of radiolabelled DDT and the soils were aged over much shorter time scales than would have occurred in orchard soils. In addition it has been reported that repeat applications of ^{14}C-DDT reduced the formation of bound residues in soil (Samuel and Pillai, 1991).

By definition, conventional solvent extractions do not extract strongly bound or sequestered organic contaminant residues from soil. Instead harsh extraction conditions including extreme pH (acidic and alkaline) and base saponification which degrade the structure of the soil matrix can be used to release bound residues (Northcott and Jones, 2000). Soil treatments which have been used to release bound DDT residues from soil and sediments include sulphuric acid (Singh and Agarwal, 1995), methanolic KOH hydrolysis, BBr_3-treatment, RuO_4-oxidation and pyrolysis gas chromatography (Schwarzbauer *et al.*, 2003). Combustion has also been used to release bound radiolabelled compounds (Boul, 1996).

The continued presence of ΣDDT in horticultural soils poses a potential hazard to ecological receptors and humans. It has been assumed that the concentration of ΣDDT in NZ soils will slowly decrease over time reducing the potential for exposure. A series of investigations were undertaken to identify factors likely to be contributing to the inhibited degradation of *p,p'*-DDT, to determine the fraction of *p,p'*-DDT and ΣDDT likely to be available for microbial degradation and to investigate the presence of bound residues of ΣDDT.

5.1.1 OBJECTIVES

The principle objectives of the work reported in this Chapter were to investigate:

- The presence and relative abundance of the *o,p'*- and *p,p'*- isomers of DDT, DDE and DDD in horticultural soils.

- Relationships between concentrations of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD, and trace elements and soil characteristics.

- The proportion of *p,p'*-DDT available for microbial oxidation using a persulfate oxidation process.

- The presence of bound residues of ΣDDT, *p,p'*-DDT, *p,p'*-DDE in orchard soils.

5.2 METHODS SUMMARY

A more detailed investigation of the data presented in Chapter Four was undertaken to identify: a) the predominant isomers of DDE, DDT and DDD present in horticultural soils for selected landuses and b) soil properties and trace elements which may be contributing to the unexpectedly low *p,p'*-DDE:*p,p'*-DDT ratios. The datasets utilised for further analysis were previously described in Chapter Four (Section 4.3.4). Tobacco, glasshouse sites and berryfruit sites were excluded from the analyses undertaken for this chapter. Tobacco sites were excluded as they are an historical landuse. Berryfruit sites were not included as some of these sites were developed after 1975 and glasshouse sites were excluded due to limited numbers.

5.2.1 PERSULFATE OXIDATION

The persulfate oxidation method developed by Cuypers *et al.* (2000) was used to estimate the fraction of *p,p'*-DDT that was available for microbial degradation in six orchard soils. It was not possible to directly measure microbial degradation of *p,p'*-DDT in soil due to its long half-life.

The orchard soils collected for the worm and seedling bioassays were utilised for the persulfate oxidation and sequential extraction experiments. Full descriptions of the methods used in this chapter are presented in Chapter Two (Sections 2.5.2, 2.5.3 and 2.5.4).

5.2.2 RESIDUES OF ΣDDT

The presence of bound residues of *p,p'*-DDT and its metabolites DDE and DDD in six orchard soils with a range of ΣDDT concentrations was investigated using a three stage sequential extraction procedure (Chapter Two, Section 2.5.4). The soil samples were initially extracted with acetone:hexane before being exhaustively extracted with dichloromethane followed by a base saponification step with methanolic KOH and subsequent extraction of the saponified soil with acetone:hexane. Three of the samples were extracted with and without the addition of H_3PO_4 in step one to determine whether H_3PO_4 also released bound residues of DDT.

5.2.3 DATA REPORTING CONDITIONS

Statistical analyses were carried out using customized Microsoft Excel worksheets and Data Desk 6.0 (Data Description Inc., New York). In this chapter, where contaminant concentrations were less than the detection limit, half of the detection limit was assigned for statistical purposes.

Significant differences in *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDE:*p,p'*-DDT ratios between regions and selected horticultural landuses were determined using analysis of variance (ANOVA) on ranked data. When significant differences were observed; differences between landuses and/or regions were determined by Tukey's multiple comparison test.

Pearson's correlation analysis on log-normalised data (excluding pH and *p,p'*-DDE:*p,p'*-DDT ratio) was used to determine significant relationships between the *p,p'*-DDE:*p,p'*-DDT ratio and concentrations of selected contaminants (arsenic, cadmium, copper, lead, zinc and ΣDDT) and soil properties.

5.3 RESULTS AND DISCUSSION

5.3.1 RESIDUES OF DDT MEASURED IN NZ HORTICULTURAL SOILS

The soil samples collected from the Auckland, Tasman and Waikato regions were analysed for the *o,p'*-and *p,p'*- iso mers of DDT, DDE and DDD. The summary statistics for the individual DDT residues are presented by region for selected landuses in Tables 5.1 to 5.3. Results for ΣDDT were also reported and discussed in Chapter Four. The *p,p'*-isomers of DDE, DDT and DDD were the predominant residues measured in horticultural soils accounting for 72 to 98% of ΣDDT. Concentrations of *p,p'*-DDD accounted for less than 12.5% of ΣDDT.

Only a limited number of significant differences in *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE concentration between landuses were identified. In both the Waikato and Tasman Districts, *p,p'*-DDD concentrations in orchards were significantly greater than in market gardens. For the Tasman samples, *p,p'*-DDT concentrations in orchards were significantly greater than in market gardens. Similarly concentrations of *p,p'*-DDT, *p,p'*-DDD and *p,p'*-DDE were significantly greater in Waikato orchard soils than in vineyard soils.

Table 5.1: Auckland soils: Concentrations (mg kg^{-1}) of *o,p'*and *p,p'*- isomers of DDT, DDE and DDD and ΣDDT.

Landuse	N	Parameter	*o,p'*-DDD	*o,p'*-DDE	*o,p'*-DDT	*p,p'*-DDD	*p,p'*-DDE	*p,p'*-DDT	ΣDDT[a]
Market garden	8	Min	<0.005	<0.005	0.006	<0.005	0.039	0.025	0.09
		Max	0.010	0.011	0.048	0.029	0.530	0.34	0.91
		Mean	0.005	0.005	0.018	0.010	0.145	0.133	0.32
		S.D.	0.003	0.003	0.013	0.009	0.166	0.118	0.28
		Geo mean	<0.005	<0.005	0.015	0.007	0.095	0.096	0.24
		Median	<0.005	<0.005	0.015	0.007	0.080	0.084	0.19
Orchards	12	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Max	0.430	0.084	1.10	1.10	6.70	15.0	24.4
		Mean	0.079	0.016	0.203	0.199	1.69	2.52	4.71
		S.D.	0.125	0.024	0.335	0.314	2.01	4.29	7.01
		Geo mean	0.019	0.008	0.036	0.039	0.25	0.196	0.68
		Median	0.029	0.006	0.066	0.102	1.28	0.720	2.23
Vineyard	5	Min	<0.005	<0.005	0.005	0.007	0.41	0.047	0.26
		Max	0.074	0.015	0.17	0.057	1.30	1.30	2.84
		Mean	0.023	0.007	0.08	0.050	0.708	0.501	1.36
		S.D.	0.029	0.005	0.066	0.043	0.472	0.490	1.04
		Geo mean	0.013	0.006	0.047	0.035	0.570	0.305	1.01
		Median	0.009	0.006	0.09	0.033	0.540	0.390	1.10
Grazing	3	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Max	<0.005	<0.005	<0.005	<0.005	0.009	<0.005	<0.03
		Mean	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	<0.03
		S.D.	0	0	0	0	0.003	0	0.003
		Geo mean	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Median	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03

[a]Sum of of *o,p'* and *p,p'*-DDT, DDE and DDD (values < 0.005 included as half of LOD), ΣDDT determined using multi-residue pesticide screen GC-ECD and GC-MS methodology.

Table 5.2: Tasman soils: Concentrations (mg kg^{-1}) of *o,p'*and *p,p'*- isomers of DDT, DDE and DDD and ΣDDT.

Landuse	N	Parameter	*o,p'*-DDD	*o,p'*-DDE	*o,p'*-DDT	*p,p'*- DDD	*p,p'*- DDE	*p,p'*- DDT	ΣDDT[a]
Market garden	5	Min	<0.005	<0.005	<0.005	<0.005	0.036	0.013	0.07
		Max	0.016	0.010	0.111	0.040	0.574	0.407	1.16
		Mean	0.006	<0.005	0.025	0.010	0.171	0.102	0.32
		S.D.	0.006	0.003	0.048	0.017	0.228	0.171	0.47
		Geo mean	<0.005	<0.005	0.006	0.005	0.098	0.042	0.17
		Median	<0.005	<0.005	<0.005	<0.005	0.061	0.025	0.12
Orchard	5	Min	0.037	0.005	0.068	0.082	0.831	0.462	1.49
		Max	0.117	0.018	0.367	0.286	4.27	2.08	7.14
		Mean	0.075	0.011	0.196	0.155	2.04	1.19	3.66
		S.D.	0.033	0.005	0.127	0.083	1.35	0.629	2.18
		Geo mean	0.069	0.010	0.159	0.140	1.74	1.05	3.19
		Median	0.084	0.010	0.201	0.120	1.49	1.24	3.09
Grazing	5	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Max	0.008	<0.005	0.097	0.061	0.638	0.565	1.30
		Mean	<0.005	<0.005	0.028	0.021	0.242	0.193	0.49
		S.D.	0.002	0	0.041	0.025	0.302	0.256	0.61
		Geo mean	<0.005	<0.005	0.010	0.010	0.063	0.037	0.16
		Median	<0.005	<0.005	<0.005	0.008	0.049	0.039	0.11

[a]Sum of of *o,p'* and *p,p'*-DDT, DDE and DDD (values <0.005 included as half of LOD).

Table 5.3: Waikato soils: Concentrations (mg kg^{-1}) of *o,p'* and *p,p'*- isomers of DDT, DDE and DDD and ΣDDT.

Landuse	N	Parameter	*o,p'*-DDD	*o,p'*-DDE	*o,p'*-DDT	*p,p'*-DDD	*p,p'*-DDE	*p,p'*-DDT	ΣDDT[a]
Market garden	7	Min	<0.005	<0.005	<0.005	<0.005	0.016	0.040	0.04
		Max	0.04	0.013	0.145	0.104	1.11	1.01	1.68
		Mean	0.011	0.005	0.045	0.024	0.296	0.245	0.63
		S.D.	0.015	0.004	0.057	0.036	0.379	0.351	0.70
		Geo mean	0.006	<0.005	0.017	0.011	0.148	0.107	0.32
		Median	<0.005	<0.005	0.015	0.011	0.165	0.151	0.39
Orchard	7	Min	<0.005	<0.005	<0.005	0.007	0.274	0.076	0.37
		Max	0.892	0.058	2.84	1.79	12.9	16.0	34.5
		Mean	0.157	0.018	0.512	0.353	3.83	3.52	8.39
		S.D.	0.325	0.020	1.04	0.640	4.50	5.71	12.1
		Geo mean	0.034	0.011	0.090	0.099	1.88	0.971	3.20
		Median	0.045	0.011	0.108	0.100	1.97	0.988	3.22
Vineyard	7	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Max	<0.005	<0.005	0.048	0.028	0.457	0.719	1.26
		Mean	<0.005	<0.005	0.009	0.007	0.092	0.115	0.23
		S.D.	0	0	0.017	0.009	0.163	0.266	0.46
		Geo mean	<0.005	<0.005	0.004	0.004	0.032	0.021	0.08
		Median	<0.005	<0.005	<0.005	<0.005	0.032	0.013	0.06
Grazing	7	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Max	<0.005	<0.005	0.020	0.016	0.223	0.551	0.75
		Mean	<0.005	<0.005	0.008	0.005	0.096	0.113	0.23
		S.D.	0	0	0.007	0.005	0.104	0.199	0.28
		Geo mean	<0.005	<0.005	0.006	<0.005	0.027	0.023	0.09
		Median	<0.005	<0.005	<0.005	<0.005	0.05	0.019	0.08
Background	7	Min	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Max	<0.005	<0.005	<0.005	<0.005	0.015	0.018	0.05
		Mean	<0.005	<0.005	<0.005	<0.005	0.005	0.005	<0.03
		S.D.	0	0	0	0	0.005	0.006	0.01
		Geo mean	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03
		Median	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03

[a]Sum of of *o,p'* and *p,p'*-DDT, DDE and DDD (values < 0.005 included as half of LOD).

5.3.1.1 RATIOS OF DDE:DDT IN HORTICULTURAL SOILS

p,p'-DDE and *p,p'*-DDT were the predominant DDT residues measured in horticultural soils (Tables 5.1 to 5.3). Under aerobic conditions, DDT in soil is progressively degraded by a range of biotic and abiotic processes to form DDE (Boul, 1995) and it would be anticipated that in horticultural soils, historical *p,p'*-DDE levels would exceed *p,p'*-DDT levels. However, *p,p'*-DDT levels were equal to or exceeded *p,p'*-DDE concentrations in 24 and 30% of the horticultural samples collected from Waikato and Auckland regions respectively. Across the three regions, the contribution of *p,p'*-DDT to ΣDDT ranged from 8 to 80%. These results differ from studies of agricultural soils in NZ in which *p,p'*-DDE tended to be the predominant DDT residue (Burke *et al.*, 1993; Boul *et al.*, 1994). Similarly, the proportions of DDE and DDT measured in soil from North Island dairy farms is reported to be 80% DDE and 20% DDT (Mashlan, 2001).

The DDE:DDT ratio, or its reciprocal value, has been used to determine whether residual DDT levels result from recent or historical inputs of DDT (e.g. Hitch and Day 1992; Strandberg *et al.*, 1998; Harner *et al.*, 1999; Tavares *et al.*, 1999). The ratio of *p,p'*-DDE to *p,p'*-DDT in formulations of technical DDT has been reported to be approximately 0.05 (WHO, 1989).

The *p,p'*-DDE:*p,p'*-DDT ratios in the NZ horticultural soils ranged from 0.4 to 9.7 (Table 5.4). There were no significant differences ($p<0.05$) in mean *p,p'*-DDE: *p,p'*-DDT ratios between either region or landuse. A comparable range of *p,p'*-DDE:*p,p'*-DDT ratios have been reported or can be calculated from data reported elsewhere for horticultural soils (Table 5.5). Boul *et al.* (1994) reported *p,p'*-DDE: *p,p'*-DDT ratios of 1.33 to 3.05 for irrigated pasture.

Table 5.4: Range of *p,p'*-DDE:*p,p'*-DDT ratios measured in selected horticultural and grazing soils.

Landuse	Auckland	Tasman	Waikato
Market gardens	0.4–2.7	1.3–9.7	0.4–1.6
Orchards	0.4–5.2	1.2–2.1	0.8–3.6
Vineyards[a]	1.0–4.0	-	0.6–2.5
Grazing[b]	-	1.1–7.3	0.3–2.6

[a]Vineyards were only sampled in Auckland and Waikato regions, [b]Ratio not calculated as *p,p'*-DDT was not detected in any Auckland grazing sample.

Higher concentrations of *p,p'*-DDT than *p,p'*-DDE have been reported for surveys of cropping and orchard soils in Canada, China, the United States of America and Europe (Table 5.5). Higher *p,p'*-DDT than *p,p'*-DDE levels have also been reported in German agricultural soils (Manz *et al.*, 2001) and soil samples from active citrus orchards in California had higher proportions of DDT relative to ΣDDT than soils used for dry farming (Odermatt *et al.*, 1993). The mean ratio of *p,p'*-DDT:ΣDDT in Romanian rural soils was 0.49 (Covaci *et al.*, 2001) and the ratio of *p,p'*-DDT:ΣDDT in Belgian, Greek, Italian and Romanian soils ranged from 0.17 to 0.66 (ΣDDT 0.6–561 μg kg^{-1}) (Covaci *et al.*, 2002).

Table 5.5: *p,p'*-DDE:*p,p'*-DDT ratios reported elsewhere for horticultural soils.

Landuse	ΣDDT (mg kg^{-1})	DDE:DDT	Reference
Orchard soils, Hawkes Bay	0.23–15.33	0.48–1.59[b]	Macaskill (2004)
Orchard soils, Canada	<0.12–14.4	1.10–1.36	Harris *et al.* (2000)
Agricultural soils, Beijing	0.08–2.2	0.02–166, median 2.63[a]	Zhu *et al.* (2005)
Canadian cropping soils	nd -70	0.15–1.07[b]	Webber and Wang (1995)
Cropping soils, US corn belt	<LOQ–11.8	0.15–2[a]	Aigner *et al.* (1998)
Cropping soils, Alabama	-	0.67–2.56[a]	Harner *et al.* (1999)
Fields, USA	3–7.8[b]	0.09–5[b]	Hitch and Day (1992)

[a]Inverse of reported DDT:DDE ratio, [b]Calculated from reported *p,p'*-DDT and *p,p'*-DDE concentrations.

It is unlikely the *p,p'*-DDE: *p,p'*-DDT ratios presented in Table 5.4 result from recent use of DDT as DDT was deregistered for use in 1989 in NZ (Buckland *et al.*, 1998). Furthermore DDT and its degradation products were not found on any of the Auckland horticultural properties developed after 1975 (Section 3.3.3, Chapter Three), concentrations of DDT measured in breast milk are declining (Bates *et al.*,

2002) and DDT was not detected in fruit and vegetables analysed as part of the 1997/98 Total Diet Survey (Cressey *et al.*, 2000).

The lower than anticipated *p,p'*-DDE:*p,p'*-DDT ratios therefore contradict a commonly held assumption (e.g. Rahm *et al.*, 2005) that elevated concentrations of DDT compared to DDE will only be found if there has been recent use of DDT. These results suggest that degradation of DDT to DDE may have been inhibited, or that DDT is being degraded via a pathway that not does lead to an accumulation of DDE.

Pearson's correlation analysis was used to investigate possible relationships between soil characteristics, trace element concentrations (arsenic, cadmium, copper, lead, tin and zinc) and the *p,p'*-DDE:*p,p'*-DDT ratios. Within each region, no significant relationships ($p<0.02$) were observed between the ratios of *p,p'*-DDE:*p,p'*-DDT and soil characteristics (% TOC, Olsen P, iron, manganese and CEC). Additionally for the Waikato and Tasman samples there were no significant correlations between the *p,p'*-DDE:*p,p'*-DDT ratio and soil particle size. NZ soils generally have lower pH levels than other countries and hence it is possible that the degradation of DDT is slower than reported elsewhere however there were no significant relationships between soil pH and the *p,p'*-DDE: *p,p'*-DDT ratio.

Significant negative correlations were found between the *p,p'*-DDE:*p,p'*-DDT ratios and copper in the Auckland ($p<0.001$) and Waikato ($p<0.02$) orchard soils (Figure 5.2). These results suggest that copper may be a contributing factor to inhibited degradation of *p,p'*-DDT to *p,p'*-DDE in orchard soils. Additionally in the Auckland orchard samples, there were also significant negative correlations ($p<0.02$) between the *p,p'*-DDE:*p,p'*-DDT ratio and, log arsenic, log cadmium and log lead concentrations. However, these observed relationships may be due to correlations between trace elements as discussed in Section 4.3.5 (Chapter Four).

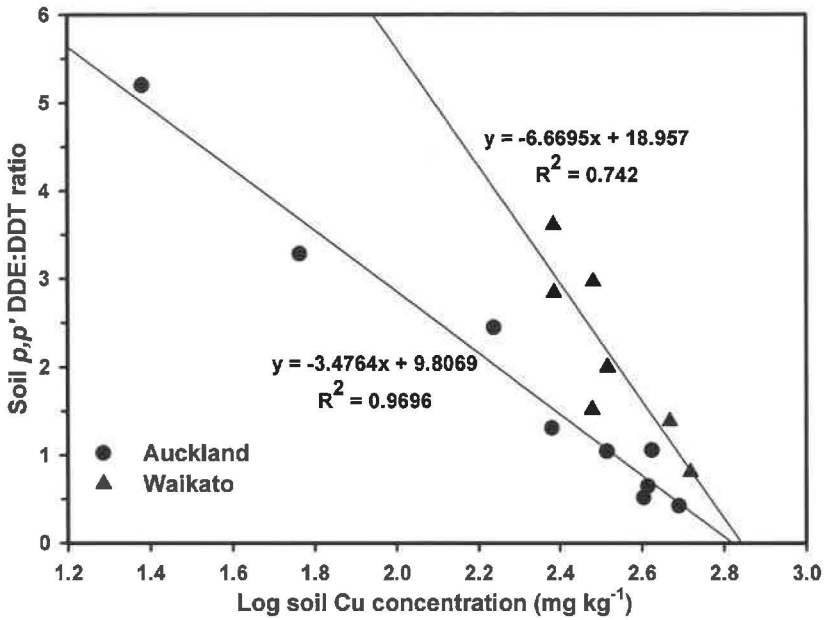


Figure 5.2: Relationship between soil copper concentration (mg kg^{-1}) and the *p,p'*-DDE:*p,p'*-DDT ratio for pip and stonefruit orchard soils in the Auckand and Waikato regions.

5.3.1.2 POSSIBLE MECHANISMS FOR INHIBITED DEGRADATION OF DDT TO DDE IN ORCHARD SOILS

The highly significant relationship between copper and the *p,p'*-DDE:*p,p'*-DDT ratio in orchard soils from the Auckland and Waikato regions (see Figure 5.2) support a hypothesis that co-contamination with elevated levels of copper, and possibly other trace elements, may have inhibited the biotic degradation of DDT in orchard soils. It has been previously reported that high levels of arsenic inhibit the degradation of DDT to DDD in Australian cattle dip soils with DDT:DDD and DDT:DDE ratios increasing with increasing arsenic concentration (Van Zwieten *et al.*, 2003). Copper has been reported to inhibit microbial degradation of a range organic compounds including phenanthrene (Sokhn *et al.*, 2001), coumaphos (Jindal *et al.*, 2000) and thiobencarb (Gunasekara *et al.*, 2005). Copper concentrations in all of the Waikato and 60% of the Auckland orchards exceeded the Oak Ridge National Laboratory Ecological Soil Screening Level (microbes) for copper of 100 mg kg^{-1} (Efroymson *et*

al., 1997a). Therefore it is plausible that either the soil micro-organisms that were able to co-metabolise DDT in NZ horticultural soils have been replaced by trace element tolerant communities or that the presence of copper inhibits the ability of the micro-organisms to co-metabolise *p,p'*-DDT to *p,p'*-DDE.

Micro-organisms have been shown to be sensitive to soil contamination, in particular contamination with heavy metals (Bååth, 1989; Giller *et al.*, 1998). Mechanisms of heavy metal toxicity to micro-organisms include functional disturbance, denaturing of proteins and destruction of the integrity of cell membranes (Leita *et al.* 1995). Reported adverse effects of trace element contamination in soils include reduced nutrient cycling (Kandeler *et al.*, 1996), inhibition of degradation of organic matter (Doelman *et al.*, 1994; Sauvé *et al.*, 1997) and changes in microbial diversity (Giller *et al.*, 1998; Zelles *et al.*, 1994) as well as inhibition of the microbial degradation of organic compounds (Giller *et al.*, 1998; Sandrin and Maier, 2003). Trace elements can also determine the type of degradative enzyme expressed by micro-organisms (Lidstrom and Semrau, 1995; Murrell *et al.*, 2000) and it has been hypothesised that micro-organisms may lose the ability to degrade organic compounds as a consequence of developing metal resistance (Doelman *et al.*, 1994).

High residual concentrations of DDT may provide further explanation of the observed low *p,p'*-DDE:*p,p'*-DDT ratios. DDT and its metabolites DDE and DDD have been shown to be toxic to soil microflora at elevated concentrations (Megharaj *et al.*, 1999) and DDT has been reported to be more persistent at high concentrations in soil (Beyer and Gish, 1980) and sediment (Pereira *et al.*, 1996). There were significant correlations between log ΣDDT concentration and *p,p'*-DDE:*p,p'*-DDT ratio in Waikato ($p<0.001$) and Auckland ($p<0.001$) orchard soils. However, the ΣDDT concentrations in NZ horticultural soils (excluding one possible outlier measured in an Auckland glasshouse soil) of <0.03 to 34.5 mg kg^{-1} (Tables 5.1 to 5.3) are below the level reported to inhibit microbial activity.

Tate (1974) found that DDT at concentrations up to 100 mg kg^{-1} did not affect microbial respiration in a NZ pasture soil. Additionally, the EC_{50} for three soil microbial parameters (basal respiration, substrate induced respiration and potential

ammonium oxidation) is greater than 1000 mg kg^{-1} (Hund-Rinke and Simon, 2005). Similarly, Welp and Brümmer (1999) did not find a toxic effect on soil micro-organisms using the Fe III reduction test at a soil DDT concentration of 11.3 mmol kg^{-1} (4000 mg kg^{-1}). Hence it is more probable that the inhibited degradation was due to the presence of co-contaminating trace elements rather than high levels of ΣDDT. Factors which contribute to the persistence of *p,p'*-DDT are also likely to increase the persistence of ΣDDT in soils.

The possibility that the degradation of DDT was inhibited by additive or synergistic impacts of contaminant trace elements cannot be excluded as there were highly significant relationships ($p<0.001$) between arsenic, copper and lead and a very significant relationship ($p<0.01$) between cadmium and copper across all horticultural soil samples. Additive and synergistic toxicity to micro-organisms has been reported previously for trace elements in soil (Fliessbach *et al.*, 1994; Castaldi *et al.*, 2004). For example, Rennella *et al.* (2003) reported additive toxic effects on soil enzyme activity when copper and zinc salts were added to soils contaminated with cadmium.

Site management practices including the frequency of application of agrichemicals, soil cultivation and irrigation will have influenced the levels and degradation of DDT in soil (Taschenberg *et al.*, 1961; Odermatt *et al.*, 1993; Boul *et al.* 1994; Spencer *et al.* 1996). DDT can also be degraded to DDE through photochemical reactions (Taschenberg *et al.*, 1961), however the constant grass cover on orchards would reduce exposure of soil bound contaminants to ultra violet light inhibiting the photolysis of DDT. A further confounding factor for many properties is the concurrent use of herbicides and soil fumigants (e.g. methyl bromide and chloropicrin) which can also have negative impacts on soil microbial activity (Roper and Gupta, 1995).

5.3.2 PERSULFATE OXIDATION

The results presented in Table 5.4 support a hypothesis that the *p,p'*-DDT residues have been sequestered within the soil matrix and are afforded some level of

protection from, or are inaccessible to, microbial degradation. The long-half life of *p,p'*-DDT in soil precluded direct measurement of degradation; hence a chemical oxidation method was used to estimate the fraction of *p,p'*-DDT that was available for microbial degradation in the experimental soils. Cuypers *et al.* (2000) found that the fraction of PAHs in soil degraded by persulfate oxidation was equivalent to that degraded by soil and sediment micro-organisms. Persulfate ($S_2O_8^{2-}$) is a strong oxidant that forms a sulfate free radical ($SO_4^{\cdot-}$) when heated, and degrades expanded organic matter in soil slurries (Cuypers *et al.*, 2000). It has been suggested that this moderate persulfate technique can be used to estimate the microbially oxidisable fraction of hydrophobic organic compounds (NRC, 2003). Persulfate has also been reported to degrade persistent and chemically stable PCBs (Killian and Bruell, 2003).

The ability of persulfate to oxidise *p,p'*-DDT was investigated using control soils. When *p,p'*-DDT was spiked onto control soil samples that were subsequently treated with persulfate, less than 30% of the *p,p'*-DDT was recovered by acetone:hexane extraction, indicating that readily available *p,p'*-DDT was degraded by persulfate treatment (Chapter Two, Section 2.5.3). Additionally more than 95% of *p,p'*-DDT was degraded by persulfate in the absence of soil. On the other hand, appreciable levels of *p,p'*-DDT were recovered when orchard soil samples were treated with persulfate (Table 5.6). This observation is consistent with the view that *p,p'*-DDT sequestered into condensed organic matter and sub-micron sized pore spaces in soil minerals is not readily oxidised by persulfate treatment.

The proportion of *p,p'*-DDT oxidised by the persulfate ranged from 4 to 37% (Table 5.6). If it is assumed that the fraction of *p,p'*-DDT degraded by persulfate is the readily available fraction, these results indicate a significant proportion of the *p,p'*-DDT in the orchard soils (up to 96% in some cases) may not be available for degradation by soil micro-organisms.

It is probable that several mechanisms have collectively contributed to inhibit the degradation of *p,p'*-DDT to *p,p'*-DDE in orchard soils. Co-contamination with copper may have initially reduced the rate of microbial degradation which resulted in the sequestration of the *p,p'*-DDT residues in a microbially unavailable form. It has

been suggested that the initial rate of degradation of a compound in soil may determine the amount that is sequestered in a microbially unavailable form (Nam and Alexander, 2001).

Table 5.6: Mean concentrations of *p,p'*-DDT and ΣDDT (μg kg^{-1}) measured in orchard soils pre and post persulfate oxidation.

	Pre-oxidation	Post-oxidation	% oxidised[a]
p,p'-DDT			
W1	16720	13490	19
W2	253	220	13
W3	6137	3869	37
W4	1907	1594	16
W5	139	133	4
W6	958	772	19
ΣDDT			
W1	32460	26360	19
W2	942	780	17
W3	14160	8606	39
W4	6577	4710	28
W5	560	496	11
W6	3377	2120	37

[a]Relative to concentration measured pre-oxidation.

5.3.3 BOUND RESIDUES OF ΣDDT

A three step sequential extraction procedure involving base saponification as described above (Section 5.2.2) was used to investigate the presence of bound residues of ΣDDT in six orchard soils. Base saponification is thought to release hydrophobic organic compounds trapped in humic acid polymers by destroying the ester bonds which hold the macromolecules together (Eschenbach *et al.*, 1994). The relative proportions of ΣDDT extracted followed the order acetone:hexane > dichloromethane (DCM) > base saponification with methanolic KOH (MSE) with the greatest proportion of ΣDDT extracted during step one (Table 5.7). These results indicate that bound ΣDDT residues may be present in orchard soils. The proportion of bound ΣDDT residues extracted from the orchard soils (0.5–1.8%) is similar in magnitude to data reported for studies using single applications of radiolabelled compounds. For example, Singh and Agarwal (1995) measured bound residues of

8.7% one year after application of ^{14}C-DDT to soil. In a second study, Agarwal *et al.* (1994) reported that the proportion of bound ^{14}C-DDE 1.5 years after application was 7%. Similarly, Boul (1995) reported that between 7 and 10% of ^{14}C labelled *p,p'*-DDT and *p,p'*-DDE formed bound residues in a microcosm experiment using a NZ pasture soil.

Table 5.7: Mean results (n = 2) for sequential extraction of ΣDDT (μg kg^{-1}) from orchard soils.

	ΣDDT extracted (μg kg^{-1})				% Extracted[b]		
Sample	**acetone:hexane**	**DCM**	**MSE**	**total[a]**	**acetone:hexane**	**DCM**	**MSE**
W1	30620	142	160	30920	99	0.5	0.5
W2	723	11	14	748	97	1.5	1.8
W3	11870	138	141	12150	98	1.1	1.2
W4	5266	38	53	5357	98	0.7	1.0
W5	468	4	8	479	98	0.8	1.6
W6	3284	33	21	3338	98	1.0	0.6
H_3PO_4 not added							
W1	30210	192	352	30760	98	0.6	1.1
W2	712	35	21	768	93	4.5	2.8
W3	12630	285	528	13440	94	2.1	3.9

[a]Sum of ΣDDT extracted in the three steps, [b]Relative to total ΣDDT extracted.

In the limited number of spiked methanolic KOH solutions that were examined it was found that DDT was degraded by the methanolic KOH used to saponify organic matter (Chapter Two, Section 2.5.4). This finding contrasts with the results of Schwarzbauer *et al.* (2003) who reported recoveries of 64% for *p,p'*-DDT and 90% for *p,p'*-DDE from spiked sediment samples using a comparable base saponification method. The observed degradation of DDT compounds by the methanolic KOH solution is consistent with earlier reports that DDT is degraded to DDE at pH levels greater than 12.5 (Smith and Parr, 1972) and can undergo dehydrochlorination in alcoholic solutions with strong alkali (Fleck and Haller, 1945 cited in Smith and Parr, 1972). While the accuracy of the results presented in Table 5.7 is not known, they do indicate that bound residues of ΣDDT may be present in orchard soils. Further work is required to identify and validate an appropriate method to release bound ΣDDT residues from NZ soils.

The addition of H_3PO_4 enhances extraction of ΣDDT from soil during the hexane:acetone extraction (Table 5.7). The amount of ΣDDT extracted by dichloromethane increased by a factor of two if H_3PO_4 was not added prior to extraction with acetone:hexane. It is thought that the H_3PO_4 causes the clay minerals to swell facilitating solvent to penetrate the soil matrix thereby enhancing extraction of ΣDDT.

It is not known if a degradation pathway which does not produce the DDE is operative in NZ orchard soils or if other metabolites of DDT are being produced. Other degradation products of DDT identified in environmental samples include DDA, DDMU, DDOH, DDMS, DDCN and DBP in surface water (Heberer and Dünnbier, 1999); DDCN, DDMU, DDNU, DDMS, DDEt, DDA, DDM and DBP in sediments (Pereira *et al.*, 1996; Schwarzbauer *et al.*, 2003) and DBP, DDA, DDMU and dicofol in soil (Kiigemagi and Terriere, 1972; Fuhremann and Lichtenstein, 1980; Xu *et al.*, 1994; Singh and Agarwal, 1995; Boul, 1996).

5.4 CONCLUSIONS

p,p′-DDE and *p,p′*-DDT are the predominant residues of DDT present in NZ horticultural soils. The *p,p′*-DDE:*p,p′*-DDT ratios in horticultural soils were lower than those reported previously reported for NZ pasture soils and were lower than would be anticipated for aged residues. These low *p,p′*-DDE:*p,p′*-DDT ratios indicate that in the soils studied, either degradation of DDT to DDE has been inhibited or that *p,p′*-DDT is being degraded by another pathway which does not form *p,p′*-DDE. The *p,p′*-DDE:*p,p′*-DDT ratios determined for horticultural soils were, however, consistent with data from horticultural soils from other countries where DDT is no longer in use.

Several factors which may inhibit DDT degradation in horticultural soils have been proposed including the rate of application, the presence of co-contaminants and site management practices. Statistical correlations of the data presented here are

consistent with the possibility that co-contamination with copper (and possibly other elements) in Auckland and Waikato orchard soils may inhibit the microbial degradation of *p,p'*-DDT to *p,p'*-DDE. These findings indicate that co-contamination with trace elements may adversely affect micro-organisms capable of degrading DDT thus enhancing its persistence. The ratio of *p,p'*-DDE:*p,p'*-DDT in horticultural soils, especially orchard soils, should not be used to determine recent (illicit) use of DDT.

Results of persulphate oxidation experiments suggest that much of the *p,p'*-DDT present in orchard soils may not be available for microbial degradation after the time periods that have elapsed in aged orchard soils. This reduced availability for microbial degradation may also have contributed to the formation of bound residues.

A preliminary investigation of six orchard soils indicated that bound residues of ΣDDT were present in orchard soils at levels similar in magnitude to those previously reported. However, the base saponification method was not suitable for releasing bound residues, as the alkaline conditions may degrade ΣDDT. Further work is required to determine the extent to which bound ΣDDT residues are present in NZ horticultural soils.

6 BIOAVAILABILITY AND ECOTOXICITY OF AGED DDT RESIDUES

6.1 INTRODUCTION

The *p,p'*-isomer of DDT and its degradation products DDE and DDD are the predominant organochlorine residues detected in New Zealand horticultural soils (Chapter Five). Internationally there are concerns regarding the continued presence of DDT and its degradation products DDE and DDD in soil because of their potential to enter the food chain (ATSDR, 2002; UNEP, 2005) and their inclusion on the list of persistent organic pollutants (POPs) for elimination under the Stockholm Convention. The bioavailability of aged ΣDDT residues in horticultural soils and the possible level(s) of risk posed by the presence of aged residues in soil to residents on former horticultural land and other ecological receptors (plants and worms) are of interest to New Zealand regulatory authorities.

In this work, it was found that concentrations of ΣDDT in 47% of New Zealand horticultural soil samples were indistinguishable from or exceeded soil criteria adopted by various overseas countries for the protection of ecological receptors (Chapter Four). Many of the early studies focused on acute rather than chronic toxicity and there have been few studies on the specific toxicity of DDD and DDE (WHO, 1989). In addition most of the ecotoxicity data available for DDT residues was determined during the time of active use of DDT or using freshly spiked rather than aged soils. There is currently only a limited amount of data specific to New Zealand on the bioavailability of aged DDT residues to terrestrial organisms.

DDT and its metabolites DDE and DDD are highly lipophilic and have low water solubilities. These physicochemical characteristics enable them to be readily taken up by organisms (WHO, 1989). However, several studies have suggested that the bioavailability of organic compounds including DDT in soil decreases with time (e.g. Kelsey and Alexander, 1997; Morrison *et al.*, 2000). This decreased availability has been attributed to the organic compounds being sequestered within the soil matrix (Semple *et al.*, 2003; Alexander, 1995). Nevertheless, recent studies have shown

uptake of aged organochlorine residues from soil by both plants (White and Kottler, 2002; Lunney *et al.*, 2004) and earthworms (Tang *et al.*, 1999; Harris *et al.*, 2000) indicating that aged DDT residues are bioavailable and there is the potential for residues in soil to enter the terrestrial foodchain.

A range of biomimetic techniques have been developed to estimate the bioavailable fraction of organic contaminants in sediments and soils. These techniques simulate uptake by organisms from the solid phase or pore water (NRC, 2003) and are based on the premise that the freely dissolved contaminant concentrations are representative of the bioavailable fraction (Sijm *et al.*, 2000). The solid phase is suspended in an aqueous solution and either a membrane or a hydrophobic polymer acts as a sink, trapping organic compounds desorbed into solution. Examples of hydrophobic polymers which have been used as adsorbing phases for biomimetic techniques include XAD-4, XAD-2, Tenax, and C-18 sorbents (Krauss and Wilcke, 2001; NRC, 2003). Krauss and Wilcke (2001) summarised the advantages of using biomimetic techniques compared to mild solvent extractions for predicting bioavailability as less alteration of the soil organic matter than during a solvent extraction, reduced depletion of contaminants from the solid phase and potential for *in situ* applications.

Tenax TA is a porous adsorbent material based on a 2,6-diphenylene oxide polymer (Sigma-Aldrich, 2005). It has been used to estimate the bioavailability of aged and spiked POPs to earthworms and oligochaetes (Macrae and Hall, 1998; Cuypers *et al.*, 2000; Morrison *et al.* 2000; Leppänen and Kukkonen, 2006); to determine the desorption kinetics of various classes of POPs from sediment (Cornelissen *et al.*, 1997); and to determine dissolution of PAHs from coal tar contaminated soil (Yeom *et al.*, 1996). Tenax TA has been specifically used to estimate the availability of aged *p,p'*-DDE residues for plant uptake (White and Kottler, 2002).

C-18 sorbents (octadecyl silanol coated silica) are used in biomimetic techniques as a surrogate for lipids (Lake *et al.*, 1996). C-18 coated silica particles have been used to estimate uptake of POPs from soil by *Lumbricus terrestris* (Krauss and Wilcke, 2001) and *E. fetida* (Tang *et al.*, 2002) and from contaminated sediment by benthic organisms (Lake *et al.*, 1996). C-18 sorbents have been specifically used to mimic uptake of *p,p'*-DDT from soil by *L. terrestris* (Awata *et al.*, 1999) and of aged DDT, DDD and DDE from soil by *E. fetida* (Tang *et al.*, 1999).

A series of experiments were undertaken to determine the bioavailability and toxicity of aged DDT residues in Auckland and Waikato orchard soils to earthworms and plants. The earthworm tissue concentrations were compared with the results of the two biomimetic extractions.

6.1.1 OBJECTIVES

The principle objectives of the work reported in this Chapter were to:

- Measure uptake of aged DDT residues by *A. caliginosa* and two edible plant species, lettuce and radish (*La. sativa* and *R. sativus*), using bioassays.
- Compare the uptake of DDT residues by *A. caliginosa* with the results of two biomimetic extraction techniques to determine whether these methods could be used to estimate the bioavailability of DDT residues in soil.
- Measure toxicity of aged DDT residues in soil to *A. caliginosa* and plants (*L. sativa*, *R. sativus* and *Lolium perenne*) using selected endpoints.
- Compare concentrations of ΣDDT measured in lettuce and radish with available regulatory standards.

6.2 METHOD SUMMARY AND DATA ANALYSIS

Details of the methods ultilised in this Chapter are presented in Chapter Two.

6.2.1 EARTHWORM ASSAY

The availability of DDT residues for uptake by the endogenous earthworm *A. caliginosa* was measured using a 28 day bioassay (Kula and Larink, 1998). The tissue concentrations from the worm bioassay were compared to the results of three

non-exhaustive extraction techniques, ethyl acetate, a moderately polar solvent extraction, and two biomimetic techniques, which ultilised Tenax TA resin and C-18 disks respectively. Toxicity of aged DDT residues to earthworms was determined by measuring mortality, changes in body mass and cocoon production.

6.2.3 PLANT ASSAYS

The phytoavailability of aged DDT residues in horticultural soils to lettuce and radish was assessed using a pot trial experiment. Lettuce (*La. sativa*) and radish (*R. sativus*) were grown on soils collected from three orchards, one vineyard, two grazing paddocks and two bushblocks in the Auckland region. A further two soils were prepared by blending an orchard soil with soil collected from an adjacent bush block. These blended soils were utilised to grow lettuce only. Phytotoxicity was determined by measuring the dry mass yield of the lettuce and radish and by seedling emergence and root elongation assay for lettuce and ryegrass (*Lo. perenne*) grown for 5 days in the sub-samples of the worm assay soils.

6.2.4 DATA ANALYSIS

In this Chapter, zero has been used for results less than the detection limits (rather than half the detection limit) to avoid overestimating worm and plant tissue ΣDDT concentrations. Since *p,p'*-isomers were the predominant isomers found in NZ soils, data analyses in this chapter are largely confined to the data for ΣDDT and the *p,p'* isomers specifically. ΣDDT includes the *o,p'*- and *p,p'*-isomers of DDE, DDT and DDD where levels were reliably measurable. Bioaccumulation factors (BAFs) for ΣDDT, *p,p'*-DDE, *p,p'*-DDT and *p,p'*-DDD were calculated as the concentration in tissue divided by the soil concentration, with both on a dry weight basis.

Concentrations of DDT residues in lettuce and radish hypocotyls have been presented on a fresh weight (FW) basis to enable comparison with literature data and regulatory standards. The lettuce and radish DDT residue concentrations were converted to

fresh weight using experimentally determined moisture contents which were comparable to those reported in the literature for lettuce and radish (Bradbury, 1986; Alloway *et al.*, 1988; USEPA, 1994).

Linear regression analysis was used to determine relationships between tissue and soil concentrations and Pearson's correlation analysis to determine correlations between soil characteristics and bioaccumulations factors (BAFs) and tissue concentrations. Spearman rank correlation analysis was used to determine relationships between toxicological endpoints and soil ΣDDT concentrations. Data was log transformed as required for statistical analyses.

6.3 RESULTS AND DISCUSSION

6.3.1 EARTHWORM ASSAY

6.3.1.1 ΣDDT CONCENTRATIONS IN SOILS

For the worm assay and the seedling emergence and root elongation assay, ten soils with ΣDDT concentrations ranging from <10 to 32460 μg kg^{-1} (Table 6.1) were collected from orchards, and where available matched grazing sites on the same soil type in the Auckland and Waikato regions. Two solvent extraction methods (ethyl acetate and 2:3 acetone:hexane) were used to extract the DDT residues from the soils used in the worm bioassay. The acetone:hexane extraction was used to extract the "total" or strongly bound fraction of DDT residues and ethyl acetate extraction to estimate the bioavailable fraction of DDT in the soil.

Table 6.1: Comparison of ΣDDT and the *p,p'*-isomers of DDE, DDT and DDD extracted by acetone:hexane and ethyl acetate from soil. Orchards and matched grazing sites have the same superscript (nc = not calculated as compound not detected).

Soil	Acetone:hexane	Ethyl acetate		Soil	Acetone:hexane	Ethyl acetate	
	μg kg^{-1}	μg kg^{-1}	% extracted[a]		μg kg^{-1}	μg kg^{-1}	% extracted
ΣDDT				***p,p'-DDE***			
orchard				*orchard*			
W1[a]	32460	33760	104	W1[a]	11850	9984	84
W2[b]	942	895	95	W2[b]	478	403	84
W3	14160	12090	85	W3	6955	5139	74
W4	6576	4061	62	W4	4389	2468	56
W5[c]	560	314	56	W5[c]	388	232	60
W6[d]	3378	3780	112	W6[d]	2101	1884	90
grazing				*grazing*			
W7[a]	223	152	68	W7[a]	145	97	67
W8[b]	10	<10	nc	W8[b]	10	<10	nc
W9[c]	46	35	76	W9[c]	32	24	75
W10[d]	<10	<10	nc	W10[d]	<10	<10	nc
p,p'-DDT				***p,p'-DDD***			
orchard				*orchard*			
W1[a]	16720	19760	118	W1[a]	647	629	97
W2[b]	253	262	104	W2[b]	89	90	101
W3	6137	5900	96	W3	409	351	86
W4	1907	1395	73	W4	100	69	69
W5[c]	139	76	55	W5[c]	25	11	43
W6[d]	958	1383	144	W6[d]	163	269	165
grazing				*grazing*			
W7[a]	67	48	71	W7[a]	<10	<10	nc
W8[b]	<10	<10	nc	W8[b]	<10	<10	nc
W9[c]	14	11	78	W9[c]	<10	<10	nc
W10[d]	<10	<10	nc	W10[d]	<10	<10	nc

[a]% extracted by ethyl acetate, relative to the acetone:hexane extraction

The ethyl acetate extraction method extracted between 56 and 112% of the ΣDDT extracted by the "total" acetone:hexane method (Table 6.1). There were significant correlations ($p<0.001$) between the concentration of ΣDDT and the *p,p'*-isomers of DDT, DDE and DDD extracted by both methods. There were however differences in the proportion of each of the *p,p'*-isomers extracted; while there was no consistent trend for *p,p'*-DDT (55–144%) and *p,p'*-DDD (43–165%), the ethyl acetate method consistently extracted less *p,p'*-DDE (56–90%) than the acetone:hexane method. This difference for *p,p'*-DDE was significant (paired t-test, $p = 0.03$). It is unlikely that the observed differences in DDE extraction are due to analytical error as the 95% confidence interval for mean recovery of spiked DDT compounds from soil was 90 ± 3% (Section 2.5.2.2, Chapter Two). No significant correlations ($p<0.05$) were found between the % ΣDDT extracted with ethyl acetate and soil properties.

6.3.1.2 BIOMIMETIC EXTRACTIONS OF AGED ΣDDT RESIDUES

TENAX

Over a 24 hour extraction, the Tenax resin adsorbed between 9 and 23% of the ΣDDT residues in soil (Table 6.2). The high percentage of DDT residues adsorbed by the Tenax indicates that a significant proportion of aged DDT soil residues remain potentially bioavailable. The proportion of DDT extracted from soil in this experiment is comparable to the 17.8% of aged *p,p'*-DDE residues desorbed from soil by Tenax TA obtained by White and Kottler (2002).

The fraction of compound desorbed from soil and sediment with Tenax by ten Hulscher *et al.* (2003) ranged from 51.9% for *p,p'*-DDE (n = 1) and 33 to 59% for *p,p'*-DDD (n = 8). The percentage of *p,p'*-DDE and ΣDDT extracted by Tenax decreased with increasing soil %TOC ($p<0.02$). Macrae and Hall (1998) have previously observed that the amount of PAHs desorbed from sediment decreased with increasing organic matter.

Table 6.2: Concentration of ΣDDT and the *p,p'*-isomers of DDE, DDT and DDD extracted by Tenax resin and C-18 disks (μg kg^{-1} soil) compared to the acetone:hexane soil extraction.

Soil	Acetone:hexane	C-18 disks		Tenax resin	
	μg kg^{-1}	μg kg^{-1}	% extracted[a]	μg kg^{-1}	% extracted[a]
ΣDDT					
W1	32460	345	1.1	2858	9
W2	942	10	1.0	213	23
W3	14160	116	0.8	2288	16
W4	6576	51	0.8	803	12
W5	560	2	0.4	68	12
W6	3378	49	1.5	783	23
p,p'-DDT					
W1	16720	179	1.1	1361	8
W2	253	2	0.9	38	15
W3	6137	47	0.8	986	16
W4	1907	15	0.8	199	10
W5	139	1	0.5	10	7
W6	958	13	1.4	251	26
p,p'-DDE					
W1	11850	109	0.9	1068	9
W2	478	5	0.9	134	28
W3	6955	60	0.9	1111	16
W4	4389	35	0.8	587	13
W5	388	2	0.4	58	15
W6	2101	30	1.4	441	21
p,p'-DDD					
W1	647	10	1.5	67	10
W2	89	1	1.0	9	10
W3	409	3	0.8	60	15
W4	100	0.4	0.4	2	2
W5	25	<0.1	0	<1	0
W6	163	4	2.5	45	27

[a]% extracted relative to acetone:hexane.

C-18 MEMBRANE DISKS

The C-18 membrane disks extracted less than 3% (0–2.5%) of the DDT residues (Table 6.2). Unlike the Tenax extractions, the percentage uptake by the C-18 membrane disks did not negatively correlate with %TOC in soil. The greater uptake by the Tenax resin compared to the C-18 membrane disks may be attributed to the increased mass of carbon sorbent and the dynamic mixing conditions used in the Tenax desorption experiments. Additionally, for the Tenax extraction there was a

higher soil to solution ratio which may have enabled more of the DDT residues to desorb.

6.3.1.3 ΣDDT CONCENTRATIONS IN WORM TISSUE

ΣDDT concentrations in the depurated worm tissue ranged from 30 to 45280 μg kg^{-1} (DW) (Table 6.3) and increased with increasing soil concentration (p<0.001) (Figure 6.1). Two of the worm tissue ΣDDT concentrations (orchard soils W1 and W3) exceeded the level of 32 mg kg^{-1} (DW) proposed by Beyer and Gish (1980) as being hazardous to sensitive bird species. Linear regression analysis showed the relationship between log concentrations in worm tissue and soil was also highly significant (p<0.001) for the *p,p'*-isomers of DDE and DDT over three orders of magnitude of soil contamination (Table 6.4). The worm tissue DDT residue concentrations also significantly correlated with the results of the soil ethyl-acetate extraction (p<0.001).

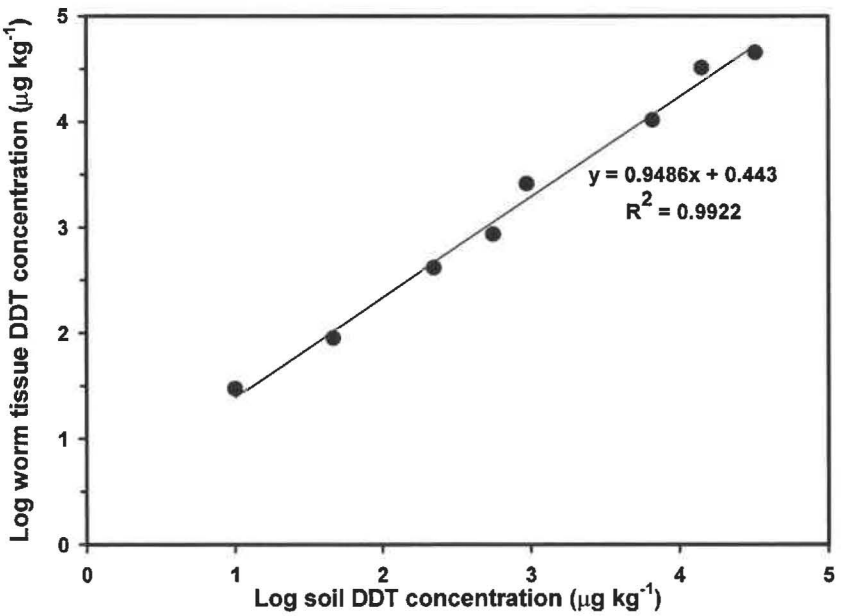


Figure 6.1: Relationship between worm tissue ΣDDT and soil ΣDDT concentration (μg kg^{-1}).

Table 6.3: Mean (n = 2) concentrations of DDT residues measured in worm tissue (μg kg^{-1} DW). Orchards and matched grazing sites have the same superscript.

	o,p -DDE	*p,p'*-DDE	*o,p'*-DDD	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	ΣDDT
baseline adults	<2	342	<2	<2	4	33	379
orchard soils							
W1[a]	54	20020	430	1205	2199	21370	45280
W2[b]	<2	1891	87	108	40	458	2584
W3	<2	18960	163	740	723	11800	32380
W4	<2	8166	<2	69	87	2028	10350
W5[c]	<2	761	<2	<2	<2	96	857
grazing soils							
W7[a]	<2	353	<2	<2	7	53	413
W8[b]	<2	23	<2	<2	<2	6	29
W9[c]	<2	63	<2	<2	5	21	89

Table 6.4: Linear regression equations for relationships between concentrations of selected DDT residues in worm tissue and soil (μg kg^{-1} DW).

	Acetone:hexane	Ethyl acetate
ΣDDT	log(worm) = 0.9486(log soil)+0.443, R^2=0.99***	log(worm) = 0.7782(log soil)+1.114, R^2=0.96***
p,p'-DDT	log(worm) = 0.9029(log soil)+0.3994, R^2=0.96***	log(worm) = 0.8937(log soil)+0.486, R^2=0.98***
p,p'-DDE	log(worm) = 0.9848(log soil)+0.4, R^2=0.99***	log(worm) = 0.8178(log soil)+1.0583, R^2=0.96***

***p<0.001.

An earlier study in New Zealand has previously demonstrated DDT accumulation from soil by earthworms from horticultural soils; Collett and Harrison (1968) measured DDT levels in earthworms before and after spraying orchards with DDT and reported that worm tissue concentrations of DDT increased from 13 mg kg^{-1} to 29 mg kg^{-1}. The worm tissue ΣDDT concentrations obtained in the bioassays reported here (Table 6.3) are consistent with tissue levels reported for *A. caliginosa* exposed to aged DDT residues in orchard soils in Canada (Harris *et al.*, 2000), and for the uptake of aged *p,p'*-DDE residues from soil by *A. caliginosa* (Kelsey *et al.*, 2005).

6.3.1.4 RELATIVE UPTAKE OF DDE AND DDT BY EARTHWORMS

The *p,p'*- isomers of DDT and DDE were the main DDT compounds detected in the test soils and the earthworm tissue (Table 6.3). Although these two compounds were measured in all earthworm samples, ratios of *p,p'*-DDE: *p,p'*-DDT were significantly higher ($p<0.003$, paired t-test on log values) in earthworm tissue than in the soils. Higher concentrations of *p,p'*-DDE than *p,p'*-DDT were also measured in a survey of *Lumbricus rubellus* collected from polluted Rhine-Delta floodplains (Hendriks *et al.*, 1995) and by Harris *et al.* (2000) for *A. caliginosa* in Canadian orchards.

Several factors may be contributing to the higher ratio of *p,p'*-DDE: *p,p'*-DDT in the worm tissue compared to soil including preferential uptake of *p,p'*-DDE and/or elimination of *p,p'*-DDT and degradation of DDT to DDE in the earthworm gut. Metabolism of DDT to DDE by earthworms has been previously reported (Davis, 1971; Edwards and Jeffs, 1974).

6.3.1.5 BIOACCUMULATION FACTORS

Bioaccumulation factors (worm tissue concentration divided by soil concentration on dry weight basis) were calculated to determine if the worms were accumulating DDT residues from soil, and hence represented a pathway for DDT residues to be mobilized from the soil. The bioaccumulation factors (BAFs) for ΣDDT were greater

than 1 (range 1.4–3.0) (Table 6.5) indicating that bioaccumulation of aged ΣDDT residues from the orchard soils had occurred.

Table 6.5: Bioaccumulation factors (BAFs) for uptake of aged DDT residues by *A caliginosa*. Orchards and matched grazing sites have the same superscript.

	p,p'-DDE	*p,p'*-DDD	*p,p'*-DDT	ΣDDT
orchard				
W1[a]	1.69	1.86	1.28	1.39
W2[b]	3.95	1.21	1.81	2.74
W3	2.73	1.81	1.92	2.29
W4	1.86	0.69	1.06	1.57
W5[c]	1.96	nc*	0.69	1.53
grazing				
W7[a]	2.44	nc	0.78	1.85
W8[b]	2.35	nc	nc	2.97
W9[c]	1.96	nc	1.46	1.94

*Not calculated as isomer not present in either soil or worm tissue.

The BAFs reported in Table 6.5 for uptake of ΣDDT, *p,p'*-DDE and *p,p'*-DDT from soil by earthworms are within the range reported in the literature. For example, BAFs of 0.9 to 7.5 were obtained for *Apporectodea sp.* in Canadian orchard soils (Harris *et al.*, 2000), 1.29 to 1.98 for *p,p'*-DDE uptake by *A. caliginosa* from aged soils (Kelsey *et al.*, 2005), and 1.8 to 9.2 for *p,p'*-DDT and *p,p'*-DDE by unspecified field collected earthworms (Ma, 1985, cited in Hendriks *et al.*, 1995).

The BAFs for *p,p'*-DDE uptake by *A. caliginosa* were consistently higher than those calculated for *p,p'*-DDT (Table 6.5). There are several possible explanations; *p,p'*-DDE is more bioavailable than *p,p'*-DDT, and is preferentially taken up by earthworms, or as previously discussed, *p,p'*-DDT could be transformed to *p,p'*-DDE within the earthworm (Edwards and Jeffs, 1974). Harris *et al.* (2000) also noted that BAFs for DDE were always greater than those calculated for DDT.

When all of the treatments were compared, there were no significant correlations between the BAFs and soil concentrations for ΣDDT and the *p,p'*-isomers of DDT and DDE (Table 6.6). However, for samples collected from within the same property, the BAF for ΣDDT for the orchard soil was consistently lower than the

BAF for the grazing soil (n = 3 pairs, paired t-test, $p<0.03$). This decreasing BAF for the same soil type is consistent with the results of Kelsey *et al.* (2005) who found that BAFs for *p,p'*-DDE uptake by *A. caliginosa* decreased with soil concentrations within the range of 82 to 406 $\mu g\ kg^{-1}$.

The BAFs for *p,p'*-DDE and ΣDDT were inversely related to %silt and the BAFs for *p,p'*-DDT and ΣDDT decreased with increasing soil pH (Table 6.6). As the soil pH and %silt were positively correlated ($p<0.01$) it is more likely that the %silt is a contributing factor. The BAF for *p,p'*-DDT decreased with increasing soil manganese concentration ($p<0.01$).

Bioaccumulation of organic compounds can also be influenced by soil properties including clay content and organic matter (Belfroid *et al.*, 1996). Davis (1971) reported that uptake of *p,p'*-DDT and *p,p'*-DDE by *A. caliginosa* decreased with increasing soil organic carbon content. Existence of such an effect was tested by assessing correlations between %TOC and BAF, but was not clearly evident in these data (Table 6.6). The BAF for *p,p'*-DDE decreased with increasing soil %TOC, however this relationship was only just significant ($p<0.05$). Possible reasons for this are that the influence of organic carbon is stronger when DDT residues are comparatively new, or that the data set is too limited to see such an underlying effect. In contrast, the % ΣDDT and % *p,p'*-DDE desorbed from soil by Tenax was inversely related to the soil organic carbon ($p<0.02$) indicating that %TOC is one of the soil properties which determines the partitioning of DDT residues between the solid and solution phases. This difference between Tenax and *A. caliginosa* may be due to additional extraction of DDT residues in the digestive system of the earthworm. *Aporrectodea caliginosa* is an endogenous earthworm which ingests soil and hence is exposed to contaminants in soil through both dermal exposure and ingestion whereas Tenax is a surrogate measure for compounds desorbed into the soil solution.

Table 6.6: Pearson's correlation coefficients for relationships between BAFs for uptake of DDT residues by earthworms and soil *p,p'*-DDT, *p,p'*-DDE and ΣDDT concentrations and soil properties.

Soil properties	*p,p'*-DDE BAF	*p,p'*-DDT BAF	ΣDDT BAF
p,p'-DDE	-0.091	0.227	-0.521
p,p'-DDT	-0.118	0.28	-0.187
ΣDDT	-0.071	0.26	-0.517
% clay	0.562	0.69	0.622
% silt	**-0.781***	-0.735	**-0.869****
% sand	-0.056	-0.318	-0.06
pH	-0.666	**-0.771***	**-0.808****
%TOC	**-0.751***	-0.325	-0.259
CEC	0.038	-0.587	0.196
OlsenP	0.215	0.647	0.089
Fe	-0.015	0.038	-0.225
Mn	-0.424	**-0.812****	-0.584

*$p<0.05$, **$p<0.01$.

6.3.1.6 CORRELATION BETWEEN WORM TISSUE CONCENTRATIONS AND BIOMIMETIC EXTRACTIONS

Correlations between the biomimetic extractions and the earthworm uptake were assessed using linear regression analysis on log transformed data. For ΣDDT and the *p,p'*-isomers of DDT, DDE and DDD there were significant relationships between the worm tissue concentration and the results of both the Tenax ($p<0.01$) and the C-18 biomimetic extractions ($p<0.05$) (Figure 6.2). The results for Tenax are consistent with the results of ten Hulscher *et al.* (2003) who found that the concentration of organochlorines measured in *L. rubellus* tissue (μg kg^{-1} lipid) after a 28 day assay was proportional to the amount desorbed from contaminated sediments in 6 h by Tenax (μg kg^{-1} organic carbon). The more significant relationship between Tenax and earthworm tissue compared with the C-18 extraction, along with the greater proportion of aged residues extracted from soil, indicates that the Tenax extraction may be a better procedure for estimating the bioavailability and uptake of aged DDT residues by *A. caliginosa.*

The results of Tenax and C-18 extractions for aged DDT, DDE and DDD residues have not previously been compared specifically to a bioassay with *A. caliginosa.*

However, experiments investigating the bioavailability of aged DDT, DDE and DDD residues in soil using *E. fetida* are available for comparison (Tang *et al.*, 1999; Morrison *et al.,* 2000). In agreement with the results presented in Figure 6.2, these studies also found the amount of aged DDT, DDE and DDD residues extracted by both Tenax and C-18 tended to increase with increasing worm tissue concentrations. In contrast with the results reported here for *A. caliginosa,* Morrison *et al.* (2000) suggested that C-18 extraction provided better results than Tenax for uptake by *E. fetida* as retention on Tenax correlated with high or low percent bioavailability but not with intermediate bioavailability. The reason for the difference between the two studies is not clear. Possible reasons include differing soil properties as well as differences in DDT uptake between *E. fetida* and *A. caliginosa.* A further possible explanation is that both Tang *et al.* (1999) and Morrison *et al.* (2000) utilised a combination of soils containing aged and freshly spiked DDT compounds for their assays whereas the results reported here are for aged soils only.

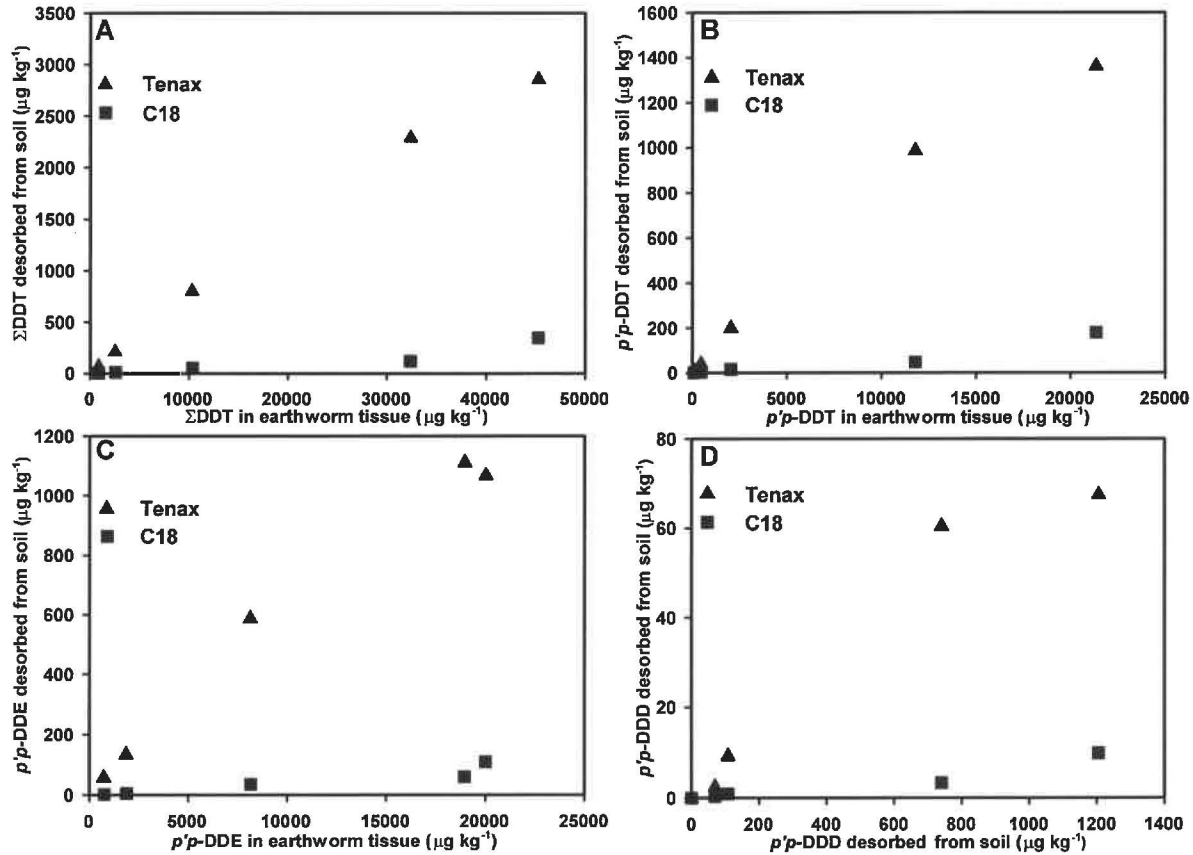


Figure 6.2: Relationships between mean concentration of DDT residue (µg kg^{-1}) desorbed from soil and mean concentration of DDT residue (µg kg^{-1} DW) measured in worm tissue. A = ΣDDT, B = *p,p'*-DDT, C = *p,p'*-DDE and D = *p,p'*-DDD.

6.3.1.7 TOXICITY OF AGED DDT RESIDUES TO *A. CALIGINOSA*

Cocoon production, change in body mass and mortality were measured to determine toxicity of the test soils to *A. caliginosa* (data presented in Chapter Seven). Across all soils, the mortality for *A. caliginosa* was 0% for the 28 day exposure and there were no relationships between change in body mass and worm tissue or soil ΣDDT concentrations (Table 6.7). This lack of acute toxicity is consistent with the results of Morrisson *et al.* (2000) for *E. fetida* exposed to similar concentrations of aged DDT, DDE and DDD residues.

Cocoon production was negatively correlated with worm tissue and soil *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT and ΣDDT concentrations ($p<0.05$) (Table 6.7). This finding was unexpected as DDT is generally considered to be non-toxic to earthworms (e.g. WHO, 1989). The highest ΣDDT soil concentration used for the worm assay was 32.5 mg kg^{-1}, an order of magnitude lower than the EC_{50} value DDT for *E. fetida* reproduction of >1000 mg kg^{-1} recently determined using spiked silty and loamy soils (Hund-Rinke and Simon, 2005). This suggests that the observed reduction in cocoon production was due to another factor which correlates with the soil ΣDDT concentration.

Table 6.7: Spearman rank correlation coefficients between earthworm cocoon production and change in bodymass, and soil and worm tissue DDT residues. Significant correlations are presented in bold.

	Cocoon production	Change in body mass
soil		
p,p'-DDE	**-0.802****	-0.238
p,p'-DDD	**-0.736***	-0.195
p,p'-DDT	**-0.802****	-0.252
ΣDDT	**-0.802***	-0.238
tissue		
p,p'-DDE	**-0.802****	-0.238
p,p'-DDD	**-0.773***	-0.61
p,p'-DDT	**-0.802****	-0.233
ΣDDT	**-0.802****	-0.223

*$p<0.05$, ** $p<0.02$

Possible relationships between trace element concentration, soil properties and ΣDDT concentration were explored using Pearson's correlation analysis. There were significant correlations between copper and ΣDDT for both worm tissue ($p<0.05$) and soil ($p<0.01$) concentrations. Cocoon production also decreased with increasing copper (worm tissue and soil) concentration (Chapter Seven). A further possible explanation is the presence of another pesticide. However, this is unlikely as the soils collected from the active orchards (n = 3) were also assayed for a multi-residue pesticide screen by HortResearch. Dicofol was detected in all samples at low concentrations (0.02 to 0.11 mg kg^{-1}) and imazalil (0.01 mg kg^{-1}) was detected in W5 (data presented in Appendix B).

6.3.2 PLANT ASSAYS

6.3.2.1 LETTUCE AND RADISH TISSUE CONCENTRATIONS

Concentrations of aged ΣDDT residues in the experimental soils ranged from 17 to 12000 μg kg^{-1} (Table 6.8) and provided corresponding plant tissue ΣDDT concentrations from <0.12 to 11 μg kg^{-1} (FW) (Table 6.9a). The dry weight concentrations are presented in Table 6.9b. There is a paucity of NZ data for organochlorine residues in vegetables with which to make comparisons. In a recent NZ total diet survey, *p,p'*-DDE concentrations of 0.03 and 0.005 mg kg^{-1} (FW) were measured in two zucchini samples (Vannoort, 2004). Root and leafy vegetables grown in a home garden on a former orchard in Hamilton, NZ with a soil ΣDDT concentration of 11 mg kg^{-1} contained *p,p'*-DDT concentrations ranging from <0.005 to 0.009 mg kg^{-1} (FW) (data supplied by Environment Waikato).

The plant tissue ΣDDT concentrations measured in vegetation from the pot trial (Table 6.9) are comparable with those reported for lettuce and radish, and other vegetables in recent overseas studies. For example, concentrations of 0.32 to 1.15 μg kg^{-1} and 0.28 μg kg^{-1} for *p,p'*-DDE and *p,p'*-DDT were measured in vegetables and vegetable products in the Canadian total diet survey for 1998/1999 (Rawn *et al.*,

2004). Mean ΣDDT concentrations of 0.06 and 0.45 μg kg^{-1} FW, and 1.44 μg kg^{-1} FW have been measured in lettuce and radish grown in West Africa (Manirakiza *et al.*, 2003) and maximum ΣDDT levels of 31.7 and 39.5 μg kg^{-1} FW in lettuce and radish grown in Nanjing, China (Gao *et al.*, 2005). White (2001) measured *p,p'*-DDE levels of 170 μg kg^{-1} (DW, estimated from graph) in the leaves of spinach grown in outdoor soil plots containing *p,p'*-DDE concentration of 360 μg kg^{-1}. Leeks grown in soil containing aged DDT residues (DDT concentration 3.6 ± 0.6 μg kg^{-1} and DDE concentration 3.5 ± 0.6 μg kg^{-1}) contained 10 and 2.8 μg kg^{-1} of DDT and DDE respectively in the aerial parts (leaves and stem) at harvest (Gonzalez *et al.*, 2003).

The order of uptake for ΣDDT, *p,p'*-DDE and *p,p'*-DDT on a dry weight basis was lettuce<radish leaf<radish hypocotyl. These differences in plant tissue ΣDDT concentrations are not explained by the mean plant lipid concentrations which followed the order radish hypocotyl<radish leaf<lettuce. Other studies demonstrating plant uptake of aged organochlorine residues from soil have been unable to identify a pattern or mechanism which explains the differential uptake between plant species and distribution of contaminants within different tissues of a plant (Webber *et al.*, 1994; Kiflom *et al.*, 1999; White, 2001).

Table 6.8: Mean concentrations of DDT residues (n = 2) (μg kg^{-1} DW) in treatment soils. Horticultural sites and their controls have the same superscript letter.

Soil	*o,p'*-DDE	*p,p'*-DDE	*o,p'*-DDD	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	ΣDDT	DDE:DDT[c]
horticulture								
Orchard 1	64	6289	530	789	396	3972	12040	1.58
Orchard 2[a]	26	3367	84	292	254	4355	8378	0.77
Orchard 3[a]	21	2670	69	229	188	3355	6532	0.80
Orchard 4[a]	13	1575	43	138	118	2007	3894	0.79
Orchard 5[b]	<10	1978	23	139	53	1421	3614	1.39
Vineyard	<10	308	<10	20	12	111	451	2.78
control								
Bushblock 1	<10	17	<10	<10	<10	<10	17	nc[d]
Bushblock 2[a]	<10	141	<10	<10	<10	163	313	0.86
Grazing 2[b]	<10	32	<10	<10	<10	<10	32	nc

[c]Ratio of the *p,p'*- isomers of DDE and DDT, [d]Ratio not able to be calculated as both isomers not detected in sample.

Table 6.9a: Mean DDT residues (n = 4) measured in plant tissue (μg kg^{-1} FW).

	o,p'- DDE	*p,p'*- DDE	*o,p'*- DDD	*p,p'*- DDD	*o,p'*- DDT	*p,p'*- DDT	ΣDDT
lettuce							
Orchard 1	<0.14	1.53	<0.14	<0.14	<0.14	0.38	1.91
Orchard 2	<0.14	1.01	<0.14	<0.14	<0.14	0.39	1.40
Orchard 3[a]	<0.14	0.87	<0.14	<0.14	<0.14	0.34	1.21
Orchard 4[a]	<0.14	0.64	<0.14	<0.14	<0.14	0.26	0.90
Orchard 5	<0.14	0.66	<0.14	<0.14	<0.14	<0.14	0.66
Vineyard	<0.14	0.21	<0.14	<0.14	<0.14	<0.14	0.21
Bushblock 1	<0.14	0.20	<0.14	<0.14	<0.14	<0.14	0.20
Bushblock 2	<0.14	0.17	<0.14	<0.14	<0.14	<0.14	0.30
Grazing 2	<0.14	0.16	<0.14	<0.14	<0.14	<0.14	0.16
radish hypocotyl							
Orchard 1	<0.12	7.45	0.67	0.73	0.44	2.15	11.4
Orchard 2	<0.12	4.59	<0.12	0.24	0.38	2.63	7.83
Orchard 5	<0.12	2.73	<0.12	<0.12	<0.12	0.56	3.29
Vineyard	<0.12	0.46	<0.12	<0.12	<0.12	<0.12	0.46
Bushblock 1	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Bushblock 2	<0.12	0.18	<0.12	<0.12	<0.12	<0.12	0.18
Grazing 2	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12

[a]Lettuce only grown in these soils.

Table 6.9b: Mean DDT residues (n = 4) measured in plant tissue (μg kg^{-1} DW).

Soil	*o,p'*- DDE	*p,p'*- DDE	*o,p'*- DDD	*p,p'*- DDD	*o,p'*- DDT	*p,p'*- DDT	ΣDDT
lettuce							
Orchard 1	<2	22	<2	<2	<2	6	28
Orchard 2	<2	17	<2	<2	<2	7	24
Orchard 3	<2	13	<2	<2	<2	5	18
Orchard 4	<2	10	<2	<2	<2	4	14
Orchard 5	<2	10	<2	<2	<2	<2	10
Vineyard	<2	3	<2	<2	<2	<2	3
Bushblock 1	<2	3	<2	<2	<2	<2	3
Bushblock 2	<2	2	<2	<2	<2	<2	2
Grazing 2	<2	2	<2	<2	<2	<2	2
radish hypocotyl							
Orchard 1	<2	124	11	12	7	36	190
Orchard 2	<2	77	<2	4	6	44	131
Orchard 5	<2	46	<2	<2	<2	9	55
Vineyard	<2	8	2	<2	<2	<2	8
Bushblock 1	<2	<2	<2	<2	<2	<2	<2
Bushblock 2	<2	3	<2	<2	<2	<2	3
Grazing 2	<2	<2	<2	<2	<2	<2	<2
radish leaf[a]							
Orchard 1	<2	53	3	4	3	14	77
Orchard 2	<2	33	<2	<2	2	16	51
Orchard 5	<2	26	<2	<2	<2	5	31
Vineyard	<2	7	<2	<2	<2	<2	7
Bushblock 1	<2	3	<2	<2	<2	<2	3
Bushblock 2	<2	6	<2	<2	<2	<2	6
Grazing 2	<2	3	<2	<2	<2	<2	3

[a]Radish leaf refers to all above ground parts of the radish i.e. stem and leaf.

6.3.2.2 ISOMERS DETECTED IN PLANT TISSUE

The main isomers of DDT detected in plant tissue were the *p,p'*- isomers of DDT and DDE (Table 6.9a,b; Figure 6.3). In all plant tissues, the *p,p'*-DDE concentrations were greater than the *p,p'*-DDT levels. This is consistent with the results of previous studies that have demonstrated preferential uptake of *p,p'*-DDE into vegetables (Pylypiw *et al.*,1991; Sadlo, 1995).

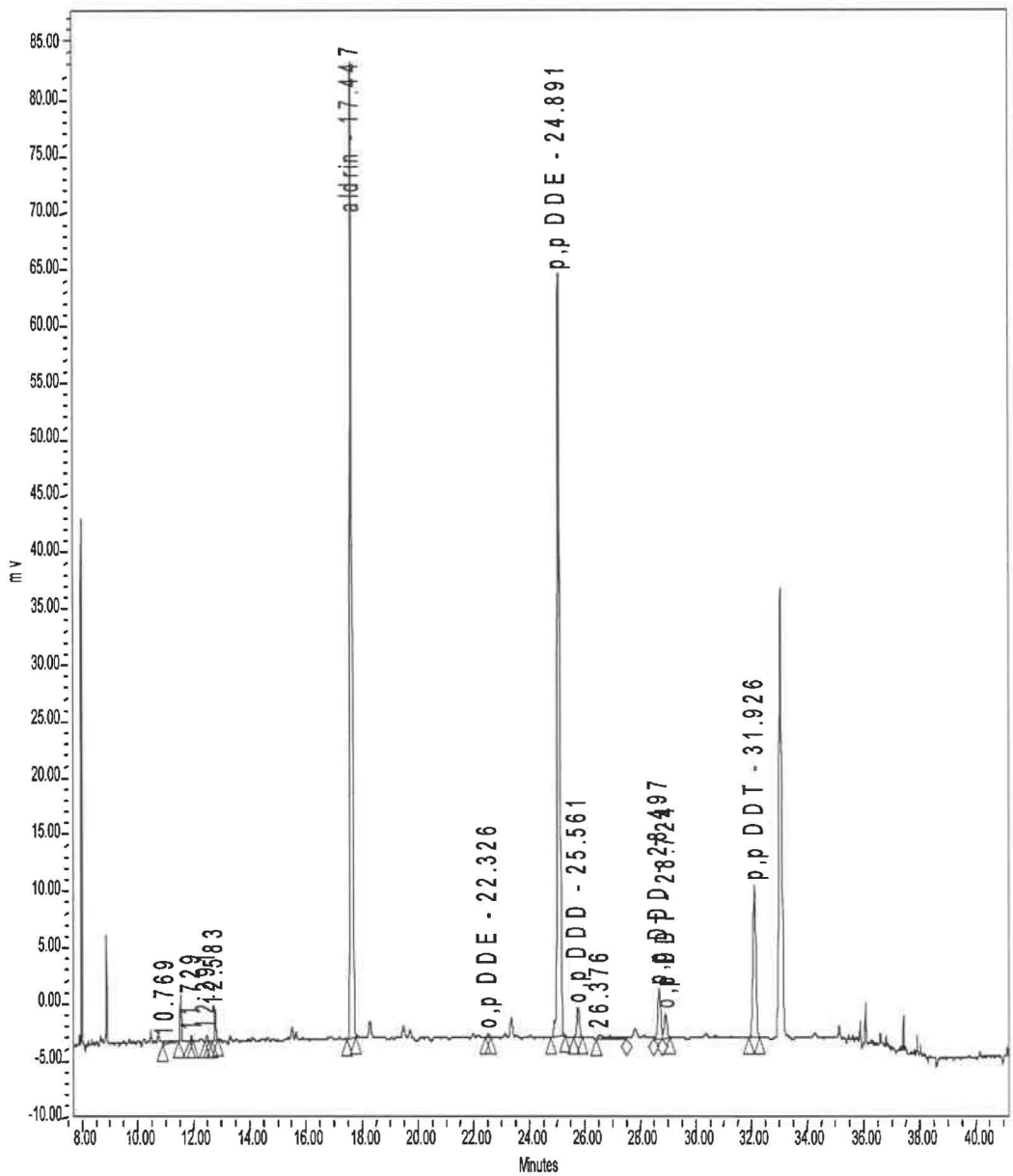


Figure 6.3: Chromatogram for DDT residue analysis of radish hypocotyl with a ΣDDT concentration of 190 μg kg^{-1} grown in soil collected from Orchard 1. Aldrin was used as an internal recovery standard and the *p,p'*- isomers of DDT and DDE were the main residues detected.

Higher *p,p'*-DDE: *p,p'*-DDT ratios were obtained for the plant tissue (DW basis) than the soils; these differences were significant for lettuce ($p<0.002$), radish hypocotyl ($p<0.03$) and radish leaf ($p<0.01$) using a paired t-test on log values. The difference in ratios between soil and plant can be explained by three possible mechanisms;

preferential uptake of DDE by the plants, degradation of DDT to DDE within the plant tissue, or, enhanced degradation of DDT to DDE in the rhizosphere followed by preferential uptake of DDE. The preferential uptake of DDE may be due to differences in the physico-chemical properties, particularly the lower Kow and Koc that combine to increase the bioavailability of DDE compared to DDT (Table 6.10). The physico-chemical data presented in Table 6.10 were sourced from ATSDR (2002), however, a wide variety of values have been reported elsewhere (CRC, 2000). Transformation of DDT to DDE and/or DDD has been measured in cell cultures of aquatic plants (Garrison *et al.*, 2000) and in hairy root cultures of *Cichorium intybus* and *Brassica juncea* (Suresh *et al.*, 2005). Additionally, cultures of lettuce cells have been reported to metabolise PCB congeners (Harms *et al.*, 2003) so it is not inconceivable that lettuce cells could metabolise DDT.

Table 6.10: Selected physical and chemical properties of the *p,p'*-isomers of DDT and DDE (ATSDR, 2002).

	***p,p'*-DDT**	***p,p'*-DDE**
Water solubility	0.025 mg L^{-1} at 25 °C	0.12 mg L^{-1} at 25 °C
Log Kow	6.91	6.51
Log Koc	5.18	4.70
Vapor pressure	1.60 x 10^{-7} at 20 °C torr	6 x 10^{-6} at 25 °C torr
Henry's law constant	8.3 x 10^{-6} atm-m^3/mol	2.1 x 10^{-5} atm-m^3/mol

6.3.2.3 RELATIONSHIP BETWEEN PLANT TISSUE AND SOIL CONCENTRATIONS

In the current study there was a significant linear correlation ($p<0.001$) between the mean soil and mean plant tissue concentrations for ΣDDT, and the principle metabolite *p,p'*-DDE (Figure 6.4 and Table 6.11). The concentration of *p,p'*-DDT in lettuce also increased with increasing soil concentration, but there were insufficient data points above the detection level to determine if similar relationships existed for radish. Increasing uptake of DDT residues with increasing soil contaminant concentration has been reported previously for various root vegetables including carrots, sweet potato and potatoes (Talekar *et al.*, 1983; Sadlo, 1995). In comparison there was no relationship between DDT levels measured in agricultural crops in

Slovakia (Schlosserová, 1992) or the levels of PCBs measured in cabbage, carrots and corn grown in PCB contaminated soil (Webber *et al.*, 1994).

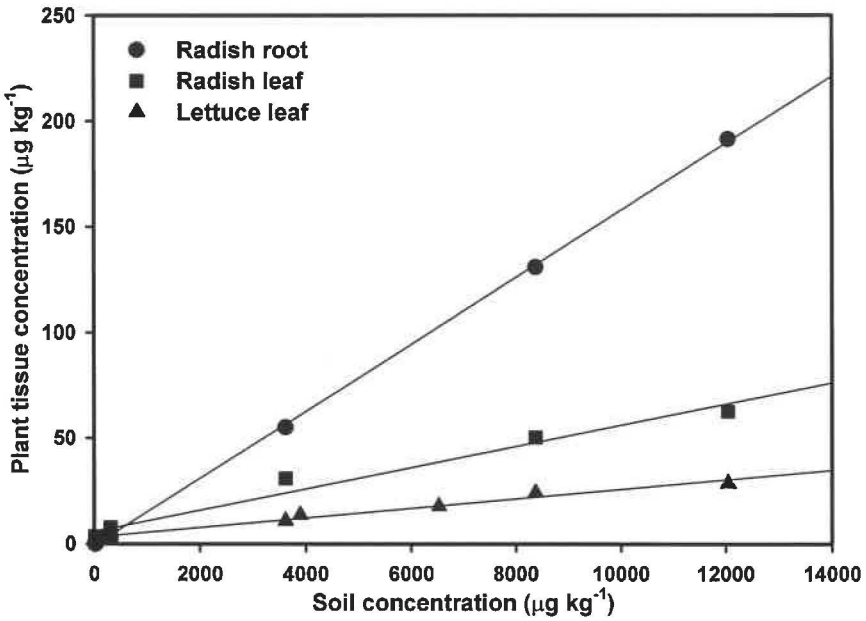


Figure 6.4: Relationship between plant tissue and soil ΣDDT concentration (µg kg^{-1} DW).

Table 6.11: Linear regression equations for the relationship between plant tissue (DW) and soil concentrations of *p,p'*-DDE, *p,p'*-DDE and ΣDDT (µg kg^{-1} DW).

	Regression equation	R^2
	lettuce	
ΣDDT	$y=0.0023 \times C_{soil} + 3.0478$	0.98***
p,p'-DDT	$y=0.0014 \times C_{soil} + 0.3235$	0.92***
p,p'-DDE	$y=0.0034 \times C_{soil} + 2.8697$	0.96***
	radish hypocotyl[a]	
ΣDDT	$y=0.0159 \times C_{soil} - 0.896$	1.00***
p,p'-DDE	$y=0.0203 \times C_{soil}l + 1.6185$	0.99***
	radish leaf[a]	
ΣDDT	$y=0.0059 \times C_{soil} + 4.557$	0.99***
p,p'-DDE	$y=0.008 \times C_{soil} + 4.8144$	0.98***

[a]Insufficient data points above the detection level to determine a relationship for *p,p'*-DDT, ***$p<0.001$

6.3.2.4 BIOACCUMULATION FACTORS

The bioaccumulation factors (BAF) calculated as the concentration in the plant tissue (DW) divided by the soil concentration were less than 1 indicating that radish and

lettuce did not bioaccumulate ΣDDT, *p,p'*-DDE or *p,p'*-DDT (Table 6.12) under the specified experimental conditions.

Table 6.12: BAFs calculated for lettuce, radish and radish leaf (*p,p'*- isomers of DDT and DDE).

	lettuce			radish hypocotyl			radish leaf		
	DDE	**DDT**	**ΣDDT**	**DDE**	**DDT**	**ΣDDT**	**DDE**	**DDT**	**ΣDDT**
Orchard 1	0.004	0.001	0.002	0.020	0.009	0.016	0.008	0.003	0.006
Orchard 2	0.005	0.001	0.003	0.023	0.010	0.016	0.010	0.004	0.006
Orchard 3[a]	0.005	0.001	0.003						
Orchard 4[a]	0.006	0.002	0.003						
Orchard 5	0.005	nc[b]	0.003	0.023	0.007	0.015	0.013	0.004	0.009
Vineyard	0.009	nc	0.008	0.025	nc	0.017	0.023	nc	0.016
Bushblock 1	0.174	nc	0.174	nc	nc	nc	0.207	nc	0.207
Bushblock 2	0.016	nc	0.013	0.021	nc	0.009	0.045	nc	0.024
Grazing 2	0.067	nc	0.067	nc	nc	nc	0.078	nc	0.078

[a]Radish not grown in these soils, [b]Not calculated as residue not present in plant tissue.

The BAFs calculated in the current study for uptake of aged DDT residues by lettuce and radish (Table 6.12) are comparable to the range reported for plants (0.00035–0.08, median 0.028) by the USEPA (2000), for potatoes grown on former orchard land contaminated by ΣDDT (0.06–0. 16, Smelt *et al.*, 1975) and for a range of 10 plant species selected for their ability to phytoextract heavy metals from soil (mean BAF value for *p,p'*-DDE of 0.18) (White *et al.*, 2005). The BAFs for the pot trial are also comparable to BAFs for spiked rather than aged soils. For example, similar BAFs (0.014–0.036) for uptake of DDT by radish from spiked soils can be calculated from the results reported by Lichenstein (1959). The BAFs obtained for ΣDDT, *p,p'*-DDT and *p,p'*-DDE in the reported experiments (Table 6.12) are lower than those reported for curcubits (e.g. stem 0.04–9.82, White *et al.*, 2003a) which have been demonstrated to bioaccumulate organochlorine pesticides to a greater extent than other types of vegetables (White *et al.*, 2003a; Lunney *et al.*, 2004).

For lettuce and radish leaf, the BAFs for ΣDDT, and the *p,p'*-DDE decreased with increasing soil concentration (Table 6.13). A similar pattern of has been observed for uptake of trace elements by lettuce and radish (Efroymson *et al.*, 2001; this study

(Chapter Seven, Section 7.3.3.2) and for uptake of DDT by vegetables (Lichenstein, 1959).

The BAF for ΣDDT uptake by radish hypocotyl (Table 6.13) was inversely related to %sand. In comparison, Beall and Nash (1969) and Lichenstein (1959) who reported that the phytoavailability of DDT decreased with increasing soil organic matter content. There were no other significant relationships between BAFs for plant uptake of ΣDDT and *p,p'*-DDE and soil properties, however the small size of the dataset may have masked significant relationships.

6.3.2.5 MECHANISM OF PLANT UPTAKE OF AGED ΣDDT RESIDUES

Tissue concentrations of both *p,p'*-DDT and *p,p'*-DDE increased with increasing soil concentration indicating that plant uptake had occurred. Several mechanisms have been identified for plant uptake of persistent organic pollutants from contaminated soil including; root uptake and translocation through the xylem, uptake from the vapour phase via the leaves and roots, and adhesion of soil particles (Simonich and Hites, 1995; Collins *et al.*, 2006). It is possible that a combination of these pathways contributed to the ΣDDT concentrations measured in the plant tissue. The experimental design employed in this study did not allow the pathways of root uptake and translocation to be distinguished from vapour phase uptake of *p,p'*-DDT and *p,p'*-DDE.

Table 6.13: Pearson's correlation coefficients for relationships between BAFs for ΣDDT and the *p,p'*-DDE versus soil ΣDDT and *p,p'*-DDE concentrations (log values) and soil properties. Significant correlations are presented in bold.

	BAFs for ΣDDT				BAFs for *p,p'*-DDE		
	Lettuce (n = 9)	**Radish (n = 5)**	**Radish leaf (n = 7)**		**Lettuce (n = 9)**	**Radish (n = 5)**	**Radish leaf (n = 7)**
ΣDDT	**-0.817****	0.483	**-0.809***	*p,p'*-DDE	**-0.802****	-0.329	**-0.818***
OlsenP	-0.611	0.706	-0.623	OlsenP	-0.615	-0.169	-0.671
%TOC	-0.348	0.061	-0.397	%TOC	-0.351	-0.741	-0.405
pH	0.230	0.766	0.234	pH	0.221	0.142	0.149
CEC	-0.271	0.051	-0.268	CEC	-0.272	-0.803	-0.279
%clay	0.126	0.771	0.133	%clay	0.125	0.578	0.096
%silt	0.162	0.844	0.003	%silt	0.151	0.138	-0.083
%sand	-0.192	**-0.995*****	-0.089	%sand	-0.183	-0.429	-0.009
Fe	-0.205	0.011	-0.180	Fe	-0.205	-0.647	-0.182
Mn	-0.625	0.081	-0.602	Mn	-0.624	-0.411	-0.607

* $p<0.05$, ** $p<0.01$, *** $p<0.001$.

The adhesion of DDT residue containing soil particles is unlikely to be a significant source of DDT residues in the plant tissues as the plant tissues were thoroughly washed to remove any adhering soil particles before freeze drying and analysis. The effectiveness of the plant washing procedure is verified by plant iron levels which can be used to provide an indication of potential contamination by soil. The plant tissue iron concentrations (Table 6.14) were within the range reported by Kabata-Pendias and Pendias (2001) of 29 to 130 mg Fe kg^{-1} DW in vegetables.

To demonstrate that the ΣDDT concentrations measured in the plant material were not primarily due to soil adhesion, the amount of adhered soil required to provide the equivalent ΣDDT concentration in the plant tissue was calculated. This figure was then used to calculate what the iron tissue concentration would have been if this amount of soil had adhered to the plant tissue. The predicted iron concentrations are compared to the measured concentrations in Table 6.14. For 50% of the plant tissue samples, the predicted iron level was at least twice the measured value indicating that soil contamination was not the main pathway for uptake of DDT and DDE into the plant material.

Table 6.14: Iron concentration (mg kg^{-1} DW) measured in plant tissue compared to predicted values calculated assuming that the ΣDDT measured was derived from adhered soil.

	Lettuce		Radish hypocotyl		Radish leaf	
	measured	predicted	measured	predicted	measured	predicted
Orchard 1	63	52	27	353	66	141
Orchard 2	64	32	41	172	59	66
Orchard 3[a]	62	32				
Orchard 4[a]	71	37				
Orchard 5	77	8	23	42	75	23
Vineyard	63	75	25	169	81	154
Bushblock 1	86	1702	39	nc[b]	99	2026
Bushblock 2	62	133	49	99	93	255
Grazing 2	85	198	31	nc[b]	94	232

[a]Radish not grown in these soils, [b]Iron tissue not able to be calculated as ΣDDT was not measured in the plant tissue.

Furthermore as discussed previously (Section 6.3.2.2), the *p,p'*-DDE:*p,p'*-DDT ratios for the plant tissue were consistently higher than those measured for the soil,

providing additional evidence that the adhering soil was not the main source of *p,p'* -DDE and *p,p'* -DDT in the plant material.

Some uptake of DDT to the plants from the vapour phase may have occurred as the soils were not covered to prevent volatilization and the small size of the pots resulted in the plants forming a canopy over the soil, thereby potentially trapping any volatilized compounds (Figure 6.5). The levels of ΣDDT compounds in the glasshouse air were not measured. Volatilisation from agricultural soils is a recognised source of DDT and other organochlorine pesticides in ambient air (Spencer *et al.*, 1996; Harner *et al.*, 1999; Bidleman and Leone, 2004). Furthermore, vegetation has been shown to take up persistent organochlorines from the vapour phase followed by partitioning into the plant tissue (Barber *et al.*, 2002). Any volatilized compounds would have most likely been absorbed by plant material directly above the soil and it is considered unlikely that volatilized compounds from higher level soils contaminated the plants growing in control soils as the ΣDDT concentrations in the plants grown in the control soils were consistently low despite the randomized trial design.

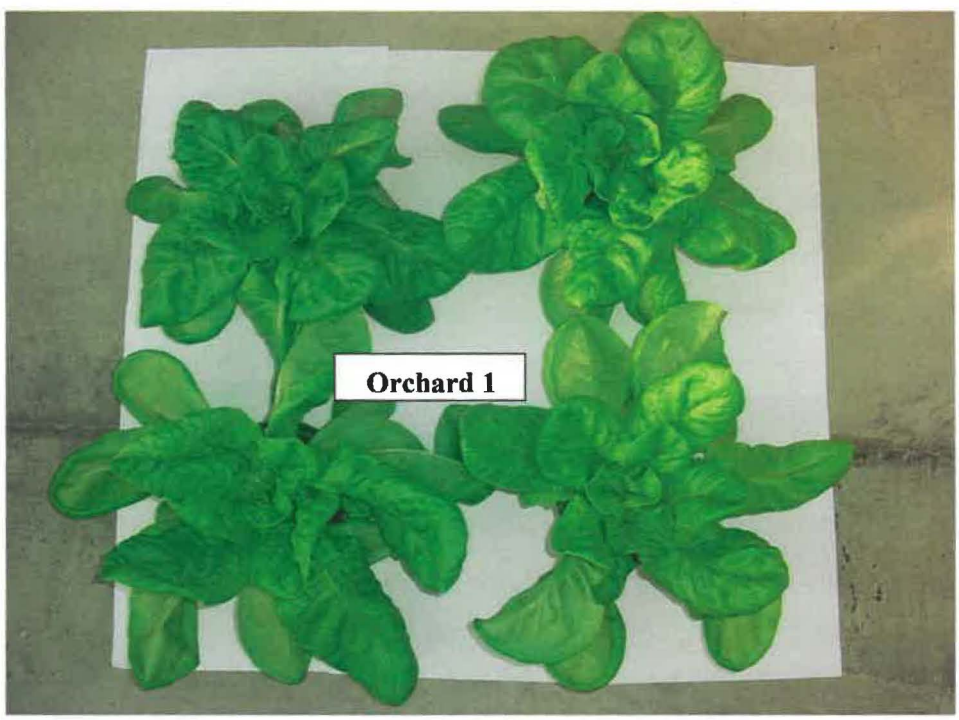


Figure 6.5: Photograph of lettuce plants grown in soil from Orchard 1 before harvest.

The presence of *p,p'*-DDE and *p,p'*-DDT in the above ground parts of the lettuce and radish indicate that root uptake and translocation of the aged DDT residues into plant tissues may have occurred despite the low water solubility of these compounds and the period of aging in the soil. Root uptake and translocation through the xylem has been observed for a range of persistent chlorinated organic pollutants including dioxins (Hülster *et al.*, 1994), ΣDDT (Lunney *et al.*, 2004), *p,p'*-DDE (White and Kottler 2002; White *et al.* 2003a) and chlordane (Mattina *et al.*, 2000; 2004). The decreasing BAFs with increasing soil concentration for lettuce and radish leaf are consistent with root uptake and translocation of *p,p'*-DDE and *p,p'*-DDT.

The uptake of *p,p'*-DDT and *p,p'*-DDE from soil to the plants may have been enhanced by the action of the growing plants and/or pre-treatment of the soils during setting up the experiment. The plants may have mobilized the *p,p'*-DDT and *p,p'*-DDE residues making them available for uptake and subsequent translocation. Plant roots release low molecular weight compounds (e.g. simple organic acids and carbohydrates) which can scavenge essential nutrients and trace elements (Marschener 1998; White and Kottler 2002; Singer *et al.* 2003), and it has recently been proposed that these root exudates are able to mobilize weathered POPs, including *p,p'*-DDE and chlordane (White *et al.*, 2003b; Mattina *et al.*, 2003), and in doing so, enhance plant uptake (White and Kottler 2002; White *et al.* 2003b). It has been suggested that these low molecular weight organic acids released by the plant roots breakdown organic and mineral phases of the soil and, in doing so, release bound organic pollutant residues (Mattina *et al.* 2003). This hypothesis is supported by experiments demonstrating that the addition of organic acids to *p,p'*-DDE contaminated soils enhanced plant uptake of *p,p'*-DDE (White and Kottler, 2002; White *et al.*, 2003b). It is likely that this effect would have occurred in the study reported here. The dimensions of the plant pots provided a higher root to soil ratio in the pots than would be typically encountered in a field situation. White *et al.* (2003a) have previously attributed a higher root to soil ratio of curcubits grown in a greenhouse trial for the higher phytoextraction of *p,p'*-DDE compared to those grown in the same soil under field conditions.

Determining the exact uptake mechanism of aged DDT contaminants to the plants is not critical to the outcomes of the experiment reported here. Regardless of which mechanism dominates uptake, the lettuce and radish plants accumulated DDT residues from the soil. This indicates that despite a considerable period of aging in soil, these historical DDT residues remain bioavailable to some extent and therefore present a hazard to ecological receptors and humans.

6.3.2.6 COMPARISON WITH REGULATORY STANDARDS

The New Zealand Food Standards 2005 do not include a maximum residue limit (MRL) for ΣDDT in vegetables and in the absence of a specified value the protocol is to assign a value of 0.1 mg kg^{-1} FW (FSANZ, 2005). Internationally, a range of regulatory levels are used (Table 6.15). The ΣDDT concentrations measured in the lettuce and radish in the reported experiments did not exceed any of these regulatory levels. However, lettuce and radish are both fast growing crops and it is possible that other crops grown in the same or similar soils could exceed these maximum residue limits. As cucurbits have been found to bioaccumulate organochlorine compounds including ΣDDT from soil (e.g. Mattina *et al.*, 2003; White *et al.*, 2003a; Lunney *et al.*, 2004), it is possible that these crops could exceed international food standards if grown on former orchard soils. Similarly, carrots have been reported to take up more DDT than other vegetables due to their higher lipid content (Lichtenstein, 1959). This specific uptake pathway may enhance uptake of DDT residues to the extent that carrots exceed regulatory standards.

Table 6.15: International standards for ΣDDT (mg kg^{-1} FW) residues in vegetables.

	Vegetable	ΣDDT
US FDA action levels[a]	lettuce	0.5 mg kg^{-1}
	radish	0.2 mg kg^{-1}
Codex aliamentarius EMRL[b]	carrot	0.2 mg kg^{-1}
European Council MRLs[c]	vegetables	0.05 mg kg^{-1}

[a]USFDA (2000), [b]Codex aliamentarius, [c]NZFSA (2004).

6.3.2.7 TOXICITY OF AGED DDT RESIDUES TO PLANTS

The dry weights of the lettuce, radish hypocotyls and radish leaves were measured to determine yield (Data presented in Chapter Seven, Section 7.3.3.3). There were no significant correlations (Spearman rank correlation, $p<0.05$) between the mean dry matter yields for lettuce and radish hypocotyls, and the mean soil and plant tissue ΣDDT, *p,p'*-DDE and *p,p'*-DDT concentrations (Table 6.16). In contrast, the radish leaf yields decreased with increasing leaf ΣDDT concentrations ($p<0.05$).

The concentrations of *p,p'*-DDT in the test soils were below levels which had been previously reported to reduce plant yields. For example, a soil concentration of 100 mg kg^{-1} ^{14}C–DDT reduced seedling height of peanuts and mustard (Mitra and Raghu,1989) and Hund-Rinke and Simon (2005) calculated an EC_{50} for DDT of >1000 mg kg^{-1} for biomass reduction of *Brassica rapa* and *Avena sativa.* An earlier study by Dennis and Edwards (1964) found that applications of DDT had no effect on the growth of lettuce, stimulated the growth of cucumbers, carrots and parsnips and decreased the growth of dwarf beans and tomatoes. As discussed in Chapter Seven (Section 7.3.3.3), it is more likely that the reduced yield for radish leaves resulted from copper rather than ΣDDT contamination as ΣDDT and copper concentrations in assay soils were correlated ($p<0.001$).

Table 6.16: Spearman rank correlation coefficients between mean plant yield and mean soil and plant tissue *p,p'*-DDE, *p,p'*-DDT and ΣDDT concentrations.

	Radish leaf (n = 7)	**Radish hypocotyl (n = 7)**	**Lettuce (n = 9)**
soil residues			
p,p'-DDE	-0.714	0.179	0.633
p,p'-DDT	-0.739	-0.126	0.502
ΣDDT	-0.714	0.179	0.667
tissue residues			
p,p'-DDE	-0.75	0.198	0.6
p,p'-DDT	-0.493	0.039	0.452
ΣDDT	**-0.821***	0.198	0.6

* $p<0.05$

The soils (refer Table 6.1) collected for the worm assay were also utilised in 5 day seedling emergence and root elongation assays for both a monocotyledonous (ryegrass) and a dicotyledonenous (lettuce) plant species (data reported in Table 7.25, Chapter 7). The germination rates and root growth of both plant species were not inhibited by the aged DDT residues as there was no correlation between germination rate or root elongation and soil ΣDDT, *p,p'*-DDE and *p,p'*-DDT levels as extracted by acetone:hexane. These results are in agreement with those of Rajanna and de la Cruz (1977) who found that soil concentrations of DDT up to 50 mg kg^{-1} had no significant effects on germination and seedling height for high quality seed of soybeans, cotton and maize.

6.4 CONCLUSIONS

6.4.1 EARTHWORM ASSAY

There were highly significant correlations between the concentrations of ΣDDT and the *p,p'*- isomers of DDT, DDE and DDD extracted using two methods – ethyl acetate and acetone:hexane. However, the ethyl acetate extraction consistently extracted less *p,p'*-DDE ($p<0.03$). Two biomimetic techniques - C-18 disks and Tenax resin were also used to estimate the bioavailable fraction of ΣDDT residues in orchard soils. The Tenax resin adsorbed up to 23% and the C-18 disks up to 2.5% of the ΣDDT residues from orchard soils.

Aporrectodea caliginosa bioaccumulated aged DDT residues during the 28 day bioassay with the worm tissue concentrations increasing with increasing soil concentration. Concentrations of DDT residues in the worm tissue were significantly correlated with soil DDT residue concentrations as measured by either ethyl acetate and acetone:hexane extraction. The ΣDDT concentrations measured in worm tissue for two of the assayed soils exceeded the concentration of 32 mg kg^{-1} considered to be hazardous to sensitive bird species.

The amount of aged DDT residues desorbed from soil by Tenax resin and C-18 disks correlated with worm tissue concentrations. The results indicated that Tenax provides an improved procedure for estimating bioavailability of aged DDT residues in soil to *A. caliginosa.* The worm tissue concentrations and the relatively high percentage of ΣDDT desorbed by Tenax indicated that a significant proportion of the aged DDT residues in orchard soils remain bioavailable.

6.4.2 PLANT ASSAYS

The *p,p'*- isomers of DDE and DDT were the predominant DDT residues measured in lettuce and radish tissues. Concentrations of ΣDDT, *p,p'*-DDE and *p,p'*-DDT in plant tissue increased with increasing soil concentration ($p<0.001$). These results show that a fraction of the aged DDT residues in NZ horticultural soils is phytoavailable. While it is likely that several uptake mechanisms occurred simultaneously, the elevated DDE:DDT ratios calculated for the plant tissue compared to those calculated for the soil indicate that root uptake and translocation of the aged residues predominated. The aged DDT residues in soil were not toxic to *La. sativa*, *R. sativus* and *Lo. perenne.*

7 BIOAVAILABILITY AND ECOTOXICITY OF TRACE ELEMENTS IN HORTICULTURAL SOILS

7.1 INTRODUCTION

In Chapter Four, orchards were identified as the horticultural landuse most likely to contain residues exceeding soil criteria for the protection of terrestrial organisms and or plant tissue concentrations. The trace elements which either frequently exceeded soil criteria or are of concern due to their toxicity to terrestrial organisms are arsenic, cadmium, copper, lead and zinc. The phytoavailability of arsenic, cadmium and lead in New Zealand soils is of interest because of their potential toxicity to humans. Concentrations of cadmium, copper and zinc in horticultural soils are likely to increase as these trace elements are still being added to horticultural soils in New Zealand through the use of agrichemicals and soil amendments. As outlined in the introduction to this thesis, there is currently a paucity of New Zealand data on the bioavailability and ecotoxicity of aged trace elements in soil to terrestrial organisms. This information is needed to support the derivation of soil quality guidelines which are appropriate in the New Zealand setting.

It is generally agreed that total trace element concentrations in soil can be a poor predictor of the bioavailability and environmental risk of trace element contamination in soils (Allen, 2002; Meers *et al.*, 2005) and it has been suggested that soil criteria based on total trace element concentrations are unnecessarily conservative (Sauvé *et al.*, 1996; McLaughlin *et al.*, 2000b; Allen, 2002). There is a need to develop robust tools based on chemical measurements which are able predict bioavailability thus avoiding the need to undertake bioassays which are often expensive and time consuming (Sauve *et al.*, 1998; Basta and Gradwohl, 2000; McLaughlin *et al.*, 2000b). One approach to assess the bioavailability of trace elements is through extractions with neutral salt solutions which simulate soil solution conditions (Gray *et al.*, 1999a). Examples of commonly used neutral salt extractants include NH_4NO_3, $NaNO_3$, $CaCl_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$ and $MgCl_2$ (McLaughlin *et al.*, 2000b).

Solutions of 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 were selected for the work presented in this Chapter - 0.01 *M* $CaCl_2$ was chosen because it has been widely used in studies assessing the availability of trace elements from soil and 1 *M* NH_4NO_3 was selected because it is used in the German regulatory method (DIN 19730:06.97) (Federal Government, 1999) for assessing the plant available fraction of trace elements in soil. Soil trigger values for plant growth impairment and plant quality for vegetable gardens and agricultural land based on the 1 *M* NH_4NO_3 extractable trace element concentrations have been developed as part of the German Federal Soil Protection and Contaminated Sites Ordinance (Federal Government, 1999).

Neutral salt solutions extract lower concentrations of trace elements than acid digestions from soil and the fraction extracted is referred to as the readily soluble fraction (NRC, 2003) or mobile fraction (Gupta *et al.,* 1996). Neutral salt extractants such as $CaCl_2$ and NH_4NO_3 remove metals from soil through desorption and ion exchange processes. The desorbing cation (e.g. Ca^{2+} or NH_4^+) replaces metal ions sorbed to the solid phase moving them from the solid phase to solution through mass action (McLaughlin *et al.*, 2000b). For $CaCl_2$, chloride complexation may also be involved in the case of some metals.

0.01 *M* $CaCl_2$ is considered to be a universal soil extractant as its ionic strength at 0.03 *M* is comparable to the average ionic strength in soil solutions (Houba *et al.,* 1996; Kabata-Pendias and Pendias, 2001). While it was initially proposed as a method for determining phytoavailability of trace elements (Houba *et al.,* 1990; Novozamsky *et al.*, 1993), extractions with 0.01 *M* $CaCl_2$ have been used to measure the availability of trace elements in spiked and aged soils to several earthworm species including *A. caliginosa, Eisenia fetida, Enchytraeus crypticus* and *Lumbricus rubellus* (Janssen *et al.,* 1997a; Marinussen *et al.,* 1997; Weltje, 1998; Peijnenburg *et al.*, 1999; Ma, 2005).

0.01 *M* $CaCl_2$ extractions have been used to measure the phytoavailable fraction of trace elements in Dutch soils (Peijnenburg *et al.,* 2000), Australian cropping soils (McLaughlin *et al.*, 1999; Nolan *et al.*, 2005; Rayment, 2005), and French and Italian vineyard soils (Deluisa *et al.*, 1996; Brun *et al.*, 1998; Brun *et al.*, 2001) among others. Two New Zealand studies have compared 0.01 *M* $CaCl_2$ extractable cadmium to plant uptake trials (Andrewes *et al.*, 1996; Gray *et al.*, 1999a). Other applications

- To assess the ecotoxicity of selected trace elements in such orchard soils to *A. caliginosa* and plants (*La. sativa, R.sativus* and *Lo. perenne*).

- To compare uptake of selected trace elements by *A. caliginosa* and edible plants (*La. sativa* and *R. sativus*) to neutral salt (0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3) extractable concentrations of trace elements in soil to determine whether these methods can be used as surrogates to measure the available fraction of trace elements in NZ soils.

- To compare concentrations of trace elements measured in the edible plants with available regulatory standards.

7.2 METHOD SUMMARY AND DATA ANALYSIS

A description of the methods used to generate the data presented in this chapter is presented in Chapter Two.

7.2.1 CHEMICAL MEASUREMENTS OF TRACE ELEMENT AVAILABILITY

Two neutral salt extractions 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3, were used to determine the available fraction of trace elements in soils. These methods were validated by comparison with the tissue results from the plant and worm assays.

7.2.2 EARTHWORM ASSAY

The availability and toxicity of trace elements to the endogenous earthworm *A. caliginosa* were measured using a 28 day bioassay. Ten soils were collected from orchard and background sites from within the Auckland and Waikato regions. Where possible for each orchard, soil was collected from an adjacent grazing site as a control.

of 0.01 *M* $CaCl_2$ extractions include determining toxicity of soil to microorganisms (Merrington *et al.*, 2002), the extractability of trace elements from Welsh soils (Rieuwerts *et al.*, 2005) and concentrations in surface runoff. For example, He *et al.* (2004) found that the 0.01 *M* $CaCl_2$ extractable fraction of copper, iron, zinc and manganese correlated with levels in runoff from Florida citrus orchards.

Extraction with 1 *M* NH_4NO_3 removes the mobile and unspecifically adsorbed fraction of trace elements in soil including the water-soluble and exchangeable heavy metals as well as slightly soluble organometallic complexes (Zeien and Brümmer, 1989 cited in Manz *et al.*1999). Extractions with 1 *M* NH_4NO_3 have been utilised in several studies measuring the phytoavailability of trace elements in soil to plants (Singh *et al.*, 1995; Hooda *et al.*, 1997; McLaughlin *et al.*, 1999; Song *et al.*, 2004; Brown *et al.*, 2005; Gryschko *et al.*, 2005; Zhou *et al.*, 2005). The 1 *M* NH_4NO_3 extractable fraction of cadmium in New Zealand pasture soils correlated with edible plant tissue concentrations (Gray *et al.*, 1999a). Other reported applications of 1 *M* NH_4NO_3 include assessment of the bioavailable fraction of copper to earthworms (Belotti, 1998), measurement of the easily soluble fraction of trace elements in topsoils impacted by the Aznalcóllar spill of mine tailings (Nagel *et al.*; 2003) and measurement of the mobile fraction of trace elements in German agricultural soils (Manz *et al.*, 1999).

Bioassays were undertaken to determine the bioavailability and ecotoxicity of aged trace element residues in orchard soils to earthworms and plants.

7.1.1 OBJECTIVES:

The principle objectives of the work presented in this Chapter were:

- To assess the availability of residual trace elements (arsenic, cadmium, copper, lead and zinc) in aged orchard soils for uptake by *A. caliginosa* and two edible plant species (*La. sativa* and *R. sativus*) which are commonly grown in home gardens.

7.2.3 PLANT UPTAKE AND PHYTOTOXICITY OF TRACE ELEMENTS

The phytoavailability of trace elements to edible plants (lettuce and radish) was assessed using a pot trial. Lettuce and radish were grown on soils collected from three orchards, one vineyard, two grazing paddocks and two bushblocks in the Auckland region. A further two soils were prepared from by blending an orchard soil with soil collected from an adjacent bush block. The blended soils were utilised to grow lettuce only. The plant tissues were analysed for both ΣDDT and trace elements. The ΣDDT data was presented in Chapter Six. Phytotoxicity was determined by measuring the dry mass yield of the lettuce and radish at the end of the assay period as well as by a five day seedling emergence and root elongation assay for lettuce and ryegrass grown in sub-samples of the worm assay soils.

7.2.4 DATA ANALYSIS

Statistical analyses were carried out using customized Microsoft Excel worksheets, Data Desk 6.0 and Minitab (version 14.20). Linear regression analysis of log transformed variables was used to determine relationships between tissue (worm or plant) and soil concentrations. Where appropriate, best subsets linear regression analysis was used to identify soil properties to improve the fit of the regression model. Pearson's correlation analysis of log transformed data was used to explore correlations between neutral salt extractable soil trace element concentrations and worm or plant tissue concentrations of trace elements. Pearson's correlation analysis was also used to determine correlations between soil characteristics and BAFs and tissue concentrations. Spearman rank correlation analysis was used to determine relationships between toxicological endpoints and soil trace element concentrations. Significant differences between data for landuse subsets were calculated using Student's t-tests. For all statistical analyses, results with $p<0.05$ were considered to be significant.

7.2.5 COMPARISON WITH LITERATURE DATA

Wherever possible, results have been compared to published data for *A. caliginosa* (previously *Allolobophora caliginosa*) in preference to data for other earthworm species. This is because the rate and extent of trace element uptake can be earthworm species dependent (Ma, 1988; Morgan and Morgan 1992; Terihuvo *et al.*, 1994; Spurgeon *et al.*, 2000; Dai *et al.* 2004; Becquer *et al.*, 2005). These differences may be explained partially by both differences in feeding behaviour and preferred habitat. The test organism used in the worm bioassay, *A. caliginosa* is an endogenous earthworm species which feed on decomposed organic matter in the soil (Belotti, 1998) whereas other commonly used test species such as *Lumbricus rubellus* and *E. fetida* are litter feeding species (Cortet *et al.*, 1999; Dai *et al.*, 2004). Additionally *A. caliginosa* may be more sensitive to the effects of trace elements than other worm species (Spurgeon *et al.*, 2000; Nahmani *et al.*, 2003).

Similarly trace element uptake by plants has been demonstrated to be both species and cultivar dependent as well as trace element specific (Davis, 1979; Crews and Davies, 1985; Xu and Thornton, 1985; Merry *et al.*, 1986b; Peijnenburg *et al.*, 2000; Naidu *et al.*, 2003; Gray and McLaren, 2005). Plant uptake of trace elements has also been shown to be concentration dependent (Alloway *et al.*, 1990; Efroymson *et al.*, 2001; Samsøe-Petersen *et al.*, 2002), hence where possible, only results from studies which utilised soils with comparable contaminant concentrations have been used here for comparative purposes.

7.3 RESULTS AND DISCUSSION

7.3.1 NEUTRAL SALT EXTRACTION OF TRACE ELEMENTS

The trace element content of the soils tested in the worm and plant assays was determined using a HNO_3/HCl digestion (Chapter Two, Section 2.6.1.2) as well as two neutral salt extraction solutions; 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 (Chapter Two, Section 2.6.3.1). The soil total and extractable trace element concentrations for the

two assays were combined into one dataset for data analysis. The results for the total and extractable trace elements are presented in Tables 7.1 and 7.2. Arsenic was not extracted at levels above the detection limit by either of the neutral salt extraction procedures. For the other trace elements, the amount of trace element extracted followed the order total >1 *M* NH_4NO_3> 0.01 *M* $CaCl_2$. With the exception of plant assay soil Bushblock 2, 0.01 *M* $CaCl_2$ only extracted detectable lead concentrations from horticultural soils i.e. properties where lead arsenate is likely to have been used.

Table 7.1: Trace element concentrations (mg kg^{-1} DW) in soils used for the worm and plant assays. Orchards and their controls have the same subscript.

	As	Cd	Cu	Pb	Zn
Worm assay					
orchards					
W1[a]	98.0	1.73	773	442	85
W2[b]	2.5	0.33	377	18	16
W3	30.1	0.78	326	142	33
W4	4.9	0.74	237	45	114
W5[c]	3.2	0.77	212	20	38
W6[d]	6.8	0.23	123	118	18
grazing soils					
W7[a]	5.6	0.55	14	34	96
W8[b]	1.7	0.61	71	19	31
W9[c]	1.9	0.40	57	15	28
W10[d]	0.4	0.06	<3	<4	5
Plant assay					
horticultural soils					
Orchard 1[a]	15.2	0.54	366	59	65
Orchard 2[b]	35.6	0.38	314	116	47
Orchard 3	28.0	0.30	243	97	44
Orchard 4	18.3	0.23	160	67	38
Orchard 5[c]	5.6	0.24	73	78	16
Vineyard	2.1	0.16	117	57	63
control soils					
Grazing 1[a]	2.3	0.28	17	34	80
Grazing 2[c]	0.4	0.09	3	4	6
Bushblock 1	1.7	0.04	18	10	9
Bushblock 2[b]	1.7	0.03	12	16	26

Table 7.2a: Mean (n = 2) 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable trace element concentrations (mg kg^{-1}) in worm assay soils.

	0.01 *M* $CaCl_2$		1 *M* NH_4NO_3		0.01 *M* $CaCl_2$		1 *M* NH_4NO_3	
	mg kg^{-1}	% extracted[a]	mg kg^{-1}	% extracted	mg kg^{-1}	% extracted	mg kg^{-1}	% extracted
	Cadmium				*Zinc*			
W1	0.0362	2.1	0.044	2.5	0.84	1.0	1.95	2.3
W2	0.0270	8.3	0.035	10.8	0.45	2.8	0.84	5.3
W3	0.0458	5.9	0.093	11.9	0.80	2.4	2.13	6.4
W4	0.0179	2.4	0.023	3.0	0.50	0.4	1.94	1.7
W5	0.0151	1.9	0.016	2.1	0.15	0.4	0.30	0.8
W6	0.0167	7.3	0.015	6.4	0.87	4.9	1.09	6.2
W7	0.0216	3.9	0.026	4.7	0.20	0.2	1.65	1.7
W8	0.0316	5.2	0.044	7.2	0.70	2.2	1.46	4.7
W9	0.0101	2.5	0.011	2.8	0.17	0.6	0.32	1.2
W10	0.0101	16.9	0.009	14.7	0.40	7.5	0.45	8.5
	Copper				*Lead*			
W1	0.675	0.1	0.915	0.1	<0.005	0	0.240	0.1
W2	1.099	0.3	1.993	0.5	<0.005	0	0.021	0.1
W3	0.505	0.2	0.782	0.2	0.010	0.01	0.152	0.1
W4	0.174	0.1	0.251	0.1	<0.005	0	0.018	0.0
W5	0.230	0.1	0.256	0.1	<0.005	0	<0.003	0.0
W6	0.332	0.3	0.377	0.3	0.072	0.06	0.406	0.3
W7	0.000	0.0	0.020	0.1	<0.005	0	0.012	0.0
W8	0.152	0.2	0.161	0.2	<0.005	0	0.031	0.2
W9	0.106	0.2	0.121	0.2	<0.005	0	<0.003	0.0
W10	<0.025	0.0	<0.013	0.0	<0.005	0	0.010	0.5

[a]Relative to total trace element concentration (Table 7.1).

Table 7.2b: Mean (n = 2) 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable trace element concentrations (mg kg^{-1}) in plant assay soils.

	0.01 *M* $CaCl_2$		1 *M* NH_4NO_3		0.01 *M* $CaCl_2$		1 *M* NH_4NO_3	
	mg kg^{-1}	% extracted[a]	mg kg^{-1}	% extracted	mg kg^{-1}	% extracted	mg kg^{-1}	% extracted
Cadmium					*Zinc*			
Orchard 1	0.0155	2.9	0.025	4.7	1.02	1.6	2.24	3.4
Orchard 2	0.0077	2.0	0.009	2.4	0.20	0.4	0.31	0.7
Orchard 3	0.0104	3.5	0.011	3.8	0.45	1.0	0.82	1.9
Orchard 4	0.0119	5.2	0.015	6.5	0.92	2.4	1.63	4.3
Orchard 5	0.0136	5.7	0.011	4.7	0.82	5.0	1.09	6.7
Vineyard	0.0187	11.7	0.024	14.8	2.57	4.1	4.76	7.6
Grazing 1	0.0087	3.1	0.014	5.0	0.84	1.1	2.07	2.6
Grazing 2	0.0114	12.7	0.010	10.8	0.50	8.0	0.62	10.0
Bushblock 1	0.0055	13.7	0.007	17.4	0.27	3.0	0.51	5.6
Bushblock 2	0.0042	14.1	0.006	18.7	1.99	7.7	3.52	13.6
Copper					*Lead*			
Orchard 1	0.569	0.2	0.618	0.2	<0.005	0	0.038	0.1
Orchard 2	0.355	0.1	0.388	0.1	<0.005	0	0.037	0.0
Orchard 3	0.391	0.2	0.389	0.2	0.012	0.02	0.062	0.1
Orchard 4	0.366	0.2	0.412	0.3	0.010	0.01	0.122	0.2
Orchard 5	0.232	0.3	0.271	0.4	0.025	0.03	0.147	0.2
Vineyard	0.386	0.3	0.535	0.5	0.030	0.05	0.330	0.6
Grazing 1	0.027	0.2	0.027	0.2	<0.005	0	0.022	0.1
Grazing 2	<0.005	0.0	0.015	0.4	<0.005	0	0.010	0.3
Bushblock 1	0.050	0.3	0.071	0.4	<0.005	0	0.042	0.4
Bushblock 2	0.037	0.3	0.055	0.4	0.020	0.13	0.201	1.2

[a]relative to total trace element concentration (Table 7.1).

Few studies have reported results for 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractions of the same soils. Consistent with the results reported in this study, 1 *M* NH_4NO_3 extracted more cadmium, copper, lead and zinc than 0.01 *M* $CaCl_2$ from soils contaminated with dust from a metal plant (Lebourg *et al.*, 1998) as well as more copper, lead and zinc than 0.01 *M* $CaCl_2$ from soils impacted by smelter emissions (Karczewska, 2002, cited in Kabata-Pendias, 2004). Similarly, 1 *M* NH_4NO_3 extracted more copper than 0.01 *M* $CaCl_2$ from NZ pasture soils spiked with copper salts (Khan *et al.*, 2005). Correspondingly, Gray *et al.* (1999a) found that 1 *M* NH_4NO_3 extracted more cadmium than 0.01 *M* $CaCl_2$ from New Zealand pasture soils and 1 *M* NH_4NO_3 extracted more cadmium than 0.01 *M* $CaCl_2$ from Australian potato cropping soils (McLaughlin *et al.*, 1999).

The differences in the amount of trace element extracted by the two neutral salt extractants may be attributed to differences in solution properties. 1 *M* NH_4NO_3 contributes protons lowering the pH during the extraction (Husz, 2001). Accordingly, Gryschko *et al.* (2005) measured the pH of soil extraction solutions of 1 *M* NH_4NO_3, water and 1 *M* KNO_3, the pH of a 1 *M* NH_4NO_3 solution was approximately 0.5 to 1 pH unit lower than a water solution. Additionally NH_4NO_3 is able to form ammine complexes with some metals (Lebourg *et al.*, 1998; Gryschko *et al.*, 2005) and the higher ionic strength of the extracting solution compared to 0.01 *M* $CaCl_2$ increases desorption of cations (Gryschko *et al.*, 2005). Chloride ions can also form strong complexes with some metals including cadmium, mercury and manganese thus enhancing desorption of metal from the solid phase (McLaughlin *et al.*, 2000b). 1 *M* NH_4NO_3 may also hydrolyse clays present in soil further releasing bound trace elements (Ure, 1996)

Arsenic was not extracted by 0.01 *M* $CaCl_2$, and 1 *M* NH_4NO_3 extracted arsenic from only three soils (Orchards 2 and 5, W6) at levels equivalent to the detection limit (0.02 mg kg^{-1}) despite both of these extraction solutions having been previously reported to extract arsenic from European soils. Gryschko *et al.* (2005) cited correlations from two trials between the amount of arsenic extracted by 1 *M* NH_4NO_3 and plant uptake, and Janssen *et al.* (1997a) reported significant correlations between 0.01 *M* $CaCl_2$ extractable arsenic and arsenic concentrations in *Eisenia Andrei.*

Additionally, there is a German trigger value for plant growth impairment for agricultural land of 0.4 mg kg^{-1}arsenic extracted by 1 *M* NH_4NO_3 (Federal Government, 1999).

This observed difference in arsenic extractability between the current study and the European data may be due to differences in soil pH for the various studies as arsenic is more mobile in alkaline soils (Adriano, 2001). For example, the soils used for the study reported by Janssen *et al.* (1997a) ranged from 3.8 to 7.9 with a median value of 6.3 (Janssen *et al.*, 1997a,b) whereas the maximum pH for the current study was 6.0 (Appendix B). In addition, calcium has been used to immobilise arsenic in contaminated soils and sediments through the formation of calcium-arsenate precipitates (Moon *et al.*, 2004).

7.3.1.1 CORRELATIONS BETWEEN TOTAL AND NEUTRAL SALT EXTRACTABLE TRACE ELEMENTS

There were significant correlations between the total and 0.01 *M* $CaCl_2$ extractable trace element concentration for cadmium and copper (Table 7.3). In contrast there was no significant correlation between total and 0.01 *M* $CaCl_2$ extractable zinc. Similarly, for the seven soils in which detectable levels of 0.01 *M* $CaCl_2$ extractable lead were measured there was also no correlation with total lead. These results for copper agree with other studies which have reported an increase in 0.01 *M* $CaCl_2$ extractable copper with increasing soil copper concentration (Pedersen *et al.*, 2000; Loland and Singh, 2004; Khan *et al.*, 2005; Ma 2005; van Vliet *et al.*, 2005). In comparison, total and 0.01 *M* $CaCl_2$ extractable copper were not correlated in French (Brun *et al.*, 1998) and Italian (Deluisa *et al.*, 1996) vineyard soils or in soil samples collected from an Australian orchard (Merrington *et al.*, 2002). Consistent with the results presented here, 0.01 *M* $CaCl_2$ extractable cadmium has been reported to increase with total cadmium (Gray *et al.*, 1999a; van Vliet *et al.*, 2005).

Table 7.3: Pearson's correlation coefficients for relationships between 0.01 *M* $CaCl_2$ extractable trace elements and total trace element concentrations (log transformed variables). Significant correlations are presented in bold.

	Cd_{CaCl_2}	Cu_{CaCl_2}	Zn_{CaCl_2}	%Cd[a]	%Cu	%Zn
Cd_{total}	**0.751*** **	**0.564** **	-0.203	**-0.827*** **	**-0.72*** **	**-0.678*** **
Cu_{total}	**0.516***	**0.922*** **	0.027	**-0.534***	**-0.524***	-0.292
Zn_{total}	0.303	0.119	0.122	**-0.724*** **	**-0.702*** **	**-0.714*** **
%clay	0.313	0.214	-0.216	-0.14	0.011	-0.246
%silt	0.144	-0.024	-0.158	-0.28	-0.358	-0.174
%sand	-0.311	0	0.115	0.274	0.255	0.264
pH	0.132	0.145	-0.562	**-0.74*** **	**-0.702*** **	**-0.727*** **
TOC	**0.444***	-0.107	0.119	**-0.63** **	**-0.577** **	**-0.469***
CEC	0.407	0.126	-0.105	**-0.7*** **	**-0.659** **	**-0.603** **
Olsen P	**0.533***	**0.856*** **	0.068	**-0.587** **	-0.286	-0.305
Mn	0.135	-0.087	0.346	**-0.79*** **	**-0.779*** **	**-0.873*** **
Fe	0.257	-0.051	-0.067	**-0.57** **	**-0.559***	**-0.66** **

[a]Percent trace element extracted by 0.01 *M* $CaCl_2$ relative to total trace element, *p <0.05, **p <0.01, ***p <0.001.

Table 7.4: Pearson's correlation coefficients for relationships between 1 *M* NH_4NO_3 extractable trace elements and total trace element concentrations (log transformed variables). Significant correlations are presented in bold.

	$Cd_{NH_4NO_3}$	$Cu_{NH_4NO_3}$	$Pb_{NH_4NO_3}$	$Zn_{NH_4NO_3}$	%Cd[a]	%Cu	%Pb	%Zn
Cd_{total}	**0.736*** **	**0.447***	0.052	0.065	**-0.744*** **	**-0.723*** **	**-0.807*** **	**-0.628** **
Cu_{total}	**0.543***	**0.932*** **	**0.468***	0.154	**-0.518***	-0.4	**-0.516***	-0.441
Pb_{total}	**0.45***	**0.618** **	**0.65** **	0.39	**-0.47***	-0.44	-0.5	-0.31
Zn_{total}	0.428	0.166	0.172	**0.493***	**-0.568** **	**-0.736*** **	**-0.641**	**-0.562** **
%clay	0.431	0.388	-0.010	-0.146	0.023	-0	-0.191	-0.26
%silt	0.036	-0.125	-0.238	-0.141	-0.362	-0.32	-0.25	-0.214
%sand	-0.405	-0.175	0.049	0.033	0.134	0.197	0.245	0.267
pH	0.066	-0.023	-0.252	-0.365	**-0.79*** **	**-0.66** **	**-0.742*** **	**-0.774*** **
TOC	**0.54***	-0.028	0.102	0.386	**-0.486***	**-0.62** **	**-0.445***	-0.344
CEC	**0.593** **	0.324	-0.021	0.183	**-0.464***	**-0.62** **	**-0.647** **	**-0.507***
OlsenP	**0.526***	**0.807*** **	0.374	0.066	**-0.518***	-0.307	**-0.542***	-0.390
Fe	**0.499***	0.144	-0.057	0.311	-0.308	**-0.56***	**-0.55***	**-0.494***
Mn	0.2	-0.172	-0.13	-0.055	**-0.715*** **	**-0.81*** **	**-0.71*** **	**-0.759*** **

[a]Percent trace element extracted by 1 *M* NH_4NO_3 relative to total trace elements, *p <0.05, **p <0.01, ***p <0.001.

There were significant correlations between the total and 1 *M* NH_4NO_3 extractable concentrations of copper (p<0.001) cadmium (p<0.001), lead (p<0.01) and zinc (p<0.05) (Table 7.4). Khan *et al.* (2005) also reported increasing concentrations of 1 *M* NH_4NO_3 extractable copper with increasing copper concentration for spiked NZ pasture soil. Gray *et al.* (1999a) measured a significant correlation between total and 1 *M* NH_4NO_3 extractable cadmium in NZ pasture soils and McLaughlin *et al.* (1999) reported a similar correlation for Australian potato cropping soils.

7.3.1.2 PERCENT OF TOTAL TRACE ELEMENT EXTRACTED BY NEUTRAL SALTS

The percent of the total trace element concentration extracted by the neutral salts (Table 7.2) followed the order cadmium>zinc>copper>lead for both 1 *M* NH_4NO_3 and 0.01 *M* $CaCl_2$. These results are comparable to the percent of trace element extracted and the order of extraction previously reported for 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3. In Polish soils, the order of extractability for 0.01 *M* $CaCl_2$ was zinc (0.5–22%)> copper (0.3–7.8%) >lead (0.3–2%) and for 1 *M* NH_4NO_3 zinc (1–25%)> copper (2–16%) >lead (1–2%) (Karczewska, 2002). This relative order of extractability is the inverse of the order for the specific adsorption of metals of Cd<Ni<Co<Zn<Cu<Pb<Hg based on the equilibrium constants (pK) for the reaction $M^{2+} + H_2O = MOH^+ + H^+$ and for metals with equal pK values, on ionic size (Brummer, 1986). It is also similar to relative order for the percent of total metal concentration extracted from sewage sludge amended soil by hot 0.01 *M* $CaCl_2$ of cadmium (0.9%) = copper (0.9%) > zinc (0.05%) reported by McBride and Evans (2002). The percent of total trace element extracted (Table 7.2) is consistent with the percent of copper (≤10%) and zinc (≤5%) extracted from agricultural soils by NH_4NO_3 (Manz *et al.*, 1999).

The percent of cadmium, copper and zinc extracted by 0.01 *M* $CaCl_2$ decreased with increasing total soil concentration ($p<0.02$). Correspondingly, the percent of cadmium, lead and zinc extracted by 1 *M* NH_4NO_3 decreased with increasing total trace element concentration. For cadmium, this outcome is inconsistent with the work of Taylor (1997), who found that $CaCl_2$-extractable cadmium increased at a higher proportional rate than total cadmium in archived New Zealand pastoral soils. For both extraction solutions, there were no significant differences (t-test, $p<0.05$) in the percent of cadmium, copper and zinc extracted from background and horticultural soils.

7.3.1.3 INFLUENCE OF SOIL PROPERTIES ON THE PERCENT OF TRACE ELEMENT EXTRACTED BY NEUTRAL SALTS

Pearson's correlation analysis was used to investigate possible relationships between the percent of trace element extracted by the neutral salt extractions and key soil properties (Tables 7.3 and 7.4). The soil properties for the worm and plant assay soils are presented in Appendix B.

Soil pH was inversely correlated ($p<0.001$), with the percent cadmium, copper, and zinc extracted by 0.01 *M* $CaCl_2$ and the percent of cadmium, copper, lead and zinc extracted by 1 *M* NH_4NO_3 ($p<0.01$). Soil pH has been found in other investigations to be an important variable determining the amount of trace element extracted by neutral salt extractions from New Zealand soils. Soil pH accounted for 30% of the variation in cadmium extracted from South Auckland market garden soils using 0.05 *M* $CaCl_2$ (Roberts *et al.*, 1995) and was an important variable in determining the amount of cadmium desorbed from NZ pastoral soils by 0.01 *M* $Ca(NO_3)_2$ (Gray *et al.*, 1998). In agreement with the results presented in Table 7.3, Singh et *al.* (1995) reported that NH_4NO_3 extractable cadmium was inversely related to soil pH. Soil pH was a determining factor for the desorption of copper from NZ soils by 0.01 *M* $Ca(NO_3)_2$ (Hogg *et al.*, 1993).

Similarly the soil pH has been found to influence desorption of trace elements in studies undertaken overseas. Examples include 0.01 *M* $CaCl_2$ extraction of cadmium, lead and zinc from Welsh soils (Rieuwerts *et al.*, 2005), copper from Tanzanian coffee orchard soils (Loland and Singh, 2004), and copper from French vineyard soils (Brun *et al.*, 1998). Similarly McLaughlin *et al.* (1999) reported that the fraction of total cadmium extracted from Australian potato cropping soils by 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 increased with decreasing soil pH. The pH was a key soil characteristic determining the partition coefficient for the distribution of copper between soil pore water and soil for cadmium, copper, lead and zinc in Dutch soils (Janssen *et al.*, 1997b).

The percent of cadmium, copper and zinc extracted by 0.01 *M* $CaCl_2$ ($p \leq 0.02$) and the percent of cadmium, copper, lead and zinc extracted by 1 *M* NH_4NO_3 decreased with increasing CEC. However, as noted above, the percent cadmium and zinc extracted was inversely related to the total trace element concentrations. As total cadmium, copper and zinc also correlated with CEC, it is not clear whether soil CEC is influencing the amount of cadmium and zinc desorbed. CEC was an important parameter for desorption of zinc from Canterbury soils by DPTA (Singh *et al.,* 1997) and the fraction of cadmium, lead and zinc extracted by 0.01 *M* $CaCl_2$ from Welsh soils was negatively correlated with CEC (Riuewerts *et al.*, 2005).

Possible relationships between Olsen P and the fraction of extractable trace elements were investigated as addition of phosphate has been used to immobilize trace elements especially lead in soil (Geebelen *et al.,* 2003; Brown *et al.*, 2005). Phosphate has also been used to immobilise cadmium in NZ pasture soils (Bolan *et al.*, 2003b). There were significant negative correlations between the soil Olsen P concentration and the percent cadmium extracted by 0.01 *M* $CaCl_2$ and the percent of lead and cadmium extracted by 1 *M* NH_4NO_3. This is consistent with the results of Brown *et al.* (2005) who reported that the addition of phosphorus as super phosphate and rock phosphate reduced the 1 *M* NH_4NO_3 extractable fraction of cadmium, lead and zinc in soil containing mine waste.

The soil organic matter content is considered to be an important soil parameter controlling the bioavailability of trace elements especially copper in soil. There was an inverse relationship between the percent of cadmium, copper and zinc extracted by 0.01 *M* $CaCl_2$ and cadmium, copper and lead extracted by 1 *M* NH_4NO_3 and the %TOC. This finding is consistent with the results of Gray *et al.* (1998) who found that the organic matter content was a key soil characteristic controlling desorption of cadmium from NZ pastoral soils. In contrast, the extractability of cadmium from South Auckland market garden soils with 0.05 *M* $CaCl_2$ was not related to soil organic matter (Roberts *et al.*, 1995). Loland and Singh (2004) reported that the 0.01 *M* $CaCl_2$ extractable copper in Tanzanian coffee soils was inversely related to soil organic matter.

Iron and manganese oxides have been shown to be important parameters controlling the partitioning of trace elements between solid and solution phases. There were significant negative correlations between iron and manganese concentrations and the percent trace element extracted by 0.01 *M* $CaCl_2$ for cadmium, copper and zinc. Similarly the percent of copper, lead and zinc extracted by 1 *M* NH_4NO_3 also decreased with increasing soil iron concentration. The percent of cadmium, copper, lead and zinc extracted by 1 *M* NH_4NO_3 decreased with increasing manganese concentration. Iron oxides may also influence the extractability of arsenic from soil as 1 *M* NH_4NO_3 extracted arsenic from only three of the orchard soils and these were the soils which had lower iron contents.

Several studies have also found iron and manganese oxides to be controlling variables for desorption of trace elements from soil. For example manganese oxide was an important variable for desorption of zinc from Canterbury (NZ) soils using DPTA (Singh *et al.*, 1997). Total iron and manganese were controlling parameters for the amount of cadmium, lead and zinc extracted by 0.01 *M* $CaCl_2$ from Welsh soils (Rieuwerts *et al.*, 2005). Similarly, iron oxyhydroxides were important for determining the partition coefficient for the distribution of trace elements between the soil pore water and soil, for arsenic, copper and lead (Janssen *et al.*, 1997b).

7.3.2 EARTHWORM ASSAY

7.3.2.1 WORM TISSUE CONCENTRATIONS

The worm tissue for each soil (n = 48 worms) was composited to provide sufficient material for analysis. Worm tissue concentrations followed the order iron ≥ zinc>copper>cadmium>arsenic>lead (Table 7.5) and were comparable to literature values for trace element tissue concentrations measured in *A. caliginosa* exposed to soils containing similar concentrations of trace elements (Table 7.6).

Table 7.5: Trace element concentrations measured in worm tissue (mg kg^{-1} DW).

	Arsenic	Cadmium	Copper	Lead	Zinc	Iron
W1	5.9	9.9	48	10.6	420	413
W2	2.8	8.0	46	1.3	364	400
W3	3.5	11.4	31	3.2	479	507
W4	3.4	9.9	16	2.1	491	394
W5	3.3	9.9	26	2.0	372	839
W7	3.2	8.6	6	1.6	482	414
W8	3.3	10.3	12	1.7	410	363
W9	3.1	8.2	12	2.3	408	452
Baseline adults[a]	4.2	6.5	12	0.8	690	394

[a]Bulk sample of adult worms collected from the same area as the worms utilised in the worm.

The assay used field harvested worms which already contained trace elements at the beginning of the assay. The trace element concentrations measured in the earthworms at the end of the 28 day assay (Table 7.5) are the combined result of uptake and elimination processes. Both the soil trace element concentrations and key soil characteristics will have determined the relative importance of uptake and elimination processes. Kinetic experiments undertaken by Peijnenburg *et al.* (1999) for uptake of trace elements from aged soils by *Eisenia andrei* indicate that the time period taken to reach steady state tissue concentrations varies with each trace element. In their assay, copper and zinc concentrations reached steady state within three days of exposure whereas for arsenic, lead and cadmium the time taken to reach steady state was longer and was also dependent on soil characteristics.

Linear regression analysis of log transformed variables was used to determine relationships between soil (Table 7.1) and worm tissue trace element concentrations after the 28 day exposure period (Table 7.5). The regression equations are presented in Table 7.7. Pearson's correlation analysis on log transformed variables was used to determine relationships between neutral salt extractable soil and worm tissue trace element concentrations (Table 7.8).

Table 7.6: Summary of literature values for tissue concentrations (mg kg^{-1} DW) for *A. caliginosa* from studies using aged contaminated soils with comparable contaminant levels.

Matrix	Cadmium		Copper		Lead		Zinc		Reference
	Soil	Worm	Soil	Worm	Soil	Worm	Soil	Worm	
Vineyard soil			55.4	10.4					Eijsackers *et al.* (2005)
Pasture contaminated with sewage sludge	0.65–0.99	7–11			28–39	6–9			Andersen (1979)
Pasture contaminated with metallurgical waste	2.5–3	19–21			31–52	3.6–78	108–176	1321–1090	Becquer *et al.* (2005)
Meadows contaminated with mine waste	0.84	36	11–38	6–10	136–355	1.8–14	151	401	Laszczyca *et al.*(2004)
Rehabilitated lead and zinc mine	2.7	214	23–62	12–20	570	662	460	1315	Morgan and Morgan (1992)
Roadside soil	0.16–0.38	0.8–1.5	17–84	5–32	11–82	13–44	62–116	286–485	Mariño *et al.* `(1992)

Table 7.7: Linear regression equations for selected relationships between worm tissue and soil trace element concentrations (mg kg^{-1}).

Regression equation	R^2	*p*
$logAs_{worm}$ = 0.132 x logAs(soil) + 0.436	0.673	0.008
$logAs_{worm}$ = 0.136 x logAs(soil) -0.369 x logFe + 0.277 x TOC + 1.79	0.952	0.001
$logCd_{worm}$ = 0.160 x logCd(soil) + 1.00	0.333	0.078
$logCd_{worm}$ = 0.271 x logCd(soil) + 0.400 x logclay + 0.438	0.780	0.01
$logCu_{worm}$ = 0.535 x logCu(soil) + 0.135	0.886	0.000
$logPb_{worm}$ = 0.486 x logPb(soil) – 0.407	0.763	0.003
$logZn_{worm}$ = 0.118 x logZn(soil) + 2.43	0.407	0.053
$logZn_{worm}$ = 0.190 x logZn(soil) - 0.145 x pH + 3.15	0.843	0.004

Table 7.8: Pearson's correlation coefficients for selected relationships between worm tissue and soil total and neutral salt extractable trace element concentrations (log transformed variables).

Soil	As_{worm}	Cd_{worm}	Cu_{worm}	Pb_{worm}	Zn_{worm}
As_{total}	**0.848****	0.474	0.49	**0.878****	0.367
Cd_{total}	**0.922****	0.652	0.34	**0.856****	0.273
Cu_{total}	0.49	0.368	**0.95*****	0.561	-0.267
Pb_{total}	**0.878****	0.519	0.466	**0.892****	0.41
Zn_{total}	0.509	0.224	-0.331	0.371	0.702
Cd_{CaCl_2}	0.411	0.563	0.444	0.382	0.21
Cu_{CaCl_2}	0.257	0.262	**0.924****	0.367	-0.466
Zn_{CaCl_2}	0.489	0.556	0.474	0.484	0.25
$Cd_{NH_4NO_3}$	0.304	0.608	0.399	0.314	0.293
$Cu_{NH_4NO_3}$	0.249	0.197	**0.958*****	0.352	-0.407
$Pb_{NH_4NO_3}$	0.594	0.494	0.424	0.572	0.377
$Zn_{NH_4NO_3}$	0.407	0.457	0.021	0.324	0.699

** p <0.01, *** p <0.001.

ARSENIC

The arsenic tissue concentrations ranged from 2.8 to 5.9 mg kg^{-1} DW over a soil concentration range of <2 to 98 mg kg^{-1} and were significantly correlated with the total soil concentrations (p<0.01). For seven of the test soils, the arsenic worm tissue levels decreased from the baseline tissue concentration at the beginning of the trial indicating that the earthworms did not accumulate arsenic from these soils during the assay. The elimination of arsenic from the earthworm tissue over the 28 day assay may have been due to the low arsenic concentration in these soils in combination with the low soil pH levels.

The tissue concentrations are in agreement with the results of Yeates *et al.* (1994) who measured arsenic uptake by field harvested *A. rosea* from a NZ pasture soil contaminated with CCA timber preservative; worm tissue arsenic concentrations ranged from 8 to 40 mg kg^{-1} and soil arsenic concentrations from 9 to 90 mg kg^{-1} (5–10 cm sampling depth, pH 5.4–5.6). In comparison, Beyer *et al.* (1987) reported a lower tissue arsenic concentration of 0.81 mg kg^{-1} for *Aporrectodea sp.* collected from a soil containing 33 mg kg^{-1} arsenic.

Linear regression analysis suggested that soil arsenic only accounted for 67% of the variability in worm tissue concentrations. The inclusion of iron and %TOC in the regression equation improved the fit of the model accounting for a further 28.2% of the variability. This finding is consistent with the results of De Brouwere *et al.* (2004) who found that oxalate extractable iron was a controlling variable for the soil-liquid distribution of arsenic (V). The addition of iron oxides has been used to immobilise arsenic in soil (Hartley *et al.*, 2004). The positive relationship with the soil organic matter (%TOC) was unexpected as arsenic is generally considered to be more mobile in soils with low organic matter contents (Rahman *et al.*, 2004). A possible explanation for the positive relationship observed between %TOC and tissue arsenic concentration is that dissolved organic matter in the earthworm gut facilitated arsenic release from soil. Dissolved organic matter has been previously reported to mobilize arsenic from soils and sediments through iron reduction and competition for binding sites (Mahimairaja *et al.*, 2005; Bauer and Blodau, 2006).

CADMIUM

Cadmium concentrations in the worm tissues ranged from 8.0 to 11.4 mg kg^{-1} and were at least six times greater than the soil concentration indicating that cadmium is bio-accumulated (Table 7.5). These results are consistent with other published studies for *A. caliginosa* (Table 7.6) which have shown that tissue concentrations of cadmium can greatly exceed soil concentrations. It has been suggested that earthworms may not able to regulate uptake of cadmium (van Gestel *et al.*, 1993). A caveat to this observation however is that the worms used in the work reported here

had already been exposed to cadmium as demonstrated by the tissue concentration for the baseline adults (6.5 mg kg^{-1}). Consistent with the lack of significant difference between soil concentrations for orchards and grazing sites, there was no significant difference ($p<0.05$) for worm tissue cadmium concentrations between orchards and controls (grazing sites).

In contrast to the results of other published studies (Janssen *et al.*, 1997a; Dai *et al.*, 2004; Laszczyca *et al.*, 2004) which have measured increasing tissue with increasing soil concentration, the worm tissue cadmium concentrations in this study were not significantly correlated with the either the total soil concentration (Table 7.7) or the 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable fractions (Table 7.8). A possible explanation for the lack of correlation between tissue and soil concentrations is that cadmium levels in the tissue may not have reached steady state over the 28 day exposure period. Worm tissue cadmium levels in other studies with longer exposure periods did not reach steady state over the exposure period. For example, cadmium levels in *Eisenia Andrei* exposed to aged contaminants in Dutch pasture soils continued to increase over a 63 day period (Peijnenburg *et al.*, 1999) and cadmium tissue concentrations in *Allolobophora tuberculata* exposed to sewage sludge contaminated soils continued to increase over the 100 day exposure period (Neuhauser *et al.*, 1995).

The inclusion of %clay improved the fit of the linear regression model describing the relationship between soil and worm tissue cadmium concentrations (Table 7.7). The positive contribution of the %clay to cadmium uptake was not expected as it would be anticipated that the bioavailability of cadmium would decrease with increasing %clay due to the resulting increase in surface area. It is possible that the %clay is correlated with another factor which is controlling cadmium uptake. Alternatively, as *A. caliginosa* have been reported to selectively ingest soil fractions (Morgan and Morgan, 1992), it is plausible that the worms preferentially ingested smaller sized soil fractions.

COPPER

Copper levels in the worm tissue (6–48 mg kg^{-1}) did not exceed the total soil concentration (<3–773 mg kg^{-1}) indicating that copper was not bioaccumulated and this observation is consistent with the results for field studies (Table 7.6). Worm tissue copper concentrations were significantly higher for the orchard soils treatments than the grazing soils (p=0.03). The worm tissue copper concentrations were significantly correlated (p<0.001), with the total soil copper as well as the 1 *M* NH_4NO_3 and 0.01 *M* $CaCl_2$ extractable concentrations. Increasing worm tissue copper concentrations with increasing soil copper concentrations have also been reported by Yeates *et al.* (1994) for *A. rosea* collected from contaminated pasture and for *A. caliginosa* exposed to spiked soil in a laboratory trial (Ma, 2005). Similarly a review of tissue concentrations in invertebrates found that body tissue copper concentrations tended to increase with increasing soil concentration (Heikens *et al.*, 2001). However, in other studies of field harvested *A. caliginosa* (Dai *et al.*, 2004), soil and tissue copper concentrations have not been correlated and it has been suggested that because copper is an essential nutrient, earthworms are able to regulate uptake of copper (Peijnenburg *et al.*, 1999; Laszczyca *et al.*, 2004). Hence different outcomes would be expected depending on the range of soil copper concentrations used in the bioassay. The significant correlation between worm tissue and 0.01 *M* $CaCl_2$ extractable copper is in agreement with the results of Janssen *et al.* (1997a) for *E. andrei* and Ma (2005) for uptake from spiked soils by *A. caliginosa* and *L. rubellus.*

LEAD

The worm tissue lead concentrations (1.3–10.6 mg kg^{-1}) did not exceed the soil concentrations (<4–442 mg kg^{-1}) (Table 7.6). There was a significant log linear relationships between the worm tissue and the total soil lead concentrations (p<0.01). Correlations between soil and worm tissue lead concentrations have been previously reported for *A. caliginosa* for spiked and aged soils (Laszczyca *et al.*, 2004; Langdon *et al.*, 2005).

ZINC

Worm tissue zinc concentrations ranged from 364 to 491 mg kg^{-1} (Table 7.6) and were elevated compared to the soil concentrations (5–114 mg kg^{-1}) (Table 7.1). Bioaccumulation of zinc by earthworms has been previously reported (Mariňo *et al.*, 1992; Neuhauser *et al.*, 1995). The final zinc tissue concentrations were lower than the initial tissue concentrations and this is mostly a result of the soil that the worms were collected from having a higher zinc concentration (134 mg kg^{-1}) than the test soils (Table 7.1). The narrow range of tissue zinc concentrations is in keeping with the results of Peijnenburg *et al.* (1999) who found that internal zinc concentrations in *Eisenia andrei* varied only five-fold despite the soil zinc concentration varying by a factor of 590.

Zinc is an essential nutrient for earthworms and hence earthworms may be able to regulate their tissue levels of zinc (van Gestel *et al.*, 1993; Laszczyca *et al.*, 2004; Ma, 2004). There were no significant correlations between worm tissue zinc concentrations and soil total or extractable zinc concentrations. The lack of correlation between 0.01 *M* $CaCl_2$ extractable zinc and worm zinc concentrations is consistent with results reported by Janssen *et al.* (1997a) for *Ei. andrei*. The addition of soil pH improved the R^2 value of the regression analysis from 40.7 to 84.3% implying that zinc uptake increases as soils become more acidic. Several other studies have also found zinc uptake by earthworms to be influenced by soil pH (Ma 1982, 2004; Van Gestel *et al.*, 1995; Rida and Bouché, 1997; Sample *et al.*, 1999).

7.3.2.2 BIOACCUMULATION FACTORS (BAFS)

The bioaccumulation factor (BAF) for each trace element (Table 7.9) was calculated as the concentration of contaminant in the worm tissue (DW) (Table 7.5) divided by the concentration of the contaminant in the soil (Table 7.1). The BAFs followed the order cadmium>zinc>arsenic>copper>lead for orchard and control grazing soils (Table 7.9) and were comparable with the ranges reported in the literature for trace element uptake by *A. caliginosa* (Table 7.10). These results agree with those of Dai

et al. (2004) who investigated metal uptake by *A. caliginosa* from pasture contaminated with metallurgical waste; the BAFs followed the order Cd>Zn>Cu>Pb as well as the concentration factors for trace element uptake by *A. caliginosa* from pasture contaminated with municipal compost followed the order Cd>Zn>Cu≥Pb (Ma 1982). This observed order of uptake for the cations is analogous to the order of the percent extracted by the neutral salts Cd >Zn >Cu >Pb (Section 7.3.1.2)

Table 7.9: Bioaccumulation factors (BAFs) for uptake of aged trace element residues by *A. caliginosa*.

Soil	Arsenic	Cadmium	Copper	Lead	Zinc
W1	0.06	5.7	0.06	0.02	4.9
W2	1.10	24.5	0.12	0.07	23
W3	0.12	14.6	0.10	0.02	14.5
W4	0.69	13.3	0.07	0.05	4.3
W5	1.04	12.8	0.12	0.10	9.8
W7	0.57	15.6	0.44	0.05	5.0
W8	1.90	16.8	0.17	0.09	13.2
W9	1.64	20.3	0.21	0.15	14.5

Table 7.10: Summary of BAFs reported in the literature for earthworms exposed to soils with similar trace element concentrations.

Species	Arsenic	Copper	Cadmium	Lead	Zinc	Reference
A. caliginosa		0.34–2.45	11–140	0.21–2.6	3.4–82	Ma (1982)
		0.27–0.89	6.18–13.45	0.08–0.38	1.95–7.91	Dai *et al.* (2004)
Ei. andrei	0.1–3.3	0.2–8	1–200	0.005–1.3	0.1–18	Janssen *et al.* (1997a)
Not identified	0.10–0.64					Geiszinger *et al.* (1998)
Not identified	0.01–0.93 (0.22)	0.00–5.49 (0.52)	0.25–190 (7.71)	0–228 (0.27)	0.02–49.51 (3.2)	Sample *et al.* (1999) (median)
Invertebrates		0.47				CCME (1999)

As the soil concentration for a given element increased the BAF decreased. The BAFs were negatively correlated (Table 7.11) with the total soil concentrations for arsenic ($p<0.001$), cadmium ($p<0.001$), copper ($p<0.001$), lead ($p<0.01$) and zinc ($p<0.001$). This pattern of uptake has been observed in other studies of trace element accumulation by earthworms (Ma, 1982; Sample *et al.*, 1999; Terihuvo *et al.*, 1994). For example, the BAF for copper uptake by *A. caliginosa* decreased with increasing

soil copper in laboratory trial using $CuSO_4$ spiked soil Ma (2005) and Geiszinger *et al.* (1998) observed the same pattern for uptake of arsenic by field collected *Lumbricidae sp.* Similarly, Spurgeon and Hopkin (1996) observed that BAFs for cadmium, copper, lead and zinc decreased with increasing soil concentration for *E. fetida.*

Neuhauser *et al.* (1995) and Geiszinger *et al.* (1998) attributed this decrease in BAFs with increasing soil concentration to an increase in elimination rate. Two further possible explanations are 1) that there is a fixed number of available binding sites for example metallothionein-like proteins for transport of trace elements within the earthworm and this physically limits the uptake of trace elements and 2) that the most available trace element pool is taken up first with replenishment being kinetically limited.

Table 7.11: Pearson's correlation coefficients for relationships between worm BAFs and soil trace element and key soil characteristics (log transformed variables) with significant correlations presented in bold.

	As_{BAF}	Cd_{BAF}	Cu_{BAF}	Pb_{BAF}	Zn_{BAF}
As_{total}	**-0.995*** **	**-0.812***	-0.52	**-0.898****	-0.421
Cd_{total}	-0.772	**-0.977*** **	-0.57	-0.669	-0.633
Cu_{total}	-0.528	-0.444	**-0.94*** **	-0.421	0.101
Pb_{total}	**-0.978*** **	**-0.835****	-0.57	**-0.903****	-0.464
Zn_{total}	-0.406	-0.644	-0.11	-0.491	**-0.991*** **
%clay	0.309	**0.712***	0.067	0.237	0.824
%silt	-0.099	-0.58	-0.33	-0.003	**-0.764***
%sand	0.017	-0.247	0.315	0.017	-0.369
%TOC	-0.294	-0.703	-0.25	-0.235	-0.597
CEC	-0.571	-0.379	**-0.76***	-0.596	0.125
OlsenP	-0.543	-0.303	-0.61	-0.369	0.449
pH	-0.004	-0.527	-0.17	0.156	-0.659
Fe	-0.495	-0.169	-0.11	-0.682	-0.36
Mn	0.068	-0.218	0.290	-0.084	-0.698

*p <0.05, ** p <0.01, *** p <0.001.

There were only a limited number of significant relationships between BAFs and soil properties. The BAF for copper was inversely related to the CEC (p<0.05). This finding for copper is in agreement with Ma (1982) who also reported a negative

correlation between the concentration factor and the soil CEC for copper, cadmium, lead and zinc. The BAF for zinc decreased with increasing %silt ($p<0.05$).

With the exception of cadmium, there were no significant relationships between the percent trace element extracted by the neutral salts and the BAFs (Appendix B). The BAF for cadmium was significantly correlated with the percent cadmium extracted by 0.01 *M* $CaCl_2$.

7.3.2.3 ECOTOXICITY

Copper concentrations in the orchard soils greatly exceeded soil quality criteria for the protection of earthworms (Table 7.12) indicating that the orchard soils were likely to be toxic to earthworms. Additionally three of the orchard soils contained 1 *M* NH_4NO_3 extractable copper levels greater than the level of 677 μg kg^{-1} which Belotti (1998) reported as a threshold for abundance of copper-susceptible endogeic earthworms.

At the end of the 28 day exposure period, mortality, cocoon production and the percent change in body mass were assessed to determine the toxicity of the test soils to earthworms (Table 7.13). Spearman rank correlation was used to determine significant relationships between the toxicological endpoints and the total and extractable soils concentrations as well as the internal worm tissue concentration (Table 7.14). It has been suggested that the internal worm tissue concentration may be better linked to the ecotoxicological effect as soil properties can influence bioavailability making comparison between different soils and studies difficult (Sijm and Hermens, 2000; Peijnenburg, 2001; Ma, 2005). The ecotoxicological endpoints were also compared to a total extractable trace element load calculated by adding the 0.01 *M* $CaCl_2$ extractable concentrations for cadmium, copper, lead and zinc. This approach has been previously used by Weltje (1998) to evaluate available data on sublethal toxicity of mixtures of cadmium, copper, lead and zinc to earthworms.

Table 7.12: Comparison of trace element concentrations (mg kg^{-1}) in worm assays soils to soil criteria for the protection of earthworms.

	Arsenic	Cadmium	Copper	Lead	Zinc
orchards					
W1	98.0	1.73	773	442	85
W2	2.5	0.33	377	18	16
W3	30.1	0.78	326	142	33
W4	4.9	0.74	237	45	114
W5	3.2	0.77	212	20	38
grazing					
W7	5.6	0.55	14	34	96
W8	1.7	0.61	71	19	31
W9	1.9	0.40	57	15	28
Soil criteria					
Eco-SSL (earthworm)[1]	60	20	50	500	200
Eco-SSL (invertebrates)[1]		110	61		
LC50[2]		540	640		
EC50 (cocoon production)[3]		35	186		
LOEC (28 day/growth)[4]	100		200		
LC50 (*E fetida*)[5]			683	4480	1010
LC50 (*E fetida*)[6]			643	5941	662

[1]Oak Ridge National Laboratory, soil guideline for earthworms (Efroymson *et al.*, 1997a), [2]USEPA Ecological Soil Screening Level (2000), [3]Khalil *et al.* (1996a), [4]O'Halloran and Booth (as cited in Markich *et al.*, 2002), [5]Spurgeon *et al.* (1994), [6]Neuhauser *et al.* (1995).

Table 7.13: Mortality, change in body mass and cocoon production for 28 day assay with *A. caliginosa*. Results are reported as mean (n = 4) ± 95% confidence interval.

	Mortality	% change in body	Cocoon count		
Soil	(%)	mass[a]	initial[b]	final[c]	cocoons/worm/week
Orchards					
W1	0	-1.8 ± 2.8	6	3 ± 2	0.1
W2	0	-14.1 ± 7.4	6	0 ± 0	0.0
W3	0	-5.0 ± 6.3	0	11 ± 14	0.2
W4	0	1.5 ± 6.1	7	13 ± 8	0.3
W5	0	10.8 ± 2	3	17 ± 10	0.4
Grazing					
W7	0	-0.1± 5.3	7	13 ± 9	0.3
W8	0	10.5 ± 10.5	9	25 ± 6	0.5
W9	0	-6.0 ± 6.6	4	22 ± 10	0.5

[a]relative to initial weight at the beginning of the 28 day exposure period, [b]Estimated from a subsample of the test soil before the bioassay, [c]Number of cocoons counted after 28 days.

Table 7.14: Spearman rank correlation coefficients for possible relationships between rate of cocoon production, and worm tissue concentration and soil total and extractable trace element concentration. Significant correlations are presented in bold.

Parameter	cocoons	Parameter	cocoons
Worm tissue		*Soil trace element concentrations*	
As	-0.192	As_{total}	-0.619
Cd	0.286	Cd_{total}	-0.167
Cu	**-0.762***	Cu_{total}	**-0.81***
Fe	0.024	Pb_{total}	-0.452
Pb	-0.095	Zn_{total}	-0.048
Zn	-0.024	Cd_{CaCl_2}	-0.476
Soil properties		Cu_{CaCl_2}	**-0.786***
Fe	-0.357	Zn_{CaCl_2}	-0.429
Mn	0.262	$\Sigma CaCl_2$ extractable[a]	-0.69
%clay	-0.024	$Cd_{NH_4NO_3}$	-0.333
%silt	0.238	$Cu_{NH_4NO_3}$	**-0.786***
%sand	0	$Pb_{NH_4NO_3}$	-0.515
pH	-0.071	$Zn_{NH_4NO_3}$	-0.476
%TOC	0.335		
CEC	-0.357		
OlsenP	-0.524		

*p <0.05, ** p <0.01, *** p <0.001, [a]$\Sigma CaCl_2$ extractable = $Cd_{CaCl_2} + Cu_{CaCl_2} + Zn_{CaCl_2}$.

MORTALITY

The soils were not acutely toxic to the earthworms as only one of the worms died during the 28 day exposure period. This is consistent with the treatment soil trace element concentrations not exceeding available LC_{50} values for earthworms (Table 7.11). In addition, the worm tissue copper concentrations were below the threshold of 60 mg kg^{-1} for mortality determined by Bogomolov *et al.* (1996) for *A. tuberculata* and Ma (2005) for *A. caliginosa.*

BODY MASS

The change in body mass per replicate over the exposure period has been used as an indication of sublethal stress rather than growth effects. Weight gain can not be interpreted as growth effects because adult rather than juvenile *A. caliginosa* were used as the test organism (Van Gestel and Weeks 2004). Food (generally finely

ground cow manure) is usually added to tests with artificial soils to improve the survival rate of the worms as the artificial soils do not contain sufficient nutrients (Eijsackers, 1998). However, during the bioassay, the worms were not fed as the addition of finely ground organic matter had the potential to mobilise the contaminants of interest. Despite the lack of supplementary feeding, the maximum weight loss for worms exposed to the grazing soils (6%) was less than the 15–20% threshold for control soils suggested by delegates at the International Workshop Earthworm Ecology II for ensuring validity of earthworm assays (Spurgeon *et al.* 2003).

There were no significant relationships between the change in body mass and soil and tissue trace element concentrations. However, the mean body mass decreased over the exposure period for the three treatments (Orchard soils W1-3) with worm tissue copper concentrations greater than 30 mg kg^{-1}. This finding is consistent with the 30 mg kg^{-1} copper tissue concentration threshold for sub lethal effects in *A. tuberculata* reported by Bogomolov *et al.* (1996). Similarly, Eijsackers *et al.* (2005) observed that body weight of *A. caliginosa* decreased with increasing body copper concentrations for grassland soil spiked with 60 mg kg^{-1} copper. In contrast, Kula and Larink (1997) found that body weight development for *A. caliginosa* was not sensitive to copper over a 28 day exposure to copper spiked artificial soil.

COCOON PRODUCTION

Cocoon production is a sub-lethal endpoint (Cortet *et al.*, 1999) and has been found in other earthworm studies (e.g. Spurgeon and Hopkin, 1995) to be the most sensitive endpoint for adult earthworms for trace element toxicity. In this study, the rate of cocoon production ranged from 0 to 0.5 cocoons/worm/week (Table 7.13). The cocoon production rate of 0.5 cocoons/worm/week measured in two of the grazing soils (W8 and W9) was comparable to the cocoon production rate for *A. caliginosa* of 0.6 cocoons/adult per week for a NZ pasture soil in a laboratory trial reported by Booth and O'Halloran (2001).

No significant relationships were found between cocoon production and soil properties. As discussed in Chapter Six (Section 6.3.1.7), cocoon production also decreased with increasing ΣDDT concentration.

Cocoon production decreased with increasing worm tissue ($p<0.05$) as well as total soil ($p<0.02$), 0.01 *M* $CaCl_2$ ($p<0.05$) and 1 *M* NH_4NO_3 extractable ($p<0.05$) copper concentrations (Figure 7.1). Ma (1988) also observed that cocoon production for *A. caliginosa* decreased with increasing copper concentration in a laboratory trial with spiked soils. A t-test revealed that the mean cocoon count for the treatments with a worm tissue copper concentration greater than 30 mg kg^{-1} was lower than the mean cocoon count for treatments with a worm tissue copper concentration less than 30 mg kg^{-1} ($p<0.05$). Similarly, Ma (2005) determined critical body residues of 40 mg kg^{-1} copper for cocoon production for *A. caliginosa* and *L. rubellus*.

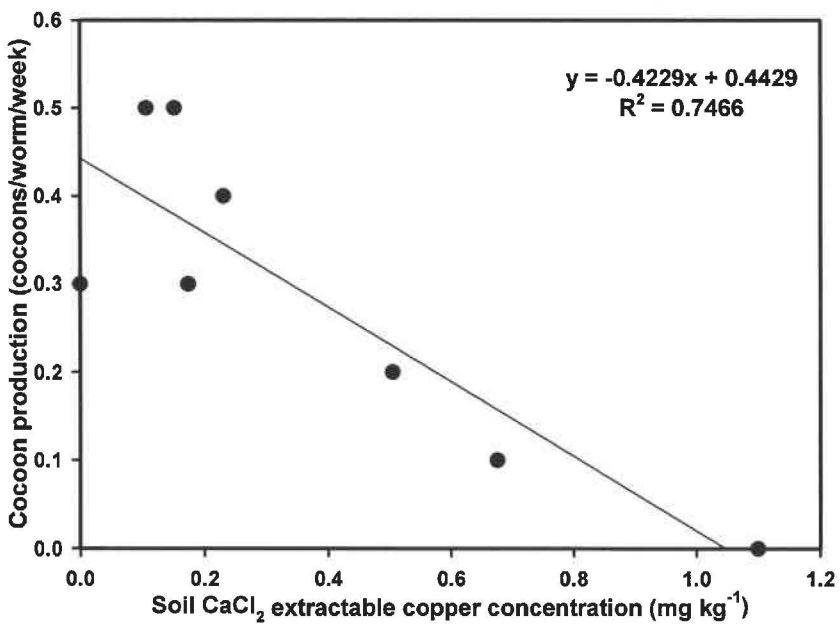


Figure 7.1: Relationship between earthworm cocoon production (cocoons/worm/week) and soil 0.01 *M* $CaCl_2$ extractable copper concentration (mg kg^{-1}).

Cocoon production was also affected by low tissue levels of copper. For the grazing soils, cocoon production increased with increasing soil total copper concentration ($p<$

0.02). Spurgeon *et al.* (1994) also reported a significant increase in cocoon production for *E. fetida* in OECD soil at the lowest spike level of 10 mg kg^{-1} copper. The observed increase in cocoon production with increasing soil copper concentration for the grazing soils is most probably due to copper being an essential nutrient. The worm tissue concentration of 6.1 mg kg^{-1} for grazing site W7 was below the minimum physiological requirement of 8 mg kg^{-1} copper for field collected *Lumbricus rubellus* reported by Ma (2005).

While significant negative relationships were only found between cocoon production and tissue and soil copper concentrations, it is likely that other trace elements present in the soils may also have contributed to the observed decrease in cocoon production. Additive and synergistic effects between contaminants can be important in determining toxicity to earthworms in soils containing multiple pollutants (Langdon *et al.*, 2003). For example, Khalil *et al.* (1996b) reported additive effects of cadmium, copper and zinc on growth of juvenile *A. caliginosa.*

COPPER AND EARTHWORMS

The toxic effects observed for body mass and cocoon production can be attributed to the presence of copper. However, concentrations of copper in aged contaminated soils comparable to those found in New Zealand horticultural soils (Chapter Four) have been shown to have other deleterious impacts on earthworms. In field surveys *A. caliginosa* have been found to either be reduced in numbers or absent from soils with elevated levels of copper (Paoletti *et al.*, 1998; Eisjackers *et al.*, 2005) and in laboratory studies earthworms have been shown to demonstrate avoidance behaviour to copper contaminated soils (Van Zwieten *et al.*, 2004). Additionally, exposure to copper has been demonstrated to make *A. caliginosa* less drought resistant (Friis *et al.*, 2004) and in combination with climatic stress such as dessication and frost to reduce the viability of *A. caliginosa* cocoons (Holmstrup *et al.*, 1998).

APPLICABILITY OF RESULTS TO THE FIELD

Further work is required to determine whether the impacts reported here occur in the field. The design of the experiment prevented the worms from demonstrating avoidance behaviour. The depth profiles presented in Chapter Three (Section 3.3.7) indicate that the contamination on orchard sites decreases with depth, hence it is possible that in the field the earthworms could choose to live and/or preferentially feed from a soil layer with a lower level of contaminants. Additionally earthworm populations may be able to develop resistance to trace elements (Langdon *et al.*, 2003). For example, Reid and Watson (2005) found that *A. rosea* collected from a lead contaminated shooting site were more tolerant of lead contaminated soil than worms collected from an uncontaminated site.

The experiment utilized adult earthworms and hence the results may not be able to be used to determine impacts on juveniles because juvenile earthworms have been found to be more sensitive to the effects of trace elements than adults. For example, juvenile *A. caliginosa* were more sensitive to arsenic and copper than adults in laboratory trials using spiked soils (O'Halloran and Booth, 2000, cited in Markich *et al.*, 2002). Similarly, Spurgeon and Hopkin (1996) measured sublethal effects of zinc at lower levels for juvenile *E. fetida* (sexual development) than adults (cocoon production).

7.3.3 PLANT ASSAYS

7.3.3.1 LETTUCE AND RADISH TRACE ELEMENT CONCENTRATIONS

The maximum plant tissue concentration followed the order zinc>iron>copper>cadmium>arsenic>lead for lettuce and radish leaf, and zinc>iron>copper>cadmium>lead>arsenic for radish hypocotyls (Table 7.15). Plant tissue concentrations were generally within the ranges reported in the literature for plants grown on soils with comparable contaminant levels (Tables 7.16 and 7.17). As previously discussed in Section 6.3.2.5 (Chapter Six) plant iron tissue concentrations were within the normal range reported by Kabata-Pendias and Pendias (2001) indicating that the concentrations of trace elements measured were unlikely to be

solely the result of adhered soil. The trace element concentration data for the assay soils were presented in Table 7.1 (Section 7.3.1). Linear regression analysis of log transformed data was used to determine significant relationships between plant tissue and soil trace element concentrations (Table 7.18). There were insufficient data points to determine relationships for arsenic in all plant tissues and for cadmium and lead in the radish leaves (Table 7.15). Pearson's correlation coefficients for relationships between plant tissue and total and neutral salt extractable soil trace element concentrations are presented in Table 7.19a,b.

Table 7.15: Mean (n = 4) concentrations of trace elements measured in plant tissue (mg kg^{-1} DW).

	Arsenic[a]	Cadmium	Copper	Lead	Zinc	Iron
lettuce						
Orchard 1	<0.2	2.10	12.1	0.18	112	63
Orchard 2	0.5	1.93	10.8	0.39	85	64
Orchard 3	0.4	1.47	9.9	0.35	76	62
Orchard 4	0.3	1.23	10.3	0.32	85	71
Orchard 5	0.7	1.49	9.4	0.53	83	77
Vineyard	<0.4	1.25	11.7	0.32	160	63
Bushblock 1	<0.4	0.51	5.4	0.19	44	86
Bushblock 2	<0.2	0.30	4.3	0.16	93	62
Grazing 1	<0.2	1.33	4.8	0.15	99	66
Grazing 2	<0.4	0.82	3.1	0.14	47	85
radish hypocotyl						
Orchard 1	0.2	0.45	14.3	0.12	73	27
Orchard 2	1.5	0.51	18.0	0.57	47	46
Orchard 5	0.9	0.50	12.9	0.97	70	22
Vineyard	<0.4	0.35	10.9	1.30	119	25
Bushblock 1	<0.4	0.30	3.8	0.22	34	39
Bushblock 2	0.2	0.34	3.1	0.76	94	49
Grazing 1	<0.2	0.24	2.5	0.13	57	39
Grazing 2	<0.4	0.54	2.0	0.07	35	28
radish leaf						
Orchard 1	0.2	0.81	34.0	0.18	105	66
Orchard 2	0.7	1.11	40.0	0.29	68	55
Orchard 5	na	na	23.4	na	107	75
Vineyard	na	na	20.3	na	218	81
Bushblock 1	na	na	6.3	na	42	99
Bushblock 2	<0.2	0.37	4.0	0.30	156	96
Grazing 1	<0.2	0.00	3.0	0.00	88	83
Grazing 2	na	na	3.2	na	44	94

[a]Samples were analysed for arsenic in two batches with differing detection limits, [b]Sample not analysed.

Table 7.16: Summary of trace element concentrations (mg kg^{-1} DW) reported in the literature for lettuce grown in soils with comparable trace element concentrations.

Matrix	Arsenic		Cadmium		Copper		Lead		Zinc		Reference
	Soil	Lettuce	Soil	Lettuce	Soil	Lettuce	Soil	Lettuce	Soil	Lettuce	
Pot trials											
Predominantly pastures soils (NZ)			0.11–0.56	0.11–0.68							Andrewes *et al.* (1996)
NZ Pasture soils			0.03–1.34	0.273–4.5							Gray *et al.* (1999a)
Lead shot contaminated pasture (NZ)							23–135	0.2–4.8			Rooney *et al.* (1999)
Mine waste	23–187	5.47–21.5	1.38–6.06	1.61–5.37			61	30	72	5.5	Cobb *et al.* (2000)
Urban soils					23–479	0.8–13			137–401	14–76	Tambasco *et al.* (2000)
Lead arsenate spiked soil (field trial)					18	3.73	38–278	1.73–5.23			Chisholm (1972)
Aerial deposition	65	6.85									Warren *et al.* (2003)
Sewage sludge	72	0.08									Warren *et al.* (2003)
Mine waste	45	<0.08									Warren *et al.* (2003)
Urban soils					32–640	8–18					Sauvé *et al.* (1996)
Field surveys											
Market gardens, Pukekohe			0.09–0.83	0.18–2.0							Roberts *et al.* (1995)
Cropping soils, British Columbia			0.41–1.09	0.28–0.39			14–61	0.09–0.21			De Pieiri *et al.* (1997)

Table 7.17a: Summary of copper and zinc concentrations (mg kg^{-1} DW) reported in the literature for radish grown in soils with comparable trace element concentrations.

Matrix	Copper			Zinc			Reference
	Soil	Hypocotyl	Leaf	Soil	Hypocotyl	Leaf	
Farming soils	37.9-286	36-563	2-29	66	39	27	Marchiol *et al.* (2004a)
Mine waste				72	24	58	Cobb *et al.* (2000)
Orchard soils	195	16	26				Merry *et al.* (1986b)
Sewage sludge soils				240–247	38–104	53–213	Lorenz *et al.* (1997)
Urban soils	32–640	16–28	15–83				Sauvé *et al.* (1996)

Table 7.17b: Summary of arsenic, cadmium and lead concentrations (mg kg^{-1} DW) reported in the literature for radish grown in soils with comparable trace element concentrations.

Matrix	Arsenic			Cadmium			Lead			Reference
	Soil	Hypocotyl	Leaf	Soil	Hypocotyl	Leaf	Soil	Hypocotyl	Leaf	
Lead shot contaminated pasture (NZ)							23–135	15–49	2.7-10	Rooney *et al.* (1999)
Mine waste	23–187	0.59–2.94	2.2–9.63	1.38–6.06	0.01–2.31	Nd–8.76	61	nd	32	Cobb *et al.* (2000)
Garden soils (not pot)							533	12		Finster *et al* .(2004)
Orchard soil	95	2.1	3.9				290	13.2	5	Merry *et al.* (1986b)
Sewage sludge soils				0.85–1.7	0.3–0.5	0.7–1.6				Lorenz *et al.* (1997)
Smelter contaminated soil				1.17	0.2	0.4				Lorenz *et al.* (1997
Geogenic				0.2	0.3	0.2				Lorenz *et al.* (1997
River flood plains contaminated by Pb/Zn mine				0.53	0.3	0.4				Lorenz *et al.* (1997
Farming soils contaminated by irrigation water				0.9	0.45	0.19	38	19	2	Marchiol *et al.* (2004a)

Table 7.18: Linear regression equations for relationship between plant tissue and soil trace element concentrations (mg kg^{-1} DW). Log transformed variables.

Regression equation	R^2	*p*
lettuce		
log Cd = 0.624 × $logCd_{soil}$ + 0.521	0.948	<0.001
log Cd = 0.677 × log Cd_{soil} – 0.246 x logCEC + 0.831	0.961	<0.001
log Cu = 0.295 × $logCu_{soil}$ + 0.350	0.922	<0.001
log Pb = 0.326 × $logPb_{soil}$ -1.12	0.548	0.009
log Pb = 0.434 × $logPb_{soil}$ -0.701 x logCEC – 0.520	0.902	<0.001
log Zn = 0.364 × log Zn_{soil} + 1.38	0.668	0.002
log Zn = 0.522 × log Zn_{soil} – 0.447 x logCEC+1.66	0.810	0.001
radish hypocotyl		
log Cd = 0.083 × $logCd_{soil}$ - 0.340	0.0	0.472
log Cd = 0.267 × $logCd_{soil}$ – 1.01 x logTOC – 0.756 x clay + 1.45	0.652	0.069
log Cu = 0.506 × $logCu_{soil}$ -0.034	0.898	0.000
log Pb = 0.726 × $logPb_{soil}$ -1.07 x pH – 2.83 x logTOC + 6.06	0.928	0.003
log Zn = 0.286 × log Zn_{soil} + 1.37	0.276	0.001
log Zn = 0.252 × log Zn_{soil} – 0.67 x pH + 4.04	0.668	0.027
log Zn = 0.268 × log Zn_{soil} – 0.538 x pH – 0.657 x Fe + 0.538	0.895	0.007
radish leaf		
log Cu = 0.621 × $logCu_{soil}$ + 0.007	0.877	<0.001
log Cu = 0.700 × $logCu_{soil}$ -0.451 x $logFe_{soil}$ + 1.67	0.990	<0.001
log Zn = 0.381 × $logZn_{soil}$ +1.40	0.307	0.089
log Zn = 0.337 × $logZn_{soil}$ -0.593 x pH + 4.79	0.692	0.023
log Zn = 0.629 × $logZn_{soil}$ -0.589 x pH- 0.449 x $logFe_{soil}$ + 6.12	0.901	0.006

Table 7.19a: Pearson's correlation coefficients for possible relationships between lettuce tissue concentrations and soil total and neutral salt extractable trace element concentrations with significant correlations presented in bold.

	$Cd_{lettuce}$	$Cu_{lettuce}$	$Pb_{lettuce}$	$Zn_{lettuce}$
Cd_{total}	**0.978*** **	**0.694***	0.438	0.443
Cu_{total}	**0.722***	**0.967*** **	**0.666***	0.53
Pb_{total}	**0.71***	**0.889*** **	**0.76***	0.634
Zn_{total}	0.537	0.605	0.181	**0.842****
Cd_{CaCl_2}	**0.759***	0.579	0.401	0.489
Cu_{CaCl_2}	0.715	**0.985*** **	**0.648***	0.367
Zn_{CaCl_2}	-0.188	0.072	-0.124	**0.701***
$Cd_{NH_4NO_3}$	**0.687***	0.595	0.124	**0.669***
$Cu_{NH_4NO_3}$	0.596	**0.987*** **	**0.723***	0.577
$Pb_{NH_4NO_3}$	-0.142	0.493	0.528	0.601
$Zn_{NH_4NO_3}$	-0.149	0.106	-0.196	**0.744***

*p <0.05, ** p <0.01, *** p <0.001.

Table 7.19b: Pearson's correlation coefficients for possible relationships between total and neutral salt extractable trace elements and radish tissue concentrations with significant relationships presented in bold.

	Radish leaf		Radish hypocotyl			
	Cu	**Zn**	**Cd**	**Cu**	**Pb**	**Zn**
Cd_{total}	0.651	0.133	0.28	0.648	-0.098	0.126
Cu_{total}	**0.946*** **	0.382	0.25	**0.954*** **	0.385	0.39
Pb_{total}	0.81	0.525	0.105	**0.86** **	0.55	0.505
Zn_{total}	0.396	0.637	-0.342	0.448	0.226	0.613
Cd_{CaCl_2}	0.513	0.328	0.355	0.497	0.043	0.338
Cu_{CaCl_2}	**0.969*** **	0.269	**0.793***	**0.965*** **	0.255	0.299
Zn_{CaCl_2}	-0.09	**0.874** **	-0.258	-0.04	0.366	**0.887** **
$Cd_{NH_4NO_3}$	0.457	0.451	0.02	0.444	-0.066	0.467
$Cu_{NH_4NO_3}$	**0.941*** **	0.511	0.228	**0.956*** **	0.557	0.526
$Pb_{NH_4NO_3}$	0.366	0.825	-0.084	0.434	**0.916** **	**0.827** **
$Zn_{NH_4NO_3}$	-0.101	**0.861** **	-0.424	-0.048	0.289	**0.872** **

*p <0.05, ** p <0.01, *** p <0.001.

ARSENIC

Arsenic levels above the detection limit were detected in four out of ten lettuce samples and four out of eight radish hypocotyls samples at maximum arsenic concentrations of 0.72 mg kg^{-1} in lettuce leaves and 1.5 mg kg^{-1} in radish hypocotyls (Table 7.15). Higher arsenic levels were measured in radish hypocotyls and leaves than in lettuce leaves for plants grown on the same soil. In agreement with the results presented in Table 7.15, both Warren *et al.* (2003) and Darmody *et al.* (2004) measured higher levels of arsenic in radish hypocotyls than in lettuce grown on the same soils. Similarly, Smilde *et al.* (1982) measured higher levels of arsenic in radish than in lettuce grown on contaminated sediments. Arsenic levels in radish roots were greater than in the tops of radish plants grown on former orchard soils (Merry *et al.*, 1986b) and arsenic levels in root crops tended to be higher than in leafy vegetables for vegetables grown on a former orchard soil (Elfving *et al.*, 1978).

Only a selection of the radish samples were analysed for arsenic. Overall for the analysed radish samples and the lettuce samples, tissue concentrations did not increase with increasing soil concentration. Arsenic concentrations in radish grown on orchard plots did not correlate with the total soil concentration and this is consistent with the results of Aten *et al.* (1980) for radish grown in soil collected

from a New York orchard. However, for the four lettuce samples grown on the blended soils (Orchards 2 to 4), the arsenic concentration in the tissue increased with increasing total soil arsenic concentration ($p<0.01$). Increasing tissue arsenic concentrations with increasing soil concentrations have been previously reported for both lettuce and radish. (Woolson, 1973; Smilde *et al.,* 1982; Xu and Thornton, 1985; Cobb *et al.*, 2000; Samsøe-Petersen *et al.*, 2002).

CADMIUM

Cadmium levels in the plant tissue followed the general order lettuce leaves> radish leaves> radish hypocotyls (Table 7.15). This order of cadmium uptake is consistent with data reported elsewhere (De Pieri *et al.,* 1997; Loganathan *et al.,* 2003; Rayment, 2005). Higher concentrations in lettuce than radish hypocotyls have been reported previously (Smilde *et al.*, 1982; Preer *et al.*, 1995; Darmody *et al.*, 2004) and several studies have measured elevated levels of cadmium in radish tops compared to hypocotyls for radish (Keefer *et al.*, 1986; Preer *et al.,* 1995; Lorenz *et al.*, 1997).

There was a significant linear relationship between total soil cadmium and lettuce leaf cadmium ($p<0.001$) (Figure 7.2). A similar relationship was not observed for radish hypocotyls. Similarly, Samsøe-Petersen *et al.* (2002) found a significant relationship between soil and cadmium lettuce concentrations but not for radish grown on the same soil. An increase in lettuce cadmium concentration with increasing soil concentration has been previously reported for both spiked (Lehoczky *et al.*, 1998; Moustakas *et al.,* 2001) and aged soils (Crews and Davies, 1985; Sterrett *et al.,* 1996; Albering *et al.*, 1999; Cobb *et al.,* 2000). The cadmium content of lettuce grown on NZ pasture soils increased with increasing soil concentration (Gray *et al.,* 1999a). Radish leaf concentrations have also been reported to increase with increasing soil concentration (Lorenz *et al.*, 1997, Cobb *et al.*, 2000). In contrast to the results presented in Table 7.17, radish root concentrations have also been reported to increase with increasing soil cadmium concentration (Sauerback and Styperek, 1985; Lorenz *et al.,* 1997; Cobb *et al.,* 2000; Moustakas *et al.,* 2001).

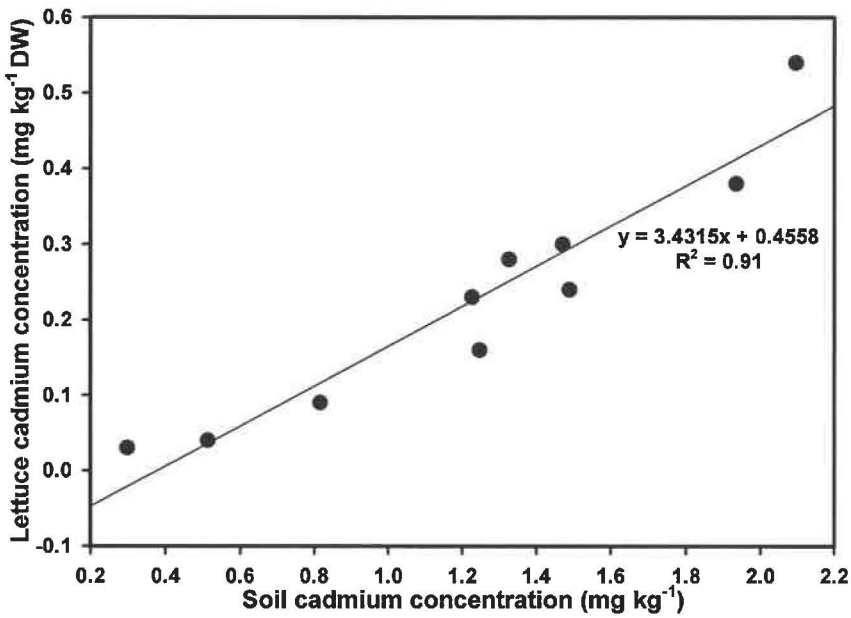


Figure 7.2: Relationship between mean lettuce tissue and total soil cadmium concentrations (mg kg^{-1} DW).

Lettuce cadmium concentrations were significantly correlated with both the 0.01 *M* $CaCl_2$ ($p<0.02$) and 1 *M* NH_4NO_3 ($p<0.05$) extractable cadmium concentrations (Table 7.19). Significant correlations between lettuce and $CaCl_2$ extractable cadmium have been reported previously for international (Novozamsky *et al.*, 1993; Peijnenburg *et al.*, 2000; Huang *et al.*, 2003) and New Zealand studies (Andrewes *et al.*, 1996). In contrast to the earlier study of cadmium uptake from NZ pasture soils by lettuce reported by Andrewes *et al.* (1996), Gray *et al.* (1999a) did not measure a significant relationship between 0.01 *M* $CaCl_2$ extractable cadmium and lettuce cadmium concentration. These contrasting results for the earlier NZ studies may be due to differences in soil properties between the two studies. 1 *M* NH_4NO_3 extractable cadmium has been previously reported to correlate with lettuce uptake (Knoche *et al.*, 1997, cited in Gryschko *et al.*, 2005; Gray *et al.*, 1999a).

The variability in cadmium concentrations observed in the radish hypocotyls was not explained by the soil cadmium concentrations (Table 7.18). The addition of soil %TOC and % clay improved the fit of the linear regression model from 0 to 65.2%, however this relationship was not quite significant ($p<0.069$). Soil organic carbon

has been identified as controlling variable for the phytoavailability of cadmium in other studies (Gray *et al.*, 1999a; Loganathan *et al.*, 2003). Cadmium uptake has been demonstrated to be dependent on the soil pH in a large number of studies (e.g. Singh *et al.*, 1995; Gray *et al.*, 1999c; McBride, 2002; Meers *et al.*, 2005). However, the multiple regression analysis did not identify soil pH as a controlling factor in the current study. This may be a result of the relatively narrow soil pH range (5.16–6.03) measured in the assay soils.

COPPER

The highest concentrations of copper were measured in the radish leaves (3–40 mg kg^{-1}) followed by the radish hypocotyls (2.0–18 mg kg^{-1}) and the lettuce leaves (3.1–12.1 mg kg^{-1}) (Table 7.15). Correspondingly the mean copper concentrations measured in plants grown in urban Canadian soils followed the order radish leaves> radish hypocotyls>lettuce (Sauvé *et al.*, 1996). However, both the results of the current study (Table 7.15) and those of Sauvé *et al.*, (1996) contrast with other studies reporting higher levels of copper in lettuce than in radish hypocotyls (Smilde *et al.*, 1982; Preer *et al.*, 1995; Darmody *et al.*, 2004). Analogous with the results presented in Table 7.15, several studies have reported higher concentrations of copper in radish leaves than in the hypocotyls (Keefer *et al.*, 1986; Merry *et al.*, 1986a,b; Preer *et al.*, 1995). This difference in tissue concentration may be due to varying physiological requirements for copper.

Copper concentrations in the lettuce leaves were significantly correlated ($p<0.001$) with the total soil copper concentration as well as with the 1 *M* NH_4NO_3 and 0.01 *M* $CaCl_2$ extractable concentrations (Table 7.19). The radish hypocotyl and radish leaf copper concentrations also significantly correlated with total soil copper concentration and the 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable copper. The observed increase in tissue concentration with increasing soil copper concentration for lettuce is consistent with the results of previously published studies (Crews and Davies, 1985; Sloan *et al.*, 1997; Tambasco *et al.*, 2000; Samsøe-Petersen *et al.*, 2002). In agreement with the results presented in Table 7.16, Samsøe-Petersen *et al.* (2002) also reported significant correlation between total soil copper and radish hypocotyl copper concentrations.

Correlations between 0.01 *M* $CaCl_2$ extractable copper and plant leaf tissue have been previously reported for spinach (Wang *et al.,* 2004) as well as for other plants grown on soils contaminated with copper-based fungicides including maize leaf and wild vineyard plants (Brun *et al.*, 1998; Brun *et al.,* 2001). In contrast, Sauvé *et al.* (1996) found that $CaCl_2$ extractable copper did not correlate with lettuce copper concentrations. Consistent with the results of the current study, correlations between tissue and 1 *M* NH_4NO_3 extractable copper have been reported for lettuce, pakchoi and radish (Knoche *et al.* 1997, cited in Gryschko *et al.*, 2005; Zhou *et al.*, 2005).

LEAD

Lead concentrations above the detection limit were measured in all analysed plant parts with lead concentrations in lettuce and radish being significantly higher ($p<0.05$) for plants grown on horticultural soils than background soils. Radish hypocotyls generally contained greater lead concentrations than those measured in lettuce leaves, whereas there was no consistent pattern for radish hypocotyl and radish leaves possibly due to limited data. Greater levels of lead were measured in radish roots than radish tops for plants grown on former orchard soils (Merry *et al.*, 1986b) whereas Keefer *et al.* (1986) measured greater lead concentrations in radish tops than hypocotyls. The order of uptake of radish > lettuce (Table 7.15) contrasts with the results of other studies reporting greater concentrations of lead in lettuce leaves than in radish hypocotyls (Hibben *et al.*, 1984; Cobb *et al.*, 2000; Darmody *et al.*, 2004). In some studies aerial deposition of lead may have contributed to the measured leaf lead concentrations.

Lettuce leaf lead concentrations increased with increasing total lead concentration ($p<0.02$). In comparison, the radish hypocotyl lead tissue concentrations correlated with 1 *M* NH_4NO_3 extractable lead ($p<0.01$) but not with total lead concentration (Table 7.19b). Lead concentrations in lettuce and radish above the detection limit were measured in all samples despite 0.01 *M* $CaCl_2$ extractable lead concentrations being measured in only five soils (Table 7.2). There were insufficient data points for lead concentration in radish leaves to determine a relationship between leaf and soil concentration. Increasing lettuce lead concentration with increasing soil concentration has been reported for studies of lead uptake (John and VanLaerhoven,

1972; Nicklow *et al.*, 1983; Crews and Davies, 1985; Sterrett *et al.*, 1996; Rooney *et al.*, 1999; Cobb *et al.*, 2000). The lack of correlation between total soil and radish lead concentration for the current study is consistent with the results for radish grown on orchard plots (Aten *et al.*, 1980). However, other studies have reported relationships between soil and both radish hypocotyl and leaf lead concentration (John and VanLaerhoven, 1972; Smilde *et al.*, 1982; Davies 1992; Rooney *et al.*, 1999; Cobb *et al.*, 2000; Samsøe-Petersen *et al.*, 2002).

There are few comparable studies relating 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable lead concentrations in soil and plant uptake reported in the literature. Reported examples include correlations between 0.01 *M* $CaCl_2$ extractable lead and lead concentrations in chinese cabbage and spinach (Wang *et al.*, 2004) and significant correlations between 1 *M* NH_4NO_3 extractable lead and lead concentrations in spinach (Knoche *et al.* 1997, cited in Gryschko *et al.*, 2005).

The soil lead concentrations did not explain all of the variability observed for plant tissue lead concentrations (Table 7.18). The fit of the linear regression model for lettuce uptake was improved by the addition of CEC. Similarly, best subsets linear regression analysis identified soil pH and %TOC as controlling variables for lead uptake by radish hypocotyls. All of these soil properties have been found to influence the bioavailability of lead in soil and hence plant tissue concentrations (Adriano, 2001).

ZINC

Zinc plant tissue concentrations exceeded soil concentrations indicating bioaccumulation. There were no significant differences in zinc concentration between lettuce and radish grown on horticultural soils and those grown on grazing and bushblock soils. The plant tissue zinc concentrations followed the order lettuce>radish leaves>radish hypocotyl (Table 7.15). Similar orders for zinc uptake by plants have been reported in the literature. For example, Keefer *et al.* (1986) and Lorenz *et al.* (1997) reported that zinc concentrations of radish tops tended to greater than those in the radish root, and zinc levels in lettuce were greater than those in radish for plants grown on river sediments (Darmody *et al.*, 2004). Consistent with

the results for the lettuce and radish grown Auckland soils (Table 7.14), Boon and Soltanpour (1992) measured higher levels of zinc in leaves than tubers.

Zinc concentrations in the lettuce tissue correlated with the 0.01 *M* $CaCl_2$ ($p<0.05$) and 1 *M* NH_4NO_3 ($p<0.02$) extractable and the total soil ($p<0.01$) zinc concentrations (Table 7.19). Radish hypocotyl and leaf zinc concentrations increased with 0.01 *M* $CaCl_2$ extractable zinc and radish hypocotyl zinc concentrations correlated with 1 *M* NH_4NO_3 extractable zinc ($p<0.01$). Comparable correlations between soil total zinc concentration and lettuce leaf zinc concentrations have been published by Davis (1979), Crews and Davies (1985); Sterrett *et al.* (1996), Lorenz *et al.* (1997), Sloan *et al.* (1997) and Albering *et al.* (2002). Correlations between $CaCl_2$ extractable zinc and leaf zinc concentrations have been previously reported for lettuce, spinach and brome grass (Novozamsky *et al.*, 1993; Hooda *et al.*, 1997; Peijnenburg *et al.*, 2000; McBride and Evans, 2002). In agreement with the results presented here, correlations between 1 *M* NH_4NO_3 extractable zinc, and plant leaf and radish hypocotyl zinc concentrations have also been previously reported. (Knoche *et al.*, 1997, cited in Gryschko *et al.*, 2005; Zhou *et al.*, 2005).

Best subsets linear regression analysis identified soil CEC as a controlling variable for zinc uptake by lettuce improving the R^2 value from 67 to 81 (Table 7.18). The relationship between radish hypocotyl zinc and total soil zinc concentration was improved by the inclusion of pH and iron. These two variables explained an additional 61.9% of the variability for radish hypocotyls and 59.4% for radish leaf. Soil pH has been previously reported to be an important variable for zinc uptake by radish (Preer *et al.*, 1995).

7.3.3.2 BIOACCUMULATION FACTORS

Bioaccumulation factors (BAFs) can be used to compare relative uptake from different studies as well as to derive soil quality guidelines which are protective of human exposure through vegetable consumption (e.g. UK CLEA model and the NZ TTGs). The BAFs were calculated by dividing the dry weight tissue concentration by the soil concentration and are presented in Table 7.20. The BAFs determined for the Auckland soils were generally comparable with BAFs reported in the literature for lettuce and radish grown on soils containing comparable trace element concentrations

as well as with uptake factors used to determine soil criteria (Table 7.21). The relative order of the bioaccumulation factors for the radish and lettuce leaves was Cd>Zn>Cu>As>Pb and Zn≥Cu>As>Pb>Cd for the radish hypocotyls. The relative order of uptake of trace elements for the leaf tissue is comparable to the order of extractability as measured by neutral salts Cd>Zn>Cu>Pb (Section 7.3.1). Similar orders of uptake have been reported in other studies. For example, the relative bioavailability of trace elements from soil to lettuce was Cd>>Zn≥Ni>Cu >> Cr >Pb 15 years after application of biosolids (Sloan *et al.*, 1997) and accumulation factors for vegetables grown on contaminated sediments followed the order Cd, Zn > Cu > As >Hg, Pb, Ni (Smilde *et al.*, 1982).

Table 7.20: Bioaccumulation factors (BAFs) for uptake of aged trace elements by lettuce and radish (nc means not able to calculate as trace element not measured in plant material).

	Arsenic	Cadmium	Copper	Lead	Zinc
lettuce					
Orchard 1	nc	3.88	0.03	0.003	1.72
Orchard 2	0.01	5.09	0.03	0.003	1.81
Orchard 3	0.01	4.90	0.04	0.004	1.74
Orchard 4	0.01	5.33	0.06	0.005	2.25
Orchard 5	0.13	6.20	0.13	0.007	5.11
Vineyard	nc	7.79	0.10	0.006	2.54
Bushblock 1	nc	12.82	0.30	0.020	4.85
Bushblock 2	nc	9.94	0.35	0.010	3.60
Grazing1	nc	4.74	0.28	0.004	1.24
Grazing 2	nc	9.06	0.93	0.036	7.61
radish hypocotyl					
Orchard 1	0.01	0.82	0.04	0.002	1.13
Orchard 2	0.04	1.34	0.06	0.005	1.00
Orchard 5	0.17	2.09	0.18	0.013	4.30
Vineyard	nc	2.20	0.09	0.023	1.89
Bushblock 1	nc	7.54	0.21	0.023	3.76
Bushblock 2	0.12	11.41	0.25	0.048	3.63
Grazing 1	nc	0.85	0.15	0.004	0.72
Grazing 2	nc	6.02	0.60	0.013	5.69
radish leaf					
Orchard 1	0.01	1.49	0.09	0.003	1.61
Orchard 2	0.02	2.91	0.13	0.002	1.44
Orchard 5	nc	nc	0.32	nc	6.56
Vineyard	nc	nc	0.17	nc	3.46
Bushblock 1	nc	nc	0.35	nc	4.57
Bushblock 2	0.00	12.41	0.32	0.019	6.03
Grazing 1	nc	nc	0.18	nc	1.11
Grazing 2	nc	nc	0.94	nc	7.03

Table 7.21: Summary of BAFs reported in the literature for uptake of trace elements by lettuce and radish grown in soils with comparable trace element concentrations. (GM = geometric mean).

Plant part	Arsenic	Cadmium	Copper	Lead	Zinc	Reference
Lettuce	0.027–0.003	0.23–1.6	0.064–0.55	0.0013–0.0036	0.064–0.55	Samsøe-Petersen *et al.* (2002)
Lettuce		1.75	0.24	0.32	0.30	Fytianos *et al.* (2001) max values
Lettuce	0.001–0.0234					Warren *et al.* 2003
Lettuce		0.28–0.98	0.14–0.54	0.001–0.016	0.14–0.26	Albering *et al.* (1999)
Lettuce	0.11–0.12	2.00–3.22		0.00	0.24–0.25	Mattina *et al.* (2003)
Radish hypocotyl	0.01–0.04	0.08-0.49	0.014–0.2	0.0074–0.021	0.083–0.57	Samsøe-Petersen *et al.* (2002)
Radish leaves		0.32	0.12	0.01	0.36	Marchiol *et al.* (2004b)
Regulatory uptake factors						
Generic		2.65	0.27			CCME (1999)
		Leaf 1.81				
		Root 15.22				
Leafy vegetables	0.009	pH dependent		0.012		DEFRA and Environment Agency (2002a)
Root vegetables	0.009	pH dependent		0.008		DEFRA and Environment Agency (2002a)
Generic	0.04	0.59	0.12	0.039	0.37	USEPA (2000) median values
Generic	0.009	0.31	0.20	0.017	0.18	Lizjen *et al.* (2001)
Leafy vegetables	0.002–0.068	0.002–14.12				US EPA (1996)
	(GM 0.036)	(GM 0.364)				
Root vegetables	0.002–0.28	0.002–1.188				US EPA (1996)
	(GM 0.008)	(GM 0.064)				

As was observed for uptake of trace elements by earthworms, the BAFs for lettuce uptake of measured trace elements decreased with increasing soil concentration (Table 7.22). Similarly, the BAFs for cadmium, copper and zinc for the radish hypocotyls and for copper and zinc for the radish leaves also decreased with increasing soil concentration. Decreases in uptake of trace elements by plants with increasing soil concentration have been reported previously (Alloway *et al.*, 1990; Efroymson *et al.*, 2001; Samsøe-Petersen *et al.*, 2002; Wang *et al.*, 2004). This pattern of uptake has also been reported for other studies investigating phytoavailability of contaminants in horticultural soils. For example, Chisholm (1972) reported differences in lead uptake by vegetables from background and contaminated orchard soils, and uptake of copper and lead from horticultural soils by oats and cress decreased with increasing soil concentration (Ferrara *et al.*, 2003).

Table 7.22: Pearson's correlation coefficients for relationships between plant BAFs and soil trace element concentrations and physical characteristics (log transformed variables). Significant relationships are presented in bold.

Soil	Lettuce (n = 10)				Radish hypocotyl (n = 8)				Radish leaf (n = 8)	
	Cd_{BAF}	Cu_{BAF}	Pb_{BAF}	Zn_{BAF}	Cd_{BAF}	Cu_{BAF}	Pb_{BAF}	Zn_{BAF}	Cu_{BAF}	Zn_{BAF}
Cd_{total}	**-0.943** ***	**-0.744** *	**-0.77** **	**-0.655** *	**-0.96** ***	**-0.722**	**-0.891** **	-0.7	-0.669	-0.7
Cu_{total}	**-0.696***	**-0.994** ***	**-0.857** **	-0.631	-0.676	**-0.952** ***	-0.577	-0.58	**-0.871** **	-0.54
Pb_{total}	**-0.743** *	**-0.899** ***	**-0.93** ***	**-0.692** *	**-0.729** *	**-0.837** **	-0.526	-0.63	**-0.828**	-0.55
Zn_{total}	**-0.733** *	-0.665	**-0.909** ***	**-0.938** ***	**-0.744** *	**-0.787** *	-0.574	**-0.89** **	**-0.889** **	**-0.8** *
Olsen P	**-0.783** **	**-0.891** ***	**-0.755**	-0.486	**-0.766** *	**-0.790** *	-0.646	-0.471	-0.668	-0.445
pH	-0.334	-0.262	-0.073	-0.106	-0.481	-0.201	-0.58	-0.25	-0.085	-0.37
%TOC	-0.572	-0.113	-0.44	-0.61	-0.628	-0.416	-0.678	-0.69	-0.544	-0.68
CEC	**-0.658***	-0.501	**-0.682***	**-0.826** **	-0.605	-0.663	**-0.754** *	**-0.82** *	**-0.761** *	**-0.85** *
%clay	-0.203	-0.496	-0.41	-0.503	-0.473	-0.598	-0.343	-0.59	-0.577	-0.6
%silt	-0.231	0.129	0.057	0.028	-0.678	-0.167	-0.643	-0.29	-0.121	-0.35
%sand	0.24	0.087	0.228	0.365	**0.745***	0.482	0.589	0.69	0.514	0.699
Mn	**-0.811** **	-0.572	**-0.797** **	**-0.879** ***	-0.667	-0.585	-0.645	**-0.85** **	-0.683	**-0.81** *
Fe	-0.456	-0.417	-0.62	**-0.863** **	-0.476	-0.619	-0.525	**-0.83***	**-0.753***	**-0.82***

*p <0.05, **p <0.01, ***p <0.001.

For arsenic, where BAFs were able to be determined, the BAFs tended to decrease with increasing soil iron content. The soil iron content has previously been reported

to be a controlling factor for plant uptake of arsenic (Xu and Thornton, 1985) and the addition of iron as $FeSO_4$ has been used as a remedial strategy to reduce uptake of arsenic by lettuce and radish (Warren and Alloway, 2003; Warren *et al.*, 2003).

The percent trace element extracted by 0.01 *M* $CaCl_2$ or 1 *M* NH_4NO_3 is theoretically a measure of the relative bioavailability of contaminants. There were positive significant correlations (Spearman rank) between the percent trace element extracted by 1 *M* NH_4NO_3 and the BAF for uptake of cadmium, zinc and lead by lettuce and radish, and for uptake of zinc by radish leaf (Appendix B). The percent trace element extracted by 0.01 *M* $CaCl_2$ correlated with the BAF for cadmium uptake by lettuce and radish and with the BAFs for zinc uptake by lettuce, radish and radish leaf. In contrast, the BAFs for copper uptake by all plant parts did not correlate with the percent copper extracted by either neutral salt.

Pearson's correlation analysis was used to determine significant relationships between uptake factors and soil properties (Table 7.21). For lettuce, significant inverse relationships were found between the BAFs for cadmium, copper and lead and Olsen P. Additional significant inverse relationships were found between the BAFs for lettuce uptake of cadmium, lead and zinc and soil properties including iron, manganese and CEC. Similarly for radish hypocotyls and leaves there were insignificant negative correlations between the BAFs for zinc and CEC and iron and manganese. The Olsen P concentration was inversely related to the BAFs for copper uptake by radish hypocotyls and leaves, as well as the BAFs for cadmium and lead uptake by radish hypocotyls. These significant inverse correlations between BAFs and soil properties could also be explained by a significant correlation between the soil property of interest and the total soil concentration, with the exception of the significant correlation between the BAF for lettuce uptake of lead and the CEC ($p<0.05$).

7.3.3.3 PHYTOTOXICITY OF AGED TRACE ELEMENTS

Concentrations of arsenic, copper, lead and zinc in most of the orchard soils exceeded the ORNL toxicological benchmarks (Efroymson *et al.*, 1997b) for the protection of plants (Table 7.23). Additionally zinc concentrations in four of the soils (two orchards and two grazing sites) exceeded the German trigger level of 2 mg kg^{-1} for 1 *M* NH_4NO_3 extractable zinc for plant growth impairment (Federal Government, 1999).

Table 7.23: Comparison of trace element concentrations measured in plant assay soils (mg kg^{-1} DW) with available soil quality criteria for the protection of plants.

	As	Cd	Cu	Pb	Zn
total trace element					
Orchard 1	15.2	0.54	366	59	65
Orchard 2	35.6	0.38	314	116	47
Orchard 3	28.0	0.30	243	97	44
Orchard 4	18.3	0.23	160	67	38
Orchard 5	5.6	0.24	73	78	16
Vineyard	2.1	0.16	117	57	63
Bushblock 1	1.7	0.04	18	10	9
Bushblock 2	1.7	0.03	12	16	26
Grazing 1	2.3	0.28	17	34	80
Grazing 2	0.4	0.09	3	4	6
NZTTG[a]	10-20		130		
ORNL[b]	10	4	100	50	50
1 M NH_4NO_3 extractable					
Orchard 1	<0.02	0.03	0.62	0.04	2.26
Orchard 2	<0.02	0.01	0.39	0.04	0.34
Orchard 3	<0.02	0.02	0.41	0.12	1.65
Orchard 4	<0.02	0.01	0.39	0.06	0.85
Orchard 5	0.02	0.01	0.27	0.15	1.12
Vineyard	<0.02	0.02	0.53	0.33	4.79
Bushblock 1	<0.02	0.01	0.07	0.04	0.53
Bushblock 2	<0.02	0.01	0.05	0.20	3.54
Grazing 1	<0.02	0.01	0.03	0.02	2.10
Grazing 2	<0.02	0.01	0.01	0.01	0.65
German standard[c]	0.4		1		2

[a]Health and Environmental Guidelines for Selected Timber Treatment Chemicals (Ministry for the Environment and Ministry of Health, 1997), [b]Oak Ridge National Laboratory toxicological benchmark for phytotoxicity of chemicals in soil (Efroymson *et al.*, 1997b), [c]Trigger value for growth impairment of cultivated plants (Federal Government, 1999).

Copper and zinc tissue concentrations in all analysed plant parts were comparable to the critical ranges for reducing plant yield reported by Kabata-Pendias and Pendias (2001). These thresholds for reducing yield by 10% were 100 to 500 mg kg^{-1} DW for zinc and 10 to 30 mg kg^{-1} DW for copper. The radish hypocotyl grown on the soil (Orchard 2) with the highest arsenic concentration (1.5 mg kg^{-1} DW) also lay within the critical range for tissue arsenic concentrations of 1 to 20 mg kg^{-1} DW (Kabata-Pendias and Pendias, 2001).

The phytotoxicity of the soils was initially assessed by measuring the dry mass yield at harvest for the lettuce and radish grown to maturity (Table 7.24).

Table 7.24: Mean dry mass yield (g) for lettuce and radish plants (n = 4) grown to maturity. Results are presented ± 95% CI.

Soil	Lettuce	Radish leaves[a]	Radish Hypocotyls[a]
Orchard 1	6.07 ± 1.31	0.59 ± 0.11	0.71 ± 0.20
Orchard 2	4.74 ± 1.39	0.64 ± 0.12	0.55 ± 0.14
Orchard 3[b]	4.97 ± 2.01	-	-
Orchard 4[b]	5.03 ± 1.42	-	-
Orchard 5	4.83 ± 2.67	0.71 ± 0.02	0.45 ± 0.11
Vineyard	5.34 ± 2.13	0.67 ± 0.08	0.71 ± 0.29
Bushblock 1	4.67 ± 1.64	0.74 ± 0.07	0.64 ± 0.23
Bushblock 2	4.53 ± 1.25	0.61 ± 0.27	0.33 ± 0.23
Grazing 1	5.52 ± 1.15	0.81 ± 0.16	1.06 ± 0.21
Grazing 2	4.09 ± 0.68	0.80 ± 0.16	0.64 ± 0.37

[a]Estimated yield per plant, [b]Radish not grown in these soils.

Overall for the lettuce plants, there were no significant differences in yield between treatments. The dry yield for lettuce increased with increasing total cadmium, zinc and iron concentrations ($p<0.05$) and with the 1 M NH_4NO_3 extractable cadmium and copper concentrations (Table 7.25). Additionally for lettuce, there were no significant negative relationships between soil properties and yield (Table 7.25). However, for the lettuce grown on the three blended soils (Orchard soils 2 to 4), the yield decreased with increasing percentage of contaminated soil.

Table 7.25: Spearman rank correlation coefficients between mean plant yield and soil and tissue element concentrations with significant correlations presented in bold.

	lettuce (n =10)	radish hypocotyl (n = 8)	radish leaf (n = 8)
Tissue			
Cd	0.588	-0.349	nc[a]
Cu	**0.673***	-0.157	-0.69
Pb	0.109	-0.374	nc
Zn	**0.709***	0.012	-0.476
Fe	-0.273	-0.325	0.429
Soil			
As_{total}	0.467	0.133	-0.381
Cd_{total}	**0.636***	0.446	-0.214
Cu_{total}	0.576	0.205	-0.595
Pb_{total}	0.358	-0.096	-0.476
Zn_{total}	**0.855****	0.602	-0.238
Cd_{CaCl_2}	0.588	0.506	-0.071
Cu_{CaCl_2}	0.626	0.12	**-0.714***
Zn_{CaCl_2}	0.43	0.229	-0.333
$Cd_{NH_4NO_3}$	**0.888*****	**0.735***	-0.048
$Cu_{NH_4NO_3}$	**0.638***	0.12	**-0.714***
$Pb_{NH_4NO_3}$	0.092	-0.358	-0.561
$Zn_{NH_4NO_3}$	0.515	0.229	-0.333
OlsenP	0.552	0.265	-0.381
%TOC	0.543	0.518	-0.143
pH	-0.317	0.104	0.422
CEC	0.527	0.253	-0.381
%clay	0.382	0.482	0.048
%silt	0.406	0.578	0.476
%sand	-0.527	**-0.771****	-0.19
Mn	0.503	0.361	-0.19
Fe	**0.648***	0.506	-0.238

[a]Not calculated as insufficient datapoints to determine a relationship, *p <0.05, ** p <0.01, *** p <0.001.

The radish hypocotyl yields were not affected by trace element concentration, but decreased with increasing %sand (p<0.05). In contrast, the radish leaf yield decreased with increasing 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable copper concentrations (Table 7.25). Copper contamination of soil has previously been reported to decrease dry matter yield of plants. For example, Bolan *et al.* (2003a) reported that dry matter yield of mustard plants decreased with increasing soil copper concentration and the biomass of ruderal plants grown in vineyard soil spiked with copper decreased with increasing copper concentration (Brun *et al.*, 2003).

SEEDLING EMERGENCE AND ROOT ELONGATION

A subsequent phytotoxicity assay was undertaken utilising sub samples of the worm assay soils (Table 7.1) to determine impacts of aged trace elements on seedling emergence and root elongation. Two plant species were used for the assays; a monocotyledon, ryegrass and a dicotyledon, lettuce. The mean results for the five day assays are presented in Table 7.26.

Table 7.26: Mean results (n = 3) for seedling emergence and root length assays.

	Root length (mm)		**Seedling emergence (%)**	
	lettuce	**ryegrass**	**lettuce**	**ryegrass**
W1	45 ± 13[a]	54 ± 6	93	93
W2	30 ± 12	34 ± 2	80	93
W3	31 ± 11	37 ± 10	70	87
W4	58 ± 10	50 ± 6	97	97
W5	46 ± 5	42 ± 14	80	93
W6	46 ± 11	42 ± 9	83	100
W7	51 ± 8	49 ± 20	93	93
W8	48 ± 21	39 ± 13	90	97
W8	54 ± 4	48 ± 12	97	93
W10	44 ± 13	41 ± 10	90	97

[a] Mean ± 95% confidence interval

Spearman rank correlation was used to explore possible relationships between soil trace element concentrations and seedling emergence and root elongation (Table 7.27). In the orchard soils, the root length of the lettuce seedlings decreased with increasing 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable copper concentration ($p<0.05$). Copper has previously been reported to reduce root length in lettuce seedlings (Inaba and Takenaka, 2005). Seedling emergence for ryegrass in the orchard soils decreased with increasing 1 *M* NH_4NO_3 extractable cadmium concentrations ($p<0.05$).

Table 7.27: Spearman rank correlation coefficients between mean root length and seedling emergence and soil trace element concentrations. Significant correlations presented in bold.

	Root length		Seedling emergence	
	lettuce	ryegrass	lettuce	ryegrass
All soils (n = 10)				
Cd_{CaCl_2}	-0.309	-0.152	-0.252	-0.426
Cu_{CaCl_2}	-0.571	-0.237	-0.511	-0.296
Zn_{CaCl_2}	-0.212	-0.079	-0.16	0.282
$Cd_{NH_4NO_3}$	-0.285	-0.224	-0.325	-0.452
$Cu_{NH_4NO_3}$	-0.539	-0.212	-0.497	-0.321
$Pb_{NH_4NO_3}$	-0.286	-0.134	-0.265	0.178
$Zn_{NH_4NO_3}$	-0.03	0.176	0.055	-0.19
As_{total}	-0.091	-0.37	-0.117	-0.344
Cd_{total}	0.018	-0.358	-0.031	-0.544
Cu_{total}	-0.406	-0.006	-0.301	-0.374
Pb_{total}	-0.018	0.358	-0.104	-0.177
Zn_{total}	0.515	**0.697**	0.387	-0.243
Orchards only (n= 6)				
Cd_{CaCl_2}	-0.6	-0.143	-0.232	-0.638
Cu_{CaCl_2}	**-0.886***	-0.429	-0.377	-0.455
Zn_{CaCl_2}	0.2	0.2	0.29	0.334
$Cd_{NH_4NO_3}$	-0.657	-0.086	-0.319	**-0.82***
$Cu_{NH_4NO_3}$	**-0.886***	-0.429	-0.377	-0.455
$Pb_{NH_4NO_3}$	-0.086	-0.029	0.087	0.213
$Zn_{NH_4NO_3}$	-0.086	0.2	0.058	-0.334
As_{total}	0.086	0.486	0.174	-0.152
Cd_{total}	-0.257	0.486	-0.087	-0.698
Cu_{total}	-0.657	0.086	0	-0.577
Pb_{total}	0.086	0.486	0.174	-0.152
Zn_{total}	0.6	**0.886***	0.638	0.091

*p <0.05, ** p <0.01, *** p <0.001.

These results indicating low phytotoxicity are consistent with the soil trace element concentrations being less than levels previously reported to inhibit seedling emergence and growth. For example, O'Halloran and Booth (2000, cited in Markich *et al.*, 2002) calculated EC_{50} values of 110 mg kg^{-1} arsenic for root length and 750 mg kg^{-1} for copper and root weight for 14 day seedling test using lettuce and spiked soils. Germination of radish, oats and lettuce in sewage sludge were not inhibited by copper spike levels of 500 mg kg^{-1} (Fjällborg and Dave, 2004).

7.3.3.4 COMPARISON WITH REGULATORY STANDARDS

The significance of the plant tissue concentrations can be determined by comparison to New Zealand and international standards for cadmium and lead in leafy and root vegetables (Table 7.28). These standards are on an "as eaten" basis. There is no New Zealand standard for arsenic in vegetables. Similarly, there is also no European Union or Codex maximum level for arsenic in vegetables. To enable comparison with regulatory standards, dry weight cadmium and lead concentrations were converted to fresh weight concentrations as discussed in Section 6.2.3 (Chapter Six). The fresh weight concentrations are presented in Table 7.29. The contribution of home grown produce to the daily intake of cadmium and lead is discussed in Chapter Eight (Section 8.3.2).

Table 7.28: New Zealand and international standards for cadmium and lead concentrations (mg kg^{-1} FW) in vegetables.

	Vegetable	Cadmium	Lead
New Zealand[a]	Leafy vegetables	0.1	0.1
	Root vegetables	0.1	0.1
Codex aliamentarius[b]	Leafy vegetables	0.2	0.3
	Stem and root vegetables	0.1	
	Vegetables		0.1
European Community maximum level[c]	Leafy vegetables	0.2	
	Stem and root vegetables	0.1	
	Brassica and leafy vegetables		0.3
	Vegetables		0.1

[a]Australia New Zealand Food Standards Code (FSANZ, 2005), [b]Codex aliamentarius maximum levels for cadmium and lead (Codex 2003, 2005), [c]EC (2001) Commission Regulation (EC) no 466/2001. Setting maximum levels for certain contaminants in foodstuffs.

Table 7.29: Fresh weight concentrations (mg kg^{-1}) of cadmium and lead measured in lettuce and radish hypocotyls. Results equivalent to NZ standards are presented in bold and results equivalent to or greater than 50% of the NZ standard are presented in italics.

Soil	Cadmium		Lead	
	lettuce	radish	lettuce	radish
Orchard 1	**0.15**	0.03	0.01	0.01
Orchard 2	**0.14**	0.03	0.03	0.03
Orchard 3	**0.10**		0.02	
Orchard 4	*0.09*		0.02	
Orchard 5	**0.11**	0.03	0.04	*0.06*
Vineyard	*0.09*	0.02	0.02	*0.08*
Bushblock 1	0.04	0.02	0.01	0.01
Bushblock 2	0.02	0.02	0.01	*0.05*
Grazing 1	*0.09*	0.01	0.01	0.01
Grazing 2	*0.06*	0.03	0.01	0.00

CADMIUM

The NZ food standard for cadmium in vegetables was lowered from 1.0 mg kg^{-1} to 0.1 mg kg^{-1} (FW) in 2002 (FSANZ, 2005). Cadmium concentrations in lettuce grown on four out of the ten soils were equivalent to or exceeded the current NZ standard for cadmium in leafy vegetables. There were no exceedances of the standard for radish hypocotyls (Table 7.29). Cadmium concentrations in lettuce exceeded the cadmium standard at soil concentrations significantly below both the maximum value measured in an orchard soil of 1.7 mg kg^{-1} (Table 7.1) and the proposed soil limit of 1.0 mg kg^{-1} for application of biosolids (NZWWA, 2003). Similarly the soil 1 *M* NH_4NO_3 extractable cadmium concentrations (Table 7.2) were significantly below the German standard of 0.04 mg kg^{-1} for agricultural soils which is protective of plant tissue concentrations (Federal Government, 1999).

There is other evidence available to suggest that cadmium concentrations in vegetables could exceed the food standard at the soil levels reported for this study under New Zealand conditions. For example, Gray *et al.* (1999a) measured cadmium uptake by vegetables from a range of NZ grazing soils in a pot trial. Cadmium levels in lettuce and carrots grown on three of the soils exceeded the current food standard. In 1995, the New Zealand Fertiliser Manufacturer's Research Association commissioned a survey of cadmium levels in South Auckland market garden produce and Mid Canterbury wheat (Roberts *et al.* 1995). Comparison of these results with

the current food standards indicates that cadmium levels in 4% of the market garden produce and 23% of the wheat would have exceeded food standards (Kim, 2005). The maximum soil cadmium concentration for market garden soils was 0.85 mg kg^{-1} and 0.69 mg kg^{-1} for wheat soil (Roberts *et al.* 1995); both of these concentrations are considerably lower than the maximum value of 1.5 mg kg^{-1} measured for horticultural soils (Chapter Four). Food standard exceedances in wheat grain have also been reported for wheat grown in New Zealand (Gray *et al.*, 2001). Kim (2005) estimated that 1.5% of potatoes purchased in the Waikato region in 2004 were likely to exceed the food standard. This estimate was derived from the results of a survey of selected vegetables (potatoes, onions, silverbeet and lettuce) purchased from within the Waikato region.

LEAD

Plant tissue lead concentrations for the edible parts of the plants grown in the pot trial did not exceed the food standards for lead. Radish hypocotyls for three of the assayed soils contained lead concentrations equal to or greater than half the standard for lead levels in root vegetables (Table 7.29). These lead levels indicate that exceedances of the food standard could occur as the soil lead concentrations used for the plant assay were significantly below the maximum lead concentration measured in an orchard soil of 440 mg kg^{-1} (Table 7.1) as well as guidelines for lead in residential soils. The soil limit for the application of biosolids to land for lead is 300 mg kg^{-1} (NZWWA, 2003) and the Ministry of Health guideline for lead in high-contact soils is 400 mg kg^{-1}(Ministry of Health, 1998).

The possibility of exceedances of the standards for vegetables grown on soils with higher lead concentrations is supported by exceedances of the lead standards for vegetable samples collected from a garden on a former Hamilton orchard with a soil lead concentration of 270 mg kg^{-1}. The lead concentrations in beetroot were 0.1 mg kg^{-1} (FW) in the tuber and 0.3 mg kg^{-1} (FW) for the leaves (Kim *pers comm.*, 2003). Lead concentrations in lettuce and radish grown in soil collected from a Canterbury (NZ) pasture contaminated with lead shot also exceeded the current food standards at

a soil lead concentration of 135 mg kg^{-1} (assuming a moisture content of 94% to convert from dry weight to wet weight concentrations) (Rooney *et al.*, 1999).

7.3.4 SUMMARY OF NEUTRAL SALT CORRELATIONS

One objective of the work presented in this chapter was to compare the bioassays results with the soil concentrations determined using neutral salt extractions. The significant relationships ($p<0.05$) found between total and extractable trace element concentration and tissue concentration for the worm and plant assays are summarised in Table 7.30 and significant relationships for toxicity endpoints in Table 7.31. Overall neither the total trace element concentrations nor the neutral salt extractable trace element concentrations were a better predictor of trace element concentrations in plant and worm tissue. As arsenic was detected in both worm and plant tissue despite not being detected in the neutral salt extractions, 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 may not be suitable extractants for determining the bioavailability/mobility of arsenic in New Zealand soils.

The neutral salt extractable concentration may be a better indicator of toxicity of copper in soil than total trace element concentrations. Additional significant negative correlations with neutral salt extractable trace concentrations were observed for toxicity endpoints measured in the plant assays (Table 7.31). In the orchard soils lettuce root length decreased with increasing 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable copper concentrations and seedling emergence for ryegrass decreased with increasing 1 *M* NH_4NO_3 extractable cadmium concentrations. These negative relationships would not have been identified if only the total trace element concentration had been measured.

The small size and limited contaminant range of the datasets may have masked significant relationships between the total and neutral salt extractable and tissue concentrations. It is possible that other significant relationships between the neutral salt extractable fraction and worm or plant tissue concentrations would have been observed if there had been a larger dataset of orchards soils containing a wider

contaminant range. Better correlations have been reported for studies utilising soils sets with contaminant concentrations which span a wide range (NRC, 2003). Of the trace elements investigated in this Chapter, copper had the widest range of concentrations in soil and was the only trace element for which tissue concentrations in both plant and worm tissues correlated with the neutral salt extractable and total soil trace element concentration (Table 7.30).

It is probable that there were differences in trace element extractability between the orchard and control soils. The trace elements in present in the background soils (possible exceptions of cadmium and zinc) are likely to be predominantly the result of soil formation processes and hence are occluded within the mineral matrix, whereas for the orchard soils the trace elements have been added and may be more available for uptake. Studies have reported differences in desorption for spiked and "native" trace elements in New Zealand soils (Hogg *et al.*, 1993; Singh *et al.*, 1997; Gray *et al.*, 1998, 1999b).

There are several contributing factors which may explain the lack of consistent correlations between the neutral salt extractable trace element concentrations for arsenic, cadmium, lead and zinc, and the worm and plant tissue concentrations. Earthworms and plants have been reported to be able to regulate tissue concentrations of copper and zinc (Laszczyca *et al.*, 2004; Peijnenburg *et al.*, 1999).

Measurement of the total amount of trace elements extracted by neutral salt solutions does not provide any information regarding the speciation of trace elements in pore water which can also determine their availability for uptake (Sauvé *et al.*, 1998; Nolan *et al.*, 2003). While the neutral salt extractions simulate exchange between the soil and the pore water, the organisms may not only be exposed to the fraction of trace elements which is able to partition between pore water and soil. For example, *A. caliginosa* ingest soil and degrade soil organic matter. It has been suggested that soil ingestion may be a more important exposure route than dermal exposure to pore water for this species (Becquer *et al.*, 2005).

In addition organisms can alter the bioavailability of contaminants in soil. For example earthworms digest soil organic matter (Oste *et al.*, 2001). Plants can also alter the bioavailability of the trace elements (Basta *et al.*, 2005). Plant roots can alter both the pH of the rhizosphere through releasing H^+, HCO_3^- and CO_2 and the redox potential of the soil surrounding the roots-through producing or using O_2. Plants may also release organic compounds (organic acids, phenolics and phytosiderophores) from their roots which can enhance the bioavailability of contaminants (Marschener, 1998; Singer *et al.*, 2003; Qin *et al.*, 2004). The addition of worms and plants to the assay soils is likely to have increased the soil microbial activity which can also enhance or reduce availability of contaminants for uptake by altering the composition of the soil solution (McLaughlin *et al.*, 2000b; Lasat, 2002).

Table 7.30: Summary of significant relationships ($p<0.05$) between soil trace element concentration (total and neutral salt extractable) and plant or worm tissue trace element concentration.

Trace element	Total				0.01 *M* $CaCl_2$				1 *M* NH_4NO_3			
	Worm	Lettuce	Radish	Radish leaf	Worm	Lettuce	Radish	Radish leaf	Worm	Lettuce	Radish	Radish leaf
Arsenic	<0.01	ns	ns	nc[a]	nc	nc	nc	nc	nc	nc	nc	nc
Cadmium	ns	<0.001	ns	nc	ns	<0.05	ns	nc	ns	<0.05	ns	nc
Copper	<0.001	<0.001	<0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Lead	<0.01	<0.05	ns	nc	ns	ns	ns	nc	ns	ns	<0.05	nc
Zinc	ns	<0.01	ns	<0.01	ns	<0.05	<0.05	<0.01	ns	<0.05	<0.05	<0.01

[a] Insufficient data points to determine a relationship.

Table 7.31: Summary of significant relationships ($p<0.05$) between soil trace element concentration (total and neutral salt extractable) and toxicity endpoints. Negative relationships are presented in bold and positive relationships in italics.

Trace element	Total					0.01 *M* $CaCl_2$			1 *M* NH_4NO_3			
	As	Cd	Cu	Pb	Zn	Cd	Cu	Zn	Cd	Cu	Pb	Zn
Cocoon production	ns	ns	**<0.05**	ns	ns	ns	**<0.05**	ns	ns	**<0.05**	ns	ns
%Change in bodymass	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Lettuce yield	ns	*<0.05*	ns	ns	*<0.01*	ns	ns	ns	*<0.001*	*<0.05*	ns	ns
Radish hypocotyl yield	ns	ns	ns	ns	ns	ns	ns	ns	*<0.05*	ns	ns	ns
Radish leaf yield	ns	ns	ns	ns	ns	ns	**<0.05**	ns	ns	**<0.05**	ns	ns
Lettuce SE[a]	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Lettuce root length[b]	ns	ns	ns	ns	ns	ns	**<0.05**	ns	ns	**<0.05**	ns	ns
Ryegrass SE[b]	ns	ns	ns	ns	ns	ns	ns	ns	**<0.05**	ns	ns	ns
Ryegrass root length	ns	ns	ns	ns	*<0.05*	ns	ns	ns	ns	ns	ns	ns

[a]seedling emergence, [b]orchard soils only

7.4 CONCLUSIONS

7.4.1 NEUTRAL SALT EXTRACTABLE CONCENTRATIONS OF TRACE ELEMENTS

Solutions of 1 *M* NH_4NO_3 extracted higher concentrations of cadmium, copper, lead and zinc from soil than 0.01 *M* $CaCl_2$. Arsenic was not extracted by either of the neutral salt solutions. The mean percent of trace element extracted followed the order cadmium>zinc>copper>lead. For both 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 there were no significant differences in the percent of cadmium, copper and zinc extracted from background and horticultural soils.

Overall neither the total trace element concentrations nor the neutral salt extractable concentrations were a better predictor of trace element concentrations in both worm and plant tissues. The neutral salt extractions may be a better indicator of toxicity of trace elements in soils than the total trace element concentration. Additional significant negative correlations existed between the neutral salt extractable copper concentrations for radish leaf yield and lettuce seedling root length (orchard soils) which were not observed for total soil copper concentrations. Ryegrass seedling emergence decreased in orchard soils with increasing 1 *M* NH_4NO_3 extractable cadmium concentrations. Further work is required to identify and validate a suitable chemical method for determining the bioavailability of trace elements to earthworms and plants.

7.4.2 EARTHWORM ASSAY

Concentrations of arsenic, copper and lead in the worm tissue correlated with total soil concentrations. *Aporrectodea caliginosa* bioaccumulated cadmium and zinc with resulting tissue concentrations up to 25 and 15 times the soil concentration for cadmium and zinc respectively. The bioaccumulation factors for arsenic, cadmium,

copper, lead and zinc decreased with increasing soil concentration indicating that uptake of trace elements by earthworms is concentration dependent.

The rate of cocoon production decreased with increasing worm tissue and soil copper concentrations (total and neutral salt extractable) indicating that the copper concentrations in present in orchard soils may have a deleterious effect on earthworms.

7.4.3 PLANT ASSAYS

Concentrations of cadmium, copper, lead and zinc concentrations in lettuce tissue and copper in radish (hypocotyl and leaf) increased with increasing total soil concentration. Copper concentrations in lettuce and radish and zinc concentrations in radish also correlated with the 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable concentration of these trace elements.

The BAFs for copper and zinc for lettuce, radish hypocotyls and radish leaf decreased with increasing soil trace element concentration. Similarly the radish hypocotyl and lettuce BAFs for cadmium and the lettuce BAF for arsenic also decreased with increasing soil concentration. Lettuce and radish (hypocotyls and leaves) bioaccumulated both cadmium and zinc with BAFs exceeding unity.

Concentrations of cadmium in lettuce tissue for four out of the ten soils assayed were equal to or exceeded the New Zealand standard of 0.1 mg kg^{-1} FW for cadmium in leafy vegetables. Lead concentrations in radish hypocotyls for three out of eight assayed soils were equivalent to or exceeded 50% of the New Zealand standard of 0.1 mg kg^{-1} FW for lead in root vegetables.

Copper was the only trace element for which phytotoxic effects were observed in both plant assays. The dry weight yield of radish leaf and the root length of lettuce seedlings grown in orchard soils for five days decreased with increasing soil copper concentration.

8 HUMAN EXPOSURE TO ΣDDT AND SELECTED TRACE ELEMENTS

8.1 INTRODUCTION

Humans are the key receptor considered for risk assessments of contaminants in residential settings. Concentrations of ΣDDT, arsenic, cadmium and lead measured in some orchard soils exceeded available New Zealand and international soil quality criteria protective of human health (Chapter Four). As horticultural land within the peri-urban fringe of New Zealand towns and cities is being increasingly developed for residential subdivision it was of interest to estimate daily intakes of these contaminants and compare them to tolerable daily intakes set by regulatory agencies. Soil ingestion, dermal absorption, inhalation of dust and consumption of home grown produce are the main contaminant exposure pathways considered for non volatile contaminants in residential settings in New Zealand.

8.1.1 TOXICOLOGY OF SELECTED CONTAMINANTS

ΣDDT

The toxicology of ΣDDT has been reviewed by several international agencies including the International Agency for Research on Cancer (IARC, 1991), the Dutch National Institute of Public Health and the Environment (RIVM) (Baars *et al.*, 2001) and the US Agency for Toxic Substances and Disease Registry (ATSDR, 2002). In animal studies long-term ΣDDT exposure has been associated with hepatotoxicity, neurotoxicity, effects on reproduction and development and cancer (Baars *et al.*, 2001). DDT was evaluated by the IARC as Group 2B, possibly carcinogenic to humans (IARC, 1991). However, as discussed further in Section 8.2.2.2, there is currently debate regarding the carcinogenicity of DDT and mode of action with regulatory agencies treating DDT compounds as both non genotoxic and genotoxic contaminants.

ARSENIC

The IARC evaluated arsenic as a Group 1, carcinogenic to humans (IARC, 2004a). Longterm exposure to arsenic has been associated with skin changes including hyperkeratosis and changes to pigmentation, cardiovascular effects and with lung, bladder, kidney and skin cancers (USEPA, 1998; WHO, 2001). Most of the information on the health effects of chronic exposure to arsenic has been derived from epidemiological studies of populations exposed to arsenic through drinking water. Toxicological reviews of arsenic have been prepared by the USEPA (1998) and RIVM (Baars *et al.*, 2001), WHO (2001) and ATSDR (2005a).

CADMIUM

The toxicity of cadmium to humans has been reviewed by several agencies including WHO (1992), USEPA (1994), ATSDR (1999), and RIVM (Baars *et al.*, 2001). Cadmium has a slow excretion rate and accumulates in the body with concentrations of cadmium in the kidneys, liver and bones tending to increase with age (WHO, 1992 Baars *et al.*, 2001). Long term exposure to cadmium has been associated with damage to the kidneys and bones (WHO, 1992; ATSDR, 1999; Baars *et al.*, 2001). Cadmium has been classified by the IARC as a Group 1 carcinogen, carcinogenic to humans and has been reported to be an endocrine disruptor (IARC, 1993). A recent epidemiological study of Swedish women observed renal tubular effects at lower cadmium levels than previously reported (Ákesson *et al.*, 2005).

LEAD

Key health effects associated with lead exposure have been reviewed by RIVM (Baars *et al.*, 2001), IRIS (2004) and ATSDR (2005b). Health effects associated with lead exposure include damage to the nervous system which can impair intellectual development in children, hypertension, anaemia, hearing damage and impaired male reproduction (ATSDR, 1999; IRIS, 2004). Children are more vulnerable to lead

exposure than adults due to their developmental stage and because they absorb more lead from their gastrointestinal tracts than adults. In utero exposure to lead has also been linked to impaired intellectual development (ATSDR, 1999) The IARC has classified inorganic lead compounds as Group 2A, probably carcinogenic (IARC, 2004b). There is some evidence to suggest that lead can cause intellectual impairment at lower levels than previously thought (Lanphear *et al.*, 2005). Lead has also been reported to be a suspected endocrine disruptor (Choi *et al.*, 2004).

8.1.2 ESTIMATING GASTRIC BIOACCESSIBILITY OF TRACE ELEMENTS

Toxicity parameters including tolerable daily intakes and index doses are generally calculated for an administered dose (Kelley *et al.*, 2002). Trace elements are generally less bioavailable from soil than other matrices such as food and drinking water (Paustenbach, 2000; Grøn and Andersen, 2003; Sarkar and Datta, 2003; Schroder *et al.*, 2003). The oral bioavailability of contaminants in ingested soil to humans is determined by the amount of contaminant which is desorbed from the soil and the amount which is absorbed into the body (Rodriguez *et al.*, 1999). Animal trials have been used to determine the bioavailability of contaminants in soil, however these methods are time consuming, expensive and raise ethical concerns (Ruby, 2004). A range of *in-vitro* models including physiologically based extraction tests (PBETs) have been developed to estimate the fraction of selected trace elements which is desorbed from soil in the human gastrointestinal tract. This fraction is commonly referred to as the bioaccessible fraction.

These laboratory based chemical extraction methods simulate conditions in the human gastric tract and results have been shown to correlate with those from animal feeding trials (Kelley *et al.*, 2002; Juhasz *et al.*, 2003). These methods are generally based on the paediatric gastrointestinal tract under fasting conditions (Kelley *et al.*, 2002). Soil is extracted at body temperature (37 °C) with a simulated gastric fluid which is prepared from hydrochloric acid and selected enzymes and amino acids. Summaries of various simulated gastric extraction techniques are presented in Oomen

et al. (2002) and Grøn and Anderson (2003). Points of difference between simulated gastric extraction methods include solid to solution ratios, the inclusion of food (dough or dairy products) and a second extraction stage which simulates processes occurring in the intestines.

To date PBET type tests have not been routinely used to estimate the bioaccessibility of trace elements from New Zealand soils and have not been validated against animal trials. However, under the Toxic Substances Amendment Regulations 1999, a comparable simulated gastric acid extraction method is used to screen children's graphic materials (i.e. paints and crayons) for toxic levels of selected trace elements.

Likely human exposures to ΣDDT, arsenic, cadmium and lead in residential settings were estimated over a range of contaminant concentrations using standard equations for exposure to contaminants in soil. The exposure pathways considered were soil ingestion, dust inhalation, consumption of home grown produce and dermal uptake. These assessments incorporated data from the plant assay (Chapters Six and Seven), the 2003/04 Total Diet Survey (Vannoort and Thomson, 2005) and a simulated gastric extraction of trace elements from soil (Section 8.3.1, this Chapter).

8.1.3 OBJECTIVES

- To determine the oral bioaccessibility of arsenic, cadmium and lead from orchard soils using the SBRC *in vitro* method.

- To estimate the daily intakes of ΣDDT, arsenic, cadmium and lead from orchard soils under residential exposure scenarios and to compare the estimated daily intakes to tolerable daily intakes set by regulatory agencies.

8.2 METHODS

8.2.1 ORAL BIOACCESSIBILITY OF TRACE ELEMENTS

A modified version of the Solubility/Bioavailability Research Consortium's Standard Operating Procedure for Stomach-Phase Extraction (Kelley *et al.,* 2002) was used to determine the oral bioaccessibility of arsenic, cadmium and lead from orchard soils. While this method has been validated for arsenic and lead, Kelley *et al.* (2002) state that the method can also be used to determine the bioaccessibility of cadmium as cadmium and lead have similar behaviours in the environment. Full details of the method are provided in Section 2.6.4.2 (Chapter Two).

8.2.2 ESTIMATING POTENTIAL HUMAN EXPOSURE TO CONTAMINANTS IN SOIL

8.2.2.1 EXPOSURE ASSESSMENT

Methodology generally consistent with that used to derive the Health and Environmental Guidelines for Selected Timber Treatment Chemicals (NZTTG) (Ministry for the Environment and Ministry of Health, 1997) was utilised to estimate likely human exposure to soil-derived contaminants in a residential setting. These guidelines represent current New Zealand government policy, although it is likely that the exposure parameters will be amended and/or updated as part of the process of preparing National Environmental Standards for contaminants in soil.

The potential exposures to ΣDDT, arsenic, cadmium and lead in soil for three receptors (adult male, adult female and child) were considered using consumption factors of 10 and 50% home grown produce which are the two default scenarios considered for residential settings in New Zealand. Additionally, the daily intakes for an adult and child have been combined to estimate a combined 30 year exposure to enable comparison with tolerable daily intakes (TDIs). This combined 30 year exposure is referred to in the text as the lifetime exposure. The female exposure

scenarios were included because many of the reported health effects for DDT relate to female reproduction (ATSDR, 2002). Similarly, for lead health concerns relate to effects on the developing foetus as well as young children making maternal exposure to lead important (ATSDR, 1999). This approach is also comparable to the UK CLEA model which bases its calculations on a female child and a female adult (DEFRA and Environment Agency, 2002b).

The likely daily exposures of residents to ΣDDT, arsenic, cadmium and lead were calculated using the exposure parameters listed in Tables 8.1 and 8.2, and equations 2 to 6. Several errors in the methodology used to derive the NZTTG guidelines have been identified (Cavanagh, 2004), and equations 1 to 6 are the corrected equations sourced from Cavanagh and Proffitt (2005) and Proffitt (2004). The range of soil concentrations for each contaminant was based on the soil results presented in Chapters Four, Six and Seven. The overall daily intake of each contaminant of concern was calculated by summing the intake from the four exposure pathways considered (soil ingestion, dermal uptake, inhalation of dust and consumption of home grown produce). An age adjusted contact rate (e.g. amount of soil ingested) derived from the child and adult contact rates using equation 6 was used to estimate the lifetime 30 year exposures for male and female residents. The acronyms are defined in Tables 8.1 and 8.2. Values for contaminant specific parameters are presented in Table 8.3.

$$\text{Intake} = \frac{\text{concentration x contact rate x exposure frequency x exposure duration}}{\text{averaging time x body weight}} \quad (1)$$

Soil ingestion

$$CDI = \frac{Cs \times IR \times CF \times ED \times EF \times MF}{AT \times BW} \quad (2)$$

Inhalation (dust)

$$CDI = \frac{Cs \times IH \times MF \times ED \times EF \times R}{AT \times BW \times PEF} \quad (3)$$

Dermal absorption

$$CDI = \frac{Cs \times CF \times AR \times AH \times ED \times EF \times AF}{AT \times BW} \quad (4)$$

Produce consumption

$$CDI = \frac{CP \times IP \times ED \times EF \times Pg}{AT \times BW} \quad (5)$$

Where

$$CP = C_{root} \times 0.29 + C_{leaf} \times 0.31 \quad (5a)$$

For the combined 30 year exposures (lifetime), the age adjusted contact rates were calculated by substituting equation 6 into equations 2 to 5. The example shown below is for soil ingestion.

$$IR_{adj} = \frac{IR_{child} \times ED_{child}}{BW_{child}} + \frac{IR_{adult} \times ED_{adult}}{BW_{adult}} \quad (6)$$

Table 8.1: Parameters used to estimate daily exposure to selected contaminants in horticultural soils through soil ingestion, dust inhalation, dermal absorption and consumption of home grown produce.

	Parameter	Units	Value	Source
CDI	Chronic daily intake	µg/kg bw/day	Contaminant and scenario specific	
Cs	Soil concentration	mg kg^{-1}	Contaminant specific	Chapter Four
MF	Matrix factor	No unit	1 (default)	NZTTG[b]
R	Proportion of particulates retained in the lungs	No unit	0.75	NZTTG
PEF	Particle emission factor	m^3/kg	1.9×10^8	NZTTG
EF	Exposure frequency	day/year	350	NZTTG
CF	Conversion factor	kg/mg	10^{-6}	NZTTG
AF	Absorption factor (skin)	no unit	Contaminant specific	USEPA (RAGS)[c]
Pg	Proportion of produce grown on-site	No unit	0.1/0.5	NZTTG
Cp	Concentration in produce	mg kg^{-1} (FW)	Contaminant specific	Chapters Six and Seven
Croot	Concentration in root vegetables	mg kg^{-1} (FW)	Contaminant specific	Chapters Six and Seven
Cleaf	Concentration in leafy vegetables	mg kg^{-1} (FW)	Contaminant specific	Chapters Six and Seven

[a]Converted from mg/kg bw/day. [b]Ministry for the Environment and Ministry of Health, 1997. [c]USEPA (2004b) Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment

Table 8.2: Age-group specific parameters used to estimate daily exposure to selected contaminants in horticultural soils through soil ingestion, dust inhalation, dermal absorption and consumption of home grown produce.

	Parameter	Units	Adult	Child	Source
	Age range	years	7–31	1–6	NZTTG[a]
BW	Body weight	kg	70	15	NZTTG
IR	Soil ingestion rate	mg/d	25	100	NZTTG
AR	Exposed skin surface area	cm^2	4700	2625	NZTTG
AH	Soil adherence (skin)	mg/cm^2	0.5	0.5	NZTTG
IP	Produce ingestion rate	kg/day (FW)	0.45	0.13	NZTTG
IH	Inhalation rate	m^3/day	20	3.8	NZTTG
AT	Averaging time[b]	days	24 years x 365	6 years x 365	NZTTG
ED	Exposure duration[b]	year	24	6	NZTTG

[a]Health and Environmental Guidelines for Selected Timber Treatment Chemicals (Ministry for the Environment and Ministry of Health, 1997), [b]For the lifetime scenario intakes, the averaging time and exposure duration was 30 years.

Table 8.3: Values of contaminant specific parameters used to estimate daily exposure to selected contaminants in horticultural soils through soil ingestion, dust inhalation, dermal absorption and consumption of home grown produce.

Parameter	ΣDDT	Arsenic	Cadmium	Lead
Dermal absorption	0.03[a]	0.03[a]	0.001[a]	0.004[b]
Bioaccessibility	100%[c]	45%[d]	100%[d]	100%[d]

[e]USEPA (2004b) Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment, [b]Florence *et al.* (1998), [c]Based on literature values refer discussion below, [d]Data derived from simulated gastric extraction (Table 8.6, this Chapter).

ORAL BIOACCESSIBILITY OF CONTAMINANTS

There is limited data on the oral bioavailability of DDT and its metabolites DDE and DDD from soils (ATSDR, 2002). Hayes *et al.*, (1959, cited in WHO, 1979) found that small repeated doses of DDT were fully absorbed and that the absorption was mediated by bile and dietary fat. The bioavailability of DDT to rats ranged from 70 to 90% when administered in vegetable oil (Keller and Yeary, 1980 cited in ATSDR, 2002). This gastrointestinal absorption efficiency is comparable to that measured for aged PCBs in spiked soils in an animal feeding trial. Approximately 67 to 82% of the spiked PCB isomers were bioavailable to rats and the PCB isomers in soil were only 20% less bioavailable than compounds administered through a corn oil gavage (Fries *et al.*, 1989). Based on these studies the oral bioaccessibility of ΣDDT from both dietary sources and soil has been assumed to be 100%.

The oral bioaccessibility of arsenic, cadmium and lead was estimated using a simulated gastric extraction method (Section 8.3.1, this Chapter). The maximum percent bioaccessible fraction was 45% for arsenic and this value was used to estimate the exposure to arsenic via the soil ingestion pathway. No adjustments were made for cadmium and lead as the maximum bioaccessible fractions were 83% and 100% for cadmium and lead respectively (Table 8.6).

DERMAL ABSORPTION OF CONTAMINANTS

The USEPA (2004) recommended dermal absorption fractions were used to estimate dermal absorption of arsenic, cadmium and ΣDDT. Dermal absorption of lead compounds is generally considered to be very low (Baars *et al.*, 2001; DEFRA and

Environment Agency, 2002c). However, Stauber *et al.* (1994) reported that 29% of radiolabelled $Pb(NO_3)_2$ applied as a solution was absorbed across the skin of a human volunteer. A subsequent study found that 0.4% of lead was absorbed through mouse skin and entered the circulatory system (Florence *et al.*, 1998). This figure of 0.4% has been used in this Chapter to estimate availability of lead for dermal absorption. This value may over estimate lead absorption as the study undertaken by Stauber *et al.* (1994) found that $PbCO_3$ is not absorbed through the skin. A comparable value of 0.3% was reported for an earlier study measuring dermal uptake of lead from hair dye (Moore *et al.*, 1980 cited in DEFRA and Environment Agency, 2002c).

BACKGROUND EXPOSURE TO CONTAMINANTS

Data on background exposure to contaminants through the diet and drinking water were sourced from the 2003/04 Total Diet Survey (TDS) (Vannoort and Thomson, 2005). The weekly intakes for the trace elements were converted to daily intakes. The figure for a child (1–6 year) was estimated by averaging the daily intake for the 5–6 year child and 1–3 year toddler age groups. The lifetime exposures were calculated as a time weighted average of the child and adult (25+ year) daily intakes and were averaged over 30 years. The daily intakes for each exposure group are presented in Table 8.4.

Table 8.4: Background exposure to contaminants from diet (μg/kg bw/day). Data sourced from the 2003/04 TDS (Vannoort and Thomson, 2005) and converted from weekly intakes to daily intakes.

Contaminant	Child[c]	Female	Male	Lifetime female[d]	Lifetime male[d]
ΣDDT	0.044	0.017	0.023	0.022	0.026
Arsenic	0.31	0.19	0.21	0.21	0.23
Cadmium[a]	0.37	0.13	0.17	0.18	0.21
Lead[b]	0.27	0.11	0.13	0.14	0.16

[a]Simulated diet excluding oysters, [b]Simulated diet excluding contaminated cornflour, [c]Average daily intake for a 5-6 year child and a 1-3 year toddler, [d]Time weighted average of child and adult exposures.

PREDICTING CONTAMINANT CONCENTRATIONS IN VEGETABLES

As discussed above, two home grown produce consumption rates, 10 and 50% were used to estimate exposure to contaminants in orchard soils in residential settings. Data from the plant assay (Chapters Six and Seven) were used to estimate contaminant concentrations in home grown produce. The use of the data for lettuce and radish to approximate contaminant uptake by leafy and root vegetables is considered to be valid as the BAFs obtained for lettuce and radish are within the ranges reported for other vegetables (refer Sections 6.3.2.4 and 7.3.3.2). The USEPA average conversion factor of 0.085 was used to convert the produce ingestion rates (Table 8.2) to dry weight (USEPA, 1996).

Where there were insufficient data points to determine a relationship between plant and soil, or no significant relationship was observed, the UK CLEA concentration factors were used to estimate vegetable contaminant concentrations (DEFRA and Environment Agency, 2002a,b). When required, median values of plant assay soil properties were selected for modeling plant uptake of trace elements (Table B1, Appendix B). The regression equations and plant uptake factors used to estimate concentrations of contaminants in home grown produce are presented in Table 8.5. By convention, contaminant concentrations in fruit are considered to be insignificant (Ministry for the Environment and Ministry of Health, 1997).

Table 8.5: Regression equations, plant uptake factors and soil properties used to estimate concentrations of contaminants in home grown produce.

Contaminant	Leafy vegetables	Root vegetables
ΣDDT	$C_{leaf} = 0.0023 \times C_{soil} + 3.0478$	$C_{root} = 0.0159 \times Csoil - 0.896$
Arsenic[b]	$C_{leaf} = 0.009 \times C_{soil}$	$C_{root} = 0.009 \times Csoil$
Cadmium	$\log(C_{leaf}) = 0.624 \times \log(C_{soil}) + 0.521$	$C_{root} = CF^{b} \times Csoil$ where $\ln(CF) = 11.174 - (1.6461 \times pH^{c})$
Lead	$\log(C_{leaf}) = 0.434 \times \log(C_{soil}) - 0.701 \times \log(CEC^{d}) - 0.520$	$\log(C_{root}) = 0.726 \times \log(C_{soil}) - 1.07 * pH^{c} - 2.83 \times \log(\%TOC^{e}) + 6.06$

[a]units are mg kg^{-1} for trace elements and μg kg^{-1} for ΣDDT, [b]UK CLEA concentration factor (DEFRA and Environment Agency, 2002a,b), [c]Calculated using a pH value of 5.66, [d]Calculated using a CEC value of 12.3 mmoles/100g, [e]calculated using a %TOC value of 3.28.

8.2.2.2 DETERMINING THE SIGNIFICANCE OF THE ESTIMATED DAILY INTAKES

Contaminants can be divided into two groups based on their mode of action; threshold contaminants including non genotoxic carcinogens, and genotoxic carcinogens. Threshold contaminants are those where it is assumed that a certain dose or threshold needs to be reached before there is a toxic effect. Non genotoxic carcinogens do not cause genetic damage and also have a threshold dose below which there is assumed to be no carcinogenic effect (Ministry for the Environment and Ministry of Health, 1997) whereas genotoxic carcinogens cause damage to genetic material with a linear relationship established between the dose or chronic daily intake, and the incidence of cancer (Lizjen *et al.*, 2001).

COMPARISON WITH TOLERABLE DAILY INTAKES FOR THRESHOLD CONTAMINANTS

The significance of daily intakes of threshold contaminants and non gentoxic contaminants can be estimated by comparison with tolerable daily intakes (TDI). A tolerable daily intake is the estimated amount of a chemical a person can ingest over their lifetime without it being likely to cause adverse health effects. Internationally, agencies differ in how they use TDIs to assess risk when deriving soil quality guidelines. For example the Dutch RIVM Maximum Permissible Risk (MPR) levels are used to derive soil criteria which are based on lifetime exposure (Baars *et al.*, 2001), one exception is the MPR for lead which is based on child exposure. The UK CLEA soil guideline values for residential settings are based on a female child (DEFRA and Environment Agency, 2002b) and the USEPA uses childhood exposure (6 years) to developing soil screening levels for threshold contaminants (USEPA, 2002).

Similarly in New Zealand, the approach promulgated in the NZTTG (Ministry for the Environment and Ministry of Health, 1997) for assessing the risk of exposure to threshold contaminants in soil has been to compare a child's exposure over 6 years to

the TDI whereas the approach taken to derive the drinking water standards (Ministry of Health, 2005) is generally based on a lifetime (70 years) exposure. Two exceptions in the drinking water standards are ΣDDT and lead which are based on a child and a bottle-fed baby respectively. The supporting documentation for the NZTTG cautions that combining the child and adult exposures over 30 years will underestimate the intake for a child and hence also underestimate the probability of adverse health effects (Ministry for the Environment and Ministry of Health, 1997). For the purposes of the risk assessments presented in this Chapter, the child and the lifetime (30 year) exposures for male and females have been compared with TDIs.

The TDIs used in this chapter for comparative purposes have been sourced from the 2005 New Zealand Drinking Water Guidelines (Ministry of Health, 2005), the 2003/04 Total Diet Survey (Vannoort and Thomson, 2005), the Dutch RIVM maximum permissible risk levels (Baars *et al.*, 2001) and the toxicological profiles collated the UK Environment Agency for the CLEA model (DEFRA and Environment Agency, 2002c,d,e).

ESTIMATING THE CANCER RISK

The cancer risk from exposure to genotoxic carcinogens is calculated by multiplying the daily intake by a slope factor. The cancer risk is the probability of a person developing cancer as result of lifetime exposure to the contaminant of concern. Regulatory authorities also differ in their acceptable cancer risk; for example the Dutch soil criteria assumed a 1 in 10,000 cancer risk (Ministry of Housing, Spatial Planning and the Environment, 2000) and the USEPA Region 9 used a 1 in 1,000,000 cancer risk to derive preliminary remediation goals for contaminated sites (USEPA, 2001b). In New Zealand the acceptable lifetime cancer risk is one extra cancer per 100,000 people over their lifetime (Ministry of Health, 2005).

IDENTIFICATION OF CANCER RISK AND SELECTION OF TOLERABLE DAILY INTAKES FOR COMPARATIVE PURPOSES

ΣDDT

Internationally agencies differ as to whether they consider DDT to be a genotoxic carcinogen, a non genotoxic carcinogen or a threshold contaminant. The IARC (1991) has classified DDT and its metabolites as Group 2B chemicals (possibly carcinogenic). Their assessment concluded that there was inadequate human evidence, but, sufficient animal evidence on the carcinogenicity of DDT and its metabolites. Similarly, the USEPA has classified the *p,p'*-isomers of DDT, DDE and DDD as probable human carcinogens (IRIS, 2005a,b,c). The ATSDR (2002) reviewed available data and concluded that there was no conclusive evidence to support the hypothesis that human exposure to DDT increased the cancer risk, however they also concluded that there was evidence to demonstrate that DDT exposure can cause cancer in animals.

The RIVM toxicological assessment (Baars *et al.,* 2001) concluded that DDT was a cancer promoting agent and that information on the genotoxicity of DDT was inconclusive. RIVM treated DDT as a threshold contaminant when deriving their maximum permissible risk level for DDT. In contrast, the World Health Organisation's provisional tolerable daily intake (PTDI) is based on developmental toxicity in rats (WHO, 2004). In order to be consistent with the Ministry of Health's drinking water guideline (Ministry of Health, 2005), ΣDDT has been considered to be a threshold contaminant for the purposes of the exposure assessment presented here.

Two TDIs have been recently used for ΣDDT in New Zealand. The Ministry of Health used the WHO PTDI of 1 mg/kg plus an uncertainty factor of 100 for the derivation of the 2005 Drinking Water Standards and the resulting TDI of 10 μg/kg bw was also used for comparative purposes in the 2003/04 Total Diet Survey. The RIVM MPR of 0.0005 mg/kg/bw (Baars *et al.*, 2001) was chosen to derive interim soil guidelines for DDT in residential settings by Proffitt (2003). Proffitt (2003)

selected the more conservative RIVM TDI to allow for the lack of international consensus on the carcinogenicity of DDT

Arsenic

Arsenic is classified by the IARC as a human carcinogen (Group 1) (IARC 2004a). Internationally regulatory agencies differ as to whether they treat arsenic as a non genotoxic or genotoxic carcinogen in risk assessments. For the derivation of the NZTTG soil arsenic guideline arsenic was considered to be a genotoxic carcinogen and a slope factor of 0.147 mg/kg bw/day was used to determine the skin cancer risk. The 2005 drinking water guidelines (NZ) use the WHO recommended guideline of 0.01 mg L^{-1} (Ministry of Health, 2005). The 2003/04 TDS compared intakes to the WHO PTWI of 15 μg/kg bw/week which is based on skin cancer risk and achievable laboratory detection levels (WHO, 1988). The UK Environment Agency (DEFRA and Environment Agency, 2002d) derived an index dose based on cancer risk whereas the derivation of the RIVM MPR for arsenic treats it as a non genotoxic carcinogen (Baars *et al.*, 2001). In the assessment presented here, the daily arsenic intakes have been compared with the WHO PTWI of 15 μg/kg bw/week used for comparative purposes in the 2003/04 TDS, the RIVM MPR of 1 μg/kg bw/day and the UK Environment Agency's index dose of 0.3 μg/kg bw/day.

Cadmium

Cadmium has also been classified by IARC as carcinogenic to humans (Group 1 carcinogen). A review of the available toxicological data on cadmium concluded that there was not sufficient evidence for the carcinogenicity of cadmium via the oral route and hence increases in cancer associated with soil contamination did not need to be considered (Baars *et al.*, 2001). In the exposure assessments presented in this Chapter, cadmium has been considered to be a threshold contaminant and the estimated daily intakes have been compared with TDIs. This is consistent with the

approach taken for the derivation of the NZ drinking water guideline for cadmium which also considers cadmium to be a threshold contaminant (Ministry of Health, 2005). Two TDIs have been used for comparative purposes – the WHO value of 1 μg/kg bw/day used in the derivation of the New Zealand drinking water standards and for comparative purposes in the 2003/04 TDS and the more conservative value of 0.5 μg/kg bw/day used by RIVM.

Lead

Inorganic lead compounds were classified by IARC as probably carcinogenic (Group 2A). However, the toxic effects of exposure to lead of primary concern are effects on the central nervous system. Lead was considered to be a threshold contaminant for the derivation of the drinking water standards because the neurotoxic effects of lead occur at lower lead exposures than carcinogenic effects. A TDI based on protecting against neurotoxic effects is also considered to be protective of carcinogenic effects (Ministry of Health, 2005). In the assessment presented here, lead has been treated as a threshold contaminant and estimated daily intakes have been compared with the WHO provisional tolerable weekly intake. This value of 25 μg lead/kg body weight was used to derive the NZ drinking water standards and for comparative purposes in the 2003/04 TDS. It is also used by RIVM as their MPR (Baars *et al.*, 2001).

8.3 RESULTS AND DISCUSSION

8.3.1 ORAL BIOACCESSIBILITY OF TRACE ELEMENTS

A modified version of the Solubility/Bioavailability Research Consortium's Standard Operating Procedure for Stomach-Phase Extraction (Kelley *et al.* 2002) was utilised to determine the bioaccessibility of arsenic, cadmium and lead from ten orchard soils. For the gastric extractions the soils were sieved to <250 μm to represent the fraction of soil likely to adhere to children's hands and hence be ingested (Kelley *et al.*,

2002). The total trace element concentrations measured in the <250 μm fraction of the orchard soils are presented in Table 8.6. The trace element concentrations in the <2 mm and the soil properties for these soils are presented in Appendix C. A paired t-test found no significant differences in the total amount of arsenic and lead extracted from the <2 mm and the <250 μm soil fractions.

Table 8.6: Total and bioaccessible concentrations (mg kg^{-1}) of arsenic, cadmium and lead measured in New Zealand orchard soils (<250 μm).

Sample	Total[a] (<250 μm fraction)				Gastric extraction			% bioaccessible[b]		
	Fe	As	Cd	Pb	As	Cd	Pb	As	Cd	Pb
AKL1[c]	9010	28	0.4	106	9	0.29	79	30	71	75
AKL2	18900	54	0.8	281	21	0.70	226	39	87	80
AKL3	21100	25	0.3	82	3	0.20	47	12	67	57
AKL4	6950	33	0.4	181	15	0.31	137	45	78	76
AKL5	22800	17	0.4	70	4	0.28	42	24	70	59
WKT1[d]	13700	116	2.2	375	43	1.66	264	37	75	70
WKT2	29800	41	1.1	202	6	0.72	114	15	65	56
TDC1[e]	8780	43	0.6	253	17	0.39	198	38	64	78
TDC2	7420	31	0.3	167	12	0.31	138	40	103	83
TDC3	7540	16	0.8	132	6	0.68	99	38	85	75

[a]Determined using US-EPA Method 200.2 (Total Recoverable Metals in Soils/Sediments/Sludges) (USEPA, 1991), [b]Relative to total extracted by acid digest, [c]Auckland, [d]Waikato, [e]Tasman.

The gastric extractable trace element concentration increased with increasing total arsenic, cadmium and lead concentration (p<0.001). The mean percent bioaccessible fraction (Table 8.6) followed the order of cadmium>lead>>arsenic reported for soils extracted using the comparable SBET method developed by the UK Geological Survey (Oomen *et al.*, 2002). The percent bioaccessible fraction for arsenic (12 to 45%) was comparable to values reported in previous studies (Table 8.7). In contrast, the bioaccessible fractions of lead (56–83%) and cadmium (64–103%) were at the upper end of the ranges previously reported.

8.3.1.1 INFLUENCE OF SOIL PROPERTIES ON BIOACCESSIBLE FRACTION

Several soil properties including iron and manganese oxide content, CEC, pH, TOC, particle size and phosphorus content (Sheppard *et al.*, 1995; Ruby *et al.*, 1996; Kelley *et al.*, 2002) have been reported to influence bioaccessibility of trace elements from soil. Pearson's correlation analysis was used to explore possible relationships between the percent bioaccessible fraction of trace elements and key soil properties where available. For iron, the concentration measured in the <250 μm fraction was used whereas for other soil properties, results from analyses of the bulk soil (<2mm) were used.

The bioaccessible fraction of lead decreased with increasing CEC ($p<0.01$) and iron concentration ($p<0.01$) (Table C2, APPENDIX C). The CEC and iron concentration were significantly correlated ($p<0.02$). CEC has been previously reported to correlate with the bioaccessibility of lead (Sheppard *et al.*, 1995, Ruby *et al.*, 1996). In agreement with the results of Fendorf *et al.* (2004) and Yang *et al.* (2002), the percent bioaccessible fraction for arsenic also decreased with increasing iron concentration (Figure 8.1). There were no relationships between the percent of trace element extracted and pH, Olsen P content and %TOC.

Table 8.7: Literature values for bioaccessible fractions (%) of arsenic, cadmium and lead determined using simulated gastric extraction tests.

Method	Material	Arsenic	Cadmium	Lead	Reference
Modified PBET	Mine waste soil			80–85	Brown *et al.* (2005)
Modified PBET	Mine waste			1–76	Geebelen *et al.* (2003)
In- vitro dilute HCl extraction	Spiked soil			30–90[a]	Sheppard *et al.* (1995)
In-vitro two-phase enzymolysis of contaminated feed	Spiked soil		89	19	Sheppard *et al.* (1995)
IVG	Arsenic herbicide contaminated soil	5–38			Juhasz *et al.* (2003)
PBET	Arsenic herbicide contaminated soil	6–43			Juhasz *et al.* (2003)
IVG, gastric extraction step	Contaminated soil		21–96		Schroder *et al.* (2003)
Artificial gastric fluid	Montana SRM	41	51	36	Hamel *et al.* (1998)
Artificial gastric fluid	Contaminated Jersey City soil	5		22	Hamel *et al.* (1998)
PBET	Metal contaminated soil			23–37	Hettiarachchi and Pierzynski (2002)
Modified PBET	Spiked soil	2.6–100			Yang *et al.* (2002)
Summary of available data (stomach phase)	Various	10–50	50–00	10–90	Grøn and Andersen (2003)
Modified in-vitro method (stomach phase)	Sodium arsenite spiked soil	39–73			Sarkar and Datta (2003)
In-vitro model which simulates mouth, stomach and small intestine	Lead pottery contaminated soil			42–66	Oomen *et al.* (2003)
In-vitro digestion model	Historically contaminated urban soils			2–88	Sips *et al.* (2001)

[a]Estimated from reported data.

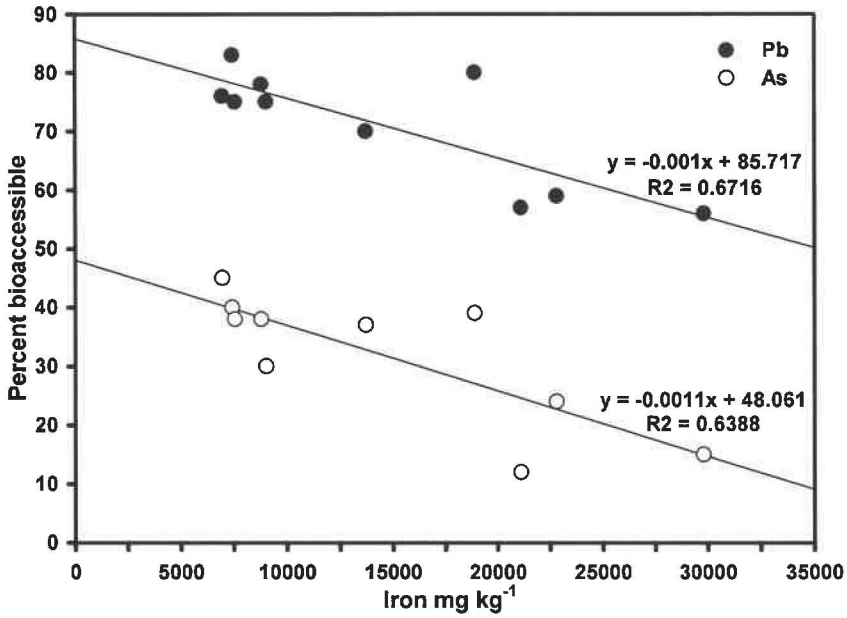


Figure 8.1: Relationships between the bioaccessible fraction (%) of arsenic and lead and the iron concentration of the <250 μm soil fraction.

8.3.2 POTENTIAL HUMAN EXPOSURE TO AGED DDT RESIDUES AND TRACE ELEMENTS

Daily intakes to ΣDDT, arsenic, cadmium and lead were estimated over a contaminant concentration range consistent with the data presented in this thesis (Chapters Three to Seven). To enable comparison with the tolerable daily intakes the adult and child exposures have been averaged over 30 years (referred to as lifetime exposure), as TDIs are generally based on lifetime exposure. The estimated exposures for adults are presented in Appendix C. The contribution from dust inhalation to the total daily intake was negligible (<0.2%) for all of the exposure scenarios considered and has not been reported. Inhalation exposures are usually much lower than exposure from dermal contact and soil ingestion (NRC, 2003).

8.3.2.1 OVERALL EXPOSURE AND COMPARISON WITH TOLERABLE DAILY INTAKES

ΣDDT

The maximum estimated daily intakes based on a soil ΣDDT concentration of 35 mg kg^{-1} were 0.42 and 0.18 μg/kg bw/day for the child and male lifetime exposures respectively (Table 8.8). The maximum estimated daily intake of 8 μg ΣDDT per day for an adult male was substantially lower than the figure of 48 μg ΣDDT per day measured for adult New Zealanders in a diet survey completed in 1974/75 (Dick *et al.*, 1978).

The maximum estimated lifetime exposure (male) over 30 years was 27 and 35% of the RIVM TDI for the 10% and 50% home grown produce ingestion scenarios respectively (Table 8.7). The estimated lifetime exposure under both produce scenarios was less than 2% of the WHO PTDI for ΣDDT for both males and females. The child exposure was 85% of the RIVM TDI for the 50% home grown produce scenario.

For both the child and the lifetime exposure scenarios, the relative contribution of the exposure pathways was soil ingestion>dermal>produce consumption for both produce ingestion scenarios. Soil ingestion was identified as the main exposure pathway to ΣDDT, contributing up to 61% of the total daily intake of ΣDDT for children from the considered sources.

Uptake through the skin or dermal exposure to aged ΣDDT residues in soil calculated using the TTG default exposure parameters was a significant exposure pathway for both adults and children contributing up to 24% and 44% of the daily intake for a child and adult male respectively for the 10% home grown produce scenario. Dermal uptake from soil has been reported to be more important for organic compounds than trace elements (DEFRA and Environment Agency, 2002b).

Table 8.8: Estimated daily intakes (µg/kg bw/day) of ΣDDT in a residential setting.

Soil (mg kg^{-1})	Soil exposure		Produce		Soil derived daily intake		Diet	Total daily intake		%TDI (WHO)		%TDI (RIVM)	
	ingestion	dermal	50%	10%	50%	10%		50%	10%	50%	10%	50%	10%
	child												
0.5	0.003	0.001	0.001	0.000	0.006	0.005	0.044	0.050	0.049	0.5	0.5	10	10
1	0.006	0.003	0.002	0.000	0.011	0.009	0.044	0.055	0.053	0.6	0.5	11	11
5	0.032	0.013	0.010	0.002	0.054	0.047	0.044	0.099	0.091	1.0	0.9	20	18
10	0.064	0.025	0.020	0.004	0.109	0.093	0.044	0.153	0.137	1.5	1.4	31	27
15	0.096	0.038	0.029	0.006	0.163	0.139	0.044	0.207	0.184	2.1	1.8	41	37
25	0.160	0.063	0.048	0.010	0.271	0.232	0.044	0.315	0.277	3.2	2.8	63	55
35	0.224	0.088	0.068	0.014	0.380	0.325	0.044	0.424	0.370	4.2	3.7	85	74
	lifetime female												
0.5	0.001	0.001	0.001	0.000	0.002	0.002	0.022	0.025	0.024	0.2	0.2	5	5
1	0.002	0.001	0.002	0.000	0.005	0.003	0.022	0.027	0.026	0.3	0.3	5	5
5	0.008	0.006	0.008	0.002	0.022	0.016	0.022	0.044	0.038	0.4	0.4	9	8
10	0.016	0.013	0.015	0.003	0.043	0.031	0.022	0.066	0.054	0.7	0.5	13	11
15	0.023	0.019	0.023	0.005	0.065	0.047	0.022	0.087	0.069	0.9	0.7	17	14
25	0.039	0.032	0.038	0.008	0.108	0.078	0.022	0.131	0.101	1.3	1.0	26	20
35	0.054	0.045	0.052	0.010	0.151	0.109	0.022	0.174	0.132	1.7	1.3	35	26
	lifetime male												
0.5	0.001	0.001	0.001	0.000	0.002	0.002	0.026	0.028	0.028	0.3	0.3	6	6
1	0.002	0.001	0.002	0.000	0.005	0.003	0.026	0.031	0.029	0.3	0.3	6	6
5	0.008	0.006	0.008	0.002	0.022	0.016	0.026	0.048	0.042	0.5	0.4	10	8
10	0.016	0.013	0.015	0.003	0.043	0.031	0.026	0.070	0.057	0.7	0.6	14	11
15	0.023	0.019	0.023	0.005	0.065	0.047	0.026	0.091	0.073	0.9	0.7	18	15
25	0.039	0.032	0.038	0.008	0.108	0.078	0.026	0.134	0.104	1.3	1.0	27	21
35	0.054	0.045	0.052	0.010	0.151	0.109	0.026	0.178	0.136	1.8	1.4	36	27

Produce consumption contributed proportionally more of the total daily intake of ΣDDT for adults than children and accounted for up to 44% of the estimated daily intake for an adult female under the 50% home grown produce scenario. The produce ingestion pathway has been demonstrated to be a significant exposure pathway for ΣDDT in residential settings under various exposure assessments. For example, Proffitt (2003) derived soil acceptance criteria for ΣDDT of 8 mg kg^{-1} and 25 mg kg^{-1} for the 50% and 10% produce consumption scenarios respectively using a higher BCF of 0.028 for plant uptake of ΣDDT. Similarly Lowe and Jamall (1994) calculated soil guidelines for ΣDDT in Californian residential soils of 7.9 mg kg^{-1} for a residential scenario including produce ingestion. Furthermore, as other vegetables such as curcubits and carrots have been reported to accumulate higher concentrations of ΣDDT (Lichtenstein, 1959; White *et al.*, 2003a; Lunney *et al.*, 2004) the potential exposure to ΣDDT from consumption of home grown vegetables could be significantly higher than that calculated under these scenarios.

ARSENIC

Daily intakes of arsenic were estimated over a soil arsenic concentration range of 20 to 100 mg kg^{-1}. The maximum estimated daily intakes of inorganic arsenic were 1.04 μg/kg bw/day for a child under the 50% home grown produce consumption scenario and 0.58 μg/kg bw/day for the lifetime male exposure under the same scenario (Table 8.9). These daily intakes were compared with three TDIs including the figure of 2.1 μg/kg bw/day used in the 2003/04 TDS (Vannoort and Thomson, 2005), the RIVM MPR of 1 μg/kg bw/day and the index dose of 0.3 μg/kg bw/day used to derive the UK CLEA soil guideline for arsenic (DEFRA and Environment Agency, 2002d). None of the estimated exposures exceeded the TDI used in the 2003/04TDS and child exposure would only exceed the RIVM value of 1 μg/kg bw/day at soil arsenic concentrations greater than 100 mg kg^{-1}.

In contrast all estimated exposures were comparable to or exceeded the UK CLEA TDI of 0.3 μg/kg bw/day. Arsenic intake through the diet under all exposure scenarios was equivalent to or exceeded the UK CLEA TDI for arsenic of 0.3 μg/kg bw/day.

The relative contributions of the exposure pathways to the daily arsenic intake followed the order diet>soil ingestion>dermal>home grown produce for a child exposure and diet>soil ingestion>dermal>home grown produce for the lifetime exposure. This is consistent with overseas data which indicates that soil ingestion is a more important exposure route for arsenic contaminated soils than uptake by vegetables (McLaughlin, 2002). Soil ingestion accounted for up to 34% of the child exposure. Increasing the soil ingestion rate to the 200 mg per day figure used by the USEPA would increase the child daily intake under the 50% produce consumption scenario to 30% of the WHO TDI used for comparative purposes in the 2003/04 TDS and 205% of the UK index dose for a soil arsenic concentration of 30 mg kg^{-1}, the current NZ soil guideline for arsenic.

Table 8:9: Estimated daily intakes (µg/kg bw/day) of arsenic in a residential setting.

Soil	Soil exposure		Produce		Soil derived daily intake		Diet	Total daily intake		%TDI (WHO)		%TDI (RIVM)		%TDI (CLEA)	
mg kg^{-1}	ingestion	dermal	50%	10%	50%	10%		50%	10%	50%	10%	50%	10%	50%	10%
	child														
20	0.06	0.05	0.04	0.01	0.15	0.12	0.310	0.46	0.43	22	20	46	43	152	142
30	0.09	0.08	0.06	0.01	0.22	0.17	0.310	0.53	0.48	25	23	53	48	176	161
40	0.12	0.10	0.08	0.02	0.29	0.23	0.310	0.60	0.54	29	26	60	54	201	180
60	0.17	0.15	0.11	0.02	0.44	0.35	0.310	0.75	0.66	36	31	75	66	249	219
80	0.23	0.20	0.15	0.03	0.58	0.46	0.310	0.89	0.77	43	37	89	77	298	257
100	0.29	0.25	0.19	0.04	0.73	0.58	0.310	1.04	0.89	50	42	104	89	347	296
	lifetime female														
20	0.01	0.03	0.03	0.01	0.07	0.05	0.214	0.28	0.26	14	12	28	26	95	87
30	0.02	0.04	0.05	0.01	0.10	0.07	0.214	0.32	0.28	15	13	32	28	106	94
40	0.03	0.05	0.06	0.01	0.14	0.09	0.214	0.35	0.31	17	15	35	31	118	102
60	0.04	0.08	0.09	0.02	0.21	0.14	0.214	0.42	0.35	20	17	42	35	141	117
80	0.06	0.10	0.12	0.02	0.28	0.18	0.214	0.49	0.40	23	19	49	40	164	132
100	0.07	0.13	0.15	0.03	0.35	0.23	0.214	0.56	0.44	27	21	56	44	188	148
	lifetime male														
20	0.01	0.03	0.03	0.01	0.07	0.05	0.23	0.30	0.28	14	13	30	28	100	92
30	0.02	0.04	0.05	0.01	0.10	0.07	0.23	0.33	0.30	16	14	33	30	112	99
40	0.03	0.05	0.06	0.01	0.14	0.09	0.23	0.37	0.32	18	15	37	32	123	107
60	0.04	0.08	0.09	0.02	0.21	0.14	0.23	0.44	0.37	21	17	44	37	146	122
80	0.06	0.10	0.12	0.02	0.28	0.18	0.23	0.51	0.41	24	20	51	41	170	137
100	0.07	0.13	0.15	0.03	0.35	0.23	0.23	0.58	0.46	28	22	58	46	193	153

CADMIUM

Daily intakes of cadmium were estimated over the concentration range of 0.25 to 2 mg kg^{-1} cadmium in soil (Table 8.10). The maximum daily intakes for cadmium were 2.29 μg/kg bw/day for a child, 1.67 μg/kg bw/day and 1.70 μg/kg bw/day for the female and male lifetime exposures respectively under the 50% produce consumption scenario. The estimated daily intakes for the 50% home grown produce scenario exceeded the current NZ TDI of 1 μg/kg bw/day at soil cadmium concentrations greater than 0.75 mg kg^{-1} for the child exposure and 1.00 mg kg^{-1} for the lifetime exposures. The mean cadmium concentration measured in Waikato orchard soils was 1 mg kg^{-1} (Table 4.7, Chapter Four). None of the estimated exposures for the 10% produce consumption scenarios exceeded the current TDI.

The estimated daily intakes were also compared with the more conservative RIVM TDI of 0.5 μg/kg bw/day. Estimated daily intakes for cadmium at soil concentrations of 1 mg kg^{-1}, the recommended soil limit for application of sewage sludge to land (NZWWA, 2003) under all exposure scenarios were twice the RIVM TDI of 0.5 μg/kg bw/day.

Homegrown produce and other food sources were the main sources of cadmium exposure. For the 50% home grown produce consumption scenarios, the relative contribution of the exposure pathways was home grown produce>diet>soil>dermal for both the child and the lifetime exposures. At a soil concentration of 1 mg kg^{-1}, homegrown produce under the 50% consumption scenario contributed 73% of the child exposure and 79% and 82% of the lifetime exposure for males and females respectively.

Table 8.10: Estimated daily intakes (µg/kg bw/day) of cadmium in a residential setting.

Soil	Soil exposure		Produce		Soil derived daily intake		Diet	Total daily intake		%TDI (NZ)		%TDI (RIVM)	
(mg kg^{-1})	ingestion	dermal	50%	10%	50%	10%		50%	10%	50%	10%	50%	10%
	child												
0.25	0.002	0.000	0.318	0.064	0.320	0.065	0.370	0.69	0.44	69	44	138	87
0.50	0.003	0.000	0.569	0.114	0.572	0.117	0.370	0.94	0.49	94	49	188	97
0.75	0.005	0.000	0.804	0.161	0.809	0.166	0.370	1.18	0.54	118	54	236	107
1.00	0.006	0.000	1.032	0.206	1.039	0.213	0.370	1.41	0.58	141	58	282	117
1.50	0.010	0.000	1.474	0.295	1.484	0.304	0.370	1.85	0.67	185	67	371	135
2.00	0.013	0.000	1.903	0.381	1.916	0.394	0.370	2.29	0.76	229	76	457	153
	lifetime female												
0.25	0.000	0.000	0.252	0.050	0.252	0.051	0.178	0.43	0.23	43	23	86	46
0.50	0.001	0.000	0.448	0.090	0.449	0.090	0.178	0.63	0.27	63	27	125	54
0.75	0.001	0.000	0.633	0.127	0.634	0.128	0.178	0.81	0.31	81	31	162	61
1.00	0.002	0.000	0.810	0.162	0.812	0.164	0.178	0.99	0.34	99	34	198	68
1.50	0.002	0.000	1.154	0.231	1.157	0.233	0.178	1.34	0.41	133	41	267	82
2.00	0.003	0.000	1.488	0.298	1.492	0.301	0.178	1.67	0.48	167	48	334	96
	lifetime male												
0.25	0.000	0.000	0.252	0.050	0.252	0.051	0.210	0.46	0.26	46	26	92	52
0.50	0.001	0.000	0.448	0.090	0.449	0.090	0.210	0.66	0.30	66	30	132	60
0.75	0.001	0.000	0.633	0.127	0.634	0.128	0.210	0.84	0.34	84	34	169	68
1.00	0.002	0.000	0.810	0.162	0.812	0.164	0.210	1.02	0.37	102	37	204	75
1.50	0.002	0.000	1.154	0.231	1.157	0.233	0.210	1.37	0.44	137	44	273	89
2.00	0.003	0.000	1.488	0.298	1.492	0.301	0.210	1.70	0.51	170	51	340	102

LEAD

Daily intakes of lead were estimated over the concentration range 100 to 500 mg kg^{-1} (Table 8.11). The maximum daily intakes estimated for the 50% home grown produce consumption were 4.1 μg/kg bw/day for the child exposure and 1.35 μg/kg bw/day and 1.33 μg/kg bw/day for the male and female lifetime exposure scenarios respectively. Only the child exposure scenario exceeded the TDI of 3.6 μg/kg bw/day at 450 mg kg^{-1} lead in soil, the UK soil guideline for lead (DEFRA and Environment Agency, 2002f).

The main exposure pathways for lead under the 50% produce ingestion scenario for a child's exposure was soil ingestion>produce>diet>dermal and for the lifetime scenarios for male and female was soil ingestion>produce>diet>dermal. Soil and dust ingestion has previously been reported to be a more significant exposure pathway for lead than plant uptake (McLaughlin, 2002). Correspondingly the soil ingestion pathway contributed up to 86% of the child exposure and 73% of the lifetime exposure for both male and female. If the child soil ingestion rate is increased from 100 to the 200 mg per day used by the USEPA, the TDI would be exceeded at a soil lead concentration of 250 mg kg^{-1} under the 50% homegrown produce consumption scenario.

Despite not exceeding the WHO TDI for lead, the estimated daily intakes exceed other regulatory levels. The USFDA has recommended Provisional Total Tolerable Intake Levels (PTTIL) of 6 μg/day lead for children up to 6 years old, 25 μg/day for pregnant women and 75 μg/day for other adults (FDA, 2003). The PTTIL for a child of 6 μg lead would be exceeded at all modeled soil lead concentrations under both home grown produce scenarios with diet contributing 4.1 μg. For pregnant women, the PTTIL would be exceeded at soil lead concentrations of 200 mg kg^{-1} for the 50% home grown produce consumption scenario and 450 mg kg^{-1} for the 10% home grown produce consumption scenario. As a point of comparison, the maximum lead concentration measured in an orchard soil was 440 mg kg^{-1} (Chapter Seven).

Table 8.11: Estimated daily intake (µg/kg bw/day) of lead in a residential setting.

Soil (mg kg^{-1})	Soil exposure		Produce		Soil derived daily intake		Diet	Total daily intake		%TDI	
	ingestion	dermal	50%	10%	50%	10%		50%	10%	50%	10%
	child										
100	0.64	0.03	0.15	0.03	0.82	0.70	0.27	1.09	0.97	30	27
200	1.28	0.07	0.23	0.05	1.57	1.39	0.27	1.84	1.66	51	46
250	1.60	0.08	0.26	0.05	1.95	1.73	0.27	2.22	2.01	62	56
400	2.56	0.13	0.36	0.07	3.05	2.76	0.27	3.32	3.03	92	84
450	2.88	0.15	0.39	0.08	3.42	3.11	0.27	3.69	3.38	102	94
500	3.20	0.17	0.42	0.08	3.78	3.45	0.27	4.05	3.72	113	103
	lifetime female										
100	0.16	0.02	0.11	0.02	0.29	0.20	0.14	0.43	0.34	12	9
200	0.31	0.03	0.18	0.04	0.52	0.38	0.14	0.66	0.52	18	15
250	0.39	0.04	0.21	0.04	0.64	0.47	0.14	0.78	0.61	22	17
400	0.62	0.07	0.28	0.06	0.97	0.74	0.14	1.11	0.89	31	25
450	0.70	0.08	0.30	0.06	1.08	0.84	0.14	1.22	0.98	34	27
500	0.78	0.09	0.33	0.07	1.19	0.93	0.14	1.33	1.07	37	30
	lifetime male										
100	0.16	0.02	0.11	0.02	0.29	0.20	0.16	0.44	0.35	12	10
200	0.31	0.03	0.18	0.04	0.52	0.38	0.16	0.68	0.54	19	15
250	0.39	0.04	0.21	0.04	0.64	0.47	0.16	0.79	0.63	22	18
400	0.62	0.07	0.28	0.06	0.97	0.75	0.16	1.13	0.90	31	25
450	0.70	0.08	0.30	0.06	1.08	0.84	0.16	1.24	0.99	34	28
500	0.78	0.09	0.33	0.07	1.19	0.93	0.16	1.35	1.08	37	30

Internationally blood lead concentrations are used as a biomarker for lead exposure. The current New Zealand level at which blood lead concentrations are required to be notified under the Health Act 1956 is 15 μg/dL. Blood lead concentrations can be calculated using empirical models. Cavanagh (2004) suggested that the model used to derive the UK soil guideline for lead may be more appropriate for use in New Zealand than the USEPA Integrated Exposure Uptake Biokinetic (IEUBK) model which has previously been used in New Zealand to estimate blood lead concentrations on a site-specific basis. The UK model was developed by the Society of Environmental Geochemistry and Health. The equation used to derive the soil lead guideline based on a target blood lead value can be rearranged and by substituting in the soil lead concentration and a baseline blood lead concentration to account for lead exposure from other sources, the blood lead concentration can be estimated. The input parameters are listed in Table 8.12 and the rearranged equation is presented below.

$$T = ((S/1000) \times \delta) + B)\ G^n$$

Table 8.12: Input parameters for the UK model for estimating blood lead concentrations (DEFRA and Environment Agency, 2002f).

Parameter	Definition	Value	Source
T	blood lead concentration ($\mu g\ dL^{-1}$)		
S	soil concentration ($mg\ kg^{-1}$)		
G	geometric standard deviation of the blood lead distribution	1.4	DEFRA and Environment Agency (2002f)
B	baseline blood lead concentration in the population from sources other than soil and dust ($\mu g\ dL^{-1}$)	1.9	NCEH (2005)
n	the number of standard deviations corresponding to the degree of protection required for the population at risk	1.645	DEFRA and Environment Agency (2002f)
δ	response of the blood lead versus soil and dust lead relationship ($\mu g\ dL^{-1}$ blood increase per 1000 $\mu g\ g^{-1}$ increment of soil or dust lead)	5	DEFRA and Environment Agency (2002f)

The model does not include the home grown produce consumption pathway. A major assumption is that the relationship between lead in soil and blood lead concentration is valid for New Zealand children. A complicating factor is the lack of information on likely baseline lead levels in New Zealand children. Available data was either collected when lead additives were still being added to petrol or was collected from children when there was reason to suspect elevated blood lead levels (Shellshear *et al.*, 1975; Reeves *et al.*, 1982; Hinton *et al.*, 1986; Silva, 1986; Bates *et al.*, 1995). In the absence of New Zealand data, data from the United States' National Center for Environmental Health (NCEH) was used to estimate children's blood lead levels. NCEH (2005) reported a geometric mean blood lead level for children aged 1–5 of 1.9 μg/dL for samples collected over the time period 1999–2002. Using this figure of 1.9 μg/dL for baseline blood lead levels, at the current Ministry of Health guideline for lead (high contact soil) of 400 mg kg^{-1} (Ministry of Health, 1998), the estimated blood lead concentration would be 6.8 μg/dL or 45% of the notification level. While the estimated blood lead concentrations are lower than the notification value of 10 μg/dL used internationally, it should be noted that effects on IQ have been reported for blood lead levels lower than 10 μg/dL (DEFRA and Environment Agency, 2002f; Lanphear *et al.*, 2005).

Indoor dust exposure

The time weighted average daily DDT and trace element intakes presented in Tables 8.8 to 8.11 were calculated using theoretical exterior soil ΣDDT and trace element concentrations. In residential settings indoor dust can be an important source of exposure to contaminants (Paustenbach *et al.,* 1997; Butte and Heinzow, 2002) as house dust can contain soil derived contaminants which are either tracked into the house through human activity or blown in on fine particles (Roberts and Dickey, 1995). Exposure to contaminants through house dust is likely to be more important for children than adults as children particularly toddlers and infants spend more time on the floor and engage in more hand to mouth behaviour (Bearer, 1995; Goldman, 1995; WHO, 2000). Additionally, enriched contaminant levels in soil adhered to skin

have been reported for several contaminants including lead and hexachlorobenzene (Sheppard and Evenden, 1994). To date, exposure through house dust has not been routinely incorporated into risk assessments for contaminated soils in New Zealand. As it has been estimated that New Zealanders spend 90% of their time indoors (PHAC, 2002; Scoggins *et al.*, 2004), potential exposures to contaminants inside the house warrant some investigation.

Soil ingestion was a significant pathway for child exposure to ΣDDT (≤60%) and lead (≤80%). The 50% home grown produce scenarios for a child for these contaminants were recalculated to include exposure to contaminants in housedust using the following assumptions; 50% of the soil ingested daily is house dust, half of the daily dermal exposure was from house dust with a soil adherence factor of 1 mg/cm^2 and house dust contained concentrations of ΣDDT and lead five times higher than external soil (Paustenbach *et al.*, 1997).

The likely level of enrichment of ΣDDT and lead in house dust compared to external soil is not known. Several studies have reported that concentrations of persistent organic pollutants are elevated in house dust are compared to soil. For example, Wilson *et al.* (2003) measured nine pre-school children's aggregate exposures to persistent organic pollutants including organochlorine pesticides at day care and at home and found that concentrations of target compounds in floor dust generally exceeded play area soil. Similarly, Chuang *et al.* (1995) measured higher concentrations of PAHs in house dust than in external soil and they suggested that these higher levels were due to soil being tracked into the house. The house dust enrichment factor selected is at the lower end of the range (3–100) reported by Fergusson and Kim (1991) for trace elements in Christchurch (NZ).

Allowing for exposure to enriched levels of contaminants in house dust increased the maximum exposures for a child threefold to 1.2 and 12.5 μg/kg bw/day for ΣDDT and lead respectively (Table 8.13). Under this scenario the conservative RIVM TDI for ΣDDT was exceeded at soil concentrations of 15 mg kg^{-1} and the WHO TDI for lead was exceeded at soil concentrations of 135 mg kg^{-1}. The magnitude of these

theoretical exposures indicate that further research on soil to house dust enrichment factors and exposure to house dust in the New Zealand context would be appropriate.

Table 8.13: Total daily intakes (µg/kg bw/day) of ΣDDT and lead estimated for the child 50% produce consumption scenario incorporating exposure to enriched concentrations of contaminants in house dust.

Soil/dust mg kg^{-1}	Soil ingestion	Dermal exposure	Produce	Diet	Total
	ΣDDT				
0.5	0.01	0.004	0.00	0.04	0.06
1	0.02	0.01	0.00	0.04	0.07
5	0.11	0.04	0.01	0.04	0.21
10	0.22	0.09	0.02	0.04	0.37
15	0.34	0.13	0.03	0.04	0.54
25	0.56	0.22	0.05	0.04	0.87
35	0.78	0.31	0.07	0.04	1.20
	Lead				
100	2.24	0.12	0.15	0.27	2.8
200	4.47	0.24	0.23	0.27	5.2
250	5.59	0.29	0.27	0.27	6.4
400	8.95	0.47	0.36	0.27	10.1
450	10.07	0.53	0.39	0.27	11.3
500	11.19	0.59	0.42	0.27	12.5

8.3.2.2 LIMITATIONS OF THE EXPOSURE ASSESSMENT

The estimated daily intakes presented in Tables 8.8 to 8.11 were calculated over the typical concentration ranges found in cropping areas of orchards. There may also be hotspots present on horticultural land with contaminant concentrations much greater than those found in cropping areas (Hogg, 2000; Gaw, 2002). Hotspots such as former spraysheds could potentially represent an acute risk for a child depending on the levels of contamination.

The intakes from the TDS are 50th percentiles and it is likely that some of the population will have higher contaminant intakes through diet. It has been suggested that the 95th percentile for daily intakes from food would be approximately three times the 50th percentile intake (Vannoort *et al.*, 2000). Exposure from drinking water was assessed as part of the 2003/04 TDS and is included in the dietary intakes. In some areas, it would be more appropriate for the intake of contaminants from

drinking water to be assessed separately as elevated levels of arsenic, cadmium and lead have been measured in a small percentage of New Zealand drinking water supplies (Ministry of Health, 2005).

Concentrations of contaminants in vegetables were estimated using data from the plant trial and the CLEA concentration factors. Further work needs to be undertaken in New Zealand to assess plant uptake of contaminants to enable robust risk assessments to be undertaken for residential settings. The assessment presented here did not consider exposure to contaminants through eating meat or eggs raised on the site and hence may underestimate potential contaminant exposures in a lifestyle block setting. Reported accumulation ratios in laying hens relative to feed range from 0.8 to 14 and 3 to 19 for eggs and abdominal fat respectively (Kan, 1978).

8.4 CONCLUSIONS

A simulated gastric extraction method was used to determine the bioaccessibility of arsenic, cadmium and lead in orchard soils. The bioaccessible fractions followed the order cadmium>lead>arsenic and were comparable to overseas data derived from physiologically based extraction tests.

The estimated daily intakes of ΣDDT over a 30 year exposure period calculated using the TTG default exposure scenarios did not exceed either the RIVM or the WHO tolerable daily intakes at the maximum soil ΣDDT concentration (35 mg kg^{-1}) measured in orchard soils. The produce ingestion pathway modeled using the results from the plant trial contributed a significant proportion of residential exposure to ΣDDT (up to 30%) and hence this pathway should be incorporated into risk assessments for ΣDDT in residential settings.

Estimated daily intakes of arsenic did not exceed the TDI of 2.1 μg/kg bw/day used for comparative purposes in the 2003/04 TDS. All of the estimated daily intakes of arsenic exceeded the more conservative index dose of 0.3 μg/kg bw/day used by the

UK Environment Agency to derive a soil guideline for arsenic. Exposure through the diet was the main exposure pathway for arsenic.

The estimated daily intakes of cadmium under the 50% home-grown produce scenario all exceeded the TDI of 1.0 μg/kg bw/day at soil concentrations greater than 0.75 mg kg^{-1} for children and 1.0 mg kg^{-1} for the lifetime exposure. Consumption of home-grown produce was the main exposure pathway for cadmium under the 50% homegrown produce consumption scenario for both the lifetime exposures and the child exposure.

Lead intakes did not exceed the TDI for the lifetime exposures and the child exposure only just exceeded the TDI at a soil concentration of 450 mg kg^{-1}. The total daily intakes of lead for a child and pregnant woman were also compared to US PTTILs for these groups. Under the 50% homegrown produce scenario, all of the estimated child exposures to lead exceeded the PTTIL for a child and the PTTIL for a pregnant woman would be exceeded at soil lead concentrations greater than 200 mg kg^{-1}.

Soil ingestion was the main exposure pathway for ΣDDT and lead. The estimated daily intakes of these two contaminants for a child were recalculated incorporating exposure to enriched levels of contaminants in housedust through ingestion and dermal exposure. Assuming an enrichment factor of five for lead and ΣDDT concentrations in soil increased the daily intakes of ΣDDT and lead threefold. The magnitude of these estimated exposures to lead and ΣDDT indicate that exposure to enriched levels of contaminants in housedust may need to be considered for risk assessments of contaminants in soil.

9 SUMMARY AND RECOMMENDATIONS

The three regional investigations of contaminant concentrations in soil presented in Chapters Three and Four have identified that land previously used for horticulture may contain elevated levels of contaminants as the result of long-term use of agrichemicals and applications of soil amendments. The key contaminants of concern were ΣDDT, arsenic, cadmium, copper and lead. With the exception of cadmium, the highest concentrations were generally measured in orchard soils.

The concentrations of ΣDDT (<0.03–34.5 mg kg^{-1}) measured in horticultural soils as part of these investigations were greater than those previously measured in grazing soils. The predominant DDT residues measured in horticultural soils were *p,p'*-DDE and *p,p'*-DDT. The lower than expected *p,p'*-DDE:*p,p'*-DDT ratios measured for some soils indicate that either DDT degradation in horticultural soils has been inhibited or that *p,p'*-DDT is being degraded by an alternative pathway which does not result in the accumulation of *p,p'*-DDE in soil. The *p,p'*-DDE:*p,p'*-DDT ratios in Auckland and Waikato orchard soils were negatively correlated with the soil copper concentration.

The results of the persulfate oxidation experiments presented in Chapter Five indicate that up to 96% of the *p,p'*-DDT present in orchard soils may not be available for microbial degradation. These aged DDT residues were however available for uptake by both plants (lettuce and radish) and earthworms (Chapter Six). Concentrations of ΣDDT in lettuce, radish and earthworms increased with increasing soil concentration. ΣDDT was bioaccumulated by earthworms by up to a factor of three. Analogous with the soil data, *p,p'*-DDE and *p,p'*-DDT were the predominant residues measured in both plant and worm tissue.

Concentrations of ΣDDT in worm tissue for two of the assayed soils exceeded the tissue concentrations of 32 mg kg^{-1} considered to be hazardous to sensitive bird species. Concentrations of DDT residues in the earthworm tissue correlated with the amount of DDT residues desorbed from soil by Tenax and C-18 disks indicating that these methods may be suitable for determining the availability of aged DDT residues in soil to *A. caliginosa*. The aged DDT residues were not toxic to plants and worms.

The results presented in this thesis indicate that under some circumstances, ΣDDT will remain an environmental hazard for longer than previously thought. ΣDDT is likely to continue to be measured in monitoring programmes as the results presented in Chapter Six indicate that ΣDDT is available for uptake by terrestrial organisms.

Elevated concentrations of arsenic were only measured in orchard soils (<2–58 mg kg^{-1}) and are mainly attributable to former use of lead arsenate as an insecticide. Concentrations of arsenic accumulated in worm tissue increased with increasing soil concentration. Despite exceeding thresholds for phytotoxicity in some soils, there were no significant relationships between plant yield and soil arsenic concentrations.

Unlike the other key contaminants, there were no significant differences between cadmium concentrations in horticultural soils (<0.1–1.5 mg kg^{-1}) and grazing soils (<0.1–1.5 mg kg^{-1}). Consistent with international studies, both worms and plants exposed to contaminated soil bioaccumulated cadmium. Cadmium concentrations in lettuce increased with increasing soil cadmium concentration and four of the lettuce treatments exceeded the New Zealand standard of 0.1 mg kg^{-1} FW for cadmium in leafy vegetables. The cadmium concentrations in grazing and horticultural soils are expected to increase with time as a result of continued phosphate fertiliser applications (Loganathan *et al.*, 2003).

Copper concentrations in horticultural soils (6–523 mg kg^{-1}) and in particular orchard soils (10–523 mg kg^{-1}) exceeded ecotoxicity criteria. In the orchard soils assayed, copper was the only trace element for which ecotoxic effects were identified in both plant assays. There were significant negative correlations between soil copper concentrations (neutral salt extractable and/or total), and the toxicological endpoints of earthworm cocoon production, plant yield and root elongation for lettuce seedlings. The negative correlations between *p,p'*-DDE:*p,p'*-DDT ratios and soil copper measured in Auckland and Waikato orchard soils are consistent with inhibitory effects on soil micro-organisms. Copper concentrations particularly in orchard soils exceeded international criteria, which are protective of micro-organisms. The copper concentrations in some horticultural soils are likely to continue to increase depending on crop type as a recent survey of pesticide sales found that the use of inorganic fungicides including copper is increasing (Manktelow *et al.*, 2005).

Lead concentrations in worm and plant tissue increased with increasing soil lead concentration (total and/or neutral salt extractable). Radish hypocotyl lead concentrations for three out of the eight assayed soil were equal to or exceeded 50% of the NZ food standard (0.1 mg kg^{-1}) for lead in root vegetables.

Worm and plant tissue trace element concentrations were compared with both total and 0.01 *M* $CaCl_2$ and 1 *M* NH_4NO_3 extractable trace element concentrations in soil. While significant correlations were observed in some instances, the neutral salt extractable trace element concentrations were not a better predictor of worm and plant tissue trace element concentrations than the soil total trace element concentrations. The neutral salt extractions may be a better indicator of toxicity of trace elements in soils than the total trace element concentration. Additional significant negative correlations were found between the neutral salt extractable copper concentrations and radish leaf yield and lettuce seedling root length (orchard soils) which were not observed for total soil copper concentrations. Seedling emergence for ryegrass decreased with increasing 1 *M* NH_4NO_3 extractable cadmium concentrations.

The bioaccumulation factors for plant and earthworm uptake of trace elements and ΣDDT tended to decrease with increasing soil concentration. This finding has implications for regulatory algorithms which are used to predict uptake and hence to set soil criteria. Depending on the bioaccumulation factor chosen, target tissue concentrations and hence the potential risk associated with contaminants in soil may be over or under estimated.

ΣDDT, arsenic, cadmium and lead were identified as being the contaminants most likely to be of concern for human protection when horticultural land is subdivided based on their toxicity and the concentrations present in soil. The estimated daily intakes of ΣDDT for residents did not exceed the WHO TDI of 10 μg/kg bw/day, however they were of the same order of magnitude as the more conservative RIVM TDI of 0.5 μg/kg bw/day. Soil ingestion was identified as the main exposure pathway for ΣDDT.

The maximum percent bioaccessible trace element fraction determined by a simulated gastric extraction method was 45, 100 and 83% for arsenic, cadmium and lead respectively. The estimated daily intakes of arsenic, cadmium and lead for lifetime exposures in residential settings developed on former orchards did not exceed the WHO tolerable intakes under the 10% homegrown produce scenario for the specified soil concentrations. Estimated arsenic intakes under the 50% homegrown produce scenario also did not exceed the WHO tolerable intake. Estimated daily intakes of cadmium under the 50% produce consumption scenario exceeded the WHO tolerable intake for cadmium at soil concentrations greater than 0.75 mg kg^{-1} for a child and 1 mg kg^{-1} for the lifetime exposure. Produce ingestion was the main exposure pathway for cadmium. Estimated child lead intakes exceeded the WHO tolerable intake at soil concentrations greater than 450 mg kg^{-1}. The estimated daily intakes for a child and a pregnant woman could also exceed the more conservative USFDA PTTILs. Soil ingestion was the main exposure pathway for lead under all scenarios.

The levels of ΣDDT, arsenic, cadmium, copper and lead identified in soils examined in this investigation can be attributed to past activities which were considered to be best practice at the time. The contamination of agricultural land can be difficult to manage as in most cases remediation options are limited (McLaughlin *et al.*, 2000a). Current applications of agrichemicals and soil amendments on agricultural land in New Zealand should be regularly reviewed to ensure that future uses of this land including the production of food are not compromised. Such reviews should identify the accumulation of degradation products and co-contaminants as well as active ingredients and would consider available evidence to determine soil criteria which are protective of soil function, waterways and human exposure.

9.1 RECOMMENDATIONS FOR FURTHER WORK

The investigations reported in this thesis have provided important and new insight into legacy contamination resulting from agrichemical use in productive horticulture. The experimental work completed in the course of these investigations has highlighted a number of knowledge gaps and identified numerous areas that would benefit from further investigation.

Work in this thesis suggests that co-contamination with copper may inhibit the degradation of DDT. It is possible that the degradation of some modern pesticides may also be inhibited by co-contamination with trace elements. As current testing generally considers agrichemicals individually it may beneficial to determine whether the degradation of other pesticides currently used in New Zealand is also likely to be inhibited by concurrent applications of inorganic agrichemicals.

The results presented in this thesis suggest that a proportion of both ΣDDT and key trace elements may be present in soil pools that are less amenable to extraction. This raises the question of longer term release of contaminants from soil. Further investigations could be undertaken to identify the conditions under which these contaminants could potentially be re-mobilised.

The results for lead from the simulated gastric extractions suggest that lead may be more bioaccessible from New Zealand soils. This has implications for exposure assessments. It would be worthwhile determining whether this higher than expected bioaccessibility only occurs for lead arsenate contaminated soils or is also the case for other types of lead contamination in soil e.g. lead based paint and lead resulting from historic use of lead additives in petrol.

The work undertaken for this thesis has also identified the following specific areas that require further investigation:

- The presence and levels of other metabolites of DDT in NZ horticultural soils.
- The efficacy of other chemical methods to release bound DDT residues from soil.
- The availability of *p,p'*-DDT in horticultural soils for microbial degradation.
- Measurement of tissue concentrations of aged DDT residues and trace elements in earthworms collected from orchard soils and determination of field based BAFs.
- Measurement of plant uptake of aged DDT residues and trace elements by a wider range of common home grown vegetables under field conditions.
- Investigation of the relative contribution of uptake of aged DDT residues by plants from the vapour phase and root uptake and translocation.
- Identification of the key soil characteristics determining bioavailability of contaminants from New Zealand soils to terrestrial organisms.
- Investigation of other chemical methods to determine the availability of trace elements in NZ horticultural soils.

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APPENDIX A REGIONAL SURVEYS

Table A1: Auckland: Trace element concentrations (mg kg^{-1}) measured in soil samples collected from horticultural sites developed before 1975.

		B	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
ARC1	glasshouse	<20	6230	18	<2	<0.1	0.6	6	7	<0.1	0.5	1	6.3	<0.4	<1	9
ARC2	glasshouse	<20	4870	85	6	0.2	0.9	8	59	<0.1	0.8	2	31.6	<0.4	<1	29
ARC3	glasshouse	<20	6520	24	<2	<0.1	0.9	5	8	<0.1	<0.4	4	8.2	<0.4	<1	17
ARC4	glasshouse	<20	19500	206	15	0.9	1.2	12	26	0.1	1.4	5	19.5	<0.4	2	76
ARC5	glasshouse	<20	15600	251	11	0.5	1.4	17	34	0.3	0.8	7	36.5	<0.4	1	115
ARC6	glasshouse	<20	12600	434	10	0.4	2.6	14	23	<0.1	1.1	7	30	<0.4	3	147
ARC7	glasshouse	<20	32900	1370	5	0.8	16.5	42	57	0.1	0.9	18	232	0.4	3	173
ARC8	glasshouse	<20	30500	1590	20	0.6	22.7	37	253	0.2	0.8	21	1250	1.7	8	510
ARC9	glasshouse	<20	31200	2410	7	0.9	27	53	230	0.2	2.3	34	93.3	0.7	1	145
ARC10	glasshouse	<20	41100	2050	10	1	28.7	44	82	<0.1	1.5	11	39.6	<0.4	1	113
ARC11	market garden	<20	29800	178	7	0.6	1.6	14	21	0.1	2.3	7	18.8	<0.4	3	45
ARC12	market garden	<20	6610	133	5	1	1.3	13	26	0.4	1.6	6	24.7	<0.4	2	46
ARC13	market garden	<20	7220	160	6	1	1.2	15	28	0.3	1.8	4	17	<0.4	1	31
ARC14	market garden	<20	36600	1840	4	0.4	22	42	36	0.1	2.2	15	22.4	<0.4	2	53
ARC15	market garden	<20	42600	2820	4	0.4	30.1	54	39	0.1	1.1	31	19.4	<0.4	1	90
ARC16	market garden	<20	46800	1450	8	0.5	9	24	44	0.3	2.3	9	29.2	<0.4	3	51
ARC17	market garden	<20	65500	2070	4	0.5	46.1	108	76	0.1	2.5	83	14.4	<0.4	3	109
ARC18	market garden	<20	49700	4570	11	1	15.3	26	137	0.3	3.4	8	45.7	<0.4	3	72
ARC19	orchard	<20	7300	88	3	0.1	0.5	5	24	<0.1	<0.4	1	11.4	<0.4	<1	22
ARC20	orchard	<20	6930	108	34	0.3	0.6	6	402	<0.1	<0.4	3	167	<0.4	1	79
ARC21	orchard	<20	11200	103	12	0.2	0.6	5	240	<0.1	0.6	0	46	<0.4	1	24
ARC22	orchard	<20	13600	134	9	0.4	0.7	6	327	0.3	0.5	1	45.6	<0.4	2	33
ARC23	orchard	<20	6960	94	6	0.2	0.9	4	58	<0.1	<0.4	3	53.2	<0.4	<1	37

Table A1: continued.

	Landuse	B	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
ARC24	orchard	<20	15900	275	34	0.8	1.2	13	490	<0.1	0.5	3	178	<0.4	2	76
ARC25	orchard	<20	14600	109	5	0.2	1.3	7	42	0.1	0.9	3	19.1	<0.4	<1	30
ARC26	orchard	<20	26700	217	17	0.3	1.7	14	173	0.1	1.3	3	64.6	<0.4	2	236
ARC27	orchard	<20	9080	336	26	0.5	1.8	8	421	0.3	<0.4	3	126	<0.4	4	58
ARC28	orchard	<20	15200	260	2	1.1	1.9	18	21	0.3	0.9	7	42.4	0.6	<1	31
ARC29	orchard	<20	19200	1470	25	0.3	11.8	12	80	<0.1	0	4	84.2	<0.4	<1	44
ARC30	orchard	<20	36100	1600	8	0.3	24.6	36	412	0.1	0.7	16	78.6	<0.4	4	78
ARC31	vineyard	<20	7260	125	14	0.6	1.1	24	152	0.2	0.5	5	87.6	<0.4	2	66
ARC32	vineyard	<20	9930	206	2	0.2	1.5	7	74	<0.1	<0.4	1	43.1	<0.4	<1	32
ARC33	vineyard	<20	11400	173	5	0.4	1	8	99	0.2	0.7	4	31.3	<0.4	1	57
ARC34	vineyard	<20	19600	328	8	0.2	4.6	12	70	0.2	0.6	14	61.7	0.4	1	79
ARC35	vineyard	<20	17400	187	7	0.7	2.4	14	139	0.2	1	6	83.9	<0.4	3	152
ARC36	grazing	<20	6800	107	<2	0.5	0.7	6	13	<0.1	<0.4	3	20.6	<0.4	<1	21
ARC37	grazing	<20	14000	1850	3	0.4	10.4	9	8	<0.1	0.6	2	15.5	<0.4	<1	24
ARC38	grazing	<20	34000	1680	3	0.4	27.7	52	45	<0.1	0.8	29	14.5	<0.4	<1	80
ARC42	multi-use	<20	3750	55	3	0.1	1	3	14	<0.1	0.50	3	7	<0.4	<1	27
ARC44	multi-use	<20	47900	2500	14	0.7	11	25	105	0.30	2.50	11	37	<0.4	3.00	83

Table A2: Auckland: Concentrations (mg kg^{-1}) of *o,p′* and *p,p′* isomers of DDT, DDE, DDD and ΣDDT and key soil characteristics measured in soil samples collected from horticultural sites developed before 1975. Units are mmoles/100g for CEC and mg kg^{-1} for Olsen P.

	Landuse	*o,p′*-DDD	*o,p′*-DDE	*o,p′*-DDT	*p,p′*-DDD	*p,p′*-DDE	*p,p′*- DDT	ΣDDT[a]	%TOC	pH	CEC	OlsenP
ARC1	glasshouse	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	6.4	5.14	1	12
ARC2	glasshouse	<0.005	<0.005	<0.005	0.022	0.01	0.011	0.043	2.6	6.45	16	67
ARC3	glasshouse	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	0.5	5.92	32	6
ARC4	glasshouse	0.063	0.027	0.33	0.34	0.61	1.4	2.77	3.9	5.89	25	222
ARC5	glasshouse	0.12	0.036	0.67	0.29	2	1.5	4.62	6.8	6	29	139
ARC6	glasshouse	0.009	0.015	0.086	0.055	0.37	0.72	1.26	3.7	5.92	31	223
ARC7	glasshouse	0.02	0.007	0.037	0.027	1.2	0.213	1.50	4.7	5.81	26	96
ARC8	glasshouse	6.8	0.200	20	25	7.2	230	289.2	3	4.71	20	163
ARC9	glasshouse	0.09	<0.005	0.23	0.1	0.4	1.7	2.52	3.7	5.67	31	180
ARC10	glasshouse	0.014	<0.005	0.02	0.022	0.057	0.12	0.233	2.2	5.75	20	186
ARC11	market garden	<0.005	<0.005	0.014	<0.005	0.05	0.087	0.151	3.3	6.33	22	88
ARC12	market garden	<0.005	<0.005	0.013	0.007	0.039	0.08	0.139	10.8	6.23	23	80
ARC13	market garden	<0.005	<0.005	0.019	0.006	0.045	0.11	0.18	8.9	6.31	23	75
ARC14	market garden	0.007	0.011	0.048	0.017	0.53	0.3	0.913	1.7	6.01	8	139
ARC15	market garden	0.009	<0.005	0.015	0.029	0.14	0.34	0.533	3.3	5.95	28	78
ARC16	market garden	<0.005	<0.005	0.006	<0.005	0.048	0.025	0.079	1.7	6.19	19	88
ARC17	market garden	<0.005	0.007	0.02	0.006	0.2	0.073	0.306	1.9	6.02	30	123
ARC18	market garden	0.01	<0.005	0.011	0.008	0.11	0.052	0.191	1.6	6.03	19	212
ARC19	orchard	<0.005	<0.005	<0.005	<0.005	0.026	0.005	0.031	4.7	5.53	19	87
ARC20	orchard	0.19	0.044	0.61	0.42	3	5.3	9.56	3.8	6.02	20	113
ARC21	orchard	0.09	0.011	0.11	0.18	1.7	1.2	3.29	3.4	6.06	22	77
ARC22	orchard	0.09	0.01	0.11	0.16	2.4	2.2	4.97	4.8	6.38	30	103
ARC23	orchard	<0.005	<0.005	0.022	0.044	0.86	0.24	1.17	4.2	5.34	17	46
ARC24	orchard	0.43	0.084	1.1	1.1	6.7	15	24.4	7.5	5.28	36	100
ARC25	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	5.5	5.62	18	44
ARC26	orchard	<0.005	<0.005	0.006	0.006	0.137	0.05	0.199	6.3	6.39	25	68

[a]Sum of of *o,p′* and *p,p′*-DDT, DDE and DDD (values < 0.005 included as half of LOD)

Table A2: continued.

	Landuse	*o,p′*-DDD	*o,p′*-DDE	*o,p′*-DDT	*p,p′*-DDD	*p,p′*-DDE	*p,p′*- DDT	ΣDDT	TOC	pH	CEC	OlsenP
ARC27	orchard	0.055	0.013	0.148	0.28	3.1	2.8	6.40	4.8	6.35	29	134
ARC28	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	15.9	5.47	26	14
ARC29	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	5.8	6.09	33	24
ARC30	orchard	0.072	0.009	0.32	0.18	2.4	3.4	6.38	3.7	5.3	23	174
ARC31	vineyard	0.074	0.015	0.09	0.12	1.1	0.58	1.97	3.8	6.22	22	154
ARC32	vineyard	<0.005	<0.005	0.005	0.007	0.19	0.047	0.249	4.6	5.98	24	37
ARC33	vineyard	0.009	<0.005	0.027	0.032	0.41	0.19	0.668	5.5	6.02	25	27
ARC34	vineyard	0.02	0.007	0.11	0.033	0.54	0.39	1.10	5.6	5.92	24	37
ARC35	vineyard	0.009	0.006	0.17	0.057	1.3	1.3	2.84	7.2	6.34	26	96
ARC36	grazing	<0.005	<0.005	<0.005	<0.005	0.009	<0.005	0.009	5.1	5.71	6	18
ARC37	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	3.7	5.78	10	27
ARC38	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	4.9	5.41	27	48

Table A3: Auckland: Trace element concentrations (mg kg^{-1}) measured in soils samples collected from horticultural sites developed after 1975.

	Landuse	B	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
ARC39	glasshouse	<20	8270	212	8	0.4	3	35	24	0.20	1.10	6	20	<0.4	2	91
ARC40	glasshouse	<20	26700	213	8	0.6	2	18	30	0.20	2.30	11	32	<0.4	2	80
ARC41	multi-use	<20	19300	608	4	0.3	4	7	24	<0.1	0.50	2	13	<0.4	<1	30
ARC43	multi-use	<20	1600	53	<2	0.4	1	12	50	0.20	<0.4	4	7	<0.4	<1	12
ARC45	orchard	<20	27000	546	11	1.0	5	20	30	0.20	1.40	8	20	<0.4	2	61
ARC46	vineyard	<20	19000	475	3	0.4	5	11	25	<0.1	0.60	3	12	<0.4	<1	30
ARC47	vineyard	<20	7800	96	4	0.2	1	7	82	<0.1	0.60	3	68	1.10	1	52
ARC48	vineyard	<20	12100	144	3	0.3	1	6	121	0.10	0.70	3	19	<0.4	1	45
ARC49	vineyard	<20	3810	101	2	0.3	1	4	16	<0.1	<0.4	1	3	<0.4	1	14
ARC50	vineyard	<20	19900	224	<2	0.3	2	16	20	<0.1	0.40	2	7	<0.4	<1	14

Table A4: Auckland glasshouse soils: Concentrations (mg kg^{-1}) of pesticides detected in the multi-residue pesticide screen.

	ARC2	ARC4	ARC5	ARC6	ARC8	ARC9	ARC10	ARC39	ARC40
Azoxystrobin	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.24	<0.02
Bifenthrin	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	0.15	<0.01
Bitertanol	<0.01	<0.01	<0.01	0.21	<0.01	<0.01	<0.01	<0.01	<0.01
Bromopropylate	<0.01	<0.01	<0.01	1.4	<0.01	<0.01	<0.01	0.4	<0.01
Bupirimate	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01
Buprofezin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01
Chlorpyrifos	<0.01	<0.01	<0.01	<0.01	0.4	<0.01	<0.01	<0.01	<0.01
Cyprodanil	<0.02	<0.02	<0.02	0.04	<0.02	<0.02	<0.02	0.56	<0.02
Dichlorvos	<0.03	<0.03	<0.03	0.01	<0.03	<0.03	<0.03	<0.03	<0.03
Dicofol	<0.05	<0.05	0.43	0.42	11	<0.05	<0.05	0.12	<0.05
Dieldrin	0.005	<0.005	0.024	<0.005	<0.005	<0.005	0.01	<0.005	0.072
Diuron	<0.02	<0.02	<0.02	0.07	<0.02	<0.02	<0.02	<0.02	<0.02
Endosulfan I	<0.005	<0.005	<0.005	0.044	<0.005	0.77	<0.005	0.15	<0.005
Endosulfan II	<0.005	<0.005	<0.005	0.11	<0.005	1.2	<0.005	0.79	<0.005
Endosulfan Sulphate	<0.005	<0.005	<0.005	0.1	<0.005	1	0.021	1	<0.005
Fludioxonil	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.29	<0.02
Fluvalinate	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	<0.01
Lindane	<0.005	0.035	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Linuron	<0.05	<0.05	<0.05	0.14	<0.05	<0.05	<0.05	<0.05	<0.05
Metalaxyl	<0.02	<0.02	<0.02	0.09	<0.02	<0.02	0.01	0.01	<0.02
Methiocarb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Myclobutanil	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	0.13	<0.01
Nithrothal-isopropyl	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	0.01	<0.01
Oxadiazon	<0.01	<0.01	<0.01	0.55	<0.01	<0.01	<0.01	7.8	<0.01
Penconazole	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01
Pendamethalin	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.11
Permethrin	<0.01	<0.01	<0.01	<0.01	<0.01	0.7	0.03	<0.01	<0.01
Pirimiphos-methyl	<0.01	0.02	<0.01	<0.01	<0.01	2.9	0.07	<0.01	<0.01
Procymidone	<0.01	<0.01	<0.01	0.15	<0.01	<0.01	0.09	0.52	<0.01
Prothiofos	<0.01	<0.01	<0.01	<0.01	4.2	<0.01	<0.01	<0.01	<0.01
Simazine	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01
Tebufenpyrad	<0.01	<0.01	<0.01	0.1	<0.01	<0.01	<0.01	<0.01	<0.01
Terbuconazole	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.2	<0.01
Terbuthylazine	<0.01	<0.01	<0.01	1.3	<0.01	<0.01	<0.01	0.24	<0.01
Terbuthylazine-desethyl	<0.01	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01

Table A5: Auckland: Concentrations (mg kg^{-1}) of pesticides detected in the multi-residue pesticide screen.

	Landuse	Dicofol	Dieldrin	Iprodione	Myclobutanil	Pendamethalin	Procymidone
ARC41	multi-use	<0.05	<0.005	0.022	0.02	<0.01	<0.01
ARC42	multi-use	<0.05	<0.005	<0.01	<0.01	<0.01	0.02
ARC43	multi-use	<0.05	<0.005	<0.01	<0.01	0.09	<0.01
ARC44	multi-use	<0.05	0.36	<0.01	<0.01	<0.01	<0.01

		Dicofol	Dieldrin	Diuron	Fenamirol	Iprodione	Procymidone	Prothiofos
ARC31	vineyard	<0.05	0.008	<0.02	<0.01	<0.01	<0.01	<0.01
ARC32	vineyard	<0.05	0.009	<0.02	<0.01	<0.01	<0.01	<0.01
ARC33	vineyard	<0.05	<0.005	<0.02	<0.01	<0.01	<0.01	0.062
ARC35	vineyard	0.54	<0.005	<0.02	0.04	<0.01	<0.01	<0.01
ARC50	vineyard	<0.05	<0.005	<0.02	<0.01	0.07	<0.01	<0.01
ARC46	vineyard	<0.05	<0.005	<0.02	<0.01	0.048	<0.01	<0.01
ARC47	vineyard	<0.05	<0.005	<0.02	0.018	<0.01	0.016	<0.01
ARC48	vineyard	<0.05	<0.005	0.2	<0.01	0.028	<0.01	<0.01

		Dicofol	Dieldrin	Dichlobenil	Myclobutanil	Oxychlordane	Oxyfluorfen	Simazine
ARC20	orchard	0.33	<0.005	<0.01	0.017	<0.005	0.013	<0.01
ARC21	orchard	0.047	<0.005	<0.01	<0.01	0.015	<0.01	<0.01
ARC22	orchard	0.065	<0.005	<0.01	<0.01	0.015	<0.01	<0.01
ARC24	orchard	0.41	<0.005	<0.01	<0.01	<0.01	<0.01	<0.01
ARC27	orchard	0.16	<0.005	<0.01	<0.01	<0.01	<0.01	<0.01
ARC30	orchard	<0.05	<0.005	0.036	0.055	<0.005	<0.01	0.16

Table A6: Auckland market garden soils: Concentrations (mg kg^{-1}) of pesticides detected in the multi-residue pesticide screen.

	Landuse	Alachlor	Dicofol	Dieldrin	Diuron	Endosulfan I	Endosulfan II	Endosulfan Sulphate	Pendamethalin	Procymidone	Simazine
ARC11	market gardens	<0.01	0.056	0.56	0.26	0.01	0.061	0.19	<0.01	<0.01	0.24
ARC12	market gardens	<0.01	<0.005	0.031	<0.02	<0.005	<0.005	0.018	<0.01	<0.01	<0.01
ARC13	market gardens	0.65	<0.005	0.039	<0.02	0.016	0.028	0.073	<0.01	<0.01	<0.01
ARC14	market gardens	<0.01	<0.005	<0.005	<0.02	<0.005	<0.005	<0.005	0.14	0.05	<0.01
ARC15	market gardens	<0.01	<0.005	0.031	<0.02	<0.005	<0.005	<0.005	<0.01	<0.01	<0.01
ARC16	market gardens	<0.01	<0.005	0.009	<0.02	<0.005	<0.005	<0.005	0.04	0.04	<0.01
ARC17	market gardens	1.7	<0.005	<0.005	<0.02	0.051	0.11	0.17	<0.01	<0.01	<0.01
ARC18	market gardens	<0.01	<0.005	0.26	<0.02	<0.005	<0.005	<0.005	<0.01	0.03	<0.01

Table A7: Tasman: Trace element concentrations (mg kg^{-1}) measured in soil samples.

Site Code	Landuse	B	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
TC1	berries	<20	2940	90	<2	0.2	0.6	3	40	<0.1	<0.4	1	10.9	<0.4	<1	11
TC2	berries	<20	17600	337	2	0.2	10	27	20	<0.1	<0.4	56	10.3	<0.4	<1	45
TC3	berries	<20	11600	235	2	0.2	5.1	11	20	<0.1	<0.4	11	7.6	<0.4	<1	43
TC4	berries	<20	13900	299	2	0.2	6.2	13	15	<0.1	<0.4	12	10.4	<0.4	<1	52
TC5	berries	<20	28400	671	4	0.6	14.9	54	111	<0.1	<0.4	57	13.6	<0.4	<1	77
TC6	market garden	<20	12200	294	2	0.1	5.4	18	6	<0.1	<0.4	15	8.3	<0.4	<1	32
TC7	market garden	<20	39700	1140	21	0.4	29.6	138	55	<0.1	0.9	131	21.2	<0.4	<1	116
TC8	market garden	<20	44200	1040	10	0.2	26.8	145	34	<0.1	<0.4	138	10.9	<0.4	<1	84
TC9	market garden	<20	44000	1250	12	0.3	35.1	170	67	<0.1	0.9	236	13.2	<0.4	<1	138
TC10	market garden	<20	43200	916	4	0.2	34.5	188	37	<0.1	0.5	320	12.3	<0.4	<1	79
TC11	orchard	<20	5020	76	3	0.4	0.7	5	10	<0.1	<0.4	5	14.7	<0.4	2	33
TC12	orchard	<20	9600	170	48	0.4	1.2	8	60	<0.1	<0.4	4	243	<0.4	3	52
TC13	orchard	<20	7620	195	33	0.3	1.6	9	67	<0.1	<0.4	6	165	<0.4	1	78
TC14	orchard	<20	8480	106	20	1	1.3	8	30	0.5	<0.4	4	131	<0.4	4	91
TC15	orchard	<20	26300	340	47	0.4	15	55	123	0.1	<0.4	33	191	<0.4	3	97
TC16	tobacco	<20	10500	240	<2	0.2	4.6	12	7	<0.1	<0.4	8	8	<0.4	<1	34
TC17	tobacco	<20	21200	559	3	0.3	8.7	28	30	<0.1	1.5	15	16.3	<0.4	<1	64
TC18	tobacco	<20	24800	335	3	0.3	7.1	35	40	<0.1	1.1	15	12.2	<0.4	<1	67
TC19	tobacco	<20	14300	520	<2	0.2	7.6	15	20	<0.1	<0.4	10	5.4	<0.4	<1	74
TC20	tobacco	<20	19900	388	<2	0.7	9	9	36	<0.1	<0.4	12	5.6	<0.4	<1	77
TC21	grazing	<20	14300	93	<2	<0.1	1.9	10	8	<0.1	<0.4	6	9.7	<0.4	<1	27
TC22	grazing	<20	6260	97	<2	0.1	2.1	6	5	<0.1	<0.4	5	5.7	<0.4	<1	24
TC23	grazing	<20	10400	274	<2	0.2	4.3	11	5	<0.1	<0.4	7	7.7	<0.4	<1	38
TC24	grazing	<20	37400	837	4	0.6	21.7	130	24	<0.1	0.4	151	8.3	<0.4	<1	71
TC25	grazing	<20	35000	978	7	0.9	30.7	127	55	<0.1	0.4	190	11.1	<0.4	<1	133

Table A8: Tasman: Concentrations (mg kg^{-1}) of *o,p′* and *p,p′* isomers of DDT, DDE, DDD and ΣDDT measured in soil samples. Units are mmoles/100g for CEC and mg kg^{-1} for Olsen P.

	o,p′-DDD	*o,p′*-DDE	*o,p′*-DDT	*p,p′*-DDD	*p,p′*-DDE	*p,p′*- DDT	ΣDDT[a]	%TOC	pH	CEC	OlsenP	%clay	%silt	%sand
TC1	0.182	0.021	0.767	0.581	1.52	2.39	5.46	3.6	5.6	12	88	12	57	31
TC2	<0.005	<0.005	0.011	0.015	0.17	0.119	0.321	2.0	5.72	15	32	19	65	16
TC3	<0.005	<0.005	<0.005	<0.005	0.018	0.016	0.046	1.3	6.32	11	27	13	49	38
TC4	0.005	<0.005	0.06	0.043	0.231	0.48	0.822	2.2	5.7	14	49	16	55	29
TC5	<0.005	<0.005	<0.005	<0.005	0.067	0.02	0.099	3.0	5.93	23	101	24	62	14
TC6	<0.005	<0.005	<0.005	<0.005	0.036	0.021	0.069	3.9	5.33	15	15	22	52	26
TC7	0.016	0.01	0.111	0.04	0.574	0.407	1.16	3.0	5.95	17	201	23	47	30
TC8	<0.005	<0.005	<0.005	<0.005	0.126	0.013	0.151	5.4	5.87	20	65	32	52	16
TC9	<0.005	<0.005	<0.005	<0.005	0.058	0.045	0.115	2.7	6.46	26	240	28	59	13
TC10	<0.005	<0.005	<0.005	<0.005	0.061	0.025	0.098	1.5	6.39	16	65	25	53	22
TC11	0.037	0.005	0.068	0.082	0.831	0.462	1.49	2.7	6.63	19	82	19	62	19
TC12	0.117	0.018	0.367	0.286	4.27	2.08	7.14	2.1	6.31	16	103	15	55	30
TC13	0.084	0.013	0.267	0.187	2.23	1.43	4.21	2.4	6.17	13	107	19	62	19
TC14	0.091	0.009	0.077	0.12	1.36	0.74	2.40	1.7	6.27	17	97	20	57	23
TC15	0.047	0.01	0.201	0.101	1.49	1.24	3.09	2.0	6.37	16	86	8	54	38
TC16	<0.005	<0.005	0.063	0.019	0.527	0.186	0.801	2.3	5.76	8	54	12	36	52
TC17	0.064	0.024	0.718	0.206	2.6	1.67	5.28	2.3	6.23	15	91	17	56	27
TC18	0.076	0.036	1.04	0.337	2.61	2.28	6.38	2.5	6.3	16	93	30	65	5
TC19	<0.005	<0.005	0.02	0.006	0.176	0.034	0.242	1.6	6.13	6	89	18	52	30
TC20	0.014	0.009	0.284	0.052	0.718	0.658	1.74	1.7	6.27	6	90	7	42	50
TC21	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.003	1.9	6.18	21	7	21	57	21
TC22	<0.005	<0.005	<0.005	0.008	0.049	0.039	0.105	3.8	5.55	17	34	15	54	31
TC23	0.008	<0.005	0.097	0.029	0.499	0.357	0.993	3.7	5.85	16	45	13	42	45
TC24	<0.005	<0.005	<0.005	<0.005	0.022	<0.005	0.037	5.6	5.96	25	52	29	63	8
TC25	<0.005	<0.005	0.034	0.061	0.638	0.565	1.30	5.2	6.24	33	48	25	67	8

[a]Sum of of *o,p′* and *p,p′*-DDT, DDE and DDD (values < 0.005 included as half of LOD)

Table A9: Tasman:Organochlorine pesticide concentrations (mg kg^{-1}) measured in soil samples.

	Landuse	Cis-Chlordane	Trans-Chlordane	Total Chlordane	Dieldrin	Endosulphan II	Endosulphan sulphate
TC1	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC2	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC3	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC4	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC5	berries	<0.005	<0.005	<0.005	<0.005	0.036	0.261
TC6	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC7	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC8	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC9	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC10	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC11	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC12	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC13	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC14	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC15	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC16	tobacco	<0.005	<0.005	<0.005	0.006	<0.005	<0.005
TC17	tobacco	<0.005	<0.005	<0.005	0.011	<0.005	<0.005
TC18	tobacco	<0.005	<0.005	<0.005	0.095	<0.005	<0.005
TC19	tobacco	<0.005	<0.005	<0.005	0.042	<0.005	<0.005
TC20	tobacco	<0.005	<0.005	<0.005	0.033	<0.005	<0.005
TC21	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC22	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC23	grazing	<0.005	<0.005	<0.005	0.005	<0.005	<0.005
TC24	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TC25	grazing	0.006	0.009	0.04	<0.005	<0.005	<0.005

Table A10: Waikato: Trace element concentrations (mg kg^{-1}) measured in soil samples.

	Landuse	B	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
EW1	berries	<20	16300	1760	8	0.6	5.2	10	74	0.2	1.1	5	29	<0.4	1	131
EW2	berries	<20	19900	1950	11	0.9	7.8	10	126	0.2	1.1	7	17	<0.4	2	158
EW3	berries	<20	21500	969	7	0.9	5.5	12	80	0.2	1.1	6	22	<0.4	2	90
EW4	berries	<20	34400	864	25	0.6	5.6	13	22	0.2	1.3	6	32	<0.4	4	93
EW5	berries	<20	22200	2940	7	1	8.1	13	60	0.2	1.2	8	20	<0.4	2	101
EW6	berries	<20	18100	1730	14	0.7	5.9	15	82	0.2	1.1	5	46	<0.4	1	119
EW7	berries	<20	24600	3190	20	1.2	9.4	16	161	0.2	1.1	11	31	<0.4	2	155
EW8	glasshouse	<20	10200	494	25	0.3	2.7	8	31	<0.1	0.7	4	26	<0.4	2	85
EW9	glasshouse	<20	18400	993	15	0.4	5.8	11	76	<0.1	0.9	8	68	0.4	2	83
EW10	glasshouse	<20	16000	1310	8	0.5	5.6	12	33	0.1	0.9	6	21	<0.4	1	111
EW11	market garden	<20	18100	2230	6	0.3	9	7	26	<0.1	1.1	4	21	<0.4	2	78
EW12	market garden	<20	56100	3160	10	0.6	12.3	37	94	0.3	3.5	10	37	<0.4	3	67
EW13	market garden	<20	50300	3160	11	0.5	12.1	25	112	0.3	3.9	10	39	<0.4	3	70
EW14	market garden	<20	30100	3720	8	0.5	12.1	13	58	0.3	1.3	7	23	<0.4	3	92
EW15	market garden	<20	44100	4640	9	0.6	12.4	20	44	0.2	3.2	8	29	<0.4	2	65
EW16	market garden	<20	32900	5570	8	0.5	17.1	13	42	0.2	1.6	8	35	<0.4	2	100
EW17	market garden	<20	51500	6090	10	0.5	20.1	25	44	0.4	2.9	8	48	<0.4	3	72
EW18	orchard	<20	15100	1900	4	1.2	3.8	7	243	0.1	1.2	5	18	<0.4	7	121
EW19	orchard	<20	18200	1240	5	1	6.9	11	301	0.4	0.8	6	22	<0.4	4	135
EW20	orchard	<20	12700	3220	5	1.2	5.1	9	303	0.2	1.4	6	17	<0.4	3	197
EW21	orchard	<20	20000	823	6	1	4	10	328	0.05	0.8	9	14	<0.4	7	123
EW22	orchard	<20	17900	753	8	0.8	5.3	13	242	0.3	0.9	5	18	<0.4	5	35
EW23	orchard	<20	34000	6140	43	1	18.9	18	466	1.1	1.7	9	198	0.7	6	114
EW24	orchard	<20	13900	682	58	1.5	4.3	14	523	0.8	0.7	12	251	0.4	5	107
EW25	vineyard	<20	26800	653	10	0.2	4.2	8	22	0.1	1.1	2	37	<0.4	2	35
EW26	vineyard	<20	22000	795	7	0.3	4.9	9	43	0.1	1.1	3	23	<0.4	2	56
EW27	vineyard	<20	23300	329	15	0.2	5.4	15	60	<0.1	0.4	5	30	0.4	<1	118
EW28	vineyard	<20	24300	487	14	0.2	5.9	17	95	<0.1	0.6	6	42	<0.4	1	91

Table A10: continued.

	Landuse	B	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
EW29	vineyard	<20	24500	1900	8	0.5	7.8	12	115	0.2	0.9	6	22	<0.4	2	104
EW30	vineyard	<20	24100	1640	8	0.7	8.1	14	81	<0.1	1.1	4	39	<0.4	2	72
EW31	vineyard	<20	33500	1140	6	0.3	8.7	20	83	0.2	1.4	3	51	0.4	4	149
EW32	grazing	<20	14000	840	5	0.6	5.1	8	12	<0.1	0.5	3	14	<0.4	<1	52
EW33	grazing	<20	11600	863	3	0.6	5.4	7	24	0.1	0.7	3	15	<0.4	<1	40
EW34	grazing	<20	17300	487	5	0.5	4.2	13	15	0.1	0.9	4	43	<0.4	2	56
EW35	grazing	<20	16100	651	8	0.7	3.2	8	17	0.1	0.9	5	18	<0.4	1	69
EW36	grazing	<20	17700	1550	8	0.7	5	10	18	0.2	1	5	26	<0.4	1	98
EW37	grazing	<20	16200	1030	3	1.5	3.2	11	19	0.1	1.1	7	12	<0.4	<1	99
EW38	grazing	<20	45200	1740	9	0.6	8.5	26	33	0.3	2.1	10	42	<0.4	3	58
EW39	background	<20	10400	679	7	0.1	3.9	6	10	0.2	0.6	3	24	<0.4	1	34
EW40	background	<20	31500	2100	4	0.2	17	8	24	0.1	0.6	6	15	<0.4	<1	74
EW41	background	<20	40600	1970	8	0.1	9.1	19	30	0.3	1.9	7	45	<0.4	2	61
EW42	background	<20	6350	765	8	0.2	1.8	5	11	0.2	0.6	3	56	<0.4	1	43
EW43	background	<20	25900	461	6	<0.1	2.5	9	20	0.4	1.1	1	13	<0.4	1	29
EW44	background	<20	19300	843	3	<0.1	11.3	26	8	<0.1	0.5	8	11	<0.4	<1	30
EW45	background	<20	10400	1040	4	0.3	3.7	5	22	0.2	1.3	4	38	0.8	2	52

Table A11: Waikato: Concentrations (mg kg^{-1}) of *o,p'* and *p,p'* isomers of DDT, DDE, DDD and ΣDDT and soil characteristics measured in soil samples. Units are mmoles/100g for CEC and mg kg^{-1} for Olsen P.

	o,p'-DDD	*o,p'*-DDE	*o,p'*-DDT	*p,p'*-DDD	*p,p'*-DDE	*p,p'*- DDT	ΣDDT	%TOC	pH	CEC	OlsenP	%clay	%silt	%sand
EW1	<0.005	<0.005	0.049	0.009	0.441	0.372	0.877	5.4	6.03	9	52	8	70	22
EW2	<0.005	<0.005	<0.005	<0.005	0.077	0.06	0.149	6.9	6.23	19	58	9	78	13
EW3	<0.005	<0.005	0.029	0.008	0.402	0.337	0.782	5.7	6.05	23	37	9	75	17
EW4	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	6.9	6.09	6	45	13	67	20
EW5	<0.005	<0.005	<0.005	<0.005	0.088	0.051	0.151	5.6	6.11	17	45	8	78	14
EW6	<0.005	0.006	0.036	0.009	0.232	0.241	0.527	3.7	5.56	8	103	9	72	19
EW7	<0.005	<0.005	0.006	0.005	0.158	0.139	0.314	7.3	5.68	26	52	8	79	13
EW8	<0.005	<0.005	0.006	<0.005	0.06	0.157	0.232	5.5	5.02	6	83	15	60	25
EW9	0.01	<0.005	0.015	0.017	0.365	0.174	0.584	3.3	5.88	19	114	19	67	14
EW10	0.015	0.006	0.062	0.033	0.51	0.335	0.961	5.4	5.33	21	55	11	66	24
EW11	<0.005	<0.005	0.015	0.011	0.243	0.151	0.426	2.6	6.13	17	130	12	70	18
EW12	<0.005	<0.005	0.04	0.011	0.165	0.172	0.394	1.7	6.23	13	172	30	66	5
EW13	0.04	0.006	0.145	0.104	0.374	1.01	1.68	1.7	6.31	14	143	32	64	4
EW14	<0.005	<0.005	<0.005	<0.005	0.11	0.04	0.162	2.5	6.46	18	90	21	71	8
EW15	<0.005	<0.005	<0.005	<0.005	0.016	0.013	0.041	2.9	6.1	21	138	24	71	5
EW16	0.022	0.013	0.104	0.029	1.11	0.292	1.57	1.6	6.06	15	180	21	65	13
EW17	<0.005	<0.005	0.005	0.007	0.052	0.04	0.11	1.9	6.04	16	96	23	74	4
EW18	0.045	0.009	0.047	0.096	0.871	0.307	1.375	8.4	6.18	26	24	6	70	24
EW19	0.049	0.011	0.153	0.248	4.98	3.29	8.73	6.9	5.97	24	48	9	77	14
EW20	<0.005	<0.005	0.017	0.007	0.521	0.176	0.727	8.1	6.26	27	39	6	72	22
EW21	0.044	0.013	0.108	0.1	1.97	0.988	3.22	6.0	6.22	23	43	12	71	18
EW22	<0.005	<0.005	<0.005	0.015	0.274	0.076	0.374	5.3	5.87	19	44	17	68	15
EW23	0.064	0.03	0.414	0.213	5.27	3.81	9.80	3.9	5.97	26	126	13	75	12
EW24	0.892	0.058	2.84	1.79	12.9	16	34.5	8.4	5.81	26	62	13	61	26
EW25	<0.005	<0.005	<0.005	<0.005	0.027	0.012	0.051	2.4	6.1	15	72	21	67	11
EW26	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	2.5	6.29	14	59	21	64	15
EW27	<0.005	<0.005	<0.005	<0.005	0.037	0.016	0.065	4.7	6.02	29	95	13	52	35
EW28	<0.005	<0.005	0.048	0.028	0.457	0.719	1.26	4.7	6.16	34	123	15	55	30
EW29	<0.005	<0.005	<0.005	<0.005	0.081	0.034	0.127	5.9	6.2	29	25	9	76	15

Table A11: continued.

	o,p'-DDD	*o,p'*-DDE	*o,p'*-DDT	*p,p'*-DDD	*p,p'*-DDE	*p,p'*- DDT	ΣDDT[a]	%TOC	pH	CEC	OlsenP	%clay	%silt	%sand
EW30	<0.005	<0.005	<0.005	<0.005	0.032	0.013	0.057	3.5	6.2	21	107	13	71	16
EW31	<0.005	<0.005	<0.005	<0.005	0.01	0.01	0.032	3.6	6.1	23	35	17	70	13
EW32	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	5.2	5.86	11	46	11	45	45
EW33	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	5.3	5.88	21	50	17	66	16
EW34	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	4.2	5.92	17	70	17	56	27
EW35	<0.005	<0.005	0.013	0.016	0.168	0.551	0.754	8.1	5.5	15	10	7	73	20
EW36	<0.005	<0.005	0.02	<0.005	0.223	0.116	0.368	5.7	5.76	18	34	9	66	25
EW37	<0.005	<0.005	0.013	<0.005	0.222	0.094	0.338	9.4	6.02	22	45	8	71	21
EW38	<0.005	<0.005	<0.005	<0.005	0.05	0.019	0.081	4.0	5.63	20	34	13	79	9
EW39	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	3.5	5.56	19	26	17	68	15
EW40	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	6.7	5.96	25	9	18	73	9
EW41	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	2.5	5.76	22	6	9	82	9
EW42	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	2.8	5.38	23	29	17	60	23
EW43	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	13.8	5.04	9	14	10	75	15
EW44	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.03	3.9	5.45	14	10	18	65	17
EW45	<0.005	<0.005	<0.005	<0.005	0.015	0.018	0.045	12.4	4.64	22	45	6	72	22

[a]Sum of of *o,p'* and *p,p'*-DDT, DDE and DDD (values < 0.005 included as half of LOD),

Table A12: Waikato:Organochlorine pesticide concentrations (mg kg^{-1}) measured in soil samples.

	Landuse	Lindane	Dieldrin	Endosulphan I	Endosulphan II	Endosulphan sulphate	Endrin	Endrin-aldehyde
EW1	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW2	berries	<0.005	<0.005	<0.005	0.011	0.098	<0.005	<0.005
EW3	berries	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	<0.005
EW4	berries	<0.005	<0.005	<0.005	<0.005	0.059	<0.005	<0.005
EW5	berries	<0.005	<0.005	0.023	0.006	<0.005	<0.005	<0.005
EW6	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW7	berries	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW8	glasshouse	<0.005	0.012	0.188	0.082	0.147	0.233	0.01
EW9	glasshouse	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW10	glasshouse	<0.005	<0.005	0.019	0.138	0.093	<0.005	<0.005
EW11	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.068
EW12	market garden	<0.005	0.016	<0.005	<0.005	<0.005	<0.005	<0.005
EW13	market garden	<0.005	0.012	<0.005	<0.005	<0.005	<0.005	<0.005
EW14	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW15	market garden	<0.005	0.006	0.071	0.109	0.113	<0.005	<0.005
EW16	market garden	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW17	market garden	<0.005	0.052	<0.005	<0.005	<0.005	<0.005	<0.005
EW18	orchard	0.017	0.012	<0.005	<0.005	<0.005	<0.005	<0.005
EW19	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW20	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW21	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW22	orchard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW23	orchard	0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW24	orchard	0.006	0.019	<0.005	<0.005	<0.005	<0.005	<0.005
EW25	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW26	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW27	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

Table A12: continued.

	Landuse	Lindane	Dieldrin	Endosulphan I	Endosulphan II	Endosulphan sulphate	Endrin	Endrin-aldehyde
EW28	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW29	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW30	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW31	vineyard	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW32	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW33	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW34	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW35	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW36	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW37	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW38	grazing	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW39	background	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW40	background	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW41	background	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW42	background	<0.005	0.011	<0.005	<0.005	<0.005	<0.005	<0.005
EW43	background	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW44	background	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
EW45	background	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005

Table A13: Duplicate data (mg kg^{-1}) used to calculate the Student's t-test error for determining when a guideline had been exceeded. Data supplied by Environment Waikato from sampling undertaken on a former orchard.

Sample	As	Cu	Pb	ΣDDT
1A	71	215	183	20.1
1B	72	206	182	18.94
2A	52	180	181	10.76
2B	59	174	204	11.67
3A	17	43	70.1	0.25
3B	20	49	73.6	0.36
4A	42	127	84.2	4.75
4B	48	137	96.1	3.91

For the Pearson's correlation analyses for regional data, the data were log transformed with the exception of soil pH and the *p,p'*-DDE:*p,p'*-DDT ratio. Each correlation matrix was calculated twice; once for trace elements and once for ΣDDT with samples below the detection limit removed.

Table A14: Pearson's correlation coefficients for log values of trace elements and selected soil characteristics for the Auckland horticultural soils samples (n = 25).

	Fe	Mn	As	Cd	Cu	Pb	Sn	Zn	pH	%TOC	CEC	Olsen P
Fe	1											
Mn	0.841	1										
As	-0.092	-0.019	1									
Cd	0.167	0.241	0.085	1								
Cu	-0.053	-0.01	0.724	-0.053	1							
Pb	-0.217	-0.095	0.752	0.086	0.794	1						
Sn	0.467	0.377	0.336	0.489	0.393	0.182	1					
Zn	0.464	0.36	0.354	0.234	0.376	0.369	0.552	1				
pH	0.029	-0.016	0.192	0.282	0.012	-0.062	0.393	0.236	1			
%TOC	-0.587	-0.573	-0.051	0.187	-0.1	0.191	-0.386	-0.136	-0.122	1		
CEC	-0.043	-0.043	0.304	0.211	0.358	0.336	0.062	0.207	0.081	0.441	1	
Olsen P	0.241	0.267	0.337	0.173	0.411	0.089	0.75	0.317	0.21	-0.578	-0.21	1

0.4227 = $p<0.05$, 0.5368 = $p<0.01$, 0.6524 = $p<0.001$

Table A15: Pearson's correlation coefficients for log values of ΣDDT, trace elements and selected soil characteristics for the Auckland horticultural soils samples (n = 22).

	Fe	Mn	As	Cd	Cu	Pb	Sn	Zn	ΣDDT	*p,p′*-DDE: *p,p′*-DDT	%TOC	pH	CEC	OlsenP
Fe	1													
Mn	0.867	1												
As	-0.133	-0.153	1											
Cd	0.188	0.272	0.251	1										
Cu	-0.069	-0.049	0.736	0.003	1									
Pb	-0.243	-0.197	0.796	0.063	0.845	1								
Sn	0.543	0.474	0.379	0.626	0.307	0.208	1							
Zn	0.481	0.369	0.335	0.28	0.307	0.369	0.486	1						
ΣDDT	-0.182	-0.136	0.645	0.036	0.832	0.805	0.195	0.182	1					
p,p′-DDE: *p,p*-′DDT	-0.111	-0.129	-0.465	-0.628	-0.254	-0.303	-0.503	-0.241	-0.476	1				
%TOC	-0.663	-0.68	0.121	0.084	0.068	0.23	-0.248	-0.007	0.165	-0.205	1			
pH	0.012	-0.093	0.053	0.396	-0.125	-0.135	0.322	0.146	-0.238	-0.262	0.042	1		
CEC	-0.061	-0.148	0.291	0.195	0.415	0.279	0.153	0.24	0.276	-0.255	0.462	0.07	1	
Olsen P	0.325	0.438	0.367	0.402	0.306	0.162	0.67	0.182	0.22	-0.282	-0.42	0.041	-0.127	1

0.4227 = $p<0.05$, 0.5368 = $p<0.01$, 0.6524 = $p<0.001$

Table A16: Pearson's correlation coefficients for log values of trace elements, ΣDDT and selected soil characteristics for the Tasman horticultural soils samples (n = 15).

	Fe	Mn	As	Cd	Cu	Pb	Sn	Zn	ΣDDT	*p,p'*-DDE:DDT	%TOC	CEC	OlsenP	pH	%clay	%silt	%sand
Fe	1																
Mn	0.964	1															
As	0.02	-0.039	1														
Cd	-0.301	-0.424	0.585	1													
Cu	0.415	0.344	0.859	0.401	1												
Pb	-0.418	-0.499	0.85	0.623	0.585	1											
Sn	-0.628	-0.785	0.489	0.739	0.176	0.787	1										
Zn	0.671	0.62	0.555	0.361	0.796	0.162	-0.162	1									
ΣDDT	-0.568	-0.621	0.745	0.717	0.425	0.885	0.799	0.007	1								
*p,p'*DDE:DDT	0.343	0.328	-0.12	-0.276	-0.076	-0.323	-0.299	0.045	-0.332	1							
%TOC	0.19	0.307	-0.299	-0.539	-0.359	-0.533	-0.527	-0.181	-0.418	0.632	1						
CEC	0.457	0.424	-0.188	0.105	0.039	-0.491	-0.244	0.374	-0.43	0.258	0.25	1					
OlsenP	0.248	0.242	0.591	0.63	0.709	0.279	0.106	0.731	0.38	-0.183	-0.285	0.444	1				
pH	-0.118	-0.225	0.279	0.609	0.428	0.322	0.472	0.251	0.409	-0.272	-0.631	0.317	0.642	1			
%clay	0.322	0.462	-0.509	-0.33	-0.357	-0.722	-0.718	0.098	-0.662	0.477	0.459	0.471	0.027	-0.268	1		
%silt	-0.625	-0.593	-0.007	0.243	-0.06	0.259	0.378	-0.219	0.284	-0.228	-0.255	0.032	0.125	0.55	-0.109	1	
%sand	-0.102	-0.212	0.353	0.162	0.17	0.487	0.435	-0.13	0.46	-0.384	-0.341	-0.604	-0.199	-0.16	-0.749	-0.488	1

0.5139 = $p<0.05$, 0.6411 = $p<0.01$, 0.7603 = $p<0.001$

Table A17: Pearson's correlation coefficients for log values of trace elements and selected soil characteristics for the Waikato horticultural soils samples (n = 21).

	Fe	Mn	As	Cd	Cu	Pb	Sn	Zn	%TOC	pH	CEC	Olsen P	%clay	%silt	%sand
Fe	1														
Mn	0.506	1													
As	0.133	-0.066	1												
Cd	-0.32	0.336	0.08	1											
Cu	-0.437	-0.073	0.272	0.799	1										
Pb	0.212	0.092	0.895	0.125	0.241	1									
Sn	-0.152	0.292	-0.037	0.767	0.634	0.121	1								
Zn	-0.301	0.114	-0.059	0.348	0.481	0.055	0.137	1							
%TOC	-0.804	-0.441	0.019	0.5	0.732	-0.053	0.279	0.499	1						
pH	0.216	0.239	-0.485	-0.212	-0.319	-0.486	-0.131	0.067	-0.324	1					
CEC	-0.5	-0.336	0.193	0.208	0.549	0.129	-0.041	0.62	0.827	-0.281	1				
OlsenP	0.609	0.348	0.372	-0.307	-0.432	0.327	-0.404	-0.304	-0.725	0.038	-0.446	1			
%clay	0.792	0.185	0.228	-0.421	-0.529	0.215	-0.197	-0.631	-0.851	0.126	-0.725	0.662	1		
%silt	0.043	0.59	-0.361	0.48	0.162	-0.162	0.61	0.107	0.044	0.098	-0.108	-0.319	-0.234	1	
%sand	-0.837	-0.648	0.05	0.006	0.314	-0.047	-0.176	0.387	0.718	-0.265	0.676	-0.415	-0.718	-0.375	1

0.4329 = $p<0.05$, 0.5487 = $p<0.01$, 0.6652 = $p<0.001$

Table A18: Pearson's correlation coefficients for log values of trace elements, ΣDDT and selected soil characteristics for the Waikato horticultural soils samples (n = 20).

	Fe	Mn	As	Cd	Cu	Pb	Sn	Zn	ΣDDT	*p,p'*DDE: DDT	%TOC	pH	CEC	OlsenP	%clay	%silt	%sand
Fe	1																
Mn	0.5	1															
As	0.125	-0.088	1														
Cd	-0.348	0.306	0.059	1													
Cu	-0.467	-0.121	0.257	0.789	1												
Pb	0.204	0.071	0.894	0.103	0.223	1											
Sn	-0.164	0.276	-0.05	0.765	0.628	0.109	1										
Zn	-0.331	0.071	-0.087	0.312	0.454	0.028	0.114	1									
ΣDDT	-0.358	0.008	0.391	0.607	0.728	0.358	0.494	0.338	1								
*p,p'*DDE:DDT	-0.405	0.037	-0.406	0.15	-0.043	-0.492	0.014	-0.051	-0.167	1							
%TOC	-0.832	-0.489	0.002	0.483	0.724	-0.074	0.266	0.481	0.375	0.153	1						
pH	0.245	0.303	-0.477	-0.167	-0.282	-0.475	-0.106	0.132	-0.317	0.037	-0.298	1					
CEC	-0.559	-0.432	0.169	0.148	0.519	0.096	-0.084	0.591	0.208	-0.035	0.829	-0.219	1				
Olsen P	0.606	0.339	0.367	-0.335	-0.463	0.321	-0.419	-0.335	-0.022	-0.293	-0.752	0.062	-0.504	1			
%clay	0.819	0.224	0.249	-0.401	-0.513	0.239	-0.182	-0.619	-0.285	-0.322	-0.847	0.091	-0.721	0.688	1		
%silt	0.034	0.582	-0.378	0.468	0.141	-0.178	0.604	0.082	-0.02	0.168	0.025	0.132	-0.156	-0.333	-0.22	1	
%sand	-0.837	-0.653	0.055	0.017	0.332	-0.042	-0.172	0.41	0.254	0.306	0.736	-0.286	0.731	-0.413	-0.736	-0.372	1

0.4438 = $p<0.05$, 0.5614 = $p<0.01$, 0.6787 = $p<0.001$

APPENDIX B BIOASSAYS

Table B1: Chemical and physical soil characteristics for bioassay soils. Units are mg kg^{-1} for Fe, Mn and Olsen P and the cation exchange capacity (CEC) is reported as mmol./100g.

Soil	OlsenP	%TOC	pH	CEC	%clay	%silt	%sand	Fe	Mn
Worm assay soils									
W1	68	6.9	6.03	21	19	63	18	14283	311
W2	49	2.7	5.55	18	35	53	12	13300	54
W3	69	4.4	5.28	23	42	53	4	22327	217
W4	17	5.5	5.95	19	26	65	8	18393	1319
W5	34	4.5	6.01	17	30	63	7	15698	1009
W6	24	3.8	5.39	11	25	62	14	4039	83
W7	12	4.4	5.77	15	24	58	18	18515	1786
W8	31	6.5	5.53	20	32	55	14	12916	157
W9	25	4.6	5.82	16	32	59	9	12447	855
W10	4	2.4	5.16	7	23	62	15	3179	41
Plant assay soils									
Orchard 1	89	5.4	5.65	24	26	64	10	22215	271
Orchard 2	85	3.1	5.88	16	33	57	10	11001	350
Orchard 3	65	3.1	5.72	14	26	49	25	11845	326
Orchard 4	41	3.7	5.55	12	27	54	19	10712	269
Orchard 5	56	3.1	5.65	8	21	64	14	2743	77
Vineyard	40	3.4	5.45	8	34	59	7	9825	131
Bushblock1	6	2.9	5.74	11	31	58	11	9767	39
Bushblock2	5	3.6	5.03	12	18	46	36	10428	177
Grazing1	12	5.6	5.67	21	28	67	5	25950	393
Grazing 2	9	3.2	5.74	7	20	62	17	2962	82

Table B2: Mean (n = 3) concentrations (μg kg^{-1}) of *o,p'* and *p,p'* isomers of DDT, DDE, DDD and ΣDDT measured in worm assay soils.

	o,p'-DDE	*p,p'*-DDE	*o,p'*-DDD	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	ΣDDT
W1	113	11850	609	647	2521	16720	32460
W2	13	478	90	89	18	253	942
W3	49	6955	158	409	456	6137	14160
W4	15	4389	32	100	133	1907	6577
W5	<10	388	<10	25	8	139	560
W6	<10	2101	47	163	109	958	3377
W7	<10	145	<10	<10	11	67	223
W8	<10	10	<10	<10	<10	<10	10
W9	<10	32	<10	<10	<10	14	46
W10	<10	<10	<10	<10	<10	<10	<10

Table B3: Concentrations of pesticides (mg kg^{-1}) measured in worm assay soils collected from active orchard soils (field-moist basis). Multi-residue pesticide screen undertaken by HortResearch.

	W2	W4	W5
p,p'-DDT	0.11	0.64	0.04
p,p'-DDE	0.20	0.90	0.16
p,p'-DDD	0.09	0.06	0.02
o,p'-DDT	0.05	0.11	0.02
o,p'-DDD	0.09	0.01	
o,p'-DDE	0.02	0.01	
dicofol	0.02	0.11	0.02
dieldrin			T
imazalil			0.01
lindane			T

Table B4: Spearman rank coefficients between BAFs for trace element uptake by earthworms and the percent of trace element extracted from soil by neutral salts. (n = 8)

	$\%Cd_{CaCl_2}$	$\%Cu_{CaCl_2}$	$\%Zn_{CaCl_2}$	$\%Cd_{NH_4NO_3}$	$\%Cu_{NH_4NO_3}$	$\%Pb_{NH_4NO_3}$	$\%Zn_{NH_4NO_3}$
Cd_{BAF}	0.762	0.667	0.405	0.571	0.762	0.275	0.286
Cu_{BAF}	0.19	0.095	-0.381	0.048	0.31	-0.31	-0.29
Pb_{BAF}	-0.214	0.429	-0.19	-0.405	0.048	-0.37	-0.62
Zn_{BAF}	0.738	0.833	0.69	0.595	0.952	0.335	0.5

0.7067 = $p<0.05$, 0.8343 = $p<0.01$, 0.9249 = $p<0.001$

Table B5: Spearman rank coefficients between BAFs for trace element uptake by lettuce and the percent of trace element extracted from soil by neutral salts. (n = 10)

BAF	$\%Cd_{CaCl_2}$	$\%Cu_{CaCl_2}$	$\%Zn_{CaCl_2}$	$\%Cd_{NH_4NO_3}$	$\%Cu_{NH_4NO_3}$	$\%Pb_{NH_4NO_3}$	$\%Zn_{NH_4NO_3}$
Cd	0.915	0.411	0.733	0.806	0.778	0.845	0.758
Cu	0.818	0.141	0.758	0.77	0.626	0.76	0.733
Pb	0.915	0.288	0.855	0.794	0.766	0.833	0.818
Zn	0.77	0.276	0.83	0.539	0.699	0.669	0.758

0.6319= $p<0.05$, 0.7646 = $p<0.01$, 0.8721 = $p<0.001$

Table B6: Spearman rank coefficients between BAFs for trace element uptake by radish and the percent of trace element extracted from soil by neutral salts (n = 8).

BAF	$\%Cd_{CaCl_2}$	$\%Cu_{CaCl_2}$	$\%Zn_{CaCl_2}$	$\%Cd_{NH_4NO_3}$	$\%Cu_{NH_4NO_3}$	$\%Pb_{NH_4NO_3}$	$\%Zn_{NH_4NO_3}$
Cd_{radish}	0.929	0.275	0.69	0.857	0.738	0.857	0.762
Cu_{radish}	0.833	-0.036	0.786	0.69	0.524	0.643	0.714
Pb_{radish}	0.905	0.443	0.619	0.881	0.786	0.905	0.738
Zn_{radish}	0.643	0.12	0.857	0.405	0.571	0.5	0.714
$Cu_{radish\ leaf}$	0.81	-0.06	0.714	0.667	0.476	0.595	0.619
Zn $Cu_{radish\ leaf}$	0.667	0.144	0.929	0.429	0.619	0.548	0.81

$0.7067 = p<0.05$, $0.8343 = p<0.01$, $0.9249 = p<0.001$

APPENDIX C HUMAN EXPOSURE

Table C1: Concentrations of trace elements (mg kg^{-1}) and selected soil characteristics in the <2mm fraction of the soils utilised in the gastric extraction experiment.

Sample	As	Pb	Fe	%TOC	pH	CEC (mmoles)	Olsen P (mg kg^{-1})	% clay	% silt	% sand
AKL1	36	116	9010	3.1	5.9	15	85	33	57	10
AKL2	49	218	18900	7.0	5.6	na	136	24	61	15
AKL3	25	84	21100	5.8	6.1	26	24	na	na	na
AKL4	34	167	6950	3.8	6.0	20	113	na	na	na
AKL5	17	65	22800	6.3	6.4	25	68	na	na	na
WKT1	98	442	13700	6.9	6.0	26	68	19	63	18
WKT2	43	198	29800	3.9	6.0	26	126	13	75	12
TDC1	48	243	8780	2.1	6.3	15	103	15	55	30
TDC2	33	165	7420	2.4	6.2	13	107	19	62	19
TDC3	18	118	7540	2.2	6.5	19	58	17	51	32

Table C2: Pearson's correlation coefficients for gastric extractable trace element concentrations, percent gastric extractable trace element and total trace element concentrations in soil and selected soil characteristics.

	$As_{gastric}$	$Cd_{gastric}$	$Pb_{gastric}$	%As	%Cd	%Pb
$As_{gastric}$	1					
$Cd_{gastric}$	0.825	1				
$Pb_{gastric}$	0.899	0.711	1			
%As	0.504	0.186	0.592	1		
%Cd	0.124	0.018	0.212	0.585	1	
%Pb	0.353	0.003	0.518	0.9	0.665	1
As_{total}	0.952	0.892	0.831	0.232	-0.035	0.098
Cd_{total}	0.796	0.988	0.674	0.092	-0.115	-0.099
Pb_{total}	0.909	0.805	0.977	0.449	0.086	0.342
Fe_{total}	-0.228	0.088	-0.224	-0.799	-0.454	-0.82
%TOC	0.382	0.404	0.203	-0.262	-0.153	-0.402
pH	-0.32	-0.165	-0.388	-0.016	-0.072	-0.146
CEC	0.091	0.404	-0.101	-0.62	-0.502	-0.877
Olsen P	0.174	0.023	0.464	0.408	0.25	0.433

0.6319= $p<0.05$, 0.7646 = $p<0.01$, 0.8721 = $p<0.001$

Table C3: Estimated daily intakes (µg/kg bw/day) of ΣDDT for adults in a residential setting.

Soil (mg kg^{-1})	Soil ingestion	Dermal exposure	Produce	TDS	Total
Adult male 50% produce					
0.5	0.000	0.000	0.001	0.022	0.023
1.0	0.000	0.001	0.002	0.022	0.025
5.0	0.002	0.005	0.007	0.022	0.035
10.0	0.003	0.010	0.014	0.022	0.049
15.0	0.005	0.015	0.022	0.022	0.063
25.0	0.009	0.024	0.036	0.022	0.090
35.0	0.012	0.034	0.050	0.022	0.118
Adult male 10% produce					
0.5	0.000	0.000	0.000	0.022	0.022
1.0	0.000	0.001	0.000	0.022	0.023
5.0	0.002	0.005	0.001	0.022	0.030
10.0	0.003	0.010	0.003	0.022	0.038
15.0	0.005	0.015	0.004	0.022	0.046
25.0	0.009	0.024	0.007	0.022	0.062
35.0	0.012	0.034	0.010	0.022	0.078
Adult female 50% produce					
0.5	0.000	0.000	0.001	0.017	0.019
1.0	0.000	0.001	0.002	0.017	0.020
5.0	0.002	0.005	0.007	0.017	0.031
10.0	0.003	0.010	0.014	0.017	0.045
15.0	0.005	0.015	0.022	0.017	0.058
25.0	0.009	0.024	0.036	0.017	0.086
35.0	0.012	0.034	0.050	0.017	0.113
Adult female 10% produce					
0.5	0.000	0.000	0.000	0.017	0.018
1.0	0.000	0.001	0.000	0.017	0.019
5.0	0.002	0.005	0.001	0.017	0.025
10.0	0.003	0.010	0.003	0.017	0.033
15.0	0.005	0.015	0.004	0.017	0.041
25.0	0.009	0.024	0.007	0.017	0.057
35.0	0.012	0.034	0.010	0.017	0.073

Table C4: Estimated daily intakes (µg/kg bw/day) of arsenic for adults in a residential setting.

Soil (mg kg^{-1})	Soil ingestion	Dermal exposure	Produce	TDS	Total
Adult male 50% produce					
20	0.003	0.019	0.028	0.210	0.261
30	0.005	0.029	0.043	0.210	0.286
40	0.006	0.039	0.057	0.210	0.312
60	0.009	0.058	0.085	0.210	0.362
80	0.012	0.077	0.113	0.210	0.413
100	0.015	0.097	0.142	0.210	0.464
Adult male 10% produce					
20	0.003	0.019	0.006	0.210	0.238
30	0.005	0.029	0.009	0.210	0.252
40	0.006	0.039	0.011	0.210	0.266
60	0.009	0.058	0.017	0.210	0.294
80	0.012	0.077	0.023	0.210	0.322
100	0.015	0.097	0.028	0.210	0.351
Adult female 50% produce					
20	0.003	0.019	0.028	0.190	0.241
30	0.005	0.029	0.043	0.190	0.266
40	0.006	0.039	0.057	0.190	0.292
60	0.009	0.058	0.085	0.190	0.342
80	0.012	0.077	0.113	0.190	0.393
100	0.015	0.097	0.142	0.190	0.444
Adult female 10% produce					
20	0.003	0.019	0.006	0.190	0.218
30	0.005	0.029	0.009	0.190	0.232
40	0.006	0.039	0.011	0.190	0.246
60	0.009	0.058	0.017	0.190	0.274
80	0.012	0.077	0.023	0.190	0.302
100	0.015	0.097	0.028	0.190	0.331

Table C5: Estimated daily intakes (µg/kg bw/day) of cadmium for adults in a residential setting.

Soil (mg kg^{-1})	Soil ingestion	Dermal exposure	Produce	TDS	Total
Adult male 50% produce					
0.25	0.000	0.000	0.236	0.17	0.41
0.50	0.000	0.000	0.422	0.17	0.59
0.75	0.000	0.000	0.597	0.17	0.77
1.00	0.000	0.000	0.767	0.17	0.94
1.50	0.001	0.000	1.095	0.17	1.27
2.00	0.001	0.000	1.413	0.17	1.58
Adult male 10% produce					
0.25	0.000	0.000	0.047	0.17	0.22
0.50	0.000	0.000	0.084	0.17	0.25
0.75	0.000	0.000	0.119	0.17	0.29
1.00	0.000	0.000	0.153	0.17	0.32
1.50	0.001	0.000	0.219	0.17	0.39
2.00	0.001	0.000	0.283	0.17	0.45
Adult female 50% produce					
0.25	0.000	0.000	0.236	0.13	0.37
0.50	0.000	0.000	0.422	0.13	0.55
0.75	0.000	0.000	0.597	0.13	0.73
1.00	0.000	0.000	0.767	0.13	0.90
1.50	0.001	0.000	1.095	0.13	1.23
2.00	0.001	0.000	1.413	0.13	1.54
Adult female 10% produce					
0.25	0.000	0.000	0.047	0.13	0.18
0.50	0.000	0.000	0.084	0.13	0.21
0.75	0.000	0.000	0.119	0.13	0.25
1.00	0.000	0.000	0.153	0.13	0.28
1.50	0.001	0.000	0.219	0.13	0.35
2.00	0.001	0.000	0.283	0.13	0.41

Table C6: Estimated daily intakes (µg/kg bw/day) of lead for adults in a residential setting.

Soil (mg kg^{-1})	Soil ingestion	Dermal exposure	Produce	TDS	Total
Adult male 50% produce					
100	0.0343	0.0129	0.1080	0.13	0.29
200	0.0686	0.0258	0.1696	0.13	0.39
250	0.0857	0.0322	0.1964	0.13	0.44
400	0.1371	0.0516	0.2682	0.13	0.59
450	0.1543	0.0580	0.2901	0.13	0.63
500	0.1714	0.0645	0.3112	0.13	0.68
Adult male 10% produce					
100	0.0343	0.0129	0.0216	0.13	0.20
200	0.0686	0.0258	0.0339	0.13	0.26
250	0.0857	0.0322	0.0393	0.13	0.29
400	0.1371	0.0516	0.0536	0.13	0.37
450	0.1543	0.0580	0.0580	0.13	0.40
500	0.1714	0.0645	0.0622	0.13	0.43
Adult female 50% produce					
100	0.0343	0.0129	0.1080	0.11	0.27
200	0.0686	0.0258	0.1696	0.11	0.37
250	0.0857	0.0322	0.1964	0.11	0.42
400	0.1371	0.0516	0.2682	0.11	0.57
450	0.1543	0.0580	0.2901	0.11	0.61
500	0.1714	0.0645	0.3112	0.11	0.66
Adult female 10% produce					
100	0.0343	0.0129	0.0216	0.11	0.18
200	0.0686	0.0258	0.0339	0.11	0.24
250	0.0857	0.0322	0.0393	0.11	0.27
400	0.1371	0.0516	0.0536	0.11	0.35
450	0.1543	0.0580	0.0580	0.11	0.38
500	0.1714	0.0645	0.0622	0.11	0.41

APPENDIX D PUBLICATIONS AND PRESENTATIONS ARISING FROM THIS THESIS

Appendix D

JOURNAL ARTICLES

PEER REVIEWED

Gaw SK, Palmer G, Kim ND and Wilkins AL. (2003) Preliminary evidence that copper inhibits the degradation of DDT to DDE in pip and stonefruit orchard soils in the Auckland region, New Zealand. *Environmental Pollution.* 122: 1–5.

Gaw SK, Wilkins AL, Kim ND, Palmer GT and Robinson P. (2006) Trace element and ΣDDT concentrations in horticultural soils from the Tasman, Waikato and Auckland regions of New Zealand. *Science of the Total Environment.* 355: 31–47.

NON PEER REVIEWED

Gaw SK, Kim ND and Wilkins AL. (2002) Contaminated Horticultural Land: A development issue for the Auckland Region. *New Zealand Journal of Environmental Health.* 25: 12–14.

Gaw SK, Kim ND and Wilkins AL. (2003) Contaminated Horticultural Land in the Auckland region: An historic legacy. *Chemistry in New Zealand.* 67: 5559.

PEER REVIEWED TECHNICAL REPORTS

Gaw SK. (2002). Pesticide Residues in Horticultural Soils in the Auckland Region. *ARC Working Report No. 96.* Auckland, New Zealand.

Gaw SK. (2003) Historic pesticide residues in horticultural and grazing soils in the Waikato region. *Report prepared for Environment Waikato.* Hamilton, New Zealand.

Gaw SK. (2003) Historic pesticide residues in horticultural and grazing soils in the Tasman District. *Report prepared for Tasman District Council.* Nelson, New Zealand.

CONFERENCE PRESENTATIONS

Gaw SK. (2002) Contaminated Horticultural Land: A Developing Issue for the Auckland Region. *New Zealand Institute of Environmental Health National Conference*, Auckland.

Gaw S, Palmer G, Kim ND and Wilkins AL. (2002) Does Copper Inhibit the Microbial Degradation of DDT? *Golden Jubilee Conference of the New Zealand Soil Science Society.* 25–29 November, Wellington, New Zealand. *Poster Presentation.*

Gaw S, Kim ND, Wilkins AL and Palmer G. (2002) Contaminated Horticultural Land: A Developing Issue for the Auckland Region (and NZ). *Waste MINZ.* Rotorua, New Zealand. (Ministry for the Environment invited speaker).

Gaw S, Palmer G, Kim ND and Wilkins AL. (2003) Impact of Copper Based Fungicides on the Degradation of *p,p'* DDT to *p,p'* DDE in Pip and Stonefruit Orchard Soils in the Waikato Region, New Zealand. *ConSoil 2003. 8th International FZK/TNO Conference on Contaminated Soil.* 12–16 May, Gent, Belgium.

Gaw S, Palmer G, Kim ND and Wilkins AL. (2003) Phytoavailability of Trace Elements to Lettuce and Radish in Horticultural Soils Contaminated with Agrichemical Residues. *SETAC Asia/Pacific/ ASE Conference 2003.* 28 September–1 October Christchurch, New Zealand.

Gaw S, Vujnovich S. and Manastyrski M. (2003) Agrichemical Residues in Horticultural Soils in the Auckland region. *New Zealand Hydrological Society Symposium.* 18–21 November, Taupo, New Zealand.

Gaw SK, Wilkins AL, Palmer G., Kim ND. and Northcott GL. (2003) Does Co-Contamination With Copper Inhibit the Microbial Degradation of *p,p'*-DDT to *p,p'*-DDE in North Island Pip and Stonefruit Orchard Soils? *New Zealand Institute of Chemistry Conference.* 30 November–4 December, Nelson, New Zealand.

Gaw SK, Northcott GL, Wilkins A and Kim ND. (2004) Uptake of Aged DDT residues from soil by lettuce and radish. An overlooked source of exposure? *Third International Workshop on Chemical Bioavailability in the Terrestrial Environment Workshop.* 12–15 September, Adelaide, Australia.

Gaw SK, Northcott GL, Wilkins AL, Palmer G and Kim ND. (2004) Uptake of Aged Arsenic, Cadmium, Copper and Lead Residues by the Earthworm *Aporrectodea Caliginosa* from North Island (NZ) Orchards Soils. *Workshop in Contaminants and Ecological Risk Assessment.* 5–7 April, Adelaide, Australia. *Poster presentation.*

Northcott GL and Gaw SK. (2004) Measuring the Bioavailability of DDT Residues in NZ Horticultural Soil - State of the Art or Just Art? *Third International Workshop on Chemical Bioavailability in the Terrestrial Environment* 12–15 September, Adelaide, Australia. (SK Gaw omitted from published programme in error)

Northcott GL, Gaw SK, Wilkins AL and Kim ND. (2004) To Be Or Not To Be Bioavailable? Comparing Chemical and Physical Availability of Soil Aged DDT Against Uptake into Earthworms. *Workshop in Contaminants and Ecological Risk Assessment.* 5–7 April, Adelaide, Australia.

Gaw SK, Kim ND, Robinson G, Northcott GL and Wilkins A. (2005) Assessing Oral Exposure to Arsenic in Former Orchard Soils Using an *In Vitro* Extraction procedure. *NZIC Trace Elements Conference.* 17–18 February, Hamilton, New Zealand.

Gaw SK. (2005) What's the problem with horticultural soils? Analytical Workshop. *Public Health Intelligence Unit, Ministry of Health.* 2 May, Wellington, New Zealand.