The Status of Iodine and Selenium in Waikato Soils

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Abstract

This thesis investigates the status of the essential trace elements iodine and selenium in Waikato soils. Soil samples (368) representing different Soil Orders, land uses and soil depths were examined.

A tetramethyl ammonium hydroxide extraction method followed by ICP-MS was validated for iodine determination. This method was suitable for total iodine determination and also gave a reliable estimate of the total selenium content of soils, based on analysis of Certified Reference Materials.

Acid extraction of selenium was unsuitable because of difficulties with recoveries and interferences in the ICP-MS, although the use of methane and DRC-ICP-MS reduced interferences. Time and equipment constraints limited the complete validation using acid extraction for total selenium determination.

Waikato soils had a mean iodine content of 20.9 mg kg^{-1}, geometric mean of 13.7 mg kg^{-1} and range of 1.5 – 122.8 mg kg^{-1}. Allophanic and Granular soils contained the highest mean iodine contents with Pumice soils displaying the lowest. The iodine content was shown to increase with soil depth, with the Waikato soils showing no evidence of coastal enrichment, though this could be explained by the losses of iodine being equal to, or exceeding the additions to soil.

Land use appeared to have an effect on the iodine content of soils with background soils displaying more iodine on average than both farmed and forestry soils. Forestry soils displayed the lowest mean iodine content. Farming and forestry both appear to reduce the amount of iodine in soils.

Iodine was correlated strongly to aluminium and iron, indicating that clay minerals and iron oxides are the most important in the retention of iodine, with organic matter appearing to be less important in iodine retention. There was also a strong correlation of iodine with selenium and mercury, suggesting an association between these elements.

The selenium status of Waikato soils showed a mean concentration of 1.77 mg kg^{-1}, geometric mean 1.33 mg kg^{-1} and a range in concentration of 0.18 – 12.1 mg kg^{-1}. Like iodine, selenium also displayed the highest mean concentrations in Allophanic and Granular soils, with the lowest concentrations in Pumice soils. The concentration of selenium also increased with soil depth, with parent material appearing to affect the selenium content of soils. Selenium appeared to be more concentrated in the soils closest to the coast than those more inland; with the relative enrichment suggesting that the losses of selenium are likely to equal or exceed the inputs from the surface.

Selenium concentration in relation to land use indicated that farming and forestry may be depleting selenium from soils, with background soils displaying more selenium on average than both farmed and forestry soils.

Again selenium showed similar behaviour to iodine in that it was strongly correlated to aluminium, iron and manganese, indicating that clay minerals and iron and manganese oxides are the most important factors in selenium retention in Waikato soils. Organic matter was less important in retention shown by the less significant correlation with selenium. Mercury and iodine were both strongly correlated to selenium suggesting that chalcophilic elements (mercury) are strongly associated to selenium.

The strong correlation between iodine and selenium also explained the similarities in the relationships of both elements with other soil properties.

The results presented for both iodine and selenium indicate that the status of both elements in the Waikato Region may be better than previously thought, with the soils showing mean concentrations that suggest they may not be as deficient as thought.

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List of Abbreviations

IDD	Iodine deficiency disorder
CEC	Cation exchange capacity
TMAH	Tetramethyl ammonium hydroxide
CRM	Certified Reference Material
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
DRC-ICP-MS	Dynamic Reaction Cell ICP-MS
XRF	X-Ray Fluorescence Spectroscopy
NAA	Neutron activation analysis
HG-AAS	Hydride generation Atomic Absorption Spectroscopy
ICP-AES	ICP-Atomic Emission spectroscopy
GF-AAS	Graphite Furnace-AAS
ETV-ICP-MS	Electrothermal volatilisation ICP-MS

1 General Introduction

Iodine and selenium are important trace elements essential to the health of most organisms. Deficiencies in one of these elements cause an individual to be susceptible to health issues. Likewise, an excess of one of these elements can also cause health problems through toxicity. Thus, an essential element produces an optimum concentration range whereby an organism's health will be the greatest (Figure 1-1).

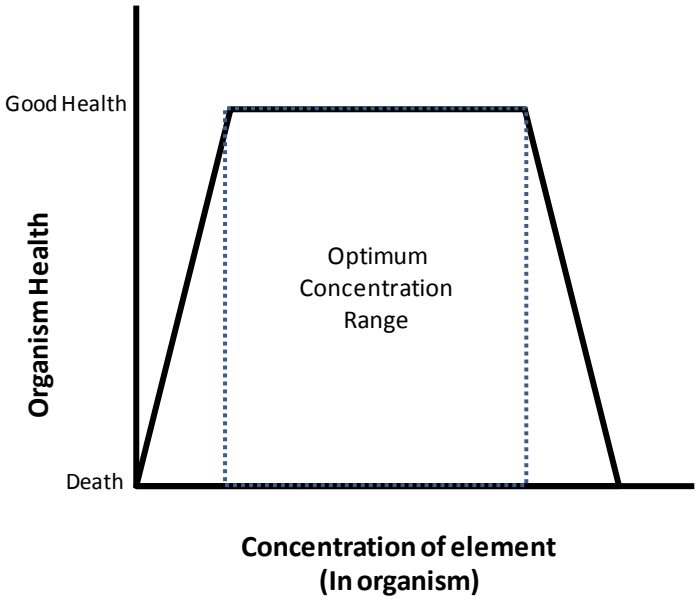

Figure 1-1 - Organism health with respect to the concentration of an essential element in the body [1].

With the exception of the marine environment, both iodine and selenium are generally introduced to organisms via ingestion of food, ultimately derived from the soil.

Generally the concentration of a trace element in the soil will affect the concentration in the food products produced from that soil. Therefore, it is important to know the status of these trace elements in soils in order to identify areas where health problems associated with deficiencies and toxicity may occur.

Soils of New Zealand are typically considered to be deficient in both iodine and selenium [2], so it would be expected that soils from the Waikato region would also be deficient in these elements.

The status of both these elements in New Zealand soils has been determined in previous decades but to differing extents. Iodine has been studied very broadly in New Zealand in relation to the incidence of goitre, with soils across the country analysed for total iodine content. However, this thesis is the first known thorough investigation in to the iodine content of soil within a region of New Zealand with respect to land use and soil type.

Selenium has been investigated extensively between 1960-1980, covering a range of soil aspects particularly relating to agriculture [3-5].

The recent status of both of these elements in the Waikato Region of New Zealand differs substantially, despite these both being essential trace elements. There is limited data available on selenium, with no current data available for iodine. This lack of current information on the status of both of these elements was reason for this project.

1.1 Iodine

Iodine plays an important role in the health of humans and mammals as it is a vital component of the hormones produced in the thyroid gland [6]. When a deficiency of iodine occurs, a series of iodine deficiency disorders (IDD) can result [7]. The most commonly recognized disorder is that of endemic goitre, the enlargement of the thyroid gland, a problem that has been well known for hundreds of years [8]. Iodine deficiency is also considered the greatest cause of preventable brain damage and mental impairment in the world, termed cretinism [6, 9]. Large populations are put at risk to this ailment due to their iodine deficient environments, characterised primarily by iodine deficient soils [8].

On the other hand, too much iodine can also affect the health of humans and animals, with hypothyroidism, goitre and hyperthyroidism also

common problems. Thus, there is an optimum range of iodine that is vital to the health of animals or humans.

In humans, the usual targeted iodine intake is 80-150 µg day^{-1}, with goitre typically seen when intakes fall below 50 µg day^{-1}, and cretinism in offspring observed when intakes of the mother fall below 30 µg day^{-1} [9].

Problems associated with iodine toxicity are observed when repeated intakes of iodine are greater than 10 mg day^{-1}. However, an upper limit of iodine intake has been suggested at 1.1 mg day^{-1} [10].

1.2 Selenium

The perception of selenium has changed substantially over past decades. The toxic effects were recognised in the 1930's before its essentiality to organism health was recognised in the 1950's [11].

Selenium is an essential trace element for many living organisms, particularly humans and animals. In humans, selenium is an essential part of selenocysteine, an amino-acid essential for the formation of a number of selenoproteins which have important enzymic functions [12]. Selenium also has other important health benefits not associated with enzymatic functions such as cancer prevention and immune defence.

Despite the essentiality of selenium to humans and animals, it is also toxic in larger concentrations with selenosis the term usually used for problems associated with toxicity [10].

The region between deficiency and toxicity of selenium is considered to be one of the narrowest out of the trace elements. This optimum range is thought to between 40-400 µg day^{-1} [13].

1.3 Objectives

The objectives of this thesis are to:

- Develop and adapt a suitable and reliable method for determining the total extractable levels of both iodine and selenium from Waikato soils,
- Provide an updated status of the iodine and selenium concentrations in Waikato Soils, and
- Identify possible relationships between the concentrations of these elements with other soil factors.

2 Literature Review: Iodine in Soil

2.1 Introduction

Iodine was discovered in 1811 when it was sublimed from ashed seaweed using concentrated sulfuric acid [14]. It is a member of Group 17 on the periodic table with the atomic number 53 and relative atomic mass of 126.9. There is only one naturally occurring stable isotope, ^{127}I, and 36 known radioactive isotopes.

Iodine is an essential trace element for animals and humans with sources of food often having deficient concentrations of iodine for optimum health. This deficiency in food ultimately results from a deficiency in its source, often the soil from which it is grown in.

Despite being an essential trace element, there is very little information available on the quantities and characteristics of iodine in soils [15], particularly in respect to New Zealand soils.

2.2 Geochemistry of Iodine

The geochemistry of iodine is well established, because of its importance as an essential trace element. The chemistry of iodine is rather complex because of the many oxidation states iodine can exist in (-1, 0, +1, +3, +5 and +7). These various oxidation states lead to iodine being capable of existing in a range of ionic forms in the soil [16]. Despite this the most common forms of iodine appear to be the simple and stable forms of iodide (I^-) and iodate (IO_3^-) [16].

Iodine is the largest known mono-atomic univalent anion (I^-) with a radius of 2.20 Å. It is highly polarisable making it favourable to substitutions with minerals containing a hydroxyl group [17]. This substitution is possible due to the similarity in structure between iodides and hydroxides of many divalent metals. This may account for the relatively high concentrations found in many silicates containing a hydroxyl (such as muscovite) and some hydroxides of iron [17].

The overall distribution of iodine in the environment is similar to that of its other halogen relatives, chlorine and bromine [16, 17]. As is the case with these elements, the distribution of iodine is largely concentrated in the oceans [17], with an average concentration of 45-60 μg L^{-1} (ppb) in seawater [14, 18, and 19].

Marine sediments contain the largest reservoir of iodine with up to 70% of global iodine considered to be contained within these [16].

Iodine, considered a biophilic element, is strongly involved in biological processes. The large concentration of iodine in marine sediments is thought to reflect this due to the uptake of iodine by plankton [16], which would ultimately be deposited to the sediments. Iodine has also been shown to be correlated strongly to the organic carbon content of sediments, as iodine is strongly fixed to organic matter [16].

In comparison to the ocean, the iodine content of the terrestrial environment and lithosphere is generally much lower with most commonly occurring rock types rarely exceeding 6 mg kg^{-1} iodine [16]. This leads to the terrestrial environment being prone to deficiencies in iodine unless the sources of iodine are sufficient to prevent deficiency.

Iodine has also been suggested to be chalcophilic, in that it is associated with sulfur [20]. This relationship was used to speculate why iodine is low in the terrestrial environment, as the earth cosmic component of sulfur has mainly been fractionated to the earth's core and in doing so would have removed the iodine as well [21].

2.3 Sources of Iodine in Soil

The natural iodine content of soil is a result of the inputs over the course of its formation and the soil's ability to retain iodine from processes that lead to the loss of iodine from soil [19].

Iodine in soil can be derived from a range of sources. Significant sources are considered to be: atmospheric deposition, the weathering of parent materials, and agricultural practices.

Losses of iodine from the soil result from processes such as volatilisation, plant uptake, removal of produce, desorption from soil particles and leaching.

A simplified view of the iodine cycle displays the cycle of iodine through the environment, from the ocean and ultimately to the land (Figure 2-1).

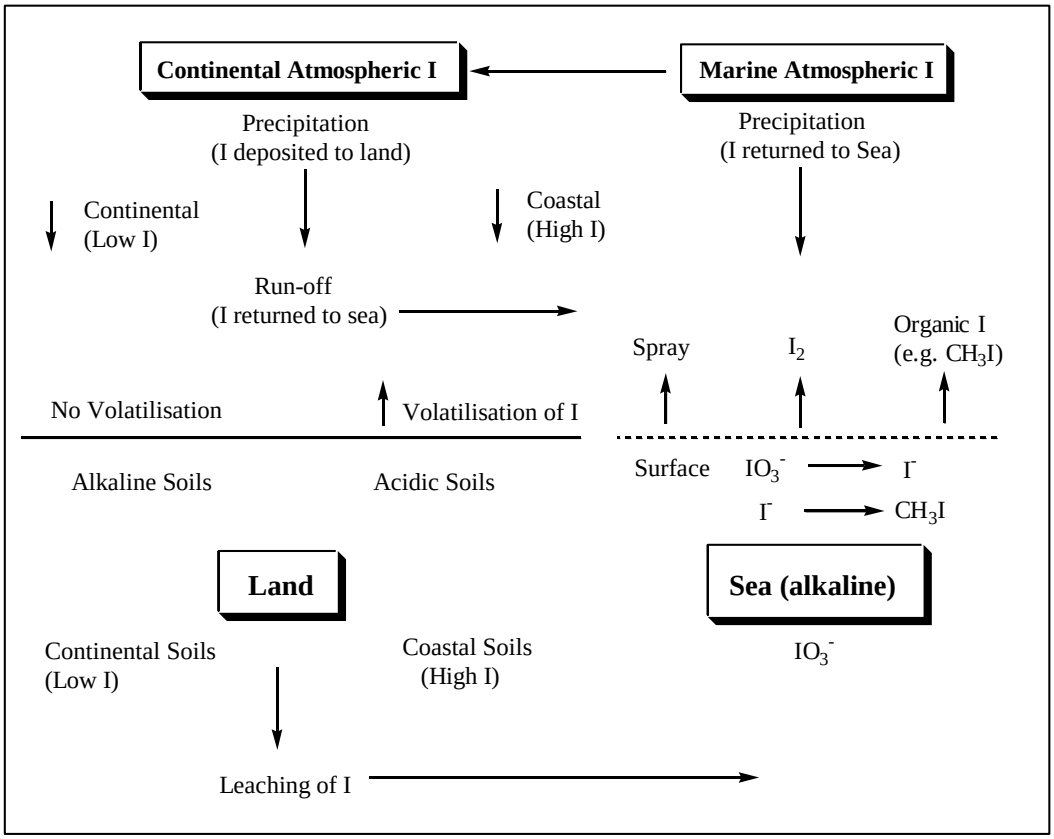

Figure 2-1 - The simplified cycle of iodine in the environment. Arrows indicate the movement of iodine. Adapted from Essentials of Medical Geology, R.Fuge (2005) [22].

2.3.1 Atmospheric Deposition

The largest source of iodine to the terrestrial environment is considered to be atmospheric deposition of iodine derived from seawater [23]. The action of sea spray would account for some of this, however, the transfer of iodine to the atmosphere directly via sea spray does not account for the larger I/Cl ratio in the atmosphere comparable to the ocean [14, 24]. If the inputs of iodine to the atmosphere were directly from sea spray, it would be expected that the I/Cl ratio would reflect the ratio seen in the water of the ocean. Therefore there are other mechanisms causing iodine to be introduced to the atmosphere.

It was suggested that there is an organic-rich film present on the surface of seawater [25] from which iodine enriched aerosols are derived [24], reflecting iodine's strong affinity towards organic matter.

More recently it was suggested that iodine was transferred to the atmosphere as methyl iodide (CH_3I) formed as a result of biological processes carried out in the ocean surface [19].

In New Zealand, it was found that 40% of the iodine in rainwater was organically bound [26], reflecting this possible contribution of iodine from biological processes and the affinity to organic matter.

The photochemical oxidation of I^- to I_2 is also thought to be responsible for volatile iodine released to the atmosphere. This occurs after the reduction of the thermodynamically stable IO_3^- to I^- in the surface of the ocean [23].

Once airborne, atmospheric iodine is primarily deposited on land via precipitation. There is suggestion that the amount of iodine deposited to soils is dependent on rainfall volume and distance from the sea [14, 16]. Coastal soils are expected to be enriched in iodine due to the close proximity to the sea [16], with inland continental soils generally considered the most likely to be deficient.

2.3.2 Weathering of Parent Materials

The iodine concentrations of parent materials in the lithosphere are generally lower compared to those found in the overlying soil.

Soil formation is largely a result of the weathering of parent materials; therefore a small amount of soil iodine would be derived from these sources. However, there is suggestion that weathering of rocks actually removes iodine, with the enrichment in iodine of weathered rock materials being due to atmospheric deposition [14, 17].

A summary of the iodine contents can be found in Table 2-1, with most common rock types containing less than 2.7 mg kg^{-1} of iodine.

Recent sediments show the only significant enrichment in iodine, thought to be largely due to the high organic matter content [14].

Table 2-1 -Iodine contents of some common rock types [14, 22].

Rock Type	Iodine Content (mg kg^{-1})
Igneous	0.25
Sedimentary	2.3
Sandstones	0.8
Carbonates	2.7
Recent Sediments	5 - 200
Rock phosphate (Germany)	440

These further display the importance of atmospheric deposition in providing an input of iodine to soil, as common rock types typically contain small amounts of iodine.

The main influence of the parent material on soil iodine concentration is through its ability to retain iodine deposited from the atmosphere from the soil characteristics unique to the material the soil is derived from [19].

2.3.3 Agricultural sources (anthropogenic iodine)

Sources of iodine in agricultural practices such as fertilisation and application of herbicides and pesticides are widely variable and often very low [19]. These types of sources are considered anthropogenic as they originate from man-made practices.

Iodine is found in a small number of herbicides and pesticides, such as Ioxynil, Iodofenphos and Benodanil [27]. The decomposition of these chemicals would release iodide to the soil in amounts dependent on the application rate. However, Iodofenphos and Benodanil are now listed as obsolete, while Ioxynil is still currently used as a herbicide [28]. In New Zealand, Ioxynil octanoate, product name: Totril® Super or Iotril® [29, 30], is used as a selective herbicide for use in onion and garlic crops and also turf grass. The use of Ioxynil is likely to only be limited to a subset of horticultural land based on its intended use as a herbicide.

Fertilisers are considered to be the largest contributor of iodine to soil of the agricultural practices. Superphosphate fertilisers derived from rock phosphate (also known as apatite), have been reported to contain up to 26 mg kg^{-1} [15]. This could be expected with rock phosphate containing up to 440 mg kg^{-1} of iodine [14].

Seaweed based fertilisers can also contain considerable amounts of iodine since seaweed is reported to contain up to 5400 mg kg^{-1} iodine [15].

2.3.4 Volatilisation

Volatilisation of iodine from soil may result from either chemical or microbial processes.

Volatilisation of iodine during soil drying is generally negligible for soils with a pH greater than 5 and organic matter greater than 3%. It is considerable for acid soils (pH <5) low in organic matter [19].

Volatilisation of organic iodine compounds as a result of microbial processes may occur in moist soils, and when conditions are favourable for microbial activity [19].

The loss of iodine through volatilisation is greatly dependent on the soil type. Iodine was completely lost from a sandy soil over a 30 day period, whereas other soil types reported minimal loss over the same period [31]. It was also found that the retention of iodine by organic matter is considered to have the greatest influence on reducing the loss through volatilisation, with the clay minerals closely following [31].

2.3.5 Plant Uptake and Removal of Produce

Living vegetation removes iodine through uptake from the soil solution. Plant uptake can be considered a way of retaining iodine in the soil if that biomass is returned to the soil. However, for the case of agriculture and horticulture, the removal of produce would result in a loss of iodine from the soil [19].

However, there has been no strong relationship found between the iodine concentration in plants and the iodine content of the soils they grow in. Therefore the actual uptake of iodine by plants varies considerably, and may depend on soil conditions, concentrations and forms of iodine, and the species of plant grown [14].

2.3.6 Desorption and Leaching

Leaching of iodine is considered to be the most important pathway for iodine loss from the soil. Iodine can be mechanically and chemically transported from the soil by the action of water movement. This water movement will cause both horizontal and vertical movement of iodine in the soil [14].

The factors which fix the iodine from the soil solution, protecting iodine from leaching are thought to be of great importance. Therefore if factors are changed such that desorption of iodine from soil particles occurs, more iodine is likely to be lost than through the process of leaching alone [14].

Soil pH is considered an important factor in iodine desorption with an increase in pH considered to increase the iodine desorption [19]. This

could be thought of as being due to competition between hydroxide and iodide (or iodate) at surface sorption sites.

Application of lime and phosphate fertilisers has been shown to increase the uptake of iodine by plants due to desorption of iodine from soil particles making it more available for plants [19].

2.4 Iodine in Soil

An understanding of the iodine content of soils and the factors that may influence the supply of iodine to crops has become more important in recent years [15].

The iodine content of soils around the world varies with location and soil type, with a world-wide average in soils thought to be in the range of 4-8 mg kg^{-1} [14]. Other estimates also point towards a mean value within this range, of 5 mg kg^{-1} [14, 32]. Despite this relatively low average content some peat soils in the United Kingdom (U.K.) have been reported to contain up to 98 mg kg^{-1} and some soils in Wales to contain up to 149 mg kg^{-1} [27, 33].

The parent material that the soil has formed from has an effect on the iodine content of soils. A summary of iodine content of soils derived from various parent materials in the U.K. is given in Table 2-2.

Table 2-2 - Iodine content of soils derived from various parent materials [14, 22].

Category of Parent Material	Mean Iodine Content (mg kg^{-1})	Range (mg kg^{-1})
Acid igneous rocks and associated till	10.4	4.4-15.7
Till associated with basic igneous rocks	10.9	3.4-16.3
Slate, shale and associated till	9.8	4.4-27.6
Sand and sandstone	3.7	1.7-5.4
Chalk, limestone	12.3	7.9-21.8
Clay	5.2	2.1-8.9
River, and river terrace alluvium	3.8	0.5-7.1
Marine and estuarine alluvium	19.6	8.8-36.9
Peat	46.8	18.7-98.2

Some Japanese soils have also been found to contain high levels of iodine. These soils, typically Andosols, are thought to contain high levels of iodine due to the high adsorption capacity due to the presence of allophane.

The direct influence of the marine environment and high rainfall in Japan is also suggested to account for these higher concentrations, through increased deposition of iodine [34].

2.4.1 Forms of Iodine in Soil

The chemical forms of iodine in soil will determine the availability to plants. Forms that are soluble or easily leached will be the fraction of iodine that is most readily available to plants and hence the food chain [22].

Studies of Eh-pH diagrams indicate that the most likely forms of iodine in the natural environment are iodide and iodate. Iodide is the dominant form of iodine in acidic soils with iodate the dominant form in alkaline soils [22]. This is evidence that pH is the main factor governing the inorganic forms of iodine in soil.

It is suggested that there may be other forms of iodine present and associated to various different fractions in soil but the low concentration of these species makes them difficult to identify directly [14]. This has lead to a generalised view of what may comprise the total iodine in the soil and the fractions of soil that iodine may be found in (Figure 2-2).

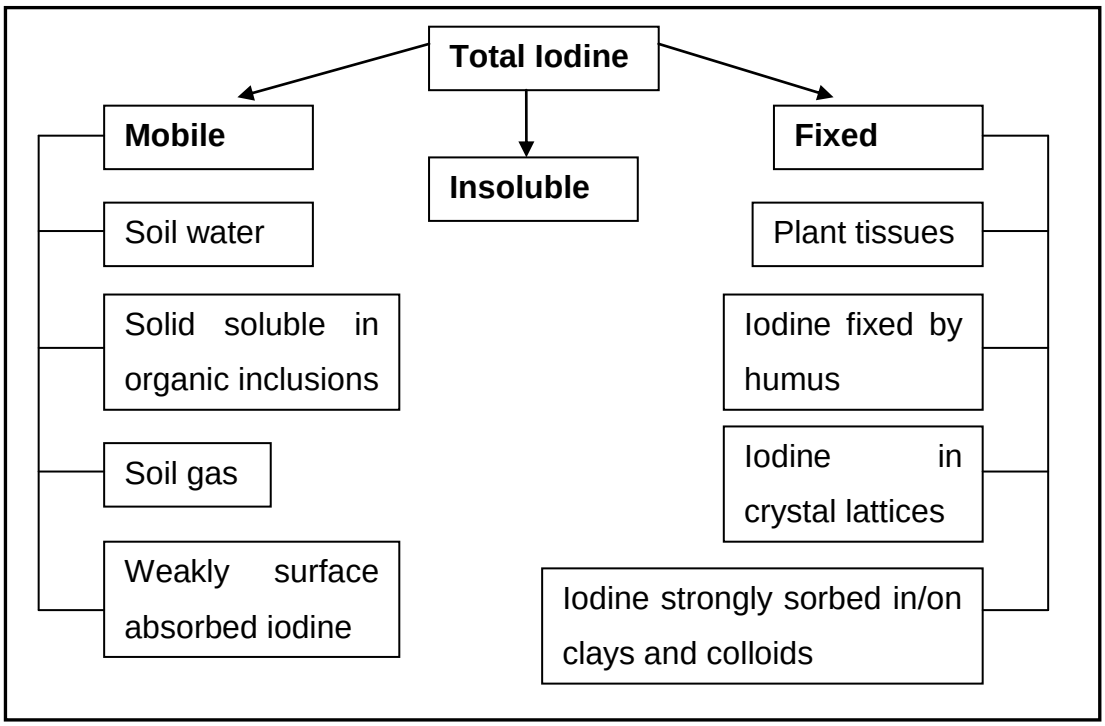

Figure 2-2 - Soil components that forms of iodine are suggested to be associated with [14].

The main mobile forms of iodine suggested to occur in the aqueous phase of soil are: I^-, IO_3^- [16].

2.4.2 Factors Influencing the Iodine Content of Soil

Iodine can be strongly adsorbed by various soil components within the soil. Therefore its concentration and behaviour in the soil will be dependent on soil composition, which in turn is strongly influenced by the parent material composition. Thus it is suggested that the parent material composition indirectly influences the iodine chemistry in soil [22].

It has been found that the most important controls on the iodine content of soils are the supply of iodine and the ability of the soil to retain it, termed the iodine fixation potential [14]. Soils with a low iodine supply and a low fixation potential will naturally have less iodine than a soil with a high fixation potential and high iodine supply, as illustrated in Figure 2-3.

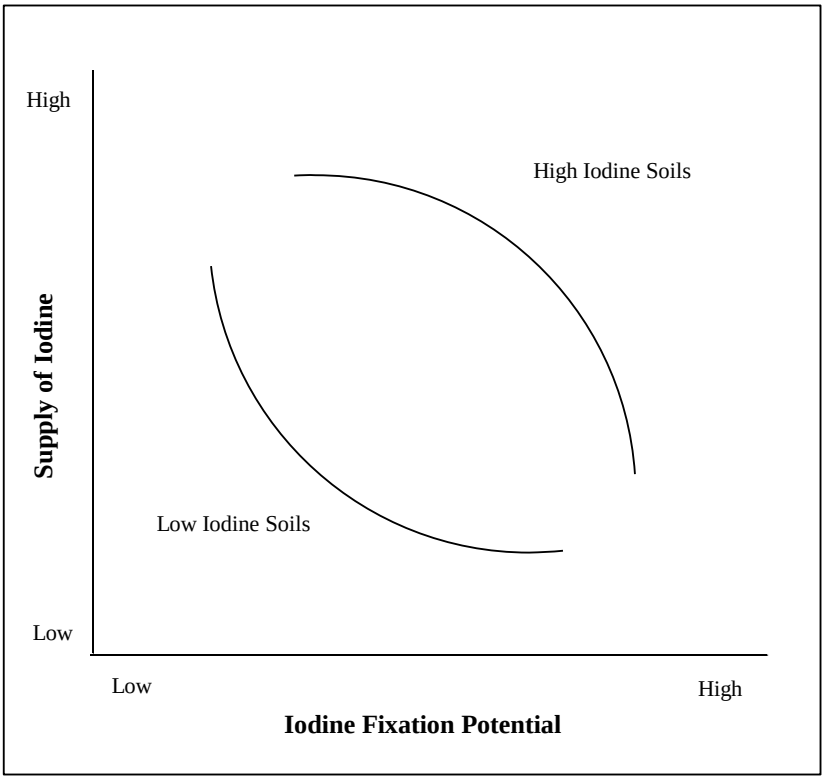

Figure 2-3 - A simple model for the iodine status of soils based on iodine supply and the soils fixation potential [14].

Organic matter is thought to be an influential soil component in regard to retaining iodine, with soils rich in organic matter generally enriched with iodine. Thus the iodine concentration in soil is thought to correlate with the organic matter content [22]. It has also been shown that iron and aluminium oxides play an important role in soil iodine retention by the

sorption of iodide and iodate [35]. This is further supported by the findings that iodine is enriched in iron-rich soils of the U.K [22].

Iodine sorption by iron and aluminium oxides strongly depends on soil pH, with sorption greatest in acid conditions (low pH), typical of anion adsorption [22]. Clay minerals have also been suggested to be involved in retention of soil iodine with this retention also pH dependent [22]. However, this is now thought to be relatively unimportant compared to the actions of organic matter [22].

Another important factor to consider is the geological age of a soil. Soils that are generally young, such as those derived from recent glaciations, are generally iodine poor as they have not had the timeframe to accumulate iodine from the atmosphere [16, 17]. However, recent research suggests that iodine in soils equilibrates to its surrounding environment relatively rapidly and it is unlikely that glacial soils are still under-saturated with iodine [36].

2.5 Iodine in New Zealand Soils

New Zealand has long been considered a naturally low iodine environment [37]. There are a number of literature sources stating that the iodine content of New Zealand soils is low [2, 38] however, this appears to originate from articles published in the early 1900's [37, 39].

The results from these studies largely centred on the investigation of goitre, a problem in New Zealand at the time. A summary of the iodine soil contents from various reports [37, 39, 40] are displayed in Table 2-3. This appears to be the most detailed work prior to this project covering the iodine content of soil in New Zealand.

Table 2-3 – Summary Statistics on the Iodine content of New Zealand and Waikato Soils, based on research conducted between 1925-1931*.

	All NZ Soils (N=427)	Waikato region soils (N=35)
Mean	7.4	22.3
Geometric mean	1.9	6.3
Median	1.5	8.0
Standard Deviation	15.0	31.1
Minimum	0.1	0.1
Maximum	135.0	135.0
Upper 95th Percentile	34.4	80.6

Data expressed in mg kg^{-1}.

*- Data reanalysed for the present work using analyses from various reports [37, 39]. All the data from these reports is also summarised in a more recent report [40].

2.6 Methods of Determination

There is limited information on the quantities of iodine in soils globally. This is due to various reasons including analytical methodology that is difficult and tedious [15], and also a lack of analytical techniques capable of measuring trace quantities of environmental iodine [41].

ICP-MS is one on the most sensitive analytical techniques for determining iodine and has been applied to environmental samples more frequently in recent years [41].

Neutron activation analysis (NAA) is another sensitive technique for determining trace quantities of iodine [42]. However, it requires a source of neutrons to irradiate the target elements before its radioactive decay is measured.

Currently, ICP-MS and NAA are the principal techniques used for sensitive multi-element determination of environmental samples [43].

2.7 Summary

Iodine is generally less concentrated in the terrestrial environment compared to the ocean. Therefore soils usually contain low levels of iodine as the parent materials soils are formed from have low iodine contents.

Iodine exists predominantly as the anionic forms of iodide and iodate and is considered to have strong involvement in biological processes. The involvement of iodine in biological process, and its ability to volatilise cause atmospheric deposition to be considered the main source of iodine to the terrestrial environment.

The dominant aspects of iodine that govern its environmental behaviour are its ability to volatilise, involvement in biological processes and its affinity for organic matter. The retention of iodine by aluminium and iron oxides also contribute to its environmental behaviour, with soil type influencing the ability of that soil to retain iodine.

3 Literature Review: Selenium in Soil

3.1 Introduction

Selenium, discovered in 1817, is found in Group 16 of the periodic table between sulfur and tellurium.

Selenium is an essential trace element for many plants and animals. However the focus of early investigations was on its toxicity. In 1933 it was shown that selenium was responsible for the poisoning of animals grazing on herbage of the Great Plains of the United States of America. This finding resulted in a large amount of analytical work being carried out relating to the distribution of the selenium in the environment [17]. This consequently led to the discovery during the 1950's that selenium deficiency was detrimental to the health of animals [11].

It is now known that selenium affects the health of humans and animals with either insufficient or excess intakes [11, 12, 44]. The actual range between selenium being deficient and toxic is one of the narrowest of all the essential trace elements. For this reason selenium has been described as a 'two-edged sword' [45].

3.2 Geochemistry of Selenium

Selenium occurs naturally in many rocks and minerals and is chalcophilic with its main geochemical behaviour similar to that of sulfur. The ionic radii of the Se^{2-} (1.91 Å) and S^{2-} (1.74 Å) ions are similar enough to permit substitution of selenium in to the sulfide lattice [17] probably explaining why it is classified as a chalcophile. Because of this substitution, selenium is commonly found in sulfur-rich deposits and environments [16].

However, many types of rocks contain selenium, with the average content of selenium in the lithosphere considered to be 0.09 mg kg^{-1} [46]. Chemical weathering of these rocks and minerals within the lithosphere releases selenium into the soil. A summary of the average selenium content of some common found rock types is presented in Table 3-1.

Table 3-1 - Selenium content some generalised common rock types [13, 16].

Major Rock Type	Selenium Content (mg kg^{-1})
Ultramafic	0.02 – 0.05
Mafic	0.01 – 0.05
Igneous	0.35
Limestone	0.03 – 0.1
Sandstone	0.05 – 0.08
Shales	0.05 – 0.06
Mudstone	0.1 – 1500
Carbonate	0.08
Phosphates	1 - 300

Atmospheric deposition of selenium compounds derived from the sea can also contribute to the selenium concentration of soils [47]. The concentration of selenium in the oceans is very low (30-200 ng L^{-1} (ppt)) [48], however the selective uptake and biotransformation of dissolved selenium in seawater by phytoplankton is considered a major pathway for the emission of selenium to the atmosphere and hence the terrestrial environment [49].

Selenium has six naturally occurring isotopes as characterised by their abundance in Table 3-2.

Table 3-2 – The naturally occurring isotopes of selenium and their relative abundances.

Selenium Isotopes	% Abundance
^{74}Se	0.87
^{76}Se	9.02
^{77}Se	7.58
^{78}Se	23.52
^{80}Se	49.82
^{82}Se	9.19

3.3 Soil Characteristics of Selenium

3.3.1 Additions and Losses of Selenium in Soil

The selenium in soil originates from a number of sources that can be classed into various categories. These are lithogenic, pedogenic, atmospheric, phytogenic, and anthropogenic. These categories and corresponding examples of sources are displayed below in Table 3-3.

Table 3-3 - Categories of the possible sources of selenium in soil [16].

Category	Selenium Source
Lithogenic	Weathering of parent materials, which are variable in selenium content.
Pedogenic	Enrichment in certain horizons due to fixation, source for lower horizons.
Atmospheric	Deposition via rainfall, volcanic exhalation (tephra), gaseous forms originating from volatilization from sea and soil surfaces.
Phytogenic	Volatilization by plants or microorganisms, which can be re-deposited, also burning of seleniferous (high Se) vegetation.
Anthropogenic	Agriculturally sourced – fertilisers, foliar sprays, seed treatments, selenium prills, stock supplements. Industrial Sourced – fly ash, wastes.

One of the main contributors of selenium in soil is the weathering of parent materials in the soil-forming process [50]. If this process was the dominant source of selenium in soil, it would be expected that the concentration in soil would reflect the concentration of the parent materials. This is not always the case because of the possibility of other sources of selenium.

Volcanic exhalation, such as tephra fallout can be a source of selenium. The tephra erupted from Mount Ruapehu in the eruptions in 1995 and 1996 covered 25000 km^2 of surrounding land [51]. The selenium content of this tephra ranged between 2-4 mg kg^{-1}. However, of this, only approximately 0.1 mg kg^{-1} of selenium was considered to be water-soluble

or immediately available for plant uptake [51]. The remaining selenium would be considered to be a source to the soil.

The discovery of selenium deficiency in arable and agricultural land has lead to the use of selenium fertilisers or prills to provide the soil with sufficient selenium for animals and humans [52]. This addition of selenium to the soil is anthropogenic and has been occurring for a very short time period compared to the other processes. Alternatively, selenium can be given directly as an animal supplement, either as a drench, injection or a slow release capsule [53]. This would act as a source to the soil through animal excreta, as not all of the supplement would be readily used by the animal.

Other fertilisers can contain significant amounts of selenium. Phosphate deposits from around the world can contain up to 55 mg kg^{-1} of selenium [54]. There is also report of rock phosphate from Idaho, America, containing 178 mg kg^{-1} selenium [55]. Fertilisers derived from these rock phosphates would act as a source of selenium to soils, although the manufacturing process involved in the production of phosphate fertiliser results in some loss of selenium through volatilisation [56]. Phosphate fertilisers in New Zealand were previously manufactured from rock phosphate sourced from Nauru, but are now mostly from North Africa [57]. Phosphate rock from Nauru contained less than 0.8 mg kg^{-1} selenium [54], with phosphate rock from North Africa containing between 3-25 mg kg^{-1}, selenium [56].

A main pathway for the loss of selenium in soil is the leaching of mobile forms of selenium (mainly selenate) from the soil profile. Selenate is weakly adsorbed to the soil and is therefore easy leached [58], during drainage from rainfall or irrigation [52].

Microbial volatilization provides another pathway for the loss of selenium from soil. Microbial activity produces volatile selenium compounds such as dimethylselenide $(CH_3)_2Se$, which are subject to losses [59].

A summary of these additions and losses of selenium in soil are shown in Figure 3-1.

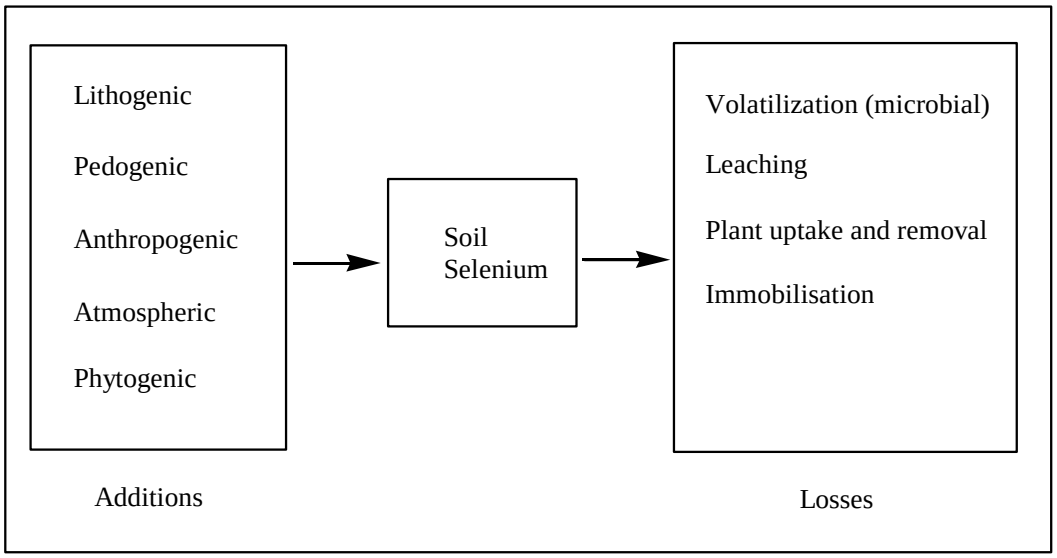

Figure 3-1 – Possible additions and losses of soil selenium.

3.3.2 Chemical Forms of Selenium in Soil

There are various different chemical forms that selenium takes in soil, all differing in solubility and bio-availability. These forms are: selenide (Se^{2-}), elemental selenium (Se^{0}), selenite (SeO_3^{2-}), selenate (SeO_4^{2-}), and organic selenium [58]. The soil type and various factors within the soil greatly affect the bio-availability of selenium to plants and hence animals, with the most important factors considered to be fixation capacity, pH and microbial activity [59]. The form and species of selenium also affects the mobility and availability in the soil.

Selenates are mobile in inorganic forms in alkaline soils, as they are not adsorbed on hydrous sesquioxides [16]. Selenate is a metastable, mobile anion, with a similar behaviour to sulfate (SO_4^{2-}) [47]. Selenite on the other hand is slightly mobile in ordinary neutral or acid soils of humid temperate regions and easily adsorbed on hydrous sesquioxides and organic matter [16]. This form of selenium, which mostly occurs as $HSeO_3^-$, is the main inorganic form expected in the acidic soils typically found in New Zealand [47]. Selenides (Se^{2-} compounds) are considered immobile in acid soils as they form stable mineral and organic compounds [16].

These different forms have different availabilities to plants. Selenate is the most available, followed by selenite, with elemental selenium (Se^0) and selenides considered not being available to plants [50].

3.3.3 Soil Factors Controlling Selenium in Soil

It is suggested that the average level of available selenium in a soil is the product, over pedological time, of the various soil-forming factors [50]. Therefore, increased weathering, which ultimately results in an increase in the clay content of soil, gives an apparent increase in the total selenium. This is further backed up with selenium being retained in the clay fraction relative to other elements in the topsoil during pedogenesis [50]. Thus soil formation and soil type are factors which cause the availability of selenium in soil to differ [59].

Several soil factors are major contributors to the mobility and availability of selenium in soil. Soil properties, such as pH and redox potential, have a large influence on the chemical form of selenium in soil [50]. A high redox value (more oxidising environment), and a pH of 7 results in selenate being the major species present in soil (Table 3-4). Conversely, when either the pH or redox potential decreases the major form of selenium changes from selenate to selenite. Furthermore, low redox potentials and low pH values yield selenides [16]. This would be a major factor when considering soils that have intermittent high water tables. The change in the water table of these soils would act to change the redox conditions of that soil [60, 61], which in turn would contribute to a likely change in selenium species. Soils affected by this would most likely be peat based soils, or low-lying soils prone to flooding.

Table 3-4 - Impact of soil conditions on the formation of soluble selenium species [16].

Redox (Eh, mV)	Value	pH	Oxidation State of Se	Major Se Species in Soil solution
High		7	+6	SeO_4^{2-} (Selenates)
>400		<2	+6	SeO_4^-
Moderate		>7	+4	SeO_3^{2-} (Selenites)
200-400		<7.3	+4	$HSeO_3^-$
Low		>3.8	-2	HSe^- (Selenides)
<200		<3.8	-2	H_2Se

Selenite anions are strongly absorbed to iron and aluminium oxides and clay minerals, effectively removing them from the soil solution [47]. In contrast, selenate anions are not adsorbed to iron and aluminium oxides and clay minerals and are usually more available to plants.

Soil organic matter has a greater fixation capacity for selenite than clay minerals; however, the nature of the fixation is different. The selenium in this organic fraction is considered to be largely associated with organic compounds or it is built in to amino acids (selenomethionine and selenocysteine) and proteins by microbial activity or plants [59]. However, very few of these organic compounds have been isolated and identified [13].

Soil pH plays a major role in determining the availability of selenium in soils. The solubility of selenium is lowest when the pH is slightly acidic to neutral, with the solubility of selenium increasing as the pH increases. This could be the result of the adsorption capacity of clay minerals and iron oxides decreasing as the pH increases [59].

As a result of this decrease in adsorption capacity, more selenium is available in the soil solution when the pH increases. The addition of lime ($CaCO_3$) is also reported to increase the selenium availability, as would be expected because this addition would act to increase the pH of the soil [62].

It is also suggested that a decrease in soil pH will cause a net increase of positive charge in the soil, which will act to adsorb the negatively charged selenate, and selenite anions. This action may result in a decrease in selenium availability [62].

Other soil factors such as cation exchange capacity (CEC) and organic matter content have all been attributed to affecting selenium adsorption in soils [58]. These factors indirectly affect the chemical forms present in soil, which have different affinities to the selenium forms in the soil.

Microbial activity in soil can adsorb available selenium fixing it into biomass. They can also act to transform strongly adsorbed selenite into more readily available selenate or soluble selenium compounds. However, microbial activity can also produce volatile selenium compounds (for example, dimethylselenide $(CH_3)_2Se$), which are subject to losses via volatilization [59].

The broad geographical variation of selenium content in soil reflects the variations in the selenium content of parent material. The weathering of this parent material is in turn dependent on a number of factors such as temperature, moisture and texture [52].

Soil factors control the chemical form of selenium in soil, which in turn controls the mobility and availability of selenium to plants and animals. Thus, selenate, which is the predominant form of selenium under ordinary alkaline and oxidising environments, is the most readily available to plants. This is followed by selenite, which is present in mildly oxidising, neutral pH environments found in many humid regions [58]. Based on this, in typical soil systems, it would be expected that selenite would be the predominant form of selenium in New Zealand soil, which would be largely associated with the clay and organic fractions of the soil.

Table 3-5 summarises a number of soil factors and the corresponding form of selenium and mobility associated with each factor.

Table 3-5 - Soil factors affecting the form and mobility of selenium [16].

Soil Factor		Se Form	Mobility
pH:	High (alkaline)	Selenates	High
	Medium (neutral)	Selenites	Moderate
	Low (acid)	Selenides	Low
Eh:	High	Selenites	High
	Low	Selenides	Low
Hydroxides (Fe, Mn):			
High content		Adsorbs all forms of Se	Low
Low Content			High
Organic Matter:			
Undecayed		Absorbed	Low
Decayed (e.g., peat)		Complexed	High
Clays:	High content	Absorbed	Low
	Low content	Not fixed	High

3.4 Ranges of Selenium Concentration in Soil

The selenium content of soils has received much attention in many countries worldwide. This has produced estimates of the worldwide surface soil concentration between 0.1 – 2 mg kg^{-1} [63], with others estimating the average worldwide soil concentration to be 0.33 mg kg^{-1} selenium [16], and 0.4 mg kg^{-1} [13].

Low selenium soils typically result from weak weathering of acid parent rock, in cool, humid regions of the world [64].

The range of selenium concentrations of surface soils vary greatly between soil types and country of origin (Table 3-6). This may indicate other factors such as climate and location which influence the selenium content of soil.

Table 3-6 - Total selenium content in soils from various regions of the World [13, 52].

Country/Soil	Selenium Concentration ($mg\ kg^{-1}$)
Worldwide average	0.1 – 2.0
New Zealand (General)	0.1 – 4.0
NZ, Semiarid Soils (Brown-grey earths)	0.12 ± 0.1
NZ, Podzols	0.37 ± 0.2
Worldwide, Orthic Humo-Ferric Podzol	0.06-1.8
Canada, Orthic Humo-Ferric Podzol	0.06-0.33
Finland, Podzols	<0.01-1.25
Denmark (general)	0.14-0.52
England/Wales (general)	<0.01 – 4.7
U.S.A (general)	<0.1 – 4.3
India (Se-deficient)	0.025 – 0.71
India (seleniferous)	2.5 – 69.5
China (general)	0.02 – 3.81
China (Se-adequate)	0.73 – 5.66
China (Se-deficient)	0.004 – 0.48
China (seleniferous)	1.49 – 59.4

3.5 Selenium in New Zealand Soils

The average total selenium content of New Zealand topsoils was reported to be 0.60 mg kg^{-1} in 1966 [5]. This was an update on the previous statement of the range of selenium concentrations in most New Zealand soils fell within 0.1 – 2.0 mg kg^{-1} [3]. It was also suggested that the soils prone to deficiencies were the ones containing less than 0.5 mg kg^{-1}, with very low selenium contents in soils considered to be less than0.3 mg kg^{-1} [3, 5].

The main Soil Orders in New Zealand, as classified by the New Zealand Soil Classification [65], that are the predominant selenium deficient soils are the Semiarid Soils (brown-grey earths), Pallic Soils (yellow-grey earths) and Pumice Soils (yellow-brown pumice) soils [66].

It is also reported that New Zealand zonal soils are low in selenium as they are derived from greywacke, an acidic rock naturally low in selenium [64]. Soil forming rock types were considered and grouped according to their selenium content in New Zealand [5].

Table 3-7 - Common soil forming rock types in New Zealand and their generalised selenium content.

Rock Type (NZ)	Selenium Content (Indicative only)
Granite and rhyolitic pumice	Very low
Ultrabasic, limestone and schist	Low
Mudstone, gneiss, sandstone, and greywacke	Average
Andesitic ash, calcareous argillite and basaltic ash	High

However, the parent material generally has less selenium than the overlying soil as the selenium contents in soils are increased as a result of weathering [5].

The central pumice plateau of the North Island is the site of extensive selenium deficiencies, which responded to administration of selenium [67]. It is also important to note that the highest incidences of selenium

deficiencies in New Zealand livestock were associated with improved pastures such as those rich in clover [67]. Plant species have the ability to take up different levels of selenium from the soil. It was found that in New Zealand soils browntop grass (*Agrostis tenuis* Sibth.) had the highest concentration of selenium, with white clover (*Trifolium repens* L.) having the least. Other grasses such as ryegrass (*Lolium perenne* L.) and cocksfoot (*Dactylis glomerata* L.) were between these two extremes [68].

It was proposed that in New Zealand the weathering intensity and soil texture may affect the selenium concentration of a soil. The degree of weathering was suggested to explain the soil texture, with less weathered soils having a higher sand content than more weathered soils which have a higher clay content. Based on soil texture, clay soils were found to have the highest selenium concentration with the sandy soils having the lowest [50].

The association of animal diseases with selenium deficiency in New Zealand soils has been well established, with approximately 6 million hectares considered to be at risk of causing selenium deficiency in young sheep and cattle [66].

Selenium deficiency was prevented in New Zealand by dosing or injecting stock with selenium [4], or by applying selenium to pasture by fertilisation, with New Zealand becoming the first country to permit this in 1982 [50]. Top dressing of permanently grazed pasture by addition of sodium selenate at rates of 8.5 g Se/ha were considered to raise blood selenium levels in sheep and cattle above deficiency levels for one year [50].

3.6 Methods of Determination

The discovery of selenium as an essential element for human and animals was recent. The lack of a sufficiently sensitive analytical method to determine selenium in low concentrations was one reason for this [59]. Since then a number of methods have been developed, with detection limits for various capabilities listed in Table 3-8.

Table 3-8 - Selenium detection limits for various instrumental techniques [69, 70].

Analytical technique	Detection limit (ppm)
ICP-AES	0.85
HG-AAS	0.02
NAA	0.05
GF-AAS	0.02
HG-ICP-MS	0.06
HPLC-ICP-MS	0.02-0.03
ETV-ICP-MS	0.40
ICP-MS	0.030
Fluorescence Spectroscopy	0.02

A hydride generation technique coupled to an atomic absorption spectrometer (HG-AAS) has been the most widely and commonly used method for a number of years. It can detect low levels of selenium of approximately 0.02 ppm [64]. Other methods include neutron activation analysis (NAA), fluorescence spectroscopy, gas chromatography (GC), X-Ray fluorescence spectrometry (XRF), inductively coupled plasma mass spectrometry (ICP-MS), and differential pulse cathode stripping voltammetry [59].

Fluorescence spectroscopy is a method using diaminonaphthalene, which reacts with selenious acid to form fluorescent complexes, which can then be extracted and detected [59]. This has been used successfully for the determination of low-level selenium previously [70], however, limitations with equipment meant this method was not investigated. This method has recently been coupled with a high performance liquid chromatography

(HPLC) instrument with a fluorescence detector to measure the fluorescence [71].

Although ICP-MS has been used in the past years to measure the levels of selenium in soils and biological samples, it has difficulties associated with polyatomic interferences with selenium isotopes. However, recent developments of reaction/collision cell ICP-MS have significantly improved the selenium measurement capability by reducing interferences [69]. ICP-MS is also the instrument of choice in many laboratories for trace element analysis. This was the main reason the ICP-MS analysis was chosen for investigation in this projcet.

3.6.1 Determination of selenium in soil fractions

It is important to know which fraction of soil the corresponding value correlates with when determining the concentration of selenium in soil. Total selenium is different to plant available selenium, with plant available selenium shown to be correlated with the concentration of selenate in the soil solution [72].

Total selenium may indicate the selenium status of a soil, with soils containing less than 0.06 mg kg^{-1} of selenium considered deficient for animals and humans [64]. However, total selenium has proved to be of little use in predicting the selenium available for plant uptake [59].

Various procedures have been designed for the fractionation and extraction of the five general forms of selenium in soil: selenates, selenites, organic selenium compounds, elemental selenium, and heavy metal selenides [72].

A sequential extraction procedure targets the selenium associated to various fractions in soil [62]. The reagents and targeted soil fractions associated with this type of extraction are displayed in Table 3-9.

Table 3-9 - Outline of a sequential extraction procedure for selenium in soil [62].

Reagent	Fraction	Availability (to plants)
1) 0.2 M K_2SO_4	Soluble – Selenate.	Available
2) 0.1 M KH_2PO_4	Exchangeable – Selenite adsorbed to hydrous oxides.	Potentially
3) 0.05 M NH_4OH	Soluble – Se associated with organic compounds, or selenite adsorbed to organic matter.	Potentially
4) 6 M HCl	Extractable – selenite occluded in sesquioxide particles, associated with amorphous material, selenium tightly to OM.	Unavailable
5) $HClO_4$ & H_2SO_4	Residual – all remaining selenium, including elemental, selenides, associated with sulphide minerals, complex humified organic matter, selenite occluded within silicate lattice. (Would be *total extractable* if only used this reagent from the start)	Unavailable

It was also found that the selenium availability pattern in untreated soils (soils not treated with fertilisers or anthropogenic practices) was: unavailable >> potentially available > available, while in selenium enriched soils the pattern was: potentially available > unavailable > available [62].

Other procedures have been used to extract different fractions of selenium in the soil. A similar sequential extraction procedure identified two exchangeable (available) and three non exchangeable selenium fractions using reagents very similar to those outlined in Table 3-9 [73].

Total selenium values are often determined using strong acid or alkali reagents that extract the selenium from all the various fractions outlined in Table 3-9.

In reality, it would be difficult to apply the sequential extraction technique for soils low in selenium because of issues with detection limits and sub-dividing already low numbers. The results may also be meaningless, as if

a soil contains very low levels of selenium, no matter what fractions the selenium is associated with the soil is likely to still have problems with deficiencies.

3.7 Summary

Selenium is an element that appears more concentrated in the soils compared to the parent materials that soil is derived from, although soils are usually low in selenium. Selenium can be added to the soil from a number of sources but the soil properties define the behaviour and retention of selenium in the soil.

Selenium may exist in a number of forms in the soil, defined by the soil properties, with selenite (SeO_3^{2-}) the form most likely in normal neutral to acid soils of humid temperate regions. This form of selenium is sorbed on to organic matter and hydrous sesquioxides.

The dominant factors influencing the behaviour of selenium in the soil environment would be the pH and reduction potential (defining the species selenium exists in) and the soil properties which influence the retention of selenium, particularly with respect to organic matter and iron and aluminium oxides.

4 Sample Information

4.1 Introduction

Environment Waikato monitors soil quality for State of the Environment reporting to determine the extent and direction of changes in soil condition. Carried out annually by Environment Waikato, this monitoring is required under the Local Government Act 2002 and the Resource Management Act 1991 [74].

The Waikato region is found in the North Island of New Zealand (Figure 4-1).

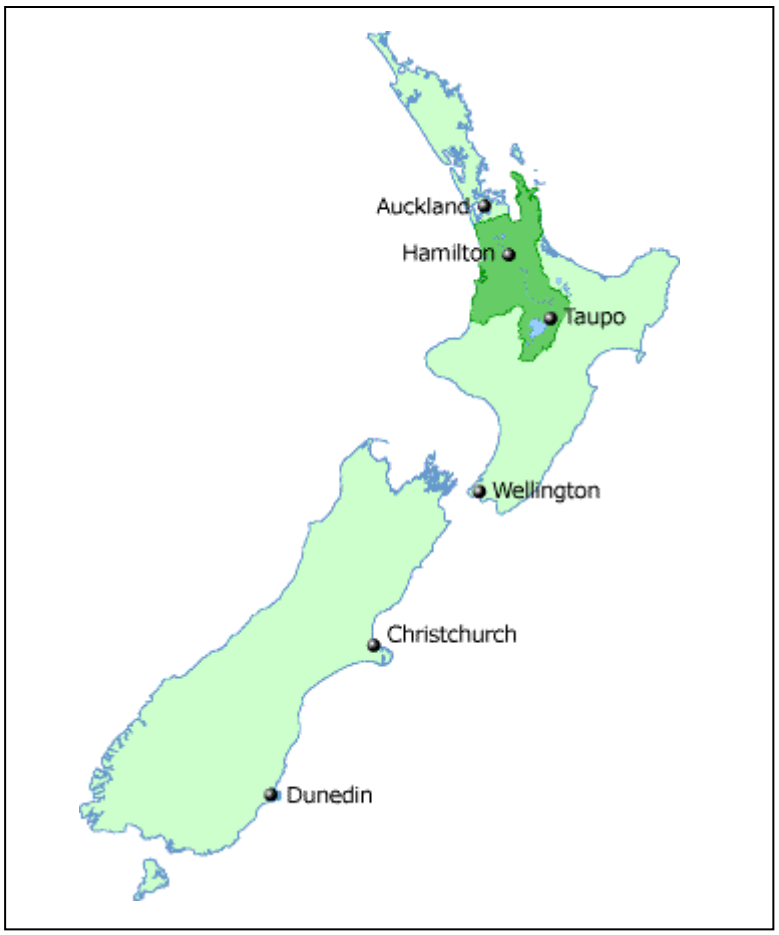

Figure 4-1 – Location of the Waikato region (Displayed in dark gray) in relation to New Zealand [74].

4.2 Soil Monitoring Sites

There are 140 soil quality monitoring sites in the Waikato region which Environment Waikato samples on a 5 year rotation.

Soil quality monitoring sites were chosen and sampled according to Land and Soil Monitoring: A guide for SoE and regional council reporting [1, 75]. Soils were classified according to the New Zealand Soil Classification [65]. Land use classes used were dairy (pasture grazed with milking cows), drystock (all other animal grazed pasture), arable (annual cultivation), horticulture (plants left in place), production forestry and background (native).

The land uses compared in this project were simplified to represent farmed, forestry and background soils. Farmed soils represented dairy, drystock, arable and horticultural soils.

Three one-off sub-regional transects across the Waikato region were also sampled. These transects were from Matamata to Raglan, Te Aroha to Huntly, and Huntly to Lake Whangape.

For confidentially purposes, the locations of the samples were withheld.

4.3 Sample Collection

Soil quality samples were collected as a composite of 50 soil cores (0 – 100 mm) collected from a 50 m transect across the sample location [76].

Sub-regional transect samples were collected based on a 2-km grid sample spacing, independent of land use or soil type. Grab samples were collected at two depths, 0-100 mm and 100-200 mm [76].

4.4 Previous Sample Analysis

Samples were analysed extensively through IANZ-accredited laboratories for various soil characteristics measured under the monitoring programme. The analyses carried out ranged from elemental composition to soil biochemical, chemical and physical properties (Table 4-1).

The samples used in this study had previously been collected and stored in plastic containers as air-dried, 2 mm sieved soil and were available for further analysis.

Table 4-1 - Previously collected soil information for the range of soil samples used in this study.

Soil Characteristics	Analyses
Elemental composition*	F, Al, Sb, As, Ba, Bi, B, Cd, Cs, Ca, Co, Cr, Cu, Fe, La, Pb, Li, Mg, Mn, Hg, Mo, Ni, P, K, Rb, Se, Ag, Na, Sr, Tl, Sn, U, V, Zn,
Physical properties	Total carbon, Total nitrogen, pH, Mineralisable nitrogen, Bulk density, Macroporosity, CEC, %C, %N, C:N, Olsen P

* Note: All elements were analysed for total acid extractable levels using the EPA 200.2 method [77], with the exception of fluorine. Total fluorine was determined using an alkali-fusion/ion-selective electrode method [78]. Full elemental analysis was also carried out using XRF analysis for a subset of samples.

5 Analytical Methods

5.1 Introduction

Analysis of trace elements by ICP-MS has become the method of choice in recent years based on the instrument's ability to analyse a range of elements simultaneously and its improved detection limit capabilities compared to other instruments [79].

Despite this, various elements remain difficult to analyse via ICP-MS because of interference problems within the instrument or from difficulties relating to the sample preparation.

Selenium analysis by ICP-MS is subject to isobaric polyatomic interferences derived from the ionising gas argon, which make analysing trace quantities very difficult. These interferences form within the ionising plasma torch of the ICP-MS. The interferences are typically due to the argon dimer ($^{40}Ar_2$) which has the same mass as the most abundant isotope of selenium (^{80}Se). Other interferences with the various isotopes of selenium are displayed in Table 5-1 [80]. Sources of interference ions may also arise from other constituents within the sample matrix (such as bromine, chlorine and sulfur).

Ideally the most abundant isotope is used for analysis as it has the greatest sensitivity; however, this is not always achievable if that isotope has major interferences associated with it (as in selenium).

Table 5-1 - Possible polyatomic interferences of the isotopes of selenium in the ICP-MS [80].

Isotope of Selenium	Possible Interferences
^{74}Se	$^{38}Ar^{36}Ar^{+}$, $^{37}Cl_2^{+}$, $^{40}Ar^{34}S^{+}$
^{76}Se	$^{40}Ar^{36}Ar^{+}$, $^{40}Ar^{36}S^{+}$, $^{31}P_2{}^{14}N^{+}$
^{77}Se	$^{40}Ar^{36}ArH^{+}$, $^{38}Ar_2H^{+}$, $^{40}Ar^{37}Cl^{+}$
^{78}Se	$^{40}Ar^{38}Ar^{+}$, $^{31}P_2{}^{16}O^{+}$
^{80}Se	$^{40}Ar^{40}Ar^{+}$, $^{79}BrH^{+}$
^{82}Se	$^{40}Ar_2H_2^{+}$, $^{34}S^{16}O_3^{+}$, $^{81}BrH^{+}$

Note: ^{40}Ar is the most abundant isotope of argon.

Soil samples to be analysed for inorganic trace element analysis by ICP-MS are commonly prepared in an acid matrix (typically HNO_3) [81]. This reflects the acid's ability to solubilise most trace elements. However, some elements may be prone to loss by volatilisation if extracted in an acid matrix. Iodine is one element that is so prone, due to the formation of gaseous HI. In order to avoid this, an alkaline extraction method is commonly used to extract iodine from solid samples. This also requires different conditions in the ICP-MS when analysing iodine compared to the conventional 2% HNO_3 matrix commonly used for most trace element analysis.

This project set out to use an acid extraction to analyse for selenium and an alkaline extraction for iodine.

However, selenium can also be extracted and analysed using the same method as analysing iodine. An alkaline extraction method (using tetramethyl ammonium hydroxide) has been used for both iodine and selenium analysis in some biological and soil samples [82-84]. For this reason the selenium concentrations were also decided to be obtained (and later validated) using the TMAH extraction during the same data acquisition stage as the iodine analyses.

This chapter outlines the methods used in attempt of determining the total concentrations of iodine and selenium. The validation of these methods proved to be a substantial part of this project and is also presented in this chapter.

5.2 Determination of Total Iodine in Soil

5.2.1 Tetramethyl ammonium hydroxide (TMAH) Extraction [85]

Iodine was extracted from the soil samples following a tetramethyl-ammonium hydroxide method used for the determination of total iodine in Japanese soils [85]. This extraction procedure most likely exploits the ability of hydroxyl (OH^-) to displace bound iodine.

A soil sample (0.25 g) was accurately weighed directly in to a 50 mL polypropylene tube with a screw cap. TMAH solution (5 mL of 5%) was added to each sample and the tubes were capped lightly. The samples were heated at 70°C for 3 hours using an extraction block capable of holding 50 mL tubes.

Samples were removed from the heat and diluted with deionised water in 25 mL volumetric flasks, giving a final concentration of 1% TMAH.

The diluted sample was centrifuged for 20 minutes at 4000 rpm.

A sample (5 mL) of the supernatant was transferred to a 15 mL polypropylene tube, by first filtering with a 45 µm syringe filter, and was analysed by ICP-MS.

Although the main intent of this extraction was for pseudo-total recovery of iodine, all the soil samples extracted using this method were also analysed for selenium.

5.2.2 Indicative Quality Control Solution

A 100 ppb potassium iodide (KI) solution was prepared as an indicative quality control solution during the ICP-MS analysis. The main purpose of this solution was to indicate any problems within the ICP-MS during the sample acquisition stage, such as calibration drift.

A 1000 ppm stock solution was prepared by dissolving 1.3093 g potassium iodide in 1 L of deionised water.

The 100 ppb solution was prepared by taking 0.1 mL of stock solution (1000 ppm) and diluting to 1 L with deionised water.

This solution was used approximately every 20-30 samples throughout each batch of samples. The values obtained were treated only as an indication of method performance and instrument drift as the solution was a different matrix to a soil sample and did not go through the same extraction procedure. The concentration of 100 ppb was chosen to minimise residual contamination of subsequent samples.

5.3 Determination of Total Selenium in Soil

The digestion and extraction of selenium from the soil samples was carried out based on two commonly used methods for trace element analysis of soil samples using ICP-MS. These were the EPA 200.2 and ISO 11466 methods.

Adaptations of these methods were also trialled in order to deduce their effectiveness. This primarily involved reversing the acid quantities used in the extraction. However, these adaptations did not improve the performance of the extractions compared to the actual methods stated below.

5.3.1 EPA 200.2: Sample Preparation for Spectrochemical Determination of Total Recoverable Elements [77]

Soil (1 g) was accurately weighed in to a 50 mL polypropylene tube. HNO_3 (4 mL, 1:1) and HCl (10 mL, 1:4) was added, the tube was capped lightly and placed on a digestion block heated to 70°C. The sample suspension was heated for 2 hours before diluting to 100 mL with deionised water in a volumetric flask.

The argon chloride ion ($ArCl^+$) is a polyatomic interference for the ^{77}Se isotope within the ICP-MS (Table 5-1). To reduce the chloride concentration the diluted suspension was further diluted by taking 10 mL and making it up to 50 mL with deionised water.

The diluted sample was then centrifuged at 4000 rpm for 20 minutes, before transferring 10 mL of filtered (45 µm syringe filter) supernatant to a 15 mL polypropylene tube ready for ICP-MS analysis.

5.3.2 ISO 11466: Extraction of Trace Elements Soluble in *aqua regia* [86]

Soil (0.5 g) was accurately weighed in to a 50 mL polypropylene tube. HCl (3 mL) and HNO_3 (1 mL) was added to the tube before capping lightly and standing at room temperature overnight. The suspension was heated on a digestion block heated to 70 °C for 2 hours before diluting in a 100 mL volumetric flask with deionised water. The diluted suspension was centrifuged at 4000 rpm for 20 minutes before 10 mL of the filtered (45 µm syringe filter) supernatant was transferred to a 15 mL polypropylene tube ready for ICP-MS analysis.

5.4 ICP-MS Analysis

Analyses were carried out on a Perkin Elmer Sciex ELAN DRC II ICP-MS. Calibration standards and matrices were unique for the two analytes targeted.

Acid extracted selenium samples required a 2% HNO_3 matrix, whereas iodine samples contained a 1% TMAH matrix. As noted above, selenium was also analysed during the iodine sample analysis as TMAH has been used as an extractant for selenium analysis in soil samples [82].

Calibration standards for both elements were also prepared in the respective matrix.

For the iodine analyses a SCP 1000 ppm liquid potassium iodide solution was used as the calibration standard with a 2% TMAH matrix.

Selenium analyses used a 2% HNO_3 matrix and a multi element Merck IV 50 ppb and 2000 ppb calibration standard. For the analysis of selenium in the TMAH extraction, the Merck IV multi element standard was prepared using 2% TMAH in place of 2% HNO_3.

5.4.1 DRC-ICP-MS

The Dynamic Reaction Cell (DRC) ICP-MS was trialled for the selenium analysis after conventional ICP-MS was not found to be acceptable for low-level selenium determination. Extractions of Certified Reference Materials (CRMs) (see Section 5.6) were used to assess analytical accuracy. Significant difficulties were encountered in achieving acceptable accuracy during ICP-MS method development for selenium. This largely was caused from interference problems within the ICP-MS. Lowering the chloride concentration of the sample matrix (as a secondary dilution step) was useful to a point, but further raises detection limit issues with samples containing low selenium because ^{77}Se is not the most abundant isotope. Interferences of the more abundant selenium isotopes also posed problems which limited their accuracy when using conventional ICP-MS.

Using a reaction gas within the DRC aims to minimise the polyatomic interferences produced within the instrument.

Various reaction gases (NH_3, CH_4, and O_2) were trialled in this project in an attempt of reducing interferences with the selenium isotopes. An overview of the results of the DRC work on both CRMs can be seen in Table 5-6 and Table 5-7 with the raw data displayed in Table A-1 and Table A-2 (Appendix 1).

Methane proved to be the most successful in reducing the argon interferences. This was also found in other literature where the argon dimer interferences were reduced by approximately five orders of magnitude [87, 88]. Methane appeared to reduce the interference of the argon dimer ($^{40}Ar_2$) enabling the most abundant selenium isotope (^{80}Se) to be analysed. This reduction of interference ions was inferred based on the improved accuracy obtained by analysis of the CRMs, particularly for the lower selenium concentration CRM.

Ammonia and oxygen gave no significant reduction in polyatomic interferences, although oxygen appeared to improve the recovery of one of the CRMs. The use of oxygen was limited to trying to reduce the immediate interferences of the selenium isotopes. It has been suggested

that oxygen could be used to form an oxide of selenium [89], as is used for the determination of sulfur by DRC-ICP-MS, where the oxide product of sulfur is analysed effectively moving the ion mass away from the interfered mass [90]. This would require the mass analysed for the selenium isotope to be adjusted to account for the oxide formation. This oxygen approach was not investigated in this project due to time limitations.

The use of the methane DRC approach gave improved accuracy, and is recommended as a good starting point for any future analysis involving low-level selenium in acid extracts on the Perkin Elmer Sciex ELAN DRC II ICP-MS.

However, for the purpose of this project, time limitations and lack of available equipment for a large part of the project constrained the possibility of fully validating the effectiveness of the DRC-ICP-MS and the respective reaction gases in determining low-level selenium in soils.

5.5 Conversion of ICP-MS Results to Concentration in Soil

The numerical value obtained from the ICP-MS analysis was adjusted to give the actual concentration of analyte in the soil. This was achieved by using the following formula:

$$C_{Soil} = ((C_{ICP\text{-}MS} - C_{Blank}) * D_f / M_{Soil})/1000$$

Where:

C_{Soil} = Concentration of analyte in the soil (mg kg^{-1}),
$C_{ICP\text{-}MS}$ = Concentration of analyte from ICP-MS analysis (ppb),
C_{Blank} = Concentration of analyte in blank solution (ppb),
D_f = Dilution Factor (25 if total volume is 25 mL),
M_{Soil} = Mass of soil used (g).

5.6 Statistical Methods

Statistical analyses of the results were carried out using DataDesk version 6. Data was log-transformed for normalisation where necessary, enabling significance testing to be achieved.

Paired Student's *t*-tests were used when comparing the significance between pairs of data, such as duplicates. Pooled Student's *t*-tests were used when comparing the significance between sample means.

Pearson's correlation coefficients were obtained between iodine and selenium with the previously collected trace elements and soil parameters. A correlation matrix was produced with respective correlation coefficients (R-values) between two parameters for each correlation. The R value was statistically assessed using p values. The significance of the p value was assessed by considering the R value and the number of sample pairs that contributed to the correlation.

Box plots were also used to display the range and variation of concentrations. These represented the minimum, 25% quartile, median, 75% quartile and maximum values.

5.6.1 Data Transformation

The natural tendency of the data collected for both the iodine and selenium is positively skewed. This is illustrated in the histogram of the selenium results of the samples analysed using the TMAH extraction method (Figure 5-1).

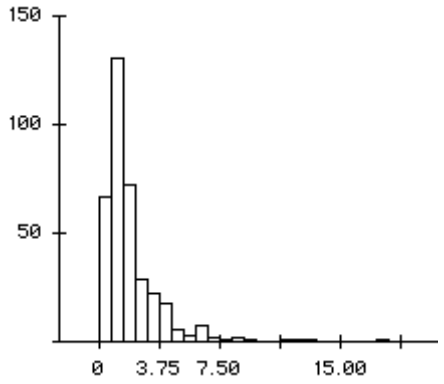

Figure 5-1 - Histogram of raw selenium analysis displaying concentration (x-axis) and count (y-axis) displaying positive skew.

Clearly the results display positive skew in that the large majority of results lie to the left of the mean, creating a tail to the right of the mean. This produces an asymmetrical probability distribution, from which interpretations of the data (such as correlations) become difficult. In order to account for this when estimating Pearson's correlation coefficients, the data first must be transformed to give a normalised distribution. This was achieved by logging the results to give a log-normal distribution (Figure 5-2).

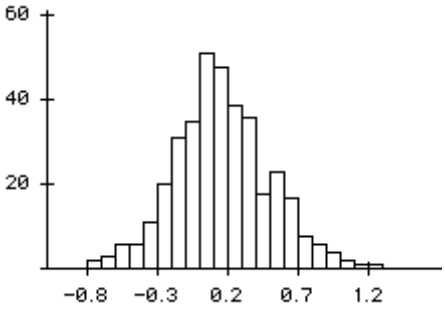

Figure 5-2 - Effect of log transformation on the raw selenium data.

Once transformed the data could be analysed effectively using Pearson's correlation, Paired Student's *t*-tests, and Pooled Student's *t*-tests.

5.7 Method Validation and Data Quality Control

During the course of the experimental work various measures were taken to assess the reliability, accuracy, precision and robustness of the methods used and data collected.

The robustness, accuracy and reliability of the method were assessed with each set of analyses carried out by use of two Certified Reference Materials (CRMs): NCS DC 73319 and NCS DC 73323. For simplicity these will be simplified to CRM 1 and CRM 2. Their selenium and iodine content is outlined in Section 5.7.1.

These two reference materials were included in each set of extractions and analysed at the start and end of every set of analyses.

The outcomes of these samples gave a good indication on the instrument performance between each set of samples analysed. Significant differences between the values of the reference materials would indicate a problem within that analysis set. These measures ensured that the results between sets of sample analyses could be compared. No significant change between the sets of samples would indicate that the method was reliable, accurate and robust.

The precision of the data collected was determined by the use of a duplicate every tenth sample. The difference between pairs of duplicates indicates the relative precision of the method. A pair of duplicates every tenth sample was used as a means of identifying possible problems with the method within a sample set during the routine analysis. This ensured that if a problem occurred within an analysis of a large number of samples, the location of that error could be indicated such that the whole analysis run is not entirely meaningless. This is important when considering the efficiency of the method with regard to time and cost in obtaining reliable results.

5.7.1 Certified Reference Materials (CRMs)

Certified Reference Materials NCS DC 73319 and NCS DC 73323 were sourced from LGC Standards, UK [91].

Both of these CRMs are reference soils from China, and were provided as sterilised and homogenised 70 g samples in glass bottles. Certified values given for these soils are provided in Table 5-2 and Table 5-3, which also gives some indication on the soil sample matrix.

Iodine and selenium were the constituents of direct interest in this project. The two CRMs selected had the advantage of having certified values for both iodine and selenium, at both low and moderate concentrations. These are also summarised in Table 5-2 and Table 5-3.

Table 5-2 - NCS DC73319 (CRM 1): Certified values of soil composition including trace elements.

Element	µgg^{-1} (mg kg^{-1})	Element	µgg^{-1} (mg kg^{-1})	Element	µgg^{-1} (mg kg^{-1})
Ag	0.35±0.05	**I**	1.8 ± 0.3	**Th**	11.6 ± 0.7
As	34 ± 4	**In**	0.08 ± 0.02	**Ti**	4830 ± 160
B	50 ± 3	**La**	34 ± 2	**Tl**	1.0 ± 0.2
Ba	590 ± 32	**Li**	35 ± 1	**Tm**	0.42 ± 0.06
Be	2.5 ± 0.3	**Lu**	0.41 ± 0.04	**U**	3.3 ± 0.4
Bi	1.2 ± 0.1	**Mn**	1760 ± 63	**V**	86 ± 4
Br	2.9 ± 0.6	**Mo**	1.4 ± 0.1	**W**	3.1 ± 0.3
Cd	4.3 ± 0.4	**N**	1870 ± 67	**Y**	25 ± 3
Ce	70 ± 4	**Nb**	16.6 ± 1.4	**Yb**	2.7 ± 0.3
Cl	70 ± 9	**Nd**	28 ± 2	**Zn**	680 ± 25
Co	14.2 ± 1.0	**Ni**	20.4 ± 1.8	**Zr**	245 ± 12
Cr	62 ± 4	**P**	735 ± 28	**SiO_2 (%)**	62.60 ± 0.14
Cs	9.0 ± 0.7	**Pb**	98 ± 6	**Al_2O_3 (%)**	14.18 ± 0.14
Cu	21 ± 2	**Pr**	7.5 ± 0.5	**TFe_2O_3(%)**	5.19 ± 0.09
Dy	4.6 ± 0.3	**Rb**	140 ± 6	**MgO (%)**	1.81 ± 0.08
Er	2.6 ± 0.2	**Sb**	0.87 ± 0.21	**CaO (%)**	1.72 ± 0.06
Eu	1.0 ± 0.1	**Sc**	11.2 ± 0.6	**Na_2O (%)**	1.66 ± 0.04
F	506 ± 32	**Se**	0.14 ± 0.03	**K_2O (%)**	2.59 ± 0.04
Ga	19.3 ± 1.1	**Sm**	5.2 ± 0.3	**CO_2 (%)**	1.12 ± 0.09
Gd	4.6 ± 0.3	**Sn**	6.1 ± 0.7	**C_{org} (%)**	1.80 ± 0.16
Ge	1.34 ± 0.20	**Sr**	155 ± 7	**TC (%)**	2.11 ± 0.19
Hf	6.8 ± 0.8	**Ta**	1.4 ± 0.2		
Hg	0.032 ± 0.004	**Tb**	0.75 ± 0.06		
Ho	0.87 ± 0.07	**Te**	0.058 ± 0.020		

Table 5-3 - NCS DC73323 (CRM 2): Certified values of soil composition including trace elements.

Element	µgg^{-1} (mg kg^{-1})	Element	µgg^{-1} (mg kg^{-1})	Element	µgg^{-1} (mg kg^{-1})
Ag	4.4 ± 0.4	**I**	3.8 ± 0.5	**Tb**	0.7 ± 0.1
As	412 ± 16	**In**	4.1 ± 0.6	**Th**	23 ± 2
Au	0.260 ± 0.007	**La**	36 ± 4	**Ti**	6290 ± 210
B	53 ± 6	**Li**	56 ± 2	**Tl**	1.6 ± 0.3
Ba	296 ± 26	**Lu**	0.42 ± 0.05	**Tm**	0.41 ± 0.04
Be	2.0 ± 0.4	**Mn**	1360 ± 71	**U**	6.5 ± 0.7
Bi	41 ± 4	**Mo**	4.6 ± 0.4	**V**	166 ± 9
Cd	0.45 ± 0.06	**N**	610 ± 31	**W**	34 ± 2
Ce	91 ± 10	**Nb**	23 ± 3	**Y**	21 ± 3
Co	12 ± 2	**Nd**	24 ± 2	**Yb**	2.8 ± 0.4
Cr	118 ± 7	**Ni**	40 ± 4	**Zn**	494 ± 25
Cs	15 ± 1	**P**	390 ± 34	**Zr**	272 ± 16
Cu	144 ± 6	**Pb**	552 ± 29	**SiO_2 (%)**	52.57 ± 0.16
Dy	3.7 ± 0.5	**Pr**	7.0 ± 1.2	**Al_2O_3 (%)**	21.58 ± 0.15
Er	2.4 ± 0.3	**Rb**	117 ± 6	**TFe_2O_3 (%)**	12.62 ± 0.18
Eu	0.82 ± 0.04	**S**	410 ± 54	**MgO (%)**	0.61 ± 0.06
F	603 ± 28	**Sb**	35 ± 5	**Na_2O (%)**	0.12 ± 0.02
Ga	32 ± 4	**Sc**	17 ± 1	**K_2O (%)**	1.50 ± 0.04
Gd	3.5 ± 0.3	**Se**	1.6 ± 0.2		
Ge	2.6 ± 0.4	**Sm**	4.0 ± 0.4		
Hf	8.1 ± 1.7	**Sn**	18 ± 3		
Hg	0.29 ± 0.03	**Sr**	42 ± 4		
Ho	0.77 ± 0.08	**Ta**	1.8 ± 0.3		

Certified Reference Materials (CRMs) were treated using the same method as the soil samples themselves depending on the respective target analyte (Se or I).

CRMs were initially used to validate the accuracy and robustness of the extraction/digestion method and ICP-MS analysis.

They were further used during each extraction and analysis as quality control measures.

Analysis of the CRMs for selenium concentration was carried out for the acid extractions (results from a number of acid extraction methods pooled together) and also for the TMAH extractions. This enabled a comparison between the acid and alkaline extractions to be made.

Statistical analysis of the CRMs was used to evaluate the effectiveness of the methods used.

5.7.1.1 Iodine CRM analysis

The iodine extraction method was validated by the use of two soils with differing certified levels of iodine, considered to be total iodine.

A total of 27 individual analyses for each reference soil were carried out for the analysis of total iodine. The summary statistics of these analyses are given in Table 5-4.

All iodine samples were extracted using the TMAH extraction method outlined previously.

Table 5-4 - Summary Statistics of the CRM analysis for iodine by TMAH extraction.

	CRM 1 (N=27)	**CRM 2 (N=27)**
Mean	1.99	3.53
Median	1.99	3.52
Minimum	1.64	2.84
Maximum	2.53	4.46
Standard Deviation	0.22	0.40
95 % Student's *t*-*i*nterval	1.91<μ<2.08	3.38<μ<3.69
Certified Value	1.8 ± 0.3	3.8 ± 0.5
Average recovery compared with CRM mean value (%)	111	92

All values expressed in mg kg^{-1} unless otherwise stated.

The mean of the CRM 1 and CRM 2 were found to be 1.99 and 3.53 mg kg^{-1}, with the median values of the two very similar to the means. The mean values for both CRMs fall within the certified concentration range, indicating that the extraction and analysis via ICP-MS yields the total iodine in the soil.

The 95% Student's *t*-interval range of both reference materials also fall within the certified concentration range, indicating the true is likely to fall within this certified range. This further reinforces and validates that the TMAH extraction followed by ICP-MS analysis was suitable for determination the total iodine concentration in soil.

The CRM values are expressed as means with ranges. Relative to the CRM mean values and on average, the TMAH extraction appeared to extract 110% of iodine from the low-iodine CRM and 92% of iodine from the higher-iodine CRM. Overall this suggests that the TMAH extraction can be regarded as being an efficient and accurate method of recovering most or all of the iodine from these soils.

5.7.1.2 Selenium CRM analysis using an acid extraction

Validation of the selenium analysis using various acid extraction methods was largely unsuccessful. The lower selenium concentration reference material (CRM 1) was consistently over-estimated while the higher concentration reference material (CRM 2) was under-estimated (Table 5-5). This is displayed by the average recovery of 300% and 54% of the two CRMs respectively.

The acid extraction results (from a range of similar acid extraction methods) are presented as a pooled set of data. As stated earlier, adaptations of the acid extractions did not appear to improve the recovery of selenium. For this reason it was decided to present a pooled data set.

Table 5-5 - Summary Statistics of the CRM analysis of Selenium using acid extraction. A range of acid extraction approaches were used with limited DRC-ICP-MS data.

	CRM 1 (N=52)	**CRM 2 (N=44)**
Mean	0.42	0.87
Median	0.43	0.70
Minimum	0.15	0.10
Maximum	0.85	2.41
Standard Deviation	0.17	0.60
95 % Student's *t*-*i*nterval	0.37<μ<0.47	0.69<μ<1.05
Certified Value	0.14 ± 0.03	1.6 ± 0.2
Average recovery compared with CRM mean value (%)	300	54

All values expressed in mg kg^{-1}.

Note – The results were based on total recoverable acid extractable selenium using a variation of the methods outlined previously.

A possible explanation for the over estimation of CRM 1 is that the detection limit of the method is very close to the actual values being analysed. In this instance the blank concentration may be under-estimated which results in an over-estimated actual value after the blank concentration is subtracted off.

CRM 2 may be under-estimated if the extraction technique is not efficiently extracting the selenium from minerals that are more resistant. This could explain the extraction efficiency of 54% in CRM 2. To get improved extraction efficiency a stronger digest may be required, or alternatively a longer extraction time may be necessary.

When DRC-ICP-MS is applied, the results of the selenium determination show little improvement to what conventional ICP-MS displays. However, the use of methane (on the most abundant selenium isotope, ^{80}Se) appears to improve the accuracy of the low-level selenium determination (CRM 1) using an acid extraction. This is shown by an average recovery of 157%, compared to the other selenium isotopes and DRC-ICP-MS reaction gases where the recovery is greater than 270%.The use of DRC-ICP-MS gave variable results for CRM 2, with oxygen showing the best recovery (94%), although the reproducibility of this was not explored as time constraints limited the investigations in this area. The majority of the results for the DRC analysis on CRM 2 either show recoveries of approximately 50%, or recoveries that are greatly over-estimated. The summary statistics for the selenium concentration of the CRMs with the various DRC-ICP-MS settings are shown in Table 5-6 and Table 5-7.

Table 5-6 - CRM 1: Summary statistics for the selenium concentration using various reaction gases in the DRC-ICP-MS.

	^{74}Se*	^{74}Se (NH_3)	^{77}Se*	^{77}Se (NH_3)	^{78}Se*	^{78}Se (O_2)	^{78}Se (CH_4)	^{80}Se*	^{80}Se (O_2)	^{80}Se (CH_4)	^{82}Se*	^{82}Se (NH_3)	^{82}Se (CH_4)	^{82}Se (O_2)
N	4	4	16	16	4	4	10	4	4	10	30	16	10	4
Mean	13.3	42.7	3.0	2.0	0.48	0.46	0.53	-84.5	2.4	0.22	0.38	0.42	0.82	8.4
Median	13.0	42.2	0.8	1.5	0.49	0.46	0.55	-84.4	2.4	0.22	0.34	0.36	0.85	8.4
Minimum	8.0	39.6	0.26	0.38	0.44	0.40	0.42	-103	2.3	0.16	0.15	0.13	0.65	7.8
Maximum	19.0	46.6	9.5	6.2	0.52	0.54	0.67	-65.8	2.5	0.27	0.75	0.99	0.95	8.9
Standard Deviation	6.1	3.0	3.3	1.7	0.04	0.06	0.09	19.9	0.10	0.03	0.17	0.25	0.10	0.44
Average recovery compared with CRM mean value (%)	9500	30500	2143	1429	343	329	379	- 22, 500	1714	157	271	300	586	6000

All values expressed in mg kg^{-1}.

Table 5-7 - CRM 2: Summary statistics for the selenium concentration using various reaction gases in the DRC-ICP-MS.

	^{74}Se*	^{74}Se (NH_3)	^{77}Se*	^{77}Se (NH_3)	^{78}Se*	^{78}Se (O_2)	^{78}Se (CH_4)	^{80}Se*	^{80}Se (O_2)	^{80}Se (CH_4)	^{82}Se*	^{82}Se (NH_3)	^{82}Se (CH_4)	^{82}Se (O_2)
N	4	4	10	10	2	2	10	2	2	10	22	10	10	2
Mean	14.8	59.5	2.2	0.83	0.80	0.74	0.83	-13.8	1.5	0.58	0.77	0.89	0.89	4.5
Median	14.5	58.4	0.36	0.48	0.80	0.74	0.73	-13.8	1.5	0.46	0.55	0.51	0.77	4.5
Minimum	7.0	57.5	-0.95	0.17	0.70	0.64	0.36	-18.6	1.4	0.20	0.10	0.20	0.40	4.2
Maximum	23.0	63.9	7.7	1.8	0.89	0.83	1.7	-9.0	1.7	1.5	1.7	1.9	1.9	1.8
Standard Deviation	9.0	3.0	3.6	0.66	0.13	0.13	0.46	6.8	0.18	0.48	0.58	0.70	0.54	0.42
Average recovery compared with CRM mean value (%)	925	3719	138	52	50	46	52	-811	94	36	48	56	56	281

All values expressed in mg kg^{-1}.

The accuracy of the low-level selenium determination appears to be improved with the use of methane DRC-ICP-MS, while the selenium determination of the moderately concentrated CRM was largely unchanged (with the exception of the limited oxygen DRC-ICP-MS results). However, this was not completely validated.

With the incomplete validation of selenium determination using an acid extraction, coupled to time and equipment constraints, it was not justifiable to run through the complete set of Waikato soil samples with the hope that the methane DRC-ICP-MS would give concentrations that were representable.

Therefore the selenium results present in Chapter 7 of this thesis were collected using the TMAH extraction (as for the iodine analysis).

However, time allowed a subset of the Waikato samples to be analysed using the methane DRC-ICP-MS to compare to results obtained from other methods (presented in Section 5.8.2).

5.7.1.3 Selenium CRM analysis using a TMAH extraction

Analysis of the CRMs using the TMAH extraction method improved the analysis of the low selenium concentration CRM (CRM 1) but was very similar to the acid extraction for the moderate selenium concentration CRM (CRM 2).

The summary statistics of the CRM analysis using the TMAH extraction are shown in Table 5-8.

The DRC-ICP-MS approach was not investigated for the analysis of samples that were extracted using a TMAH method. This is primarily because the problem with polyatomic interferences seemed to be reduced, possibly because of a lighter sample matrix.

Table 5-8 - Summary Statistics of the CRM analysis of Selenium using TMAH extraction.

	CRM 1 (N=21)	CRM 2 (N=21)
Mean	0.15	0.61
Median	0.15	0.62
Minimum	0.09	0.36
Maximum	0.29	0.80
Standard Deviation	0.04	0.10
95% Student's *t*-interval	0.13<μ<0.17	0.57<μ<0.65
Certified Value	0.14 ± 0.03	1.6 ± 0.2
Average recovery compared with CRM mean value (%)	107	38

All values expressed in mg kg^{-1}.

The 95% Student's *t*-interval for CRM 1 fell within the certified value (0.14 ± 0.03 mg kg^{-1}). This suggested that the TMAH method was appropriate to analyse low levels of selenium in soil, compared to that of an acid extraction where interferences within the ICP-MS are problematic with low level selenium determination.

The Student's *t*-interval for CRM 2 is lower than the certified value with an extraction efficiency of 38%. This may reflect the inability of TMAH to remove selenium from soil fractions that are harder to access. The recovery of selenium for this CRM using TMAH is less than the recovery using an acid extraction (38% compared to 54%). This most likely further reflects a weaker extraction using TMAH.

However, based on these results, the TMAH method appears to be more reliable for the determination of low level selenium than an acid extraction. The low-level selenium recovery was deemed to be more important for the soil samples in this project. It was known that the soils used in the project were most likely low in selenium based on the previous sample analysis and the nature of selenium in New Zealand soils. For these reasons selenium was analysed alongside iodine during the ICP-MS sample

acquisition. This decision also enabled a full set of selenium data to be collected for the Waikato soils, and was hence further reason the TMAH extracted selenium values were decided to be presented for the selenium results in Chapter 7.

It must also be noted that given the TMAH and acid extraction methods both under-recovered selenium in CRM2, it is possible that the certified selenium concentration provided for CRM2 is an over-estimate.

5.7.2 Blank Solutions

Blank solutions were prepared in the same way as the soil samples, without the addition of soil. Blank solutions were included as an indication of sources of contamination within the reagents used throughout the extraction process.

The blank values collected during each analysis were also used to adjust the ICP-MS raw data when calculating the sample concentration.

The blank values were consistently low in both selenium and iodine such that the contribution of these to the concentration of the sample would be negligible. Statistical analysis of the blank concentrations for both selenium and iodine using TMAH and acid extractions are displayed in Table A-3 (Appendix 2).

5.7.3 Duplicate Analyses

Duplicate sample analyses were carried out every tenth sample during each subsequent extraction/digestion and analysis. Duplicates were treated the same as other samples prepared in the respective methods. Statistical analysis of the duplicates was used to give a measure on the accuracy, precision and reproducibility of the method.

5.7.3.1 Iodine Duplicate Analysis

Initial statistical analysis of the duplicate pairs using a (paired Student's *t*-test) indicates that there was a statistical difference between the duplicates (p=0.0119, n=52) throughout the concentration range tested.

When the iodine concentration in the soil increases (>50 mg kg^{-1}) it appears that the difference between the pairs becomes more significant (p=0.0094, n=7). Of the seven pairs that fell above 50 mg kg^{-1}, 5 of the 7 had differences of 5 mg kg^{-1} and higher.

Of the lower concentration samples (<50 mg kg-1), all samples showed a difference of less than 3 mg kg^{-1}, of which a paired *t*-test fails to rule out statistical significance (p=0.2209, n=45).

Therefore, as the iodine concentration increases the absolute error is also shown to increase.

However, when taking the relative percentage error into account, 17 of the 52 (33%) duplicates show a relative error greater than 5% (Table 5-9). These are not limited to a certain range of iodine concentration as is mainly observed with the absolute errors. The relative error appears greatest at a concentration of 4 mg kg^{-1} (27.1%). However, five of the seven duplicates with concentrations higher than 50 mg kg^{-1} had relative errors greater than 5%.

Statistically, no significant difference is observed between pairs that have a relative error of less than 5% (p=0.0526, n=35). However, statistically this is not a lot of margin between them still being different, based on the p-value. For duplicate pairs that have a relative error of 5% or greater, the difference becomes statistically significant (p<0.0221, n=17).

The higher relative error along with the higher absolute error at iodine concentrations above 50 mg kg^{-1} could reflect decreased precision of the methodology in high iodine concentrations. This could largely be due to the calibration of the instrument or the relatively low iodine concentrations (1.8 and 3.8 mg kg^{-1}) in both CRMs relative to the concentrations that were actually obtained during the analysis of the Waikato soil samples.

The precision of the TMAH method in extracting iodine seems to be sufficient at low iodine concentrations, but decreases as the concentration of iodine increases.

A simpler approach to expressing precision statistics is as the Percent Relative Standard Deviation, or %RSD.

For each pair:

%RSD = Standard deviation / mean x 100

Over all 52 pairs of duplicate analyses for iodine, %RSD values for iodine concentrations in soil ranged from 0% to 19.3%, with 10^{th} and 90^{th} percentiles of 0.4% to 6.8%, respectively. The overall arithmetic average %RSD (N=52 pairs) was 3.4% with a narrow 95% confidence interval of 2.4-4.4%. Overall these results show a good degree of precision for the iodine analyses.

In summary, it can be concluded that the TMAH-ICP-MS method for iodine was acceptably accurate (Section 5.7.1.1) and precise (this section).

Table 5-9 - Relative error analysis of the iodine duplicates (mg kg^{-1}).

Measurement 1	2.6	3.7	3.8	3.9	4.2	4.2	4.9	5.2	5.4	6.3	6.7	7.6	8.3	8.5	8.5	8.6	8.9	9.2	9.8
Measurement 2	2.5	3.8	5.0	3.6	4.2	4.9	5.0	5.3	5.0	6.4	6.6	7.4	7.4	8.4	9.1	7.9	9.1	9.3	9.5
Average	2.5	3.8	4.4	3.8	4.2	4.6	5.0	5.2	5.2	6.3	6.6	7.5	7.8	8.5	8.8	8.3	9.0	9.2	9.7
Difference	0.0	0.1	1.2	0.2	0.1	0.6	0.1	0.0	0.4	0.2	0.1	0.2	0.9	0.0	0.6	0.7	0.3	0.2	0.3
Relative error (%)	**1.6**	**2.7**	**27.1**	**6.2**	**2.1**	**13.5**	**2.3**	**0.6**	**7.6**	**2.7**	**1.0**	**2.5**	**11.3**	**0.4**	**6.4**	**8.9**	**3.0**	**1.9**	**3.4**

Measurement 1	10.4	11.0	11.5	11.6	12.0	12.4	12.7	12.7	14.4	15.3	16.0	16.4	16.5	17.3	19.4	20.6	22.1	25.3	26.8
Measurement 2	10.7	11.0	11.6	12.0	12.2	12.1	12.9	13.3	15.2	16.6	16.1	17.3	17.4	16.8	17.9	20.7	22.1	26.7	28.1
Average	10.6	11.0	11.6	11.8	12.1	12.3	12.8	13.0	14.8	16.0	16.1	16.8	16.9	17.0	18.7	20.6	22.1	26.0	27.5
Difference	0.3	0.0	0.1	0.4	0.2	0.3	0.2	0.6	0.7	1.3	0.1	0.8	0.9	0.5	1.5	0.1	0.1	1.3	1.3
Relative error (%)	**2.5**	**0.5**	**0.8**	**3.8**	**1.9**	**2.6**	**1.9**	**4.9**	**4.9**	**8.2**	**0.4**	**4.8**	**5.4**	**3.1**	**8.0**	**0.7**	**0.3**	**5.1**	**4.6**

Measurement 1	26.9	27.1	31.8	31.9	37.0	37.6	41.0	55.9	56.9	60.4	67.0	69.5	79.4	79.9
Measurement 2	25.8	28.2	32.4	33.0	36.2	34.4	40.9	62.6	68.6	61.0	71.7	74.6	85.8	79.2
Average	26.3	27.7	32.1	32.5	36.6	36.0	40.9	59.3	62.7	60.7	69.4	72.1	82.6	79.5
Difference	1.1	1.1	0.6	1.0	0.9	3.1	0.1	6.7	11.7	0.6	4.8	5.1	6.4	0.7
Relative error (%)	**4.2**	**4.1**	**1.9**	**3.2**	**2.4**	**8.7**	**0.3**	**11.3**	**18.7**	**1.0**	**6.9**	**7.1**	**7.8**	**0.8**

5.7.3.2 Selenium Duplicate Analysis

The selenium duplicate analysis using the acid extractable methods was limited to 7 pairs because of the limited collection of samples and duplicates. Statistical analysis of these pairs, using paired Student's *t*-tests, showed that there was no significant difference (p=0.4192, n=7) between them. This suggests that the precision of the acid extraction method is reasonable. However, as the accuracy is not suitable (based on CRM analysis) an acid extraction seems limited for the purpose of this project.

Statistical assessment is more complete using the duplicates collected using the TMAH extraction.

Analysis of the selenium duplicates collected using the TMAH method was more meaningful as the results presented in Chapter 7 were based on the TMAH method.

Thirty nine duplicate pairs were analysed using the TMAH extraction method for selenium. Statistical analysis of these pairs shows a significant difference between the pairs (p=0.0068, n=39). However, if the relative percentage errors (Table 5-10) are considered, 20/39 (51%) of the duplicate pairs have relative errors of 5% or more of which a paired *t* test displays more significant difference, with a decreased p value (p=0.0066, n=20). The pairs that have relative errors less than 5% display no statistical difference (p=0.3334, n=19).

The precision of the TMAH method for selenium analysis is reduced as the relative error increases. With 51% of duplicate pairs showing a relative error greater than 5% it would be suggested that the TMAH is not very precise. This would introduce a source of error through the variability from one sample to the other.

As for iodine, precision of the selenium results can also be summarised using the %RSD.

Over all 39 pairs of duplicate analyses for selenium, %RSD values for selenium concentrations in soil ranged from 0% to 21.5%, with 10^{th} and

90^{th} percentiles of 0.3% to 10.5%, respectively. The overall arithmetic average %RSD (N=39 pairs) was 4.4% with a narrow 95% confidence interval of 3.1-5.7%. Overall these results show a good degree of precision for the selenium analyses.

In summary, it can be concluded that the TMAH-ICP-MS method for selenium was acceptably precise.

Table 5-10 - Relative error analysis of the selenium duplicates (mg kg^{-1}) analysed using the TMAH method.

Measurement 1	0.72	2.98	0.96	1.08	1.11	2.09	1.34	1.37	1.64	0.97	0.80	1.24	0.80	0.73	2.05
Measurement 2	0.72	3.04	0.95	1.07	1.15	2.21	1.14	1.31	1.73	1.01	0.75	1.38	0.75	0.71	2.33
Average	0.72	3.01	0.96	1.07	1.13	2.15	1.24	1.34	1.69	0.99	0.78	1.31	0.77	0.72	2.19
Difference	0.01	0.06	0.00	0.01	0.04	0.13	0.20	0.05	0.10	0.04	0.05	0.14	0.05	0.02	0.27
Relative Error (%)	**1.22**	**1.98**	**0.27**	**1.09**	**3.16**	**5.87**	**16.36**	**3.98**	**5.70**	**3.66**	**6.95**	**11.00**	**5.85**	**3.09**	**12.36**
Measurement 1	2.01	1.39	0.40	0.81	1.73	1.09	3.59	7.81	11.62	0.75	0.63	1.05	1.04	3.69	0.92
Measurement 2	2.05	1.34	0.35	0.77	2.35	1.15	3.64	8.48	12.27	0.70	0.63	1.01	0.99	3.82	0.93
Average	2.03	1.36	0.37	0.79	2.04	1.12	3.61	8.14	11.95	0.73	0.63	1.03	1.01	3.76	0.92
Difference	0.04	0.05	0.04	0.04	0.62	0.06	0.05	0.67	0.65	0.05	0.00	0.04	0.05	0.13	0.02
Relative Error (%)	**1.84**	**3.64**	**11.90**	**4.48**	**30.29**	**5.33**	**1.42**	**8.25**	**5.45**	**6.66**	**0.47**	**3.86**	**4.93**	**3.34**	**1.72**
Measurement 1	3.18	2.34	2.24	4.37	2.52	0.61	3.80	1.80	1.47						
Measurement 2	3.59	2.41	2.50	4.87	2.37	0.66	3.75	1.72	1.37						
Average	3.38	2.37	2.37	4.62	2.45	0.63	3.78	1.76	1.42						
Difference	0.40	0.07	0.26	0.51	0.15	0.05	0.05	0.09	0.10						
Relative Error (%)	**11.94**	**3.16**	**10.93**	**11.00**	**6.07**	**7.56**	**1.31**	**4.98**	**6.69**						

5.7.4 XRF Analysis

A number of the samples analysed in this project were also analysed via X-Ray Fluorescence (XRF) spectroscopy for selenium and iodine as part of a separate project. The results from the XRF analysis were compared with the methods used in this project for iodine and selenium, as XRF is considered to represent the total elemental composition of a sample. This acts as a useful quality control measure.

Statistical analyses of the XRF results for selenium are displayed in Table 5-12 and Table 5-13 and are discussed in more detail in Section 5.8.

The comparison of iodine analysed by XRF and TMAH are present below.

5.7.4.1 Comparison of Total Iodine values collected by TMAH Extraction (ICP-MS) and XRF

The results from a sub-set of Waikato soil sample analysed by XRF were compared to the values obtained using the TMAH extraction method.

Initial comparisons using summary statistics (Table 5-11) indicated that there was most likely no difference between the two methods. This is largely due to the mean and geometric means being close to one another and the 95% Student's *t*-intervals for both methods overlapping. The true value for each mean may lie within the interval range (with 95% confidence), and as the two overlap, they can be considered to be very similar.

Table 5-11 - Comparison of the total iodine concentration of samples analysed using TMAH extraction and X-Ray Fluorescence*.

	Iodine Concentration (mg kg^{-1}) TMAH Method	Iodine Concentration (mg kg^{-1}) XRF Method
Mean	26.9	24.1
Geometric Mean	18.9	17.5
Median	18.6	16.9
Minimum	3.8	3.7
Maximum	112.6	135.3
Standard Deviation	24.0	21.2
95% Student's *t*-interval	21.9>μ>32.0	19.6>μ>28.5

*- Based on 90 samples (N=90) analysed by both methods.

However, the mean and geometric means for both methods indicates that the TMAH extraction may on average be extracting more iodine than the XRF method.

A paired *t*-test of the difference between the sample means shows a statistical significance between the two sample methods for total iodine in soil ($p=0.0007$, $n=90$). This difference indicates that the TMAH extraction method extracts on average more iodine than the XRF analysis.

XRF analysis (in theory) gives total determination of elements in various environmental samples. Therefore, the TMAH method could be considered to represent the total iodine fraction of soil. This also agrees with the method validation step of this project where the TMAH extraction successfully obtained the total iodine in the certified reference materials.

The results also agree with other studies where a TMAH extraction has been used to determine the total iodine in soil [85].

The method where iodine is extracted using a TMAH solution appears to be a reliable and effective method for obtaining the total iodine concentration of soil. It also may be a better representation of the total iodine content in soil compared to XRF. With TMAH extracting on average more iodine than XRF, it suggests that XRF analysis is not obtaining all the iodine present in the sample. It is uncertain what may cause this, but it could be through a subset of samples being measured near the detection limit of the instrument, or because of a matrix correction issue in the XRF spectrometer.

However, a factor in favour of using XRF is that it is capable of multi-element analysis. This would be possible using a multi-element standard in the TMAH method coupled to ICP-MS, however, the TMAH may not be strong enough to give total concentrations of some elements that are more strongly bound to soil.

5.8 Identification of the preferred method choice for the determination of total selenium in soils

Different approaches to analysing the total selenium in soil were assessed. Both acid and alkaline extraction methods analysed by ICP-MS were assessed along with limited XRF analyses. Various reaction gases were also trialled using the DRC-ICP-MS.

Method development was a significant component of this project, particularly when attempting to present the status of selenium in Waikato soils based on the total selenium values.

The following section evaluates the various methods used in determining the total selenium in soils for this project.

5.8.1 Determination of Selenium using TMAH extraction

As discussed earlier, TMAH extraction was validated and hence the method of choice for determining low-level selenium concentration of soils in this project. It also ended up being a convenient method for the purpose of this project as it allowed both selenium and iodine to be determined simultaneously. Therefore, the status of selenium in Waikato soils (as presented in Chapter 7) was based on the determination of selenium from this method.

The TMAH method proved to be relatively precise based on the duplicate analysis. However, the actually accuracy of the method is not entirely known. It can be assumed that the low selenium concentration results (<1 $mgkg^{-1}$) are most likely more accurate than the higher concentration selenium samples (>1 $mgkg^{-1}$). This suggested that the higher concentration samples may not represent the true total selenium concentration of the soil but may be better thought of as the total available selenium concentration.

Alternatively, given that both the TMAH method and the refined acid extraction approaches consistently showed a low recovery of selenium in

CRM2 despite numerous attempts, it is plausible that the certified value in CRM2 is an over-estimate. In support of this idea, there was also found to be a very good overall agreement between the TMAH method for selenium and the results of X-ray Fluorescence (XRF) analyses on the same sample (Section 5.8.4), indicating that the TMAH method is likely to be accurate across the concentration range. However, establishing that the selenium value specified in CRM2 should be revised would require further work with a separate high-selenium soil CRM.

5.8.2 Determination of Selenium using acid extraction (aqua regia) and ICP-MS

Analysis of the Certified Reference Materials indicated that an acid extraction for soils low in total selenium was not suitable (section 5.7.1.2).

This was largely due to polyatomic interferences in the ICP-MS interfering with all the isotopes of selenium [89]. The nature of an acid extraction also seems to create more interference, possibly relating to the matrix the sample is in (matrix effects). An acid extraction can be a relatively strong extraction technique which produces a heavy matrix requiring dilution of the extracted sample in order to lower the total dissolved solids. This dilution may also dilute the extracted selenium such that issues are raised concerning the detection limit.

DRC-ICP-MS, using various reaction gases was also trialled to reduce the polyatomic interferences of the selenium isotopes. Methane displayed the most promise in reducing the interferences such that the recovery of the low selenium CRM improved. However, issues that caused the validation to be incomplete meant that this method was still deemed unsuitable to analyse the full set of soil samples from the Waikato region.

Despite the findings that an acid extraction was not suitable, soil samples from the Matamata to Raglan transect (44 samples) were analysed using an acid extraction with ICP-MS (using conventional ICP-MS and DRC modes). The summary statistics of this analysis can be seen in Table 5-12.

These results are also compared to the results of TMAH and XRF analysis for the same samples.

The methane DRC mode displays lower mean selenium concentrations for the subset of Waikato soils compared to an acid extraction using conventional ICP-MS of the ^{82}Se isotope and also both the TMAH and XRF methods.

The Student's *t*-intervals of the acid extracted selenium analysed by ICP-MS (^{82}Se) overlap with the corresponding Student's *t*-intervals of both the TMAH and XRF methods. This suggests that there may be no significant difference between the mean concentrations of these methods, as the true mean values may all be similar (in theory). The overlap of the acid extraction with TMAH and XRF method occurs on the upper range of the acid extraction interval and lower range of the other two intervals. As this overlap occurs on the outer range of all three, it suggests that there may be a difference between the acid extraction and other two methods, as the probability of the three means having the same of similar true mean would be low. Therefore, this suggests that the acid extraction method extracts less selenium on average than both the TMAH and XRF methods.

The Student's *t*-interval of the selenium results collected using methane DRC-ICP-MS shows no overlap with the Student's *t*-intervals of the TMAH or XRF methods. This indicates that there is a significant difference between the means for these methods, with the DRC mode returning the lowest selenium concentrations, on average, than the others.

Table 5-12 -Summary Statistics of the ICP-MS analysis using normal and DRC modes of selenium following an acid extraction, compared to TMAH method for the same set of soil samples (Matamata-Raglan Transect).

	^{82}Se Concentration (conventional ICP-MS)	^{80}Se Concentration (DRC Mode with Methane)	^{82}Se TMAH Method	XRF Analysis
Mean	1.8	1.1	2.7	2.2
Geometric Mean	1.6	0.9	2.0	2.0
Median	1.5	1.0	1.7	2.0
Minimum	0.5	0.2	0.4	1.0
Maximum	4.6	3.2	12.1	5.1
Standard Deviation	0.9	0.6	2.4	0.9
95% Student's *t*-Interval	1.52<μ<2.09	0.93<μ<1.32	1.95<μ<3.43	1.90<μ<2.47

All values expressed in mg kg^{-1}. Summary statistics based on 44 Waikato soil samples along the Matamata to Raglan transect.

The results of the acid extractions for the 44 soil samples compared in reasonable agreement with the TMAH and XRF methods, although both acid extraction methods produced lower mean values for the total selenium. The lower mean values of the acid extraction could indicate a number of possibilities. The first is that the extraction is not recovering all of the selenium, or less selenium compared to the other methods. This could be due to the acid extraction promoting loss of selenium via the formation of volatile selenium products. However, analysis of the CRMs indicated that the TMAH method may also have reduced recovery.

The heavy matrix caused by aqua regia extraction (known by the ICP-MS blockages) may also cause the selenium to be interfered with in the ICP-MS, although dilution of the extracted sample should have accounted and minimised this.

The length (time) of the extraction could be an important factor in the lower recovery of selenium. The extraction time may not have been sufficient to target selenium from all of the fractions in the soil. This would also relate to the strength of the extraction. Various soil fractions (such as the aluminosilicates) are hard to fully solubilise with standard aqua regia, therefore any elements associated with these fractions may not entirely be recovered. Because of this, extractions using stronger acids (hydrofluoric acid or nitric acid with perchlorate) are often needed to ensure a total recovery of some elements in the soil. These stronger extraction techniques can be dangerous and are avoided where possible. For this reason, the use of these stronger extractions was not investigated in this project.

Although a stronger extraction may cause the extraction efficiency of selenium to improve, the method used in this project was based on common methods used for trace element analysis. Therefore, the lower recovery of selenium may be associated with other areas of the sample analysis than the extraction.

The main difficulties in this project were associated with the ICP-MS in the sample analysis. This was most likely due to the concentrations of selenium in the samples being close to the detection limits of the ICP-MS. The dilution stage after sample extraction was investigated to see whether it could be reduced. The total dilution factor for acid extraction by the methods described earlier was either 100 or 500. This depended on whether HCl was the major component of the aqua regia and if the need for a secondary dilution step to lower the chloride concentration was needed. The total dilution was reduced by trialling a total dilution factor of 50 and 25. This was conducted with the idea that having less dilution of the sample would increase the amount of selenium in the sample aliquot that was to be introduced in to the ICP-MS. In doing this it was hoped that the quantity of selenium may be high enough to produce a large enough signal such that interferences would not be a problem. The decreased dilution was unsuccessful as it caused the sample introduction and nebuliser of the ICP-MS to block. The sample matrix also became heavier because of the high total dissolved solids such that various elements

(aluminium and iron) were too high for the ICP-MS to cope with without necessary dilution. Increasing the mass of soil used in the extraction also had similar results as this effectively decreased the dilution factor of the sample.

The DRC-ICP-MS method using methane as the reaction gas resulted in a lower mean selenium concentration of the 44 soil samples. This indicates that it may also extract less selenium on average than the other methods, although it was the method that produced the lowest selenium concentration compared to others. This suggests that the DRC method may be better at estimating the selenium concentration of soils containing low levels of selenium, but less effective at analysing higher concentration samples. Time constraints and equipment availability limited the development and validation of this particular method and also a full analysis of Waikato soil samples.

5.8.3 Determination of Selenium using XRF analysis

XRF analysis of a subset of Waikato soils was also carried out during a separate project. This provided values for the total selenium content on a subset of the soil samples analysed by TMAH and acid extractions.

A comparison of XRF with two acid extraction methods and TMAH extraction for 44 Waikato soil samples is displayed in Table 5-12.

Summary statistics of a larger subset of Waikato soils with the TMAH extraction method is shown in Table 5-13 (section 5.8.4).

One apparent difference of the XRF analysis with the other methods is the ability in determining low level selenium. In looking at the minimum values of the two subsets of soils (Table 5-12 and Table 5-13), XRF displays the highest minimum values of all the methods. This may reflect the detection limit capabilities of the instrument.

Compared to the TMAH method, the results of XRF analysis are very similar, with statistical analysis of the two methods discussed in more detail in the following section (Section 5.8.4).

The CRMs were not analysed by XRF (as this was separate to this project) so a true assessment of the total selenium recovery was not available as it was for the other methods using ICP-MS. The relative comparison of XRF to the TMAH method would give some indication on the effectiveness of the method. However, the TMAH method was not 100% efficient at extracting the total selenium at concentrations greater than 1 mg kg^{-1} (as noted in section 5.7.1.3), therefore the relationship of the obtained concentrations to the total selenium content is not entirely known. It can only be assumed that the XRF concentrations for the soil samples represent the total selenium content based on the nature of XRF analysis.

5.8.4 Comparison of Total Selenium Concentration using TMAH extraction (coupled to ICP-MS) with XRF analysis

The subset of Waikato soils analysed by XRF was compared to the results of the TMAH method. This was done to assess the performance of the TMAH method in determining the total selenium concentration of soil.

The summary statistics of the selenium concentration between the two methods were very similar (Table 5-13). The TMAH method has the largest range of the two methods as it produced the smallest and largest selenium concentrations in the soil samples. Despite this, the Student's *t*-intervals for both methods are very similar, and as they both overlap it suggests they are indifferent. The interval for XRF analysis is narrower than the interval for TMAH extraction, most likely indicating less sample to sample variation in the XRF analysis than the TMAH method.

Table 5-13 - Summary Statistics of selenium in 90 soil samples following TMAH and XRF analysis.

	Selenium Concentration (TMAH)	**Selenium Concentration (XRF)**
Mean	2.2	2.1
Geometric Mean	1.7	1.9
Median	1.5	1.8
Minimum	0.2	0.8
Maximum	12.1	5.2
Standard Deviation	1.9	0.9
95% Student's *t*-interval	1.80<μ<2.61	1.88<μ<2.25

All values expressed in mg kg^{-1}. Summary statistics based on 90 Waikato soil samples along the Matamata to Raglan transect.

A paired Student's *t*-test fails to rule out any statistical difference between the two sample means (p=0.1754, n=90). Therefore, it can be assumed that the TMAH extraction method coupled to ICP-MS gives the same selenium concentrations as is observed with XRF analysis. However, as the extraction of CRM 2 by TMAH was approximately 30-40% efficient, the

actual relevance of both of these methods to the total selenium content is largely unknown.

It is assumed that the XRF (in theory) represents the total selenium content. Therefore it can also be assumed that the TMAH extracted results for selenium also represent the total selenium concentrations. This further points towards the real possibility that the certified value of CRM 2 is an over-estimate.

In order to better deduce the ability of both these methods in evaluating the total selenium concentration, analysis of certified reference materials (covering a greater concentration range) would be recommended. Also analysis of CRMs by XRF would indicate the ability of the instrument in quantifying the total selenium content of soils.

5.8.5 Summary

The results of the various methods trialled in determining the total selenium in Waikato soils indicate that XRF analysis or TMAH extraction (analysed ICP-MS) were the most suitable for analysing total selenium. However, because the XRF method was not fully validated it was assumed that these values best represent the total selenium concentration in soil. Results obtained by acid extraction followed by ICP-MS proved to be prone to interferences, troublesome and largely variable. The use of DRC-ICP-MS using methane gas appeared to improve the low-level selenium recovery but showed lower recovery of selenium concentration (on average) compared to the other methods.

The limitations encountered during this part of the project meant that the effectiveness of these methods was not fully validated. However, it was assumed that the TMAH extraction method best represented the total selenium concentration in soil. Therefore the results of selenium present in this project are based on the values collect using TMAH extraction.

6 Iodine Status of Waikato Soils: Results and Discussion

6.1 Introduction

The iodine status of the Waikato region in relation to Soil Order, land use and other soil properties is unknown.

Chapter 6 presents the iodine status of Waikato Soils and discusses the behaviour of iodine in the Waikato soils in relation to soil properties and land use.

Raw data for the analyses are displayed in Appendix 3.

6.2 Overall Iodine Status of the Waikato Region

The Waikato Region was found to have a mean iodine content of 20.9 mg kg^{-1} with standard deviation of 22.2 mg kg^{-1}. The 95% Student's *t*-interval indicates that the "true" mean may lie within the range of 18.6 – 23.2 mg kg^{-1}. The summary statistics of the soil samples analysed and a raw histogram of results are shown in Table 6-1 and Figure 6-1, respectively. These results showed that iodine concentrations in Waikato soils have a large amount of variation, relating to the properties of soil.

Table 6-1 – Summary Statistics for the Iodine Concentrations in the Waikato Region.

	Iodine Concentration (mg kg^{-1}) **N = 368**
Mean	20.9
Geometric Mean	13.7
Median	11.8
Standard Deviation	22.2
Minimum	1.5
Maximum	122.8
95 % Student's *t*-interval	$18.6 < \mu < 23.2$
Upper 95th Percentile	68.6

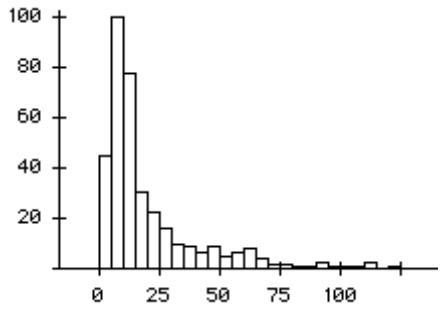

Figure 6-1 - Histogram of iodine analyses displaying concentration (x-axis) vs count (y-axis).

The difference between the median and mean (11.8 mg kg^{-1} compared to 20.9 mg kg^{-1}) indicates the skewed nature of the mean. The geometric mean has a value of 13.7 mg kg^{-1} which shows better agreement with the median. The geometric mean and the median are a better representative of the central tendency of the iodine data than the arithmetic mean as a result of the positive skew of the data. The small number of samples with concentrations of iodine higher than 60 mg kg^{-1} will naturally skew the mean concentration of the samples. For this reason, the geometric mean was chosen to be the statistic of choice for comparison in subsequent sections.

The upper 95th percentile showed that 95% of samples lie within 68.6 mg kg^{-1} iodine, with only 5% of soil samples containing higher than this concentration.

These results compare in reasonable agreement to the samples that were analysed some 80 years previously (Table 2-3, Section 2.5). This previously collected data was from individual soil samples across New Zealand. From these samples the soils that fell within the Waikato region (as currently defined) were pooled together and statistically analysed.

The mean concentrations of Waikato soils are similar: 20.9 mg kg^{-1} compared to 22.3 mg kg^{-1}, with the results from 1925-1931 having a higher mean iodine content. However, comparisons of the geometric means show greater difference. The samples collected in this project showed a geometric mean content of 13.7 mg kg^{-1}, which was approximately double the geometric mean content of the soils analysed between 1925 and 1931 (6.3 mg kg^{-1}). This suggests there may be generally more iodine in the Waikato soils currently compared to approximately 80 years ago. This comparison must be taken with caution as the location and soil type of the early samples were not entirely known, and the methods of iodine determination are different. Therefore this comparison is more indicative rather than being a direct comparison.

The variation in the range of the data displayed by the box plots (Figure 6-2) is very similar but it indicates that there may be more of a skewed relationship to the data observed from approximately 80 years ago, based on the difference between the mean and maximum values. The previously collected data displays the lower minimum and larger maximum values compared to the results of this project, and coupled with the larger standard deviation suggests that the data collected previously had more sample to sample variation.

The difference between the geometric mean and the highest value for each set of samples also indicates that the data from 80 years previous is likely to be more skewed. The data collected previously shows the highest iodine concentration but the smaller geometric mean. This indicates that the tail of the skewed data would lie more to the right of the majority of the data, and hence be more skewed.

Box plots were represented by the minimum, 25% quartile, median, 75% quartile and maximum values.

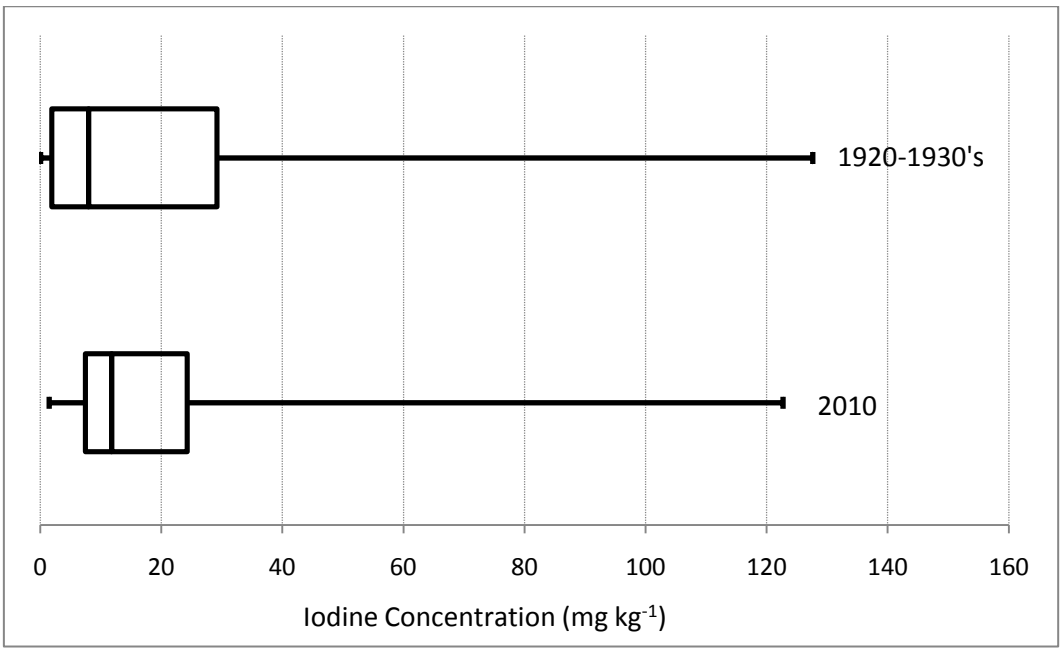

Figure 6-2 - Boxplots comparing the iodine concentration of Waikato soils determined in this study (2010) with that of the samples conducted in the 1925-1930 period.

The worldwide mean soil iodine content has been reported as 5.1 mg kg^{-1} with the geometric mean 3.0 mg kg^{-1} (based on data from 2151 cited sources) [40]. Both these statistics are lower than the mean and geometric mean calculated for the soils of the Waikato region, however, there is a larger sample size for the worldwide soils than for the Waikato soils. Despite this, the geometric mean concentration of iodine in Waikato soils is much larger than the worldwide geometric mean content (13.7 mg kg^{-1} compared to 3.0 mg kg^{-1}), indicating that Waikato soils contain more iodine.

The mean iodine concentration of Waikato soils is higher than other iodine deficient soils from around the world. Soils in Derbyshire, England and Missouri, USA, which are classic regions of iodine deficiency, have iodine contents of 5.44 mg kg^{-1} and 1.27 mg kg^{-1} respectively [92].

New Zealand is considered an iodine deficient country according to the studies carried out on goitre between 1925-1931 [37, 39]. This is despite soil iodine concentrations, both those previously reported and those from this study being higher than other areas considered iodine deficient. However, there is no accepted threshold figure for soil that defines it as iodine deficient [93]. This is partly due to soil iodine content being a poor

indicator of the greater environmental status of iodine [94]. It is also important to note that the soils analysed in this study were only from one region of New Zealand, making it difficult to predict the status of iodine on a national scale.

The higher concentration of iodine in Waikato soils could suggest that Waikato soils may be less prone to iodine deficiencies than other regions of the country. This agrees with the previous studies, where the iodine content from the Waikato region was on average higher than the New Zealand mean iodine content (Table 2-3, Section 2.5). However, in medical studies conducted in the mid 1990's, 50% of Waikato participants were considered to be at risk of mild iodine deficiency, with 7% at risk of severe iodine deficiency disorders [2]. Three percent of Waikato residents are also suggested to show some sort of thyroid disease from iodine deficiency [95]. Based on these findings along with the higher average iodine contents of Waikato soils, it could suggest that the iodine in Waikato soils may be less available for plant uptake and is therefore not being transferred through the food chain effectively. This would assume that the food consumed from Waikato residents is produced locally. However, in reality, food is also imported where it has been produced from soils with differing iodine contents. Thus, the diet of Waikato residents could be mostly to blame for iodine deficiencies in the region, rather than the soil iodine status.

6.3 Soil Iodine Content in Relation to Soil Order

It is apparent the iodine content of Waikato soils varies with Soil Order (Figure 6-3 and Table 6-2). Two Soil Orders have only 2 samples each (Ultic and Podzol soils). Geometric means and summary statistics of these two Soil Orders are presented as indicative only and the samples have consequently been left out of further statistical analysis and the box plots of Figure 6-3.

Allophanic and Granular soils had the highest iodine contents on average shown by the highest geometric mean contents. The order, from highest geometric mean concentration to lowest was: Allophanic > Granular > Recent > Brown > Organic > Gley > Pumice.

Allophanic and Granular soils also provide the highest values for iodine concentrations (113.3 mg kg^{-1} and 112.7 mg kg^{-1} respectively) closely followed by Gley soils (100.6 mg kg^{-1}).

Pumice soils show the lowest iodine concentrations on average, based on the geometric means.

Allophanic, Granular and Gley soils show the largest variation and spread in the concentrations of iodine, while Recent, Pumice and Organic soils show the least amount of variation and spread. This spread represents the difference between the maximum and minimum values for the respective Soil Orders. The soils showing the most variation are also the soils showing the largest concentrations of iodine.

The Student's *t*-interval for the various Soil Orders gave an indication of the range that the true mean may fall within (with 95% confidence). The range of the Students *t*-interval indicates the amount of uncertainty in the sample mean and hence the sample to sample variation. The largest uncertainty in the means occurred for the soils that also displayed the greatest variation between sample concentrations. Basing the Student's *t*-interval on the geometric means helped to account for some of this sample to sample variation but generally displayed the same trends as the intervals based on the arithmetic means. The range of each interval was

reduced slightly using the interval based on the geometric means indicating less uncertainty in the position of the true mean. The concentration range of each interval was also slightly reduced as the geometric mean accounted for the skew of the data. Recent soils showed increased uncertainty in the mean when using the Student's *t*-interval based on the geometric mean. This is due the concentrations of Recent soils showing less skew than the other soil types.

The ranges of these *t*-intervals are shown in numerical format in Table 6-2 and pictorial format in Figure 6-4 (based on geometric means only).

The overlap of the Student's *t*-intervals is an indicative way of determining if there is likely to be a difference between mean iodine content of the various Soil Orders. No overlap indicates that a difference between the means is likely, while an overlap indicates there is most likely no significant difference between the means.

Based on the relative overlap of the Student's *t*-intervals it can be concluded that there is most likely no difference between the mean iodine content of Brown, Gley, Granular, and Recent soils. The mean iodine content of Organic soils has a reasonably small confidence interval, but still overlaps with that of Gley soils and the lower end of the intervals for Brown and Recent soils, suggesting that Organic soils show similar mean concentrations. The intervals were most use in confirming that Allophanic soils display the highest average iodine content of all the soil types with Pumice soils displaying the lowest.

Table 6-2 - Summary Statistics of the iodine concentration of soils in relation to the Soil Order.

	Allophanic (N=69)	Brown (N=35)	Gley (N=45)	Granular (N=42)	Organic (N=21)	Podzol (N=2)	Pumice (N=29)	Recent (N=11)	Ultic (N=2)
Mean	34.4	19.5	14.1	22.2	11.2	14.7	8.1	16.6	6.8
Geometric Mean	24.8	12.9	9.4	16.8	10.8	12.6	7.2	14.4	6.2
Median	32.3	10.3	9.6	16.7	10.7	14.7	7.1	14.8	6.8
Minimum	3.2	2.8	2.1	5.0	6.2	7.2	3.5	2.5	4.0
Maximum	113.3	69.5	100.6	112.7	21.4	21.1	21.3	27.9	9.5
Standard Deviation	24.9	20.1	17.4	21.2	3.3	10.5	4.2	7.2	3.9
95 % Student's *t*-Interval	28.4<μ<40.4	12.6<μ<26.4	8.9<μ<19.3	15.6<μ<28.8	9.7<μ<12.7		6.5<μ<9.7	11.7<μ<21.5	
95 % Student's *t*-Interval**	20.0<μ<30.8	9.5<μ<17.5	7.4<μ<12.1	13.5<μ<20.9	9.5<μ<12.2		6.1<μ<8.6	9.3<μ<22.5	

All values expressed in mg kg^{-1}. ** - Student's *t*-interval based on geometric means.

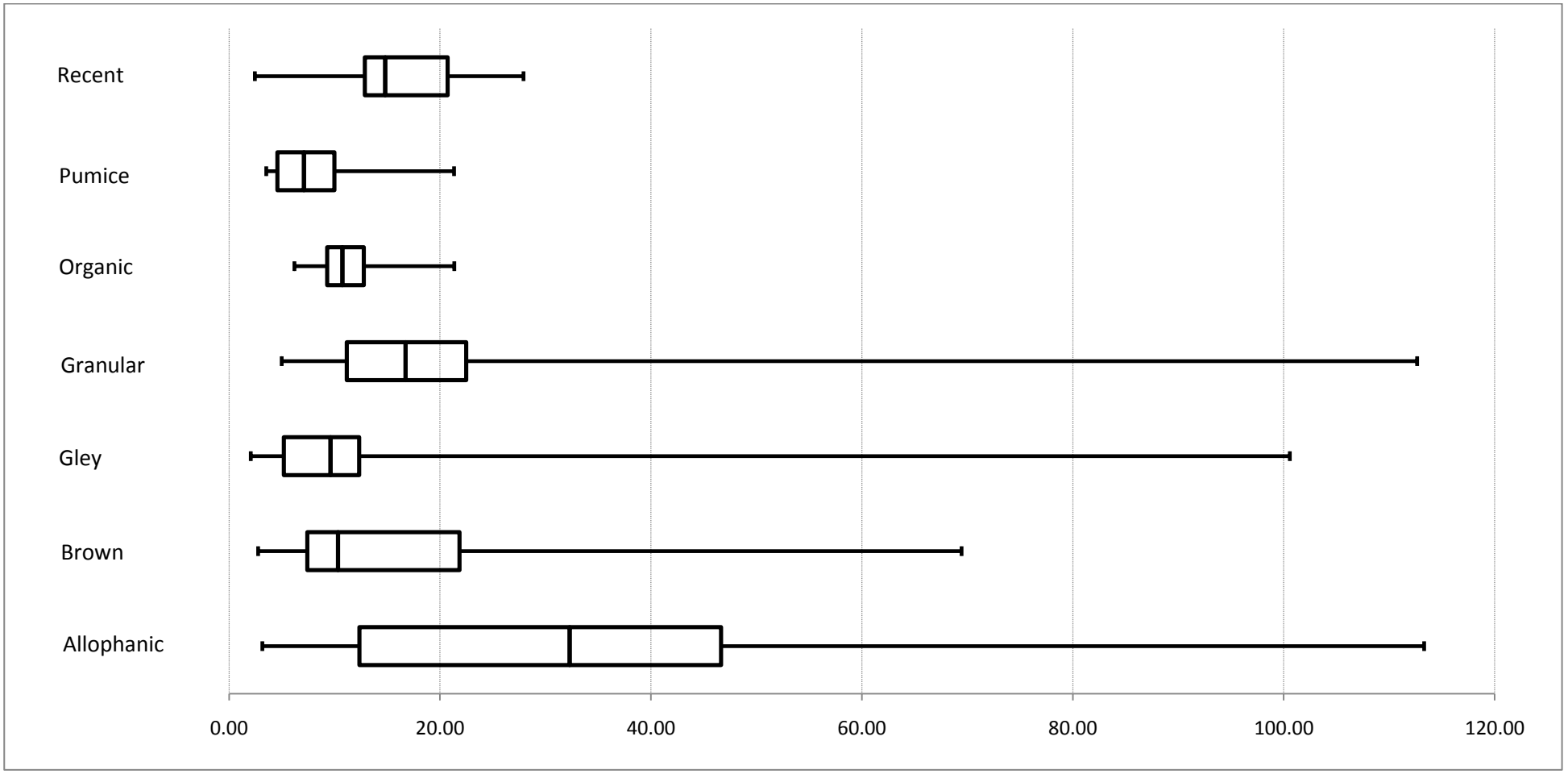

Figure 6-3 - Box plots showing the range of iodine concentrations (mg kg^{-1}) of the various Soil Orders in the Waikato Region.

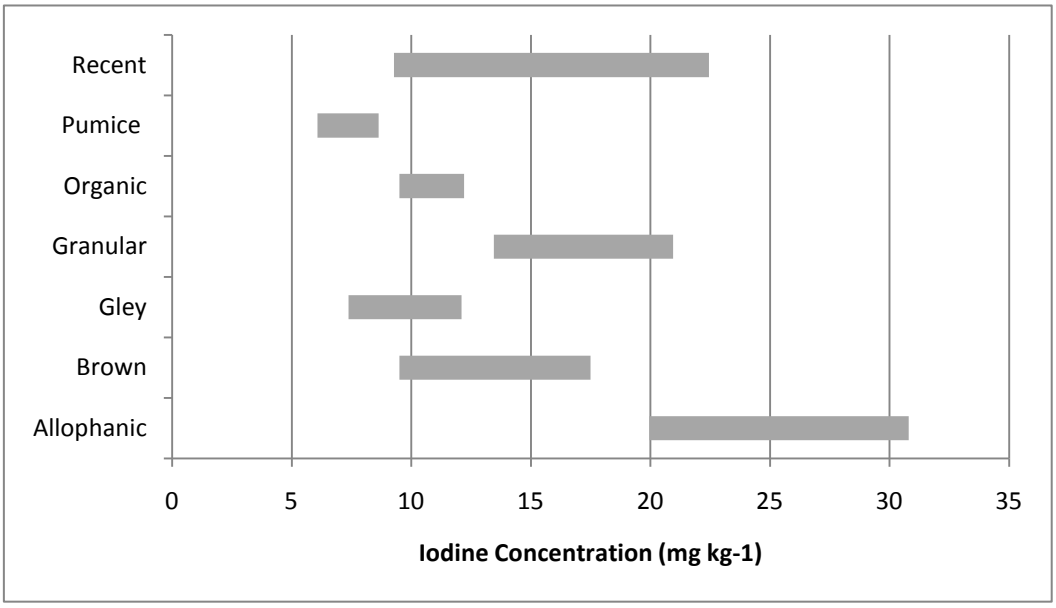

Figure 6-4 - The 95% Student's t-interval for the iodine concentration from various soil orders.

Previous work has found soil texture is an important influence on iodine content of a soil. In one study, the relationship between the soil texture and geometric mean content of iodine follows the trend: peat (7.0 mg kg^{-1}) > clay (4.3 mg kg^{-1}) > silt (3.0 mg kg^{-1}) > sand (2.2 mg kg^{-1}) [40].

Based on soil texture alone, it would be expected that the peat based soils in the Waikato Region would contain the highest levels of iodine (as is observed with peat soils in the U.K) [27]. This was found not to be true, with the peat soils containing less iodine on average than many of the other Soil Orders. This may suggest that the role of organic matter in Waikato soils is not the dominant factor in iodine retention.

Both a source of iodine and an ability to retain iodine would be needed to return high levels of iodine in a soil. Therefore the lower concentrations of iodine in the organic (peat based) soils of the Waikato region may also indicate that the source of iodine to these is also low. Waikato peats are largely dome bogs [96, 97], which are defined by having rainfall as the dominant hydrological input [97]. This rainfall would also act as the dominant source of iodine in these peats and peat based soils. This would tend to suggest that the source of iodine through rainfall and atmospheric

deposition is low, or the hydraulic effects of this rainfall on the peat may remove iodine through processes such as leaching before the organic matter has the ability to retain it. If this was the case these organic soils may be a poor indicator of the true retention characteristics that organic matter has on iodine. However, Gley soils usually contain high organic matter [98], which if true could indicate the importance organic matter has in retaining iodine in soils. This was found not to be the case in the Waikato soils, with Gley soils showing the fifth highest carbon content of the Soil Orders. Therefore the affinity of organic matter to iodine is not displayed well in the Waikato soils.

The four Soil Orders that return the highest iodine concentrations (Allophanic, Brown, Gley, and Granular) are all soils that have a clay/colloid contribution. Clays and colloids increase the adsorption capacity of a soil [14]. Therefore, based on these results the adsorption capacity (related to the clay/colloidal fraction of the soil) in the Waikato soils may be more important than the organic matter contribution in iodine retention.

Another possible explanation in the difference in organic soils compared to clay based soils is that the soil pH may play an equally important role in iodine retention, as the effectiveness of aluminium and iron oxides, and organic matter in sorbing iodine is influenced by soil pH [27]. The sorption of iron oxides is greatest with pH<5, aluminium oxides between pH 5-7, and organic matter with pH>7 [27]. Therefore, based on soil pH, it would be expected that the aluminium oxides would be the most important in iodine retention as Waikato soils have average pH values of 5.1 (background soils) and 5.9 (farmed soils) with a overall average pH of 5.4 [76].

The mineral allophane, found in Allophanic soils, can protect organic matter [99] and as organic matter is believed to be important for iodine fixation, this could explain the high concentrations seen in these soils compared to others. Then again, the high adsorption capacity of Allophanic soils could lead to a greater iodine fixation potential, which in turn will result in greater iodine retention.

The low iodine concentration seen in the Pumice soils of the Waikato can be explained by the soil texture. Pumice soils are sandy, gravelly soils dominated by pumice and pumice sand [98]. Sand contains the least iodine of the textural groups, most likely due to its low adsorption capacity. However, the pumice soils contain the fourth highest carbon contents (Appendix 4) of the soils tested, which may explain the higher values observed in the pumice soils compared to other sand based soils, due to the fixation of iodine by organic matter.

6.4 Soil Iodine Content in Relation to Land use

Summary statistics of the iodine content of Waikato soils in relation to their generalised land use (farmed, forestry or background) are displayed in Table 6-3 and Figure 6-5.

Background soils, considered to have minimal to no influence from anthropogenic activities, displayed the highest mean iodine content, based on geometric means (17.3 mg kg^{-1}), with forestry soils displaying the lowest mean iodine content with (11.6 mg kg^{-1}). Farmed soils had on average an iodine content between background and forestry soils (14.2 mg kg^{-1}) but contained the highest individual iodine content of the three categories (113.3 mg kg^{-1}), probably as a result of the larger data set.

Farmed soils display the largest range and spread of iodine concentrations based on the difference between the minimum and maximum concentrations, with the forestry soils showing the smallest range. However, all three generalised land uses are positively skewed as displayed in the box plots.

All three categories of soils appear to have no significant difference between the means, based on the 95% Students *t*-interval calculated using both the arithmetic and geometric means. These intervals all overlap with the other corresponding intervals which indicate that there is a possibility that the true means may have very similar values.

There appears to be greater uncertainty with the background and forestry soils in that the respective *t*-intervals show a large range that the actual arithmetic mean may fall within. This is most likely to reflect the smaller sample size and larger sample to sample variability for both these categories compared to the farmed soils where there is less uncertainty. The Student's *t*-interval based on the geometric mean is a better representation of the true mean, and also displays less sample to sample variation from the result of log normalising the data.

Table 6-3 - Summary statistics of iodine concentration relating to farmed, forestry and background soils.

	Farmed Soils (N=219)	Forestry Soils (N=17)	Background Soils (N=12)
Mean	20.9	17.2	25.9
Geometric Mean	14.2	11.6	17.3
Median	12.0	9.5	12.0
Minimum	2.1	3.8	5.2
Maximum	113.3	69.5	100.6
Standard Deviation	20.7	19.0	28.2
95th Percentile	61.7	66.2	96.5
95% Student's *t*-interval	18.2<μ<23.7	7.5<μ<27.0	8.0<μ<43.8
95% Student's t-interval**	12.6<μ<15.9	7.5<μ<18.0	9.8<μ<30.4

****** - Student's *t*-interval based on geometric mean.

All values are in mg kg^{-1}.

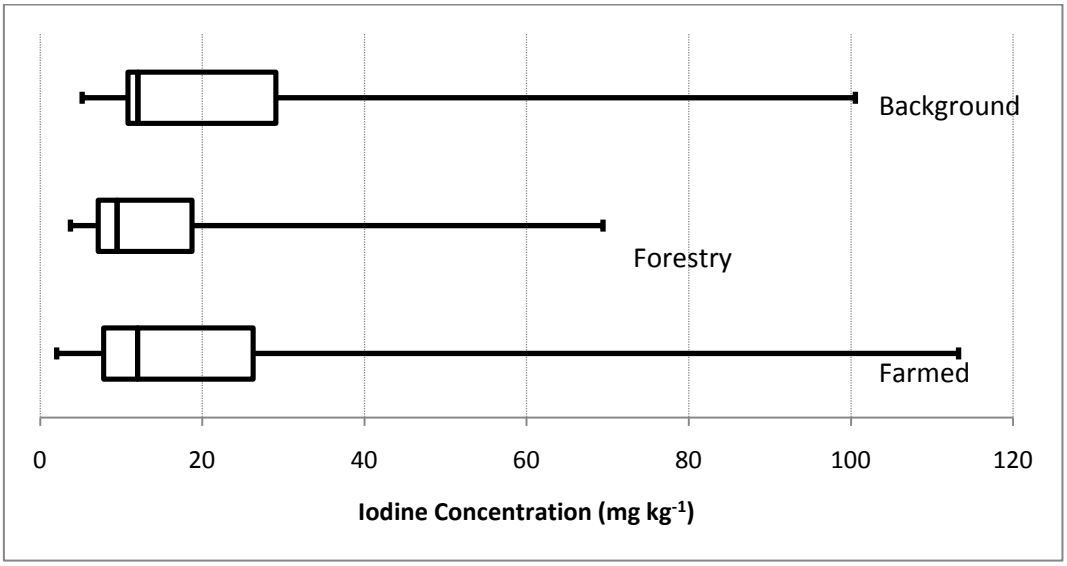

Figure 6-5 - Boxplots showing the iodine content distribution of farmed, forestry and background soils.

Background soils showed the highest concentrations of iodine compared to farmed and forestry soils. This is likely to reflect the influence of soil properties in retaining iodine as the sources of iodine would theoretically be less than both farmed and forestry sources (no anthropogenic).

Organic content is one property that explains the increased iodine concentration of these soils. The background soils of the Waikato displayed the highest organic carbon content (%C) of the three land use categories (Appendix 4). This indicates that organic matter in these soils is important in retaining iodine, however no correlation was observed between %C and iodine (Table 6-5) which would be expected if this was the case.

As the background soils are considered to have no anthropogenic influences it also may indicate that farming and forestry practices such as produce removal or irrigation may cause iodine to be lost from the soil.

However, the highest concentration of iodine was observed in a farmed soil suggesting that some farming practices, such as fertilisation, may also act as an additional iodine source. Fertilisation could also be used to explain the lower mean iodine content compared to background soils, through desorption of adsorbed iodine as is seen with some other elements [100, 101].

A possible explanation for the low mean iodine content in the forestry soils is that there is typically be less organic matter (carbon content) in forestry soils compared to farmed and background soils. This may be due to reduced carbon turnover occurring in forestry soils because of the nature of the plant species commonly used in New Zealand forestry (Radiata pines [102]). This is supported with the forestry soils having the lowest percentage carbon (on average) of the three categories (Table A-6, Appendix 4). If this was the case, it would be expected that forestry soils may have a reduced adsorption capacity (reduced iodine fixation potential), which would explain the lower iodine concentrations in these soils.

If this was valid, it would also be expected that the correlation between the percentage carbon (%C) and iodine concentration would become significant in the forestry soils. This was supported by forestry soils displaying an increased correlation with %C ($p<0.01$) compared to all Waikato soils and the farmed and background soils (Table 6-5).

Another possible explanation is that forestry is generally planted on erosion-prone land that is less suitable for farming. Soil organic matter tends to be lost during the erosion process [103] and this land could have a lower capacity for adsorbing and retaining iodine, which would result in decreased soil iodine concentrations. Forestry was generally planted on areas less suitable for pastoral farming with a large proportion of forestry planted on pumice soils of the South Waikato that were associated with bush sickness (cause by cobalt deficiency) [102, 104]. These pumice soils were shown in previous studies to be hydrological and erosion sensitive [105].

6.5 Soil Iodine Content in Relation to Soil Depth

The iodine content in relation to soil depth was assessed using the sub-regional transect samples which were collected over two soil depths. Initial results, based geometric means, suggest that there is an enrichment of iodine lower down in the soil profile (10-20 cm) than the surface (0-10 cm). This is due to the difference in the geometric mean iodine contents of the two soil depths of 10.8 and 12.4 mg kg^{-1} respectively (Table 6-4).

The 95% Student's *t*-interval can be used as a guide to the range that the true mean may fall within (based on 95% confidence). The range observed for both depths is higher when this interval is based on arithmetic means as opposed to the geometric means. The Student's *t*-interval based on geometric means appears narrower because of less sample to sample variation, a result of log-normalising the data.

However, regardless of the two methods used, the intervals for both soil depths overlap indicating that there may be no difference in the mean iodine concentration between the two soil depths.

Table 6-4 - Summary statistics of the Iodine content of two different soil depths.

	Soil Depth A (0-10 cm)	**Soil Depth B (10-20cm)**
Mean (N=105)	15.0	19.6
Geometric Mean	10.8	12.4
Median	10.1	11.4
Minimum	2.1	1.5
Maximum	100.6	113.0
Standard Deviation	14.6	22.6
95th Percentile	45.6	64.8
95 % Student's *t*-interval	12.1<μ<17.8	15.2<μ<24.0
95 % Student's t-interval**	9.3<μ<12.6	10.4<μ<14.8

****** - Student's *t*-interval based on geometric mean. All values expressed in mg kg^{-1}.

To deduce whether a difference occurs between the two soil depths a paired Student's *t*-test was carried out. This was carried out to test

whether depth B (10-20 cm) was higher on average than depth A (0-10 cm).

The results of the paired Students *t*-test ($p<0.0001$, $N=105$) indicates that there is a statistical difference between the iodine concentration of the two soil depths. Therefore, it was found that on average, the iodine concentration of soils at most sample sites is lower at the surface (0-10 cm) than it is at depth (10-20 cm).

The results from this project are consistent with other findings from Turkey, where iodine is reported to peak in concentration lower in the soil profile (~30-40 cm) compared to the surface (0-20 cm) [106]. This was found to be largely due to the leaching of iodine through the surface soil to lower in the soil profile where the clay content was generally higher providing increased iodine retention [106].

However, other studies suggest that iodine is generally greatest in the soil surface and decreases with depth [107] of which the findings of this project display the opposite.

Iodine distribution in the soil profile is considered dependent on the parent material, due to the soil being derived from differing parent materials, with differing retention characteristics [108]. Therefore, the iodine content in relation to soil depth could be considered to be variable and dependent on the retention characteristics defined by the parent material. This would explain the differing trends observed around the world in relation to the iodine content and soil depth.

6.6 Soil Iodine Content and Distance from the Coast

There appears to be no clear relationship between the iodine concentration and distance from the coast supporting coastal enrichment of iodine in the surface (0-10 cm) soils (Figure 6-6).

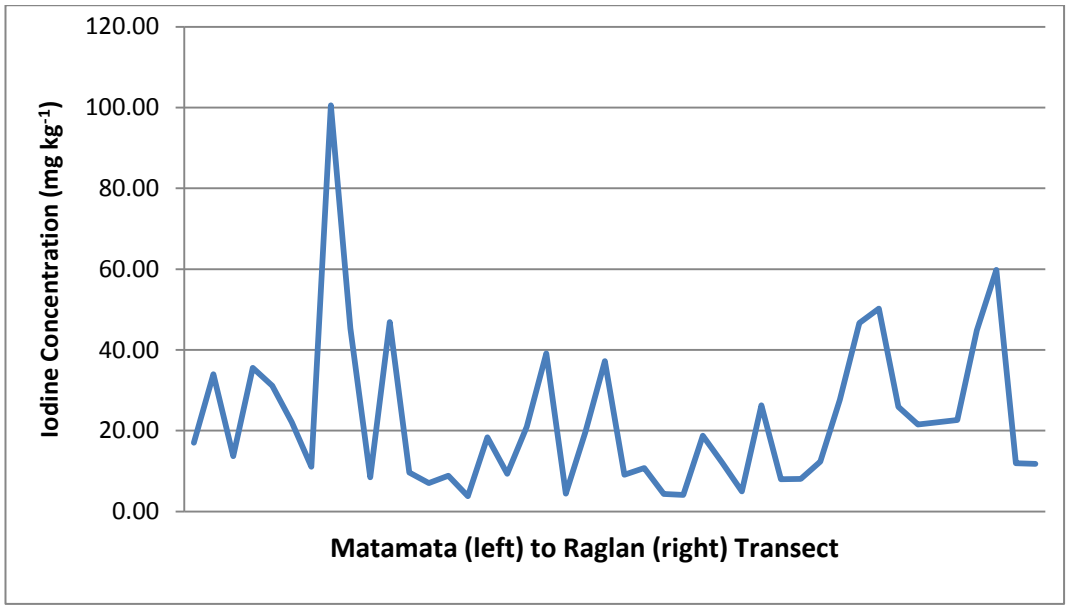

Figure 6-6 - Iodine concentration (mg kg^{-1}) in relation to distance from the coast along the Matamata (86km from coast) to Raglan (0 km from coast) transect.

Using the ratio of the two soil depths along the Matamata to Raglan transect there also appears to be no significant increase in concentration of iodine at coastal sites compared to those more inland (Figure 6-7).

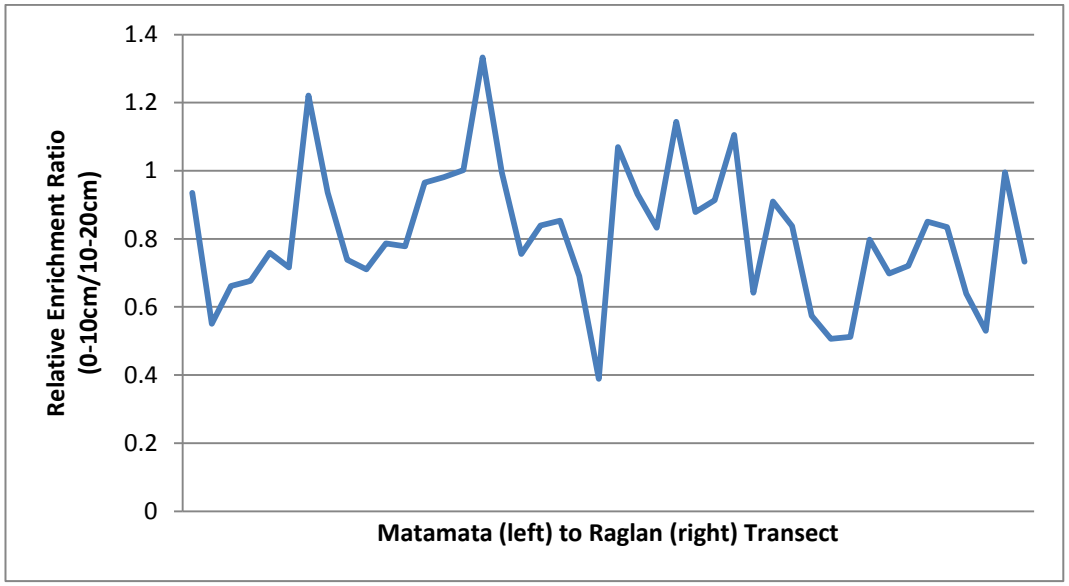

Figure 6-7 – Relative Enrichment (ratio) of iodine concentration between the two soil depths (0-10cm/10-20cm) along the Matamata to Raglan Transect.

If there was enrichment in the surface soils closer to the coast, due to increased atmospheric deposition, it would be expected that the relative enrichment ratio between the two soil depths (0-10 cm and 10-20 cm) would increase. This would be because of the top layer of soil receiving more iodine from atmospheric deposition.

This relative enrichment in the surface soil was not observed, therefore no relationship between iodine concentration and distance from the coast can be drawn. The variation in the ratios seen is most likely an effect of the different soil properties in retaining iodine – noting in particular that the proportion of various adsorptive phases with depth is likely to differ between different soil types.

This agrees with findings that small island based nations generally do not have a noticeable change in iodine content in relation to distance from the coast. In England, there was no correlation found between the iodine content of soils and distance from the coast with some coastal soils containing high levels of iodine with others containing low levels [15, 109]. However, it was noted that soils within 50 km from the coast had on average higher iodine contents than soils greater than 50 km from the coast [109].

The effect of soil type and the differing soil properties are most likely the main factors causing the variation of iodine concentration and relative enrichment ratio across the Matamata to Raglan transect.

However, if the rate of loss of iodine was greater than the addition rate there would be no evidence of enrichment, despite the fact it could be occurring. As iodine is suggested to arise from atmospheric deposition (precipitation) [14], the source may act to also leach the iodine through the surface of the soil profile before it has time to be retained. Therefore, the iodine content of rainfall across a coastal-inland transect may vary, which would act as an indication of potential coastal enrichment.

6.7 Correlation Analysis

Pearson's correlation analysis was used to show the correlations between iodine (TMAH extracted) and various soil chemical characteristics and total acid recoverable elements (refer to Table 4-1 for previous sample analysis). A total correlation matrix (Table 6-5) was carried out for all the soil samples pooled together, and the soils based on land use (farmed, forestry and background soils). This was done in an attempt to deduce whether farmed, forestry and background soils were correlated to different soil components as it was assumed these sites had minimal to no anthropogenic influences.

The data was log-normalised (prior to the derivation of the correlation matrix) where histograms showed signs of a skew distribution, which was necessary for most elements. However some did not need log-normalising (such as pH) as they were normally distributed.

The correlation matrix consisted of correlation coefficients (R values) which had a significance based on the number of pairs that contributed towards the correlation. Therefore, the R value defined the significance of the correlation according to respective p values, based on the number of sample pairs between the two variables correlated. For example, a correlation between 12 pairs of data representing iodine and pH, would require an R value of 0.576 or higher for a significance of $p<0.05$, 0.708 ($p<0.01$), and 0.823 ($p<0.001$).

The number of data pairs that were analysed varied between each two correlated components. The regression values and corresponding number of pairs (N value) for each correlation are displayed in Appendix 5.

Table 6-5 - Correlation analysis of iodine in Waikato soils with relation to land use. The significance of each variable is based on the respective p value defined by the N value (number of pairs, N varies) and regression coefficient.

	All Soils	Farmed	Forestry	Background
Se	***	***	***	**
pH	ns	ns	ns	ns
% C	*	*	**	ns
% N	***	***	**	ns
Al	***	***	***	ns
Sb	ns	*	**	ns
As	***	***	*	ns
Ba	***	***	ns	ns
Bi	***	***	*	*
B	***	***	ns	ns
Cd	**	***	*	ns
Cs	ns	ns	ns	ns
Ca	ns	ns	ns	ns
Co	***	***	ns	ns
Cr	*	**	ns	ns
Cu	***	***	**	ns
F	ns	*	ns	ns
Fe	***	***	ns	ns
La	***	***	**	*
Pb	***	***	*	ns
Li	***	***	ns	ns
Mg	**	***	ns	ns
Mn	***	***	*	ns
Hg	***	***	***	***
Mo	***	***	*	*
Ni	***	***	ns	ns
P	*	***	*	ns
K	ns	ns	ns	ns
Rb	ns	ns	ns	ns
Ag	***	***	**	**
Na	ns	ns	*	ns
Sr	***	***	ns	ns
Tl	***	***	*	ns
Sn	***	***	**	ns
U	***	***	**	ns
V	***	***	ns	ns
Zn	***	***	ns	ns
Olsen P	***	***	ns	ns

Significance: ns: not significant, *: p<0.05, **: p<0.01, ***: p<0.001.

It was expected that iodine should have a good correlation with the organic content of the soil [14]. However, for the soils analysed from the Waikato region the correlation between the percentage carbon (%C) and iodine was only just significant for all soils and farmed soils ($p<0.05$). Forestry soils show greater correlation ($p<0.01$), with the background soils displaying no significant correlation between iodine concentration and %C. The finding that the background soils show no correlation with %C indicates that %C may not a dominant factor in retaining iodine in these soils. However, the sample size for background soils (N=12) is smaller than the other categories which may limit the statistical comparison. The smaller sample size would require the correlation coefficient between the two properties to be larger to be considered significant.

Iodine in all the Waikato soils was strongly correlated to aluminium, iron and manganese ($p<0.001$). This reinforces the idea that iodine retention in soil is strongly influenced by clays (which are aluminosilicate minerals) and hydrated iron and manganese oxides [15, 22], and further reinforces the point that these oxides are likely more important in the Waikato soils at retaining iodine than organic matter.

Aluminium appears to be the most strongly correlated ($p<0.001$) element to iodine for all the Waikato soils along with the farmed and forestry sites, but is not significant for background soils.

Iron is also strongly correlated ($p<0.001$) to iodine in all the soils, however, when the forestry soils are considered, it becomes non-significant ($p>0.05$). This suggests that iron oxides play an important role in the iodine retention in soils, particularly the farmed soils, but this role appears to be less significant than that of the aluminium oxides.

Manganese is also strongly correlated to iodine in the farmed soils ($p<0.001$) and slightly correlated in the forestry soils ($p<0.05$). There is no correlation observed in the background soils.

Farmed soils show correlations to the greatest number of chemical properties, and based on the large sample size, causes all the Waikato soils to show similar correlations when they are pooled together.

Using the Point of Zero Charge (PZC) of the iron and manganese oxides in soil, the correlation of many of the other trace elements and heavy metals can be explained. Waikato soils have an average pH of 5.6. At this pH the PZC in iron oxides would carry a net positive charge, while the manganese oxides would carry a net negative charge. Based on this, elements such as arsenic (arsenate), molybdenum (molybdate), and vanadium (vanadate) will be associated and bound to the net positive iron oxides. Other elements such as barium (Ba^{2+}) and other positively charged anions will be associated with the net negative manganese oxides [1].

The aluminium oxides (and aluminosilicates) will also have elements associated to them (such as boron, lithium, and lanthanum).

Therefore, many of the elements may only be showing a strong correlation to iodine through their own respective strong correlations with aluminium, iron, and manganese. Thus, these elements are most likely indirectly related to iodine.

Farmed soils show strong correlations between iodine content and Olsen P, zinc, uranium, phosphorus which are all associated with fertiliser use (and facial eczema remedies for zinc [1]). This could suggest that farming is having an effect on the concentrations of iodine in the soil, as these correlations are not seen in background soils.

The forestry soils largely show the same correlations as farmed soils, though the correlations are less extensive. Background soils only display significant correlations with mercury ($p<0.001$), silver and selenium ($p<0.01$), molybdenum, bismuth and lanthanum ($p<0.05$).

The difference in the nature of correlations between farmed, forestry and background soils, suggest that anthropogenic activities may alter the interactions of soil chemical properties with iodine. However, the sample size is considerably larger for farmed soils (N=368) compared to forestry (N=23) and background (N=12) soils. Therefore, the correlations for forestry and background soils may be under-represented compared to farmed soils.

Despite this, iodine appears to be strongly correlated with mercury ($p<0.001$), and silver ($p<0.01$) for all the various land uses, possibly reflecting the formation and insolubilities of HgI_2 and AgI in soil. However, one particular similarity between these elements is they are considered chalcophilic in which they are chalcogen-loving (Chalcogens: S, Se, Te, Po) [14, 17]. This suggests that iodine, mercury and silver may be related to chalcogens in the soil. This would explain the correlation between iodine and selenium, and would suggest that iodine and the other chalcophilic elements would also be expected to be correlated to sulfur. However, no information on sulfur was collected or analysed in this project, and there was no previous data on sulfur available for the Waikato soils.

It is also important to note that the type of extraction technique used in this study (TMAH) may only target inorganic and ionic forms of iodine, and not the organically bound iodine. If this was true it would explain the lack of correlations between organic content of soils and iodine that is often stated in literature.

6.7.1 Summary

The main findings of the correlation analysis indicate that the iodine retention in soils is likely to be more strongly influenced by aluminium and iron oxides compared with organic matter. The strong correlation of iodine in Waikato soils to a large number of elements is most likely through the indirect correlation of these elements to aluminium and iron.

It is also apparent that iodine in soil may have chalcophilic properties through the strong correlation with other chalcophilic elements (Se, Hg and Ag).

Farming and forestry practices may also cause iodine to be correlated to a greater number of elements compared to background soils, although the small sample size of both forestry and background soils may cause some correlations to be under-estimated.

7 Selenium Status of Waikato Soils: Results and Discussion

7.1 Introduction

Data on the selenium status of soils in the Waikato region in recent years is very limited. There were extensive studies carried out on selenium in New Zealand until the 1980's [3-5, 66, 70]. Since then the selenium status or any changes that may have been occurring remains largely undetermined, and selenium is not routinely reported in soils because of the low levels close to instrumental detection limits.

Chapter 7 presents the status of selenium in Waikato soils and discusses the behaviour of selenium in these soils in relation to soil properties and land use. The selenium results discussed in this section were all based on the TMAH extraction method, which was considered to best represent the total selenium content of the methods tested.

The results in this chapter should be viewed in the light of potentially low level selenium determination being possible compared to complete recovery at higher selenium concentrations, as discussed in Section 5.7.1.3.

Raw data for these analyses are displayed in Appendix 3.

7.2 Overall Selenium status of the Waikato Region

Summary statistics for selenium in Waikato soils is presented in Table 7-1. The selenium concentration of Waikato soils has a mean concentration of 1.77 mg kg^{-1}, a geometric mean of 1.33 mg kg^{-1}, and median of 1.35 mg kg^{-1}. The geometric mean gives a better representation of the central tendency of the data as there is a skewed nature to the results of the 256 samples analysed. The skew of the raw data is shown in Figure 5-1.

The 95% Students *t*-interval indicates the actual mean may fall within the range of 1.6 to 2.0 mg kg^{-1} with 95% confidence.

The maximum selenium concentration observed in the soils tested was 12.1 mg kg^{-1}, with the minimum concentration 0.18 mg kg^{-1}. The range of results between these two values indicates a large amount of variation of selenium between the soils of the Waikato (Figure 7-1).

Table 7-1 - Summary statistics of the selenium concentration of Waikato Soils, using a TMAH extraction method.

	Selenium Concentration (mg kg^{-1}) N=256
Mean	1.77
Geometric Mean	1.33
Median	1.35
Standard Deviation	1.51
Minimum	0.18
Maximum	12.1
95 % Student's *t*-interval	1.6<μ<2.0
Upper 95th Percentile	4.4

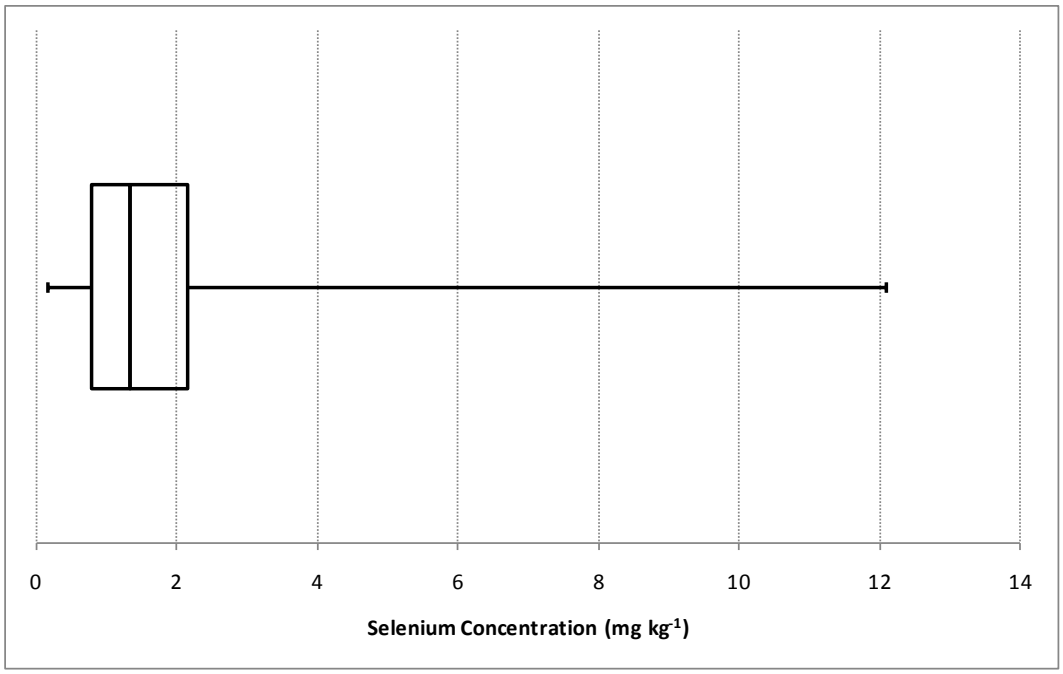

Figure 7-1 - Box plot displaying the variation of selenium concentration in the Waikato soils (N=256).

The mean and geometric mean selenium concentration of the Waikato soils are both higher than the worldwide mean selenium content of soils of 0.4 mg kg^{-1} [13, 110].

The Waikato soils, despite having a mean content higher than the worldwide mean content (0.04 mg kg^{-1}), show a similar range to most soils (between 0.01-2.0 mg kg^{-1} [13]).

The selenium content of Waikato soils analysed in this project (mean 1.77 mg kg^{-1}, and range, 0.18-12.1 mg kg^{-1}), compare in good agreement with previous studies [3] which found the selenium content of most New Zealand soils to be in the range of 0.1 to 2 mg kg^{-1}. The mean selenium content of New Zealand soils was also suggested to be 0.6 mg kg^{-1} in a similar study [5]. Concentrations of up to 17.2 mg kg^{-1} selenium were observed [5], however, it should be noted that the soil containing 17.2 mg kg^{-1} was an Organic soil from an offshore Island (Campbell Island) and not from mainland New Zealand.

The previously suggested mean selenium content of New Zealand soils (0.6 mg kg^{-1}) is lower than the mean selenium content determined by this project, suggesting that Waikato soils may have more selenium than other regions nationally. However, this value was reported prior to the adopted use of selenium prills and supplementation in New Zealand (beginning 1959, with fertilisers permited to allow addition of selenium in 1982 [50]) to prevent selenium deficiency. The use of these prills and supplements may explain why there was a higher mean selenium content obtained from this project. Despite this, the range of selenium concentrations observed for the Waikato soils are similar to what has previously been obtained nationally.

Total selenium has been considered to be the primary factor in relating to the selenium status of New Zealand soils, with no deficiencies observed over concentrations of 0.6 mg kg^{-1} [50]. This would suggest that the current status of selenium in Waikato soils is sufficient to prevent deficiencies (based on the mean content). However, the soils analysed which contained less than 0.6 mg kg^{-1}, could be considered to be at risk of causing selenium deficiencies. This assumes that the food source is

limited to localised production and does not consider the inputs of selenium from imported food.

On the contrary, some soils may have the potential to pose problems through toxicity, particularly the few soils that returned above average concentrations. The level of selenium in soil that causes potential toxicity was suggested to be as low as 0.5 mg kg^{-1} [3, 111]. This value is misleading as it is smaller than the value stated above which indicates the concentration that if soils are below they are likely to be deficient. However, this value was stated back in the 1930's with no such figure being able to be found in the literature since and it is most likely to be linked to the bio-availability of the selenium in the soil. This is because the bio-available selenium would be the fraction available for plant uptake and hence consumption. Using this threshold value, a number of soils in the Waikato contain levels of selenium that may be potentially toxic if a significant proportion of it is bio-available. Despite this, there are no known areas in New Zealand where selenium toxicity has been an issue [3].

7.3 Soil Selenium Content in relation to Soil Order

The selenium status of soils appears to relate to the Soil Order. The underlying geology (parent material) is thought to be the primary control on selenium concentration in soil [13]. Therefore, it could also be expected that the selenium concentration of soil is influenced by the Soil Order because of the influence the parent material has in defining it.

Two Soil Orders have only 2 samples each (Ultic and Podzol soils) and the samples have consequently been left out of further statistical analysis and the box plots

There is a large amount of variation seen when the selenium concentrations are compared by soil order. Summary statistics and box plots of the selenium concentration of nine soil orders are displayed in Table 7-2 and Figure 7-2.

The geometric means are likely to better represent the mean selenium concentration because of the positive skew causing the arithmetic mean values to be also skewed to higher values. Using the geometric means, Granular soils display the highest concentrations of selenium (on average), while pumice soils display the lowest selenium concentrations, closely followed by Podzol soils. The order from highest geometric concentration to lowest was: Granular > Allophanic > Organic > Gley > Brown > Recent > Pumice.

Pumice and Podzol soils appear to have on average less selenium than all other soil orders. This is consistent with the finding that selenium adsorption of New Zealand soils was the lowest in Podzol soils [66], while Pumice soils of New Zealand are generally considered to be the predominant selenium deficient soils [5, 66].

The highest concentration of selenium in all the soils tested was found in a Granular soil, while the lowest concentration was seen in a Recent soil. This would be expected as Recent soils are likely to reflect the concentration of the parent material they are derived from because of their limited pedological time to develop adsorption sites.

Granular soils show the largest range in concentration, as defined by the box plots, followed by Allophanic soils. Brown, Gley, and Organic soils all show a similar amount of variation and range between the selenium concentrations, while Podzol soils show a very small range. The box plot of Pumice soils appears to be skewed because of the maximum concentration observed being much higher than the majority of the samples.

The range of these Student's *t*-intervals for the various Soil orders are displayed in Figure 7-3 (based on geometric means). Using the relative overlap of the 95% Student's *t*-interval it can be seen that Granular and Allophanic soils are likely to have higher average selenium concentrations than the Brown, Gley, Organic, and Recent soils. It is likely that no difference can be drawn between the mean selenium concentration of Brown, Gley, Organic, and Recent soils because the Student's *t*-intervals showing some degree of overlap with each other.

Pumice soils show significantly less selenium, on average, than most soil types other than Recent soils where a small overlap (insignificant) in the intervals is seen.

Table 7-2 - Summary Statistics of the Selenium Concentration (mg kg^{-1}) for various Soil Orders of the Waikato.

	Allophanic (N=69)	Brown (N=35)	Gley (N=45)	Granular (N=42)	Organic (N=21)	Podzol (N=2)	Pumice (N=29)	Recent (N=11)	Ultic (N=2)
Mean	2.17	1.47	1.52	2.85	1.49	0.58	0.66	1.03	0.97
Geometric Mean	1.80	1.27	1.28	2.10	1.31	0.54	0.50	0.89	0.89
Median	1.80	1.12	1.19	1.64	1.50	0.58	0.43	1.01	0.97
Minimum	0.42	0.47	0.39	0.64	0.19	0.37	0.24	0.18	0.57
Maximum	8.87	3.75	4.31	12.1	2.59	0.80	4.28	1.90	1.37
Standard Deviation	1.43	0.85	0.95	2.41	0.64	0.30	0.76	0.50	0.57
95 % Student's *t*-interval	1.82<μ<2.51	1.18<μ<1.77	1.24<μ<1.81	2.10<μ<3.60	1.20<μ<1.78		0.37<μ<0.95	0.70<μ<1.37	
95 % Student's *t*-interval**	1.55<μ<2.09	1.06<μ<1.53	1.08<μ<1.53	1.60<μ<2.66	0.99<μ<1.72		0.39<μ<0.64	0.59<μ<1.37	

All values expressed in mg kg^{-1}. ** - Student's *t*-interval based on geometric means.

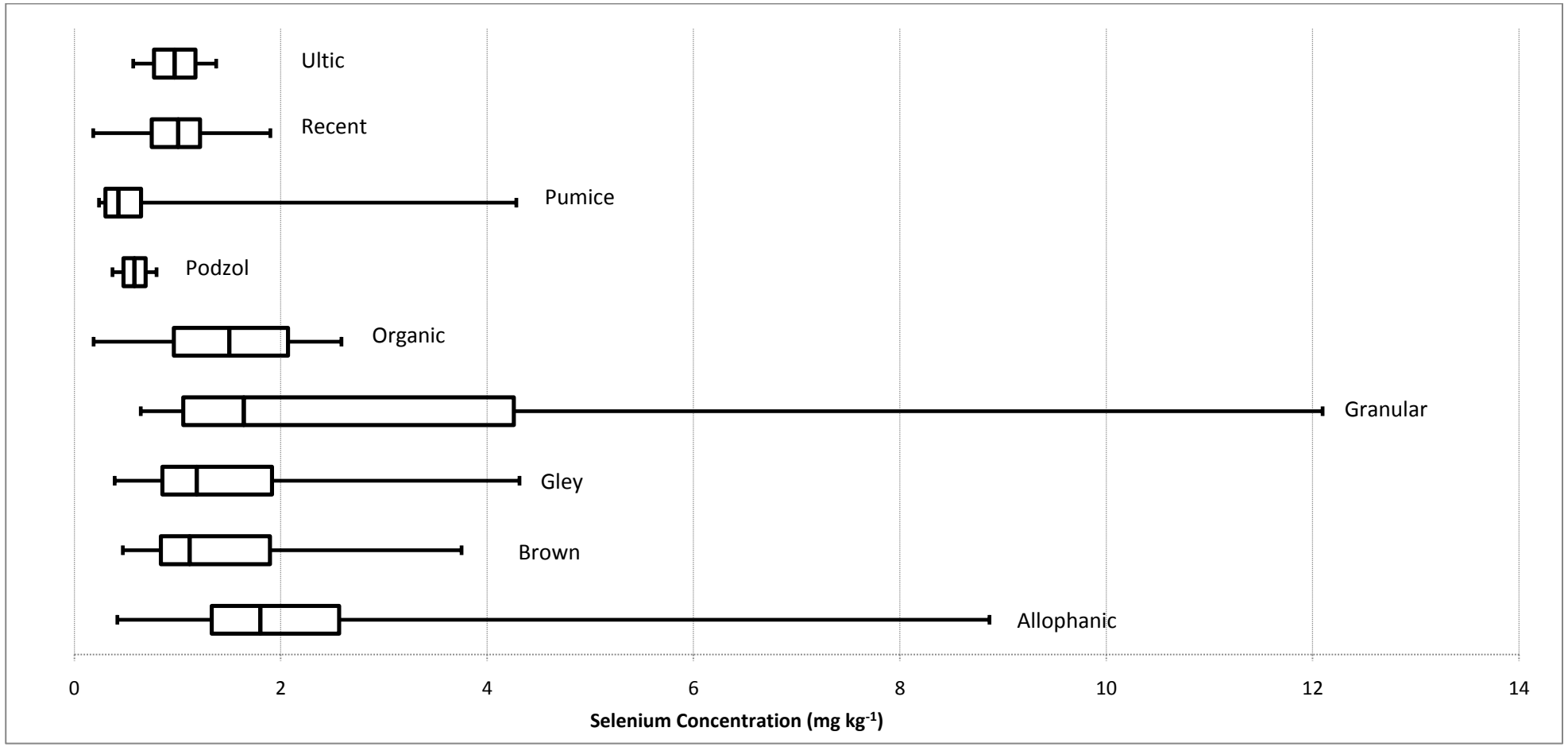

Figure 7-2 - Box plots showing the range of selenium concentrations of the various Soil Orders in the Waikato Region.

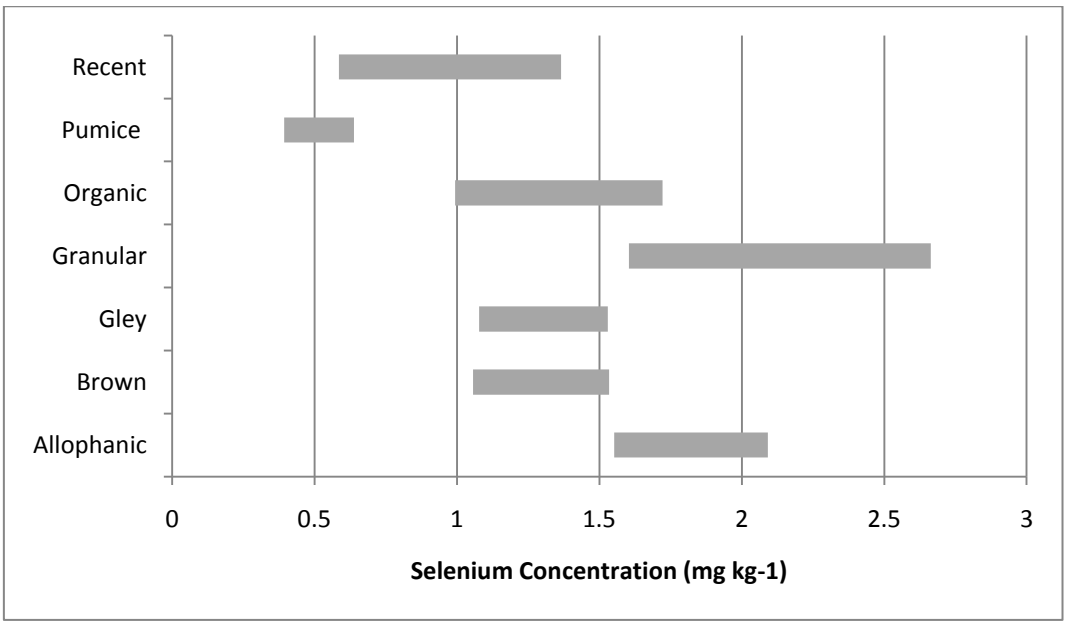

Figure 7-3 - The 95% Student's *t*-interval for the selenium concentration of soils from various Soil Orders.

The sorption of selenium to soils has previously been found to be affected by a range of soil properties, and the selenium sorption generally followed the order: high organic carbon soil>calcareous soil>normal soil>saline soil>alkali soil [112]. Previously the factors that were shown to have a positive influence on the sorption of selenium were organic carbon, clay content, $CaCO_3$, and the cation exchange capacity. The negative influences were high salt content, alkalinity and pH [112]. From these findings it would be expected that the Organic soils in the Waikato region would contain the highest levels of selenium, because of the strong sorption selenium has to organic matter. However, this was not the case as the Organic soils contained the fourth highest selenium content (on average) of the Soil Orders that were analysed.

The soils that contained more selenium than the Organic soils have a strong associated with clay content of the soil. Allophanic, Gley, Granular, and Brown soils all have a significant contribution of clay/colloids. This suggests that the selenium retention in the Waikato region is more influenced by the clay fraction of the soil than the organic fraction. This agrees with the findings that in New Zealand the total selenium content increases with clay content [50]. Selenium is also suggested to be retained

by the clay content of a soil during pedogenesis [50]. This is also supported using the correlation analysis results discussed later.

The selenium content of soils in the Waikato derived from limestone was not investigated in this project. Calcium carbonate ($CaCO_3$) is suggested to have a positive influence on selenium sorption in soil [112], in which case soils derived from limestone may show significant concentrations of selenium. The high selenium concentrations in limestone soils may be due to the presence of insoluble calcium selenate and selenides.

The predominant selenium deficient soils in New Zealand are the Pumice, Pallic and Semi-arid soils [66]. The findings of this project agree with Pumice soils being the most prone to deficiencies shown the low selenium concentration. It would also be important to suggest that Podzol, Ultic, and Recent soils may also be prone to cause selenium deficiency due to their low average selenium contents. However, the species and bio-availability of selenium are likely to have a major influence on plant uptake [16], and hence affect the susceptibility of soils to deficiency.

7.4 Soil Selenium Content in relation to Land use

The selenium content of soils between farmed, forestry and background soils appears to be very similar based on the summary statistics (Table 7-3). Background soils, considered to be uninfluenced by anthropogenic activities, show the highest selenium concentrations (on average), with forestry soils displaying the lowest. The farmed soils show the maximum selenium concentration of the soils tested (probably because of the large number of samples), and also display the largest variation (spread) of the soils (Figure 7-4).

However, the three different categories are likely to be indifferent based on the individual 95% Student's *t*-intervals all appearing to overlap. This indicates that the true mean value for the generalised land uses may all have the same value.

Table 7-3 - Summary statistics of the selenium concentration (mg kg^{-1}) in soil in relation to farmed, forestry and background soils.

	Farmed Soils (N=219)	Forestry Soils (N=17)	Background Soils (N=12)
Mean	1.79	1.13	2.06
Geometric Mean	1.39	0.84	1.50
Median	1.39	1.08	1.66
Minimum	0.25	0.24	0.19
Maximum	8.87	3.42	4.88
Standard Deviation	1.39	0.93	1.49
95th Percentile	4.36	3.34	4.82
95% Student's *t*-interval	$1.60<\mu<1.98$	$0.65<\mu<1.61$	$1.11<\mu<3.00$

All values expressed in mg kg^{-1}.

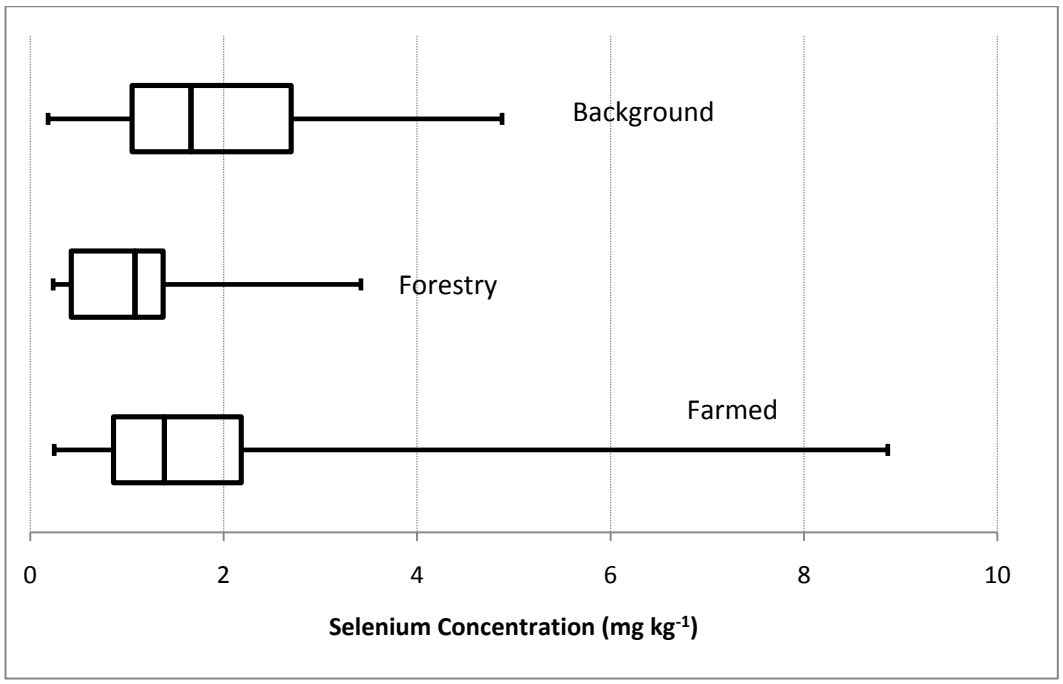

Figure 7-4 - Boxplots showing the selenium distribution of farmed, forestry and background soils.

Farmed soils could be expected to display the highest concentration of selenium due to the widespread use of selenium prills (fertilisers) and supplements that were introduced as a method to reduce selenium deficiency in livestock [4, 50]. High use of prills or supplementation may help explain the observation that the highest selenium concentration occurred in a farmed soil, and that this was approximately twice the concentration of the maximum selenium concentrations observed in the forestry and background soils.

However, this trend is not definitive due to the background soils displaying the highest mean selenium levels. The background soil concentrations for selenium could be considered to represent the natural background selenium concentrations of the various Soil Orders prior to anthropogenic activities. If this was the case it would indicate the selenium concentration and retention characteristics relative to the parent material the soil was derived from.

It is also important to note that no selenium would be removed from the background soils through produce, as would be the case for both farmed and forestry soils. Therefore, the higher selenium content in background soils could suggest that removal of produce in farmed and forestry soils

may be responsible for removing a proportion of selenium. Whatever the reason, it is significant that despite the widespread use of selenium supplements on farmed soils, these soils show no evidence of selenium accumulation, and in fact may be depleted in selenium relative to background soils, suggesting that routes of selenium loss are significant.

The carbon content of the soils may also explain the average selenium concentrations between the three generalised land use categories. Backgrounds soils display the highest percentage carbon with forestry soils containing the least percentage carbon (Appendix 4). The organic matter may act to retain selenium in the soil. This agrees with findings from Japan, whereby it was suggested that organic matter contributes to the accumulation of selenium in soil [71]. However, it was also suggested that the effects of organic matter and volcanic materials on the selenium content of soil was indistinguishable, as they were both strongly correlated [71]. Therefore the influence of volcanic materials on selenium retention may also be important, particularly as the Waikato soils are largely derived from volcanic materials (Appendix 6).

The use of phosphate fertilisers may act as a source of selenium, as rock phosphate can contain significant amounts of selenium [54, 55].However, other fertilisers may also act as a source of selenium. If this was the case it would be expected that the fertilised soils would contain significantly more selenium than the other soils. This was found not to be the case with non-fertilised soils (background sites) containing more selenium on average than fertilised soils (Table 7-4). However, a pooled *t* test fails to rule out any difference between the two means (p=0.3588).

The largest concentration of selenium was found in a farmed soil and was approximately double the concentration of the highest concentration found in non-fertilised soils. This could reflect the influence of fertiliser or anthropogenic activities which may have an increased source of selenium.

Table 7-4 - Selenium concentration of fertilised and non-fertilised soils.

	Selenium Concentration Fertilised Soils	**Selenium Concentration Non-Fertilised Soils**
N	219	12
Mean	1.8	2.1
Geometric mean	1.4	1.5
Median	1.4	1.7
Minimum	0.2	0.2
Maximum	8.9	4.9
Standard Deviation	1.4	1.5
95% Students *t*-interval	1.6<μ<2.0	1.1<μ<3.0

All values expressed in mg kg^{-1}.

Fertiliser use on agricultural land could also be used to explain why there is generally a lower mean selenium concentration in farmed soils compared to the background soils. Phosphates and sulphates are known to reduce selenium adsorption [16]. This is primarily through the action of competitive adsorption, where by introduced ions (from fertiliser) may compete with selenium for adsorption sites. It has been observed that an increase in concentration of a specific metal ion results in a decrease in adsorption of another metal ion [100]. The competition of a more concentrated metal ion may also desorb a lower concentrated species, increasing its concentration in the soil solution [101].

Desorption of selenium from soil particles could make selenium more prone to losses through leaching and plant uptake. However, desorbing selenium from the soil particles would cause it to be available in the soil solution and free for plant uptake, which in turn would allow it to be transferred through the food chain. This would have a beneficial effect for the health of animals grazing agricultural land. However the desorption of one element by competitive desorption of another may cause an increase in the desorbed element in the soil solution [101] but may not necessarily result in an increase in plant uptake. This is because of the element responsible for desorbing the other element likely to have a higher concentration in the soil solution (a result of fertiliser application).

Therefore fertiliser application may act to further dilute any free selenium in the soil solution that would be available for plant uptake.

The selenium concentration in relation to the land use of Waikato soils indicates that anthropogenic activities (farming and forestry) may reduce the amount of selenium in the soil (such as fertilisation and produce removal). However, the loss of selenium by other routes such as volatilisation and methylation was not determined.

Therefore despite the use of fertilisers and selenium supplements, farmed soils appear to display less selenium on average than background soils. This indicates that if anything (and on average) combined losses of selenium, through various pathways, equal or exceed the sum of inputs from various sources.

7.5 Soil Selenium Content in relation to Soil depth

Summary statistics of the selenium concentration for the two soil depths indicate that there may be an increase in selenium in the 10-20 cm soil depth than that of the surface samples (Table 7-5). The largest concentration of selenium is also observed lower in the soil (18.0 mg kg^{-1}) compared to that of the surface (12.1 mg kg^{-1}). Both the arithmetic and geometric means also show an increase in the selenium concentration lower in the soil profile, although the difference between the geometric means is smaller.

The Student's *t*-intervals (based on both the arithmetic and geometric means) overlap to some extent, indicating a chance that the two sample means are no different.

However the more refined approach of paired Student's *t*-test (examining changes in depth on a site by site basis) shows there is a significant difference between the two soil depths ($p<0.0001$, $N=105$). Therefore, there is more selenium on average lower in the soil profile (10-20 cm depth) compared to the surface of the soil (0-10 cm depth).

The increase in selenium lower in the soil profile would be expected because of the action of leaching moving selenium through the soil profile and the increased selenium retention from the general increase in clay content with soil depth [5].

Table 7-5 - Summary statistics of the selenium concentration (mg kg^{-1}) between two different soil depths.

	Soil Depth A (0-10 cm)	Soil Depth B (10-20 cm)
Mean (N=105)	1.79	2.32
Geometric Mean	1.34	1.61
Median	1.22	1.42
Minimum	0.18	0.21
Maximum	12.1	18.0
Standard Deviation	1.81	2.69
95 % Student's *t*-interval	1.44<μ<2.14	1.80<μ<2.84
95 % Student's t-interval**	1.16<μ<1.53	1.38<μ<1.87

****** - Student's *t*-interval based on geometric mean. All values expressed in mg kg^{-1}.

Previous research from New Zealand, found that selenium concentration is greatest in the B horizons of soils, with maximum concentrations observed in the concretion layer of ironstone soils and the iron pan layer of Podzols [5]. Although the lower depth soil samples collected in this study did not always represent the B horizon, the findings that the selenium concentrations show an increase lower in the soil profile agrees with these previous findings. It also suggests that the selenium concentration reflects the ability of a soil to retain it, as the lower horizons in a soil profile generally have a higher clay content [5].

7.6 Soil Selenium Content and Distance from the Coast

The concentration of selenium in the top 10 cm of soil appears to be greatest in the soils nearest to the coast, and lowest in soils farthest from the coast (

Figure 7-5). This suggests that the influence of sea spray and selenium derived from the ocean may play an important role in the concentration of selenium in soils (coastal enrichment).

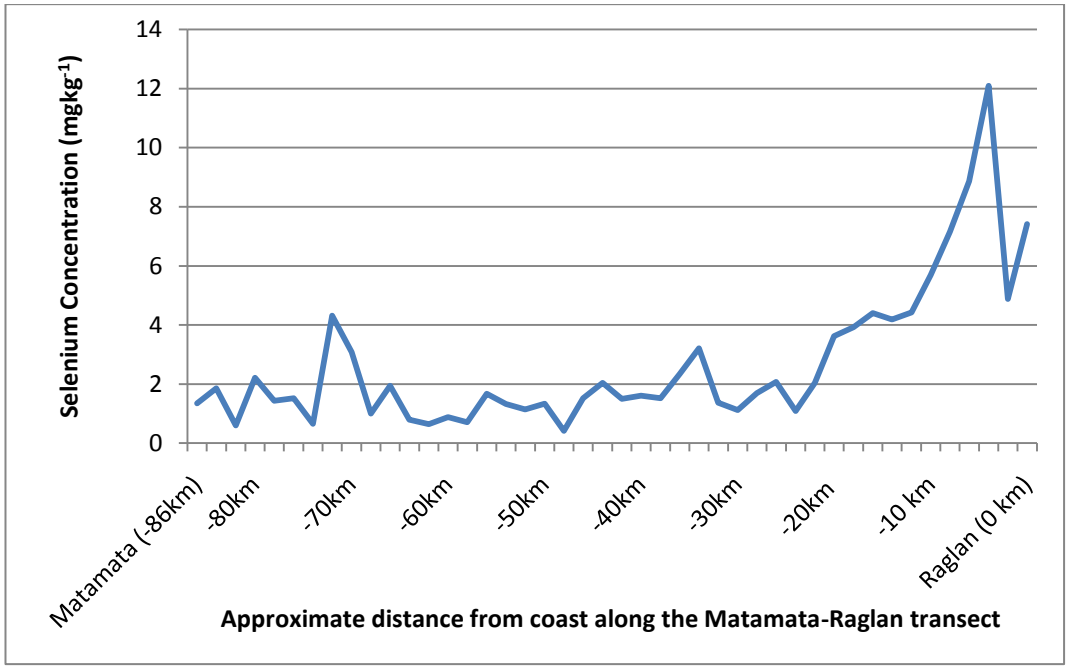

Figure 7-5 - Selenium concentration and distance from the coast, assuming Raglan is 0 km from coast and Matamata is -86 km (Based on 2 km sample collection).

However, this does not take in to account the effect that soil type may have on the concentration of selenium. In order to deduce the effect of coastal enrichment on selenium concentration, the relative enrichment of the soils were plotted against distance from the coast (Figure 7-6). The use of the relative enrichment of selenium in the soils effectively corrects for the variation in soil type.

Relative enrichment in this project was defined by using the ratio between the concentrations of the two soil depths. A relative enrichment in the soil surface would be defined by a ratio greater than one, indicating that the

surface soil has a higher concentration of selenium compared to the lower soil depth. A ratio less than one would indicate that there was a greater concentration of selenium lower in the soil profile compared to the surface.

It would be expected that the relative enrichment of the soils would increase towards the coast if coastal enrichment was a factor in the selenium concentration of soil. However, the relative surface enrichment of the soils along the transect show no conclusive trend supporting coastal enrichment, despite the surface soils displaying clear evidence supporting surface enrichment.

It could therefore be suggested that the losses of selenium are equal or exceed the inputs from the surface. If the loss rate was equal or greater than the addition rate the relative ratio would not reflect enrichment in the surface soil. This would explain the apparent coastal enrichment in the surface soils (Figure 7-5) but the lack of evidence supporting this idea using the relative enrichment ratios (Figure 7-6).

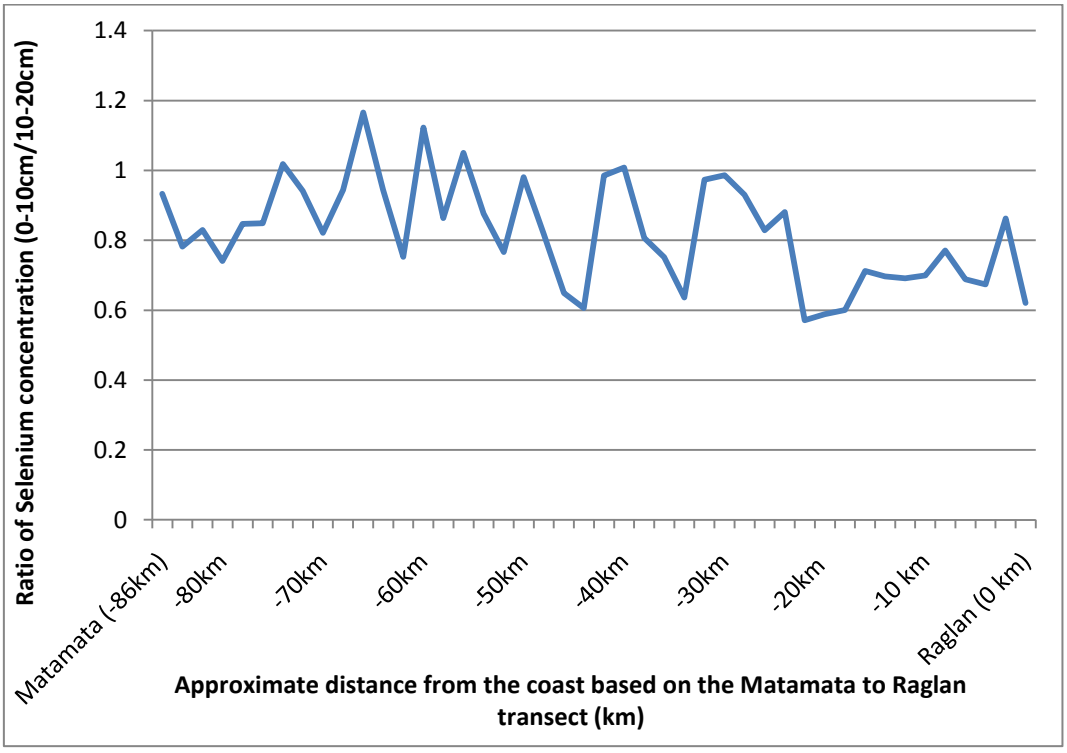

Figure 7-6 – Relative enrichment (0-10cm/10-20cm) of selenium in soil in relation to the distance from the coast.

Another possibility to explain the increased surface soil selenium concentrations is that the soils near Raglan are generally basalt-derived soils, from which basaltic rock (igneous) typically contain more selenium than other rock types [13]. Therefore, the increase soil selenium content could be due to the influence of the parent material. However, if this were to be the case, it would be expected that the selenium would be enriched in samples showing higher chromium and nickel concentrations as is generally the case in basaltic rock types [113, 114].

Correlation analysis between selenium, nickel, and chromium (Table 7-6), indicate that selenium is strongly correlated to the nickel ($p<0.001$) in the soils but is only slightly correlated to the chromium content ($p<0.1$). However, chromium is strongly correlated to the nickel content of soil ($p<0.001$).

Therefore, it could be assumed that the selenium concentration in soil is correlated to the nickel content, which in turn correlates to the chromium content. This correlation suggests that basalt rock (and hence, the parent material) may influence the selenium concentration of soil, and this factor is likely to be the cause of any increase in selenium nearer to the coast (Raglan) than the action of coastal enrichment.

Table 7-6 - Correlation analysis of selenium, nickel, and chromium.

	Se	Cr
Cr	0.196*	
Ni	0.451***	0.547***

Significance: * $p<0.1$, *** $p<0.001$.

When the selenium concentrations along this transect are compared against the parent material that the soil is derived from it suggests there is a relationship between the two. The highest concentrations of selenium occur in the basalt and ash derived soils, with the lowest mean concentrations seen in the Taupo pumice derived soils (Appendix 6). This finding further reinforces the idea suggested above and also shows agreement with findings from Japan where volcanic ash soils had higher total selenium than non-volcanic ash soils [71].

Previous studies also found New Zealand topsoils developed from basalt to have high concentrations of selenium [5]. In these studies, concentrations up to 9.2 mg kg^{-1} were observed in basaltic derived soils.

This also agrees with the suggestion that in most cases there is a strong correlation between the parent material and the selenium concentration of the soil derived from them [110]. The exceptions to these are soils that have been modified by anthropogenic activities.

Soil factors, such as pH, redox conditions, mineralogy, and organic matter, may also play an equally if not more important role in the selenium concentration of soils [110].

7.7 Correlation Analysis

Pearson's correlation analysis between the TMAH extracted selenium values and other soil characteristics and elements (generally total acid recoverable, refer to Table 4-1) was carried out. The statistical significance for each correlation is displayed in Table 7-7. A correlation matrix was carried out for all the Waikato soils pooled together and also carried out for the generalised land use categories (farmed, forestry and background soils).

The number of data pairs that were analysed varied between each two components. The regression values and corresponding number of pairs (N value) for each correlation are displayed in Appendix 5.

Generally, the farmed soils reflected the same correlations as was seen in all the Waikato soils combined, as farmed soils made up the majority of the samples. Forestry soils showed very similar correlations to the farmed soils differing by significance, while background soils showed fewer and less significant correlations to the other categories. This was most likely because of the limited sample size for both forestry (N=23) and background (N=12) soils. The limited sample size most likely result in under-estimated correlations compared to a larger sample size as the correlation coefficient (R value) must be that much larger to be considered significant. The variability between categories will be larger in the background and forestry because of the reduced sample size, but the R value between a sample size of 20 and 200 would not be expected to change a lot when considering soil samples. This is displayed in Appendix 5 where the R values between the categories for a specific correlation do not appear to change significantly, but the statistical significance differs largely because of the sample size.

Table 7-7 - Correlation analysis for the concentration of selenium in soil for all soils, farmed soils, and background/forestry soils.

	All Soils	Farmed	Forestry	Background
pH	ns	ns	ns	ns
%C	**	**	ns	ns
%N	**	*	*	ns
Al	***	***	***	**
Sb	ns	ns	*	ns
As	***	***	**	ns
Ba	**	**	ns	ns
Bi	***	***	*	*
B	***	***	***	ns
Cd	**	**	**	ns
Cs	*	*	ns	*
Ca	ns	ns	ns	ns
Co	***	***	***	ns
Cr	***	***	**	ns
Cu	***	***	***	ns
F	ns	ns	*	ns
Fe	***	***	**	*
La	***	***	**	*
Pb	***	***	***	ns
Li	***	***	***	ns
Mg	***	***	*	ns
Mn	***	***	ns	*
Hg	***	***	***	**
Mo	***	***	***	***
Ni	***	***	***	ns
P	***	*	*	ns
K	ns	ns	ns	ns
Rb	ns	ns	ns	ns
Ag	***	***	**	**
Na	**	ns	ns	ns
Sr	***	***	*	ns
Tl	***	***	**	**
Sn	***	***	***	**
U	***	***	***	ns
V	***	***	***	ns
Zn	***	***	*	ns
I	***	***	***	**

Significance: ns: not significant, *: p<0.05, **: p<0.01, ***: p<0.001.

Selenium shows a strong correlation to iodine ($p<0.001$) in all the soils sampled. One possibility is that this strong correlation reflects that both these elements are derived from a similar source. This agrees with the findings in Sweden where both elements were strongly correlated, reflecting the contribution atmospheric deposition has in supplying these elements to the soil [115].

Selenium also appears to be strongly correlated to aluminium, iron and manganese when all the Waikato soils are considered ($p<0.001$).

Aluminium is associated with clay minerals in the soils. Therefore, the strong correlation between selenium and aluminium suggests that selenium is also associated and bound to the clay minerals in soil.

Iron and manganese oxides are known to be important for sequestering elements because of their occurrence in soils, large surface area, and strong affinity for a range of elements, including selenium [116]. Because of this it would be expected that there would be a strong correlation between the selenium content of soil and the iron and manganese content. However, at a given pH, selenium is suggested to have a stronger affinity to iron oxides than to manganese oxides because of the intrinsic differences in the binding ability of the two surfaces [116]. This stronger affinity of selenium could explain the correlation coefficients of selenium with iron and manganese. Both iron and manganese show strong correlation to selenium in the Waikato soils, however, the correlation coefficients (Appendix 5) of iron are much larger (more significant) than manganese. This could reflect the fact that there is typically more iron in soils compared to manganese, therefore the iron would dominate as there is more iron oxides around. This is displayed by a mean iron content of 21672 mg kg^{-1} compared to 1026 mg kg^{-1} for the mean manganese content (in the Waikato soils sampled).

The organic fraction of a soil has been considered to be a strong carrier of selenium [117]. However, recently it has been suggested that the association of selenium with organic matter is due to the indirect association of surface iron oxides or clays [117]. It was also found that the selenium associated with soil particles was correlated strongly to the

presence of iron and aluminium [117]. This explains the strong correlation ($p<0.001$) of selenium to both iron and aluminium, but the weaker correlation ($p<0.01$) to the carbon percentage in the Waikato Soils. The stronger correlation of selenium to aluminium and iron compared to carbon suggests that aluminium and iron may control the sorption of selenium in soil more so than carbon.

The strong correlation of selenium to iron and aluminium also suggests that the iron oxide and clay fraction of the Waikato soils is the most important in retaining selenium. The dominant species of selenium could also be speculated to be selenite as it binds strongly to iron oxides and clay minerals [110].

Another interesting relationship seen is the correlation between sodium and selenium. These elements show a significant negative correlation for all the Waikato Soils. This suggests that as the concentration sodium increases the concentration of the selenium is likely to decrease (but unlikely that the increase in selenium results in a decrease in sodium). This could be linked somewhat to the salinity of the soil, whereby, an increase in the salt content of a soil decreases the adsorption capacity of selenium in that soil [118]. A decrease in the adsorption capacity of the soil could cause the retention of selenium in the soil to also decrease, resulting in a lower total selenium concentration. However this correlation may not be a true representation of sodium as an acid extraction does not completely recover the sodium from soil. However, when limited XRF data ($N=44$) was correlated to the selenium of the corresponding soils, a negative correlation ($p<0.05$) was still observed.

The strong correlation between selenium and mercury may reflect the preference mercury has in binding to sulfur-donating ligands [1]. Mercury is also considered chalcophilic [17], so the strong correlation may reflect mercury's preference to bind to chalcogens (selenium and sulfur), of which HgSe is insoluble.

Selenium is very similar chemically to sulfur so mercury may also bind to selenium-containing compounds in the soil. The binding preference of mercury would be for the lower oxidation species of selenium (Se^{2-}) and

for organic selenium compounds, but not for selenite and selenate. Thus, the correlation between mercury and selenium may indicate the form selenium is in. These low oxidation state selenium, or organic selenium compounds, would act as retention sites for mercury.

7.7.1 Summary

The main findings from the correlation analysis for selenium indicate that aluminium (probably as clay minerals) and iron (iron oxides) may play a more important role in selenium retention than organic matter.

Selenium also shows strong correlation to mercury which may indicate that selenium acts as a binding site for mercury.

8 Summary and Recommendations

8.1 Research Approach

The status of two essential trace elements, iodine and selenium, was investigated in Waikato soils covering a range of Soil Orders and land-uses.

Regional soil samples (up to 368) from Environment Waikato's soil monitoring sites were analysed in this study which allowed comparisons of the iodine and selenium concentrations with other previously collected soil properties.

Various methods were trialled in order to develop a method that best represented the total iodine and selenium content of the Waikato soils. The methods used were developed and validated using Certified Reference Materials.

8.2 Key Findings

8.2.1 Method Development

A tetramethyl ammonium hydroxide method was successfully validated for the use of determination of total iodine in Waikato soils using ICP-MS.

This same alkaline TMAH extraction was also shown to best represent the total selenium of soil and was thus used to also present the status of selenium in Waikato soils. Validation of this method was achieved by the use of CRMs.

Various acid extraction methods were trialled for the determination of total selenium in soils using ICP-MS and DRC-ICP-MS (Sections 5.3 and 5.4).

Analysis of CRMs showed that the low concentration CRM was consistently over-estimated and the high concentration CRM under-estimated. The use of methane in the DRC-ICP-MS proved to be the most successful in reducing interferences and improving the low level selenium determination, but not to the accuracy needed for the actual soil samples (Sections 5.7.1 and 5.8).

Comparison of the TMAH extracted concentrations of iodine and selenium with limited results of XRF analysis also showed that the TMAH method best represented the total concentrations of both elements (Sections 5.7.1, 5.7.4.1 and 5.8).

8.2.2 Iodine in Waikato Soils

The Waikato Region was found to have a mean iodine content of 20.9 mg kg^{-1}, geometric mean 13.7 mg kg^{-1} and range of 1.5 – 122.8 mg kg^{-1}. The results displayed a higher mean content than previous samples collected in New Zealand and some other iodine deficient areas from around the world. This suggested that the Waikato Region may be less iodine deficient than previously thought.

There was large variation in iodine content with Soil Order, with the order from highest geometric mean to lowest: Allophanic > Granular > Recent > Brown > Organic > Gley > Pumice. The soils showing the highest iodine content were those with a significant clay/colloid contribution, indicating the importance of these in iodine retention.

Land use appeared to have an effect on the iodine content of soils with background soils displaying the highest mean concentrations of iodine, followed by farmed soils, with forestry soils containing the lowest iodine. This suggests that anthropogenic activities typical act to reduce the iodine content of soils, or reflects the higher organic content of background soils.

The iodine concentration in soil showed a significant ($p<0.0001$) increase with depth (10-20 cm) compared to the surface (0-10 cm). The iodine concentration did not appear to increase in the surface soils nearest to the coast, with the highest iodine concentration observed inland. There was also no apparent relative enrichment in the surface soil of coastal soils

compared to inland soils causing no relationship to be seen between iodine concentration and distance from the coast. However, this could reflect the losses of iodine being greater than the additions of iodine to the soil.

Iodine was strongly correlated to aluminium and iron in Waikato soils, although this correlation was less apparent for background soils. The correlation between iodine and organic content was less significant for Waikato soils, but non-existent for background soils. This suggested that in Waikato soils aluminium (presumably in the form of clay minerals) and iron (as hydrated iron oxides) play a more important role in iodine retention than organic matter.

Iodine was also strongly correlated to the chalcophilic elements mercury and silver. There was also strong correlation between iodine and selenium (a chalcogen).

8.2.3 Selenium in Waikato Soils

The selenium content of the Waikato Region had a mean concentration of 1.77 mg kg^{-1}, geometric mean of 1.33 mg kg^{-1} and range 0.18 – 12.1 mg kg^{-1}. The mean content of Waikato soils was higher than the worldwide mean, and the previous New Zealand mean selenium content of 0.6 mg kg^{-1}. This suggested that the selenium status of Waikato soils may be better than other regions New Zealand, though selenium concentrations were observed that would potentially cause deficiencies or toxicities.

Selenium concentrations varied with Soil Order with the order from highest geometric mean to lowest being: Granular > Allophanic > Organic > Gley > Brown > Recent > Pumice.

Pumice soils were shown to have the lowest selenium concentrations and be the most prone to selenium deficiencies, consistent with previous work. The soils showing the highest mean selenium indicate that selenium in the Waikato Region is influenced by the clay/colloid fraction rather than the organic fraction.

Land use had a marked difference on the selenium content of soils, with background soils displaying the highest mean concentrations and forestry the lowest. No accumulation of selenium was seen in farmed soils, despite the use of selenium supplements and prills. It was suggested that anthropogenic activities (farming and forestry) appear to reduce the net selenium content of soils, i.e. that exports of selenium may equal or exceed the sum of inputs from fertilisers, supplements and natural sources.

Selenium was also shown to increase with depth (10-20 cm) in the soil compared to the surface (0-10 cm). There was evidence of increased selenium in the surface soils nearest to the coast but no relative surface enrichment between selenium concentration and distance from the coast observed. This further suggested that losses of selenium equalled or exceeded the inputs from the surface.

There was a relationship seen between the parent material and selenium content of soil, with basalt and ash derived soils showing higher mean selenium concentrations compared to pumice derived soils.

Like iodine, selenium was strongly correlated to aluminium, iron and manganese, but was not correlated as strongly to organic content. This suggested that the clay minerals and iron and manganese oxides play a more important role in selenium retention than organic matter.

Selenium and mercury also showed strong correlation indicating that chalcophilic elements (like mercury) have a strong affinity for selenium, with selenium acting as a potential binding site for mercury.

8.3 Recommendations

TMAH followed by negative ion ICP-MS was found to be a good method for determining total iodine from soils, but when it comes to selenium, some uncertainty remains about the best approach to use. TMAH appeared to give a low recovery (40%) for selenium in the higher of the two Certified Reference Materials. With acid extraction and ICP-MS in positive-ion mode, the DRC-ICP-MS method using methane seemed the most reliable, but full investigation was constrained by limited time and equipment availability. In this method development area, the following is recommended to further improve validation of selenium measurements:

1. Method validation of the TMAH method for selenium at higher levels against one or more mid-to-high selenium Certified Reference Soils. This would eliminate the possibility that the low recovery observed in this study in one CRM is in fact an issue with the reported certified value.
2. Further method development of the methane DRC-ICPMS approach.

In terms of the selenium and iodine status of soils, a number of findings have been made in this wok that could be subject to further investigation. Recommendations for future work could usefully focus on the following aspects:

1. Relationships between iodine in soils and levels in food are not well understood. Soils tested in this study appear to contain reasonable total amounts of iodine, suggesting the moderate to severe iodine deficiencies previously experienced in New Zealand may be mostly related to the low bioavailability of iodine in New Zealand soils. The chemical form and bioavailability of iodine and selenium in different soils would therefore be useful in determining their full status.
2. Whether iodine deficiency may also be an issue for grazing livestock in some cases. (Iodine deficiencies in the human New Zealand population have recently been addressed by requiring mandatory addition of iodine to flour used for making bread.)

3. Selenium shows no evidence of being enriched in farmed soils despite the widespread use of selenium supplements and fertiliser. There is some indication that farmed soils may lose selenium at a faster rate than it is being added. Future work could quantify the addition and loss pathways for selenium in soils, and identify the types of soils or farming systems that are most likely to be subject to selenium deficiency.
4. At the other end of the spectrum, high selenium results in soils suggest the possibility of future selenium toxicity that has not previously been thought to be a problem in New Zealand. Further work could be undertaken to quantify the risks to grazing animals or the environmental receptors on the high selenium soils that were identified. This could also clarify whether these high selenium results are due to natural processes or overly heavy selenium supplementation.

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Appendices

Appendix 1 – DRC-ICP-MS raw data

Table A-1 – Comparison of the selenium concentration (mg kg^{-1}) of CRM 1 (0.14 ± 0.03 mg kg^{-1}) for the various isotopes of selenium using various gases in the DRC.

CRM 1													
74	NH3 74	77	NH3 77	78	O2 78	CH4 78	80	O2 80	CH4 80	82	NH3 82	CH4 82	O2 82
		0.46	1.21							0.16	0.39		
		0.52	1.32							0.16	0.37		
		0.65	1.35							0.15	0.35		
		0.66	1.37							0.15	0.33		
		7.30	2.99							0.42	0.99		
		9.47	3.40							0.43	0.93		
		5.57	5.49							0.31	0.31		
		7.20	6.20							0.30	0.29		
		0.47	0.43							0.25	0.19		
		0.44	0.38							0.23	0.18		
		0.26	1.56							0.16	0.13		
		0.80	1.80							0.18	0.14		
8	46.62	0.79	0.50							0.25	0.58		
8	42.92	0.81	0.52							0.24	0.54		
18	41.41	5.44	1.77							0.33	0.53		
19	39.64	6.72	2.10							0.35	0.51		
						0.47			0.18	0.57		0.68	
						0.43			0.16	0.54		0.65	
						0.42			0.20	0.62		0.79	
						0.44			0.23	0.67		0.79	
						0.55			0.26	0.62		0.95	
						0.57			0.27	0.75		0.93	
						0.55			0.22	0.58		0.82	
						0.59			0.23	0.55		0.87	
						0.61			0.22	0.59		0.89	
						0.67			0.21	0.54		0.87	
				0.46	0.54		-68.96	2.38		0.37			8.32
				0.44	0.46		-65.80	2.25		0.34			7.83
				0.52	0.45		-99.91	2.51		0.33			8.91
				0.51	0.40		-103.4	2.36		0.32			8.46

Note: Each row of the table corresponds to a separate sample.

Table A-2 - Comparison of the selenium concentration (mg kg^{-1}) of CRM 2 (1.6 ± 0.2 mg kg^{-1}) for the various isotopes of selenium using various gases in the DRC.

CRM 2													
74	NH3 74	77	NH3 77	78	O2 78	CH4 78	80	O2 80	CH4 80	82	NH3 82	CH4 82	O2 82
		-0.80	0.50							0.39	0.53		
		-0.83	0.46							0.38	0.49		
		-0.91	0.35							0.28	0.36		
		-0.95	0.33							0.27	0.35		
		7.72	1.78							1.71	1.91		
		5.75	1.61							1.58	1.77		
7	59.04	0.32	0.17							0.10	0.20		
7	57.45	0.39	0.17							0.11	0.22		
22	63.89	5.90	1.46							1.62	1.54		
23	57.81	5.89	1.44							1.63	1.51		
						0.62			0.29	0.39		0.56	
						0.60			0.25	0.41		0.53	
						0.36			0.21	0.42		0.40	
						0.36			0.20	0.45		0.41	
						0.79			0.53	0.66		0.85	
						0.76			0.49	0.59		0.87	
						1.63			1.44	1.66		1.84	
						1.69			1.50	1.70		1.90	
						0.70			0.42	0.51		0.71	
						0.78			0.49	0.68		0.82	
				0.89	0.83		-9.03	1.66		0.84			4.78
				0.70	0.64		-18.58	1.40		0.64			4.18

Note: Each row of the table corresponds to a separate sample.

Appendix 2 – Methods: Blank analysis

Table A-3 - Summary statistics of the concentration of selenium and iodine in the respective experimental blanks.

	Selenium Blank (acid extraction)	Selenium Blank (TMAH)	Iodine Blank (TMAH)
N	44	81	81
Mean	0.0003	-0.0001	0.0003
Median	0.0002	-0.0002	0.0002
Standard Deviation	0.0006	0.0004	0.0008
Minimum	0.00002	-0.001	-0.002
Maximum	0.004	0.002	0.003
95% Students *t* interval	0.0001 <μ< 0.0005	-0.0002 <μ< -0.00005	0.0001 <μ< 0.0004

Values expressed in mg kg^{-1}.

Appendix 3 – Raw data

Table A-4 - Raw iodine and selenium concentrations for the Waikato soil samples analysed.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
EW02-1	27.45		2.07		Gley	Farmed
EW02-2	58.92		3.18		Gley	Farmed
EW02-3	7.59		1.16		Allophanic	Farmed
EW02-4	8.60		0.71		Allophanic	Farmed
EW02-5	10.71		0.64		Gley	Farmed
EW02-6	7.84		2.57		Allophanic	Farmed
EW02-7	8.81		2.51		Allophanic	Farmed
EW02-8	21.33		1.31		Pumice	Farmed
EW02-9	18.44		4.28		Pumice	Farmed
EW02-10	32.13		4.11		Allophanic	Farmed
EW02-11	6.04		1.52		Allophanic	Farmed
EW02-12	7.36		1.30		Gley	
EW02-13	18.56		4.31		Granular	Farmed
EW02-14	14.47		4.73		Granular	Farmed
EW02-15	49.54		4.26		Granular	Farmed
EW02-16	68.52		6.38			
EW02-17	18.42		3.32			
EW02-18	12.42		2.95			
EW02-19	122.75		8.38			
EW02-20	72.05		5.58			
EW02-21	11.54		3.39			
EW02-22	7.98		3.98			
EW03-01	69.35	50.9	3.75	4.3	Brown	Farmed
EW03-02	7.55	5.9	1.10	1.85	Brown	Forestry
EW03-03	33.24	26.9	1.45	1.8	Allophanic	Farmed
EW03-04	22.21	17.1	1.10	1.9	Allophanic	Forestry
EW03-05	37.77	26.8	1.56	2	Allophanic	Farmed
EW03-06	32.28	26.2	1.57	2	Allophanic	Farmed
EW03-07	6.49	7.3	0.34	1.5	Pumice	Farmed
EW03-08	5.10		0.26		Pumice	Farmed
EW03-09	12.91		0.93		Organic	Farmed
EW03-10	13.01		0.92		Organic	Farmed
EW03-11	19.24		0.74		Recent	Farmed
EW03-12	26.32	20.00	1.13	1.8	Recent	Farmed
EW03-13	87.19		3.76		Allophanic	Farmed
EW05-1	12.28	10.9	2.01	2.3	Allophanic	Farmed
EW05-2	46.66	33.3	1.62	1.7	Allophanic	Farmed
EW05-3	53.90	39.6	1.79	1.7	Allophanic	Farmed
EW05-4	8.19	7.8	1.13	1.7	Allophanic	Farmed
EW05-5	38.41	29.15	1.65	1.2	Gley	Farmed
Cont. -						

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
EW05-6	16.11	12.9	1.49	2.2	Gley	Farmed
EW05-7	13.13	10.3	1.50	1.6	Brown	Farmed
EW05-8	12.03	12.6	1.05	1.6	Brown	Farmed
EW05-9	7.62	8.2	2.10	2.6	Gley	Farmed
EW05-10	82.58	53.1	4.62	4.1	Granular	Farmed
EW05-11	112.65	81.3	6.39	5.2	Granular	Farmed
EW05-12	8.60	10	1.23	1.9	Allophanic	Farmed
EW05-13	26.01	21.5	2.82	2.6	Granular	Farmed
EW05-14	47.58	37.2	2.12	2	Brown	Farmed
EW05-15	5.00	4.4	1.79	1.8	Gley	Farmed
EW05-16	10.33	9.2	0.75	1.2	Brown	Farmed
EW05-17	8.80	8.6	0.90	1.8	Brown	Farmed
EW05-18	8.44	9	1.05	1.8	Brown	Farmed
EW05-19	10.62	9.8	1.19	1.7	Gley	Farmed
EW05-20	20.64	14.75	2.47	2.1	Brown	Background
EW05-21	23.06		2.31		Brown	Farmed
EW05-22	15.73	11.15	1.36	1.55	Brown	Forestry
EW06-1	60.73		3.38		Allophanic	Background
EW06-2	93.73	66.05	3.44	3.1	Allophanic	Farmed
EW06-3	92.58	66.7	3.17	1.85	Allophanic	Farmed
EWO6-4	10.10		1.54		Brown	Background
EW06-5	9.92		1.48		Brown	Farmed
EW06-6	14.83	11.1	1.51	2.2	Brown	Forestry
EW06-7	27.92		1.78		Recent	Background
EW06-8	12.94	10.9	1.08	1.85	Recent	Farmed
EW06-9	11.87		1.14		Gley	Farmed
EW06-10	10.56		2.37		Gley	Farmed
EW06-11	9.49	7.00	1.37	1.65	Ultic	Forestry
EW06-12	4.02		0.57		Ultic	Farmed
EW06-13	16.74		2.17		Granular	Farmed
EW06-14	13.33		1.70		Granular	Farmed
EW06-15	34.51		1.91		Gley	Farmed
EW06-16	77.29	64.7	3.04	1.7	Allophanic	Farmed
EW06-17	11.44	10.2	0.95	1.65	Brown	Farmed
EW06-18	37.60	28.05	2.06	2.7	Allophanic	Farmed
EW06-19	34.84		1.95		Allophanic	Farmed
EW06-20	32.47		2.37		Allophanic	Background
EW07-1	6.63	7.50	0.38	0.90	Pumice	Farmed
EW07-2	7.17		0.29		Pumice	Forestry
EW07-3	11.11	10.25	0.62	1.20	Pumice	Forestry
EW07-4	10.03		0.98		Pumice	Farmed
EW07-5	9.99	8.65	0.52	1.05	Pumice	Farmed
EW07-6	3.76	4.10	0.24	0.80	Pumice	Forestry
EW07-7	8.07		0.42		Pumice	Farmed
EW07-8	6.42		0.30		Pumice	Forestry

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
EW07-9	7.21		0.37		Podzol	Forestry
EW07-10	22.09		0.80		Podzol	Forestry
EW07-11	20.41		1.66		Gley	Farmed
EW07-12	19.02		2.72		Gley	Farmed
EW07-13	43.46	33.30	1.80	1.50	Allophanic	Farmed
EW07-14	10.76		2.38		Organic	Farmed
EW07-15	29.96	23.05	1.19	1.25	Allophanic	Farmed
EW07-16	43.75	34.90	1.47	1.65	Allophanic	Farmed
EW07-17	9.62		0.68		Gley	Farmed
EW07-18	10.16		1.42		Gley	
EW07-19	55.83	46.95	1.76	1.50	Allophanic	Farmed
EW07-20	62.72	51.85	2.05	1.40	Allophanic	Farmed
EW07-21	113.31		6.24		Allophanic	Farmed
EW07-22	12.81		1.31		Recent	Farmed
EW07-23	7.95		0.61		Gley	Farmed
EW07-24	7.47		0.52		Pumice	Farmed
EW07-25	11.03		0.75		Pumice	Farmed
EW07-26	58.93		2.87		Allophanic	Farmed
EW07-27	44.28		2.67		Allophanic	Farmed
EW07-28	14.27		1.02		Pumice	Farmed
EW08-01	59.26		2.19		Allophanic	Farmed
EW08-02	12.06		0.79		Recent	Farmed
EW08-03	69.45		3.20		Brown	Forestry
EW08-04	65.10		3.10		Brown	Farmed
EW08-05	54.16		2.43		Allophanic	Farmed
EW08-06	60.39		2.36		Allophanic	Farmed
EW08-07	17.68		1.03		Allophanic	Farmed
EW08-08	47.36		2.31		Allophanic	Farmed
EW08-09	6.20		0.19		Organic	Background
EW08-10	36.60		2.04		Allophanic	Farmed
EW08-11	11.83		1.19		Granular	Background
EW08-12	48.09		4.25		Granular	Farmed
EW08-13	10.57		1.39		Gley	Farmed
EW08-14	9.95		1.03		Gley	Farmed
EW08-15	43.88		4.63		Granular	Farmed
EW08-16	24.23		4.22		Granular	Farmed
EW08-17	24.47		3.17		Granular	Farmed
EW08-18	5.20		0.57		Gley	Background
EW08-19	22.21		1.90		Recent	Farmed
EW08-20	12.13		1.37		Pumice	Background
EW08-21	18.70		3.14		Granular	Farmed
EW08-22	20.03		3.41		Granular	Farmed
EW08-23	20.40		4.08		Granular	Farmed
EW08-24	38.98		4.21		Gley	Farmed

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
EW09-01	8.81		0.65		Pumice	Farmed
EW09-02	8.16		0.59		Pumice	Forestry
EW09-03	6.06		0.46		Pumice	Farmed
EW09-04	6.88		0.44		Pumice	Farmed
EW09-05	10.46		0.96		Organic	Farmed
EW09-06	10.04		0.84		Organic	Farmed
EW09-07	22.27		1.43		Allophanic	Farmed
EW09-08	10.42		0.88		Allophanic	Farmed
EW09-09	3.16		0.42		Allophanic	Farmed
EW09-10	3.90		0.43		Allophanic	Forestry
EW09-11	79.54		3.77		Allophanic	Farmed
EW09-12	60.23		3.42		Allophanic	Forestry
EW09-13	14.81		0.76		Recent	Farmed
EW09-14	18.22		1.01		Recent	Farmed
EW09-15	60.26		3.27		Brown	Farmed
EW09-16	4.54		1.08		Brown	Forestry
EW09-17	4.59		0.40		Pumice	Farmed
EW09-18	3.53		0.34		Pumice	Farmed
EW09-19	4.59		0.38		Pumice	Farmed
EW09-20	19.13		1.26		Granular	Farmed
EW09-21	26.39		1.75		Allophanic	Farmed
EW09-22	27.05		1.65		Allophanic	Farmed
EW09-23	7.81		0.67		Pumice	Farmed
EW09-24	4.34		0.29		Pumice	Farmed
EW09-25	7.11		0.43		Pumice	Farmed
EW09-26	4.58		0.27		Pumice	Farmed
EW09-27	4.16		0.25		Pumice	Farmed
EW09-28	4.51		0.30		Pumice	Farmed
EW09-29	18.73		1.41		Allophanic	Forestry
RT 1A	17.02	15.6	1.34	2.4	Allophanic	Farmed
RT 1B	18.20		1.44			
RT 2A	33.97	34.6	1.86	1.9	Allophanic	Farmed
RT 2B	61.67		2.38			
RT 3A	13.70	22.2	0.59	1	Allophanic	Farmed
RT 3B	20.71		0.71			
RT 4A	35.57	33.8	2.22	2.40	Allophanic	Farmed
RT 4B	52.61		2.99			
RT 5A	31.10	30.2	1.43	1.70	Allophanic	Farmed
RT 5B	40.94		1.69			
RT 6A	22.11	26.4	1.52	2.00	Granular	Farmed
RT 6B	30.87		1.79			
RT 7A	11.09	10.2	0.65	1.10	Granular	Background

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
RT 7B	9.08		0.64			
RT 8A	100.58	135.3	4.31	5.10	Gley	Background
RT 8B	107.42		4.58			
RT 9A	45.29	42.1	3.08	2.60	Allophanic	Farmed
RT 9B	61.31		3.75			
RT 10A	8.45	10	1.00	1.60	Gley	Farmed
RT 10 B	11.89		1.06			
RT 11 A	46.91	48.4	1.94	2.00	Brown	Farmed
RT 11 B	59.64		1.66			
RT 12 A	9.66	11.2	0.79	1.10	Gley	Farmed
RT 12 B	12.42		0.84			
RT 13 A	6.99	7.9	0.64	1.10	Granular	Farmed
RT 13 B	7.25		0.86			
RT 14 A	8.82	8.9	0.87	1.60	Granular	Farmed
RT 14 B	8.99		0.78			
RT 15A	3.76	4.3	0.71	1.40	Allophanic	Farmed
RT 15B	3.75		0.82			
RT 16A	18.32	17.9	1.68	2.00	Allophanic	Farmed
RT 16B	13.75		1.59			
RT 17A	9.31	8.9	1.32	1.50	Allophanic	Farmed
RT 17B	9.36		1.51			
RT 18A	20.96	21.6	1.14	1.50	Allophanic	
RT 18B	27.75		1.48			
RT 19A	39.10	36.5	1.33	1.50	Allophanic	Farmed
RT 19B	46.61		1.36			
RT 20A	4.41	4.8	0.42	1.10	Allophanic	Farmed
RT 20B	5.17		0.51			
RT 21A	19.63	19.9	1.52	1.80	Allophanic	Farmed
RT 21B	28.43		2.35			
RT 22A	37.20	32.8	2.04	1.80	Allophanic	Farmed
RT 22B	95.76		3.37			
RT 23A	9.12	13.8	1.50	2.10	Organic	Farmed
RT 23B	8.52		1.52			
RT 24A	10.74	16.2	1.61	1.80	Organic	Farmed
RT 24B	11.54		1.60			
RT 25A	4.36	4	1.52	1.90	Gley	Farmed
RT 25B	5.24		1.89			
RT 26A	4.12	3.7	2.34	2.60	Gley	Farmed
RT 26B	3.60		3.12			
RT 27A	18.78	16.6	3.21	3.00	Gley	Farmed
RT 27B	21.37		5.05			
RT 28A	11.98	11.7	1.37	1.30	Gley	Farmed

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
RT 28B	13.12		1.41			
RT 29 A	4.99	5.2	1.12	1.40	Granular	Farmed
RT 29 B	4.52		1.13			
RT 30 A	26.24	25.9	1.69	1.70	Brown	Farmed
RT 30 B	40.91		1.82			
RT 31 A	7.96	7.6	2.07	2.40	Allophanic	Farmed
RT 31 B	8.75		2.50			
RT 32 A	8.05	7.9	1.08	1.30	Gley	Farmed
RT 32 B	9.62		1.23			
RT 33 A	12.35	14.3	2.03	2.00	Allophanic	Farmed
RT 33 B	21.51		3.56			
RT 34 A	27.66	30.8	3.62	3.50	Allophanic	Farmed
RT 34 B	54.62		6.16			
RT 35 A	46.66	57.1	3.92	3.50	Allophanic	Farmed
RT 35 B	91.14		6.53			
RT 36 A	50.23	54.2	4.40	3.70	Allophanic	Farmed
RT 36 B	62.92		6.18			
RT 37 A	25.88	24.4	4.18	2.80	Granular	Farmed
RT 37B	37.04		6.00			
RT 38 A	21.49	19.6	4.42	2.60	Granular	Farmed
RT 38 B	29.83		6.40			
RT 39 A	22.12	20.2	5.69	3.50	Allophanic	Farmed
RT 39 B	26.01		8.13			
RT 40 A	22.63	20.7	7.15	3.50	Granular	Farmed
RT 40 B	27.11		9.28			
RT 41 A	44.87	44.8	8.87	3.60	Allophanic	Farmed
RT 41 B	70.24		12.88			
RT 42 A	59.83	62.2	12.10	4.10	Granular	
RT 42 B	112.98		17.96			
RT 43 A	11.95	9.3	4.88	1.80	Granular	Background
RT 43 B	12.01		5.66			
RT 44 A	11.76	9.7	7.42	2.00	Granular	Farmed
RT 44 B	16.05		11.94			
TA 1 A	14.81		0.72		Granular	Farmed
TA 1B	17.32		0.87			
TA 2A	4.99		0.69		Gley	Farmed
TA 2B	6.67		0.71			
TA 3A	5.00		0.84		Allophanic	Farmed
TA 3B	5.31		1.05			
TA 4A	4.23		0.87		Gley	Farmed
TA 4 B	3.78		1.07			
TA 5 A	6.43		0.61		Gley	Farmed

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
TA 5 B	6.83		0.63			
TA 6 A	4.56		0.55		Allophanic	Farmed
TA 6 B	4.44		0.59			
TA 7 A	12.33		1.03		Gley	Farmed
TA 7 B	16.46		1.22			
TA 8 A	6.23		1.06		Gley	Farmed
TA 8 B	6.51		1.35			
TA 9 A	2.27		0.60		Gley	Farmed
TA 9 B	2.39		0.75			
TA 10 A	4.19		1.02		Gley	Farmed
TA 10 B	4.60		1.19			
TA 11 A	5.82		0.75		Gley	Farmed
TA 11 B	6.66		0.84			
TA 12 A	4.86		0.69		Gley	Farmed
TA 12 B	4.35		0.87			
TA 13 A	16.74		1.15		Granular	Farmed
TA 13 B	25.77		1.55			
TA 14 A	4.26		0.47		Brown	Farmed
TA 14 B	3.50		0.54			
TA 15 A	6.99		0.79		Brown	Farmed
TA 15 B	10.98		1.01			
TA 16 A	2.76		0.52		Brown	Farmed
TA 16 B	2.83		0.48			
TA 17 A	6.34		0.73		Brown	Farmed
TA 17 B	11.25		1.06			
TA 18A	9.71		0.98		Granular	Farmed
TA 18B	10.82		1.21			
TA 19A	21.20		1.29		Granular	Farmed
TA 19 B	24.12		1.54			
TA 20A	9.62		2.86		Gley	Farmed
TA 20 B	9.86		3.59			
TA 21 A	15.40		2.80		Gley	Farmed
TA 21 B	11.58		3.02			
TA 22 A	11.67		2.59		Organic	Farmed
TA 22B	16.09		2.86			
TA 23A	9.31		1.65		Organic	Farmed
TA 23 B	10.63		2.25			
TA 24 A	7.00		2.17		Organic	Farmed
TA 24 B	7.49		2.25			
TA 25A	3.09		1.62		Gley	Farmed
TA 25B	2.49		1.91			
TA 26A	4.28		0.85		Gley	Farmed

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
TA 26B	5.25		1.20			
TA 27 A	5.21		0.96		Gley	Farmed
TA 27 B	5.34		0.91			
TA 28 A	2.06		0.39		Gley	Farmed
TA 28 B	1.52		0.43			
TA 29 A	5.43		0.89		Gley	Farmed
TA 29 B	7.55		1.09			
TA 30 A	12.01		1.22		Organic	Farmed
TA 30 B	11.38		1.21			
TA 31A	8.33		0.54		Organic	
TA 31B	11.77		1.31			
TA 32 A	9.45		1.27		Organic	Farmed
TA 32 B	13.48		2.31			
TA 33 A	5.28		0.92		Granular	Farmed
TA 33 B	5.40		0.94			
TA 34 A	5.58		0.73		Granular	Farmed
TA 34 B	6.63		0.90			
TA 35 A	34.92		1.88		Brown	Farmed
TA 35 B	59.14		1.79			
TA 36 A	9.67		0.77		Brown	Farmed
TA 36 B	11.28		0.99			
TA 37 A	2.91		0.58		Brown	Farmed
TA 37 B	3.92		0.79			
TA 38 A	5.60		0.80		Brown	
TA 38 B	5.94		0.86			
TA 39 A	7.88		0.82		Granular	Farmed
TA 39 B	11.05		1.17			
TA 40 A	11.35		1.12		Granular	Farmed
TA 40 B	12.13		1.22			
TA 41 A	7.48		0.72		Granular	Farmed
TA 41 B	5.02		0.62			
TA 42 A	13.63		0.66		Recent	
TA 42 B	5.53		0.62			
TA 43 A	2.45		0.18		Recent	
TA 43 B	2.72		0.21			
HW 1 A	12.78		1.07		Organic	Farmed
HW 1B	14.89		1.42			
HW 2A	11.48		1.91		Brown	Farmed
HW 2B	17.52		2.83			
HW 3A	7.28		0.88		Brown	Farmed
HW 3B	9.92		1.18			
HW 4A	5.85		0.75		Brown	Farmed

Table A-4 cont.

Sample ID (Lab)	Iodine (TMAH)	Iodine (XRF)	Se 82 (TMAH)	Se (XRF)	Soil Order	Land use
HW 4B	6.31		0.80			
HW 5A	7.74		0.93		Brown	Farmed
HW 5B	9.24		1.13			
HW 6a	11.55		1.12		Brown	Farmed
HW 6B	11.77		1.20			
HW 7A	10.91		1.89		Organic	Farmed
HW 7B	13.60		3.37			
HW 8A	21.36		1.42		Organic	Farmed
HW 8B	19.98		1.83			
HW 9A	13.36		1.68		Organic	Farmed
HW 9B	11.95		1.68			
HW 10 A	16.85		2.15		Organic	Farmed
HW 10B	16.05		2.10			
HW 11A	9.51		2.23		Organic	Farmed
HW 11B	9.92		2.48			
HW 12 A	14.48		0.94		Granular	Farmed
HW 12 B	15.49		1.81			
HW 13 A	18.21		1.58		Granular	Farmed
HW 13 B	18.81		1.67			
HW 14 A	11.42		1.35		Granular	Farmed
HW 14 B	14.02		1.68			
HW 15 A	7.09		1.05		Granular	Farmed
HW 15 B	7.83		1.26			
HW 16 A	10.07		1.31		Brown	Farmed
HW 16 B	4.18		1.15			
HW 17 A	9.05		2.07		Organic	Farmed
HW 17 B	8.02		2.16			
HW 18 A	10.62		1.08		Granular	Farmed
HW 18 B	10.54		0.87			

Appendix 4 – Carbon content of Waikato soils

Table A-5 - Carbon Content (%C) of the various Soil Orders

	Allophanic	Brown	Gley	Granular	Organic	Podzol	Pumice	Recent	Ultic
N	69	35	45	42	21	2	29	11	2
Mean	8.9	7.2	7.3	6.5	31.2	8.5	7.5	5.9	6.1
Geometric Mean	8.3	6.5	6.6	5.9	29.4	8.2	7.2	5.8	6.1
Median	8.4	6.6	6.4	6.1	30.4	8.5	7.1	6.0	6.1
Standard Deviation	3.4	3.3	3.2	2.7	11.1	3.2	2.0	1.2	0.6
Minimum	3.9	2.8	2.2	2.2	15.0	6.3	4.0	3.5	5.7
Maximum	20.1	17.0	14.4	13.0	51.5	10.8	11.3	7.8	6.6
95% Students *t*-interval	8.1<μ<9.7	6.0<μ<8.3	6.3<μ<8.2	5.6<μ<7.3	26.2<μ<36.3	-20.3 <μ< 37.3	6.7<μ<8.2	5.1<μ<6.7	0.3<μ<12.0

Table A-6 - Percentage Carbon (% C) content of Waikato soils, categorised in to Farmed, Forestry, and Background Soils.

	Farmed	Forestry	Background
N	218	17	12
Mean	9.4	8.0	11.8
Geometric Mean	7.8	7.4	8.7
Median	7.1	6.7	7.0
Minimum	2.2	4.1	3.7
Maximum	50.7	18.2	51.5
Standard Deviation	7.6	3.6	13.1
95% Students *t*-interval	8.4<μ<10.4	6.1<μ<9.8	3.4<μ<20.2

Appendix 5 – Correlation Analysis

Table A-7 - Correlation analysis of iodine with various other soil properties and elements. The regression values and number of sample pairs for each category.

	All soils R Value	N	Farmed R Value	N	Forestry R Value	N	Background R Value	N
Se	0.704	368	0.717	219	0.803	17	0.727	12
pH	0.063	361	0.106	219	0.468	17	0.249	12
%C	0.141	361	0.138	219	0.683	17	0.008	12
%N	0.213	282	0.246	201	0.698	17	0.23	12
Al	0.59	325	0.583	201	0.726	17	0.56	12
Sb	0.081	270	0.188	170	0.746	13	-0.136	10
As	0.215	321	0.291	197	0.511	17	0.338	12
Ba	0.223	325	0.238	201	0.272	17	0.104	12
Bi	0.57	295	0.588	175	0.559	15	0.637	12
B	0.506	254	0.578	168	0.331	14	0.072	11
Cd	0.18	358	0.317	219	0.529	17	0.195	12
Cs	0.044	324	0.098	200	0.216	17	0.201	12
Ca	0.033	325	0.118	201	0.311	17	-0.027	12
Co	0.455	325	0.511	201	0.345	17	-0.152	12
Cr	0.157	325	0.196	201	0.441	17	0.132	12
Cu	0.477	325	0.495	201	0.667	17	0.336	12
F	0.089	333	0.151	194	0.258	15	0.38	12
Fe	0.37	325	0.405	201	0.434	17	0.216	12
La	0.623	325	0.624	201	0.674	17	0.628	12
Pb	0.224	361	0.29	219	0.525	17	0.099	12
Li	0.371	321	0.389	200	0.314	17	-0.128	11
Mg	0.205	325	0.255	201	0.089	17	-0.373	12
Mn	0.413	325	0.454	201	0.492	17	0.38	12
Hg	0.579	343	0.539	219	0.825	17	0.889	12
Mo	0.635	325	0.65	201	0.547	17	0.641	12
Ni	0.332	325	0.401	201	0.375	17	-0.254	12
P	0.148	325	0.237	201	0.521	17	0.317	12
K	0.017	325	0.015	201	-0.2	17	-0.375	12
Rb	-0.098	325	-0.058	201	-0.255	17	-0.223	12
Ag	0.613	298	0.602	178	0.756	15	0.738	12
Na	-0.018	325	-0.026	201	-0.538	17	-0.273	12
Sr	0.226	325	0.308	201	0.326	17	0.15	12
Tl	0.42	320	0.439	199	0.486	17	0.474	12
Sn	0.398	325	0.402	201	0.687	17	0.493	12
U	0.433	361	0.47	219	0.506	14	0.416	12
V	0.37	280	0.387	164	0.672	17	0.066	12
Zn	0.263	343	0.271	219	0.44	17	0.055	12
Olsen P	-0.223	361	-0.244	219	-0.267	17	-0.335	12

Table A-8 - Correlation analysis of selenium with various other soil properties and elements. The regression values and number of sample pairs for each category.

	All Soils		Farmed		Forest		Back-ground	
	R value	N	R value	N	R value	N	R value	N
I	0.702	361	0.684	315	0.862	23	0.726	12
pH	-0.006	361	-0.095	315	0.277	23	0.289	12
%C	0.153	361	0.183	315	0.195	23	-0.49	12
%N	0.162	282	0.142	240	0.462	21	-0.185	12
Al	0.7	325	0.689	279	0.783	23	0.716	12
Sb	0.077	270	0.116	234	0.498	18	-0.138	10
As	0.317	321	0.342	275	0.599	23	0.403	12
Ba	0.179	325	0.161	279	0.345	23	0.089	12
Bi	0.601	295	0.594	253	0.537	20	0.653	12
B	0.49	254	0.481	218	0.74	18	-0.201	11
Cd	0.141	358	0.093	314	0.605	22	-0.062	12
Cs	0.13	324	0.138	278	0.202	23	0.605	12
Ca	0.062	325	0.016	279	0.331	23	-0.163	12
Co	0.58	325	0.613	279	0.691	23	0.197	12
Cr	0.267	325	0.203	279	0.556	23	0.446	12
Cu	0.536	325	0.53	279	0.662	23	0.464	12
F	0.029	333	-0.05	290	0.451	21	0.419	12
Fe	0.557	325	0.551	279	0.639	23	0.621	12
La	0.466	325	0.432	279	0.591	23	0.612	12
Pb	0.382	361	0.4	315	0.645	23	0.364	12
Li	0.498	321	0.486	277	0.742	22	-0.009	11
Mg	0.241	325	0.237	279	0.414	23	-0.142	12
Mn	0.283	325	0.237	279	0.389	23	0.59	12
Hg	0.699	343	0.678	297	0.884	23	0.723	12
Mo	0.701	325	0.693	279	0.711	23	0.83	12
Ni	0.559	325	0.612	279	0.727	23	0.031	12
P	0.185	325	0.14	279	0.427	23	0.306	12
K	0.09	325	0.114	279	0.167	23	-0.145	12
Rb	0.002	325	0.008	279	-0.066	23	0.148	12
Ag	0.573	298	0.533	255	0.641	21	0.748	12
Na	-0.168	325	-0.115	279	-0.229	23	-0.569	12
Sr	0.234	325	0.239	279	0.452	23	0.096	12
Tl	0.354	320	0.282	275	0.545	22	0.769	12
Sn	0.603	325	0.581	279	0.684	23	0.786	12
U	0.599	361	0.619	315	0.851	23	0.386	12
V	0.627	280	0.629	238	0.782	20	0.427	12
Zn	0.222	343	0.209	297	0.495	23	0.226	12
Olsen P	-0.210	361	-0.261	315	-0.236	23	-0.435	11

Appendix 6 – Concentration of iodine and selenium in soil in relation to parent material

Table A-9 - Iodine concentration (mg kg^{-1}) of soils based on the parent material they are derived from.

	N	Mean	Geometric Mean	Median	Minimum	Maximum	Standard Deviation	95th Percentile	95% Students *t*-interval
Alluvium	30	17.2	14.0	12.0	5.0	50.2	12.8	47.6	12.5<μ<22.0
Alluvium (Taupo Pumice)	4	19.6	19.2	18.7	14.8	26.3	4.8	26.3	12.0<μ<27.3
Basalt	1	12.0*	-	-	-	-	-	-	-
Colluvium	4	76.8	70.6	79.9	34.5	112.7	32.2	112.7	25.5<μ<128.0
Greywacke	7	21.3	18.2	14.8	9.9	46.9	13.5	46.9	8.8<μ<33.7
Hamilton Ash	5	29.9	17.2	11.1	7.0	100.6	39.9	100.6	-19.7<μ<79.5
Hinuera	9	17.4	12.4	18.3	3.8	39.1	13.6	39.1	7.0<μ<27.9
Peat	9	9.4	9.0	10.0	4.4	13.0	2.9	13.0	7.2<μ<11.6
Sandstone/Siltstone	7	23.8	13.0	9.5	4.0	69.4	28.2	69.4	-2.3<μ<49.9
Tephra	81	33.4	25.4	25.9	3.2	113.3	23.6	83.0	28.2<μ<38.7
Tephra (Taupo Pumice)	34	10.4	8.4	7.6	3.5	58.9	10.0	26.0	6.9<μ<13.9

All values in mg kg^{-1}.

*-Caution must be taken for the basalt value as it is based on only one sample. Therefore it is not a true mean value.

Table A-10 - Selenium concentration (mg kg^{-1}) of soils based on the parent material they are derived from.

	N	Mean	Geometric Mean	Median	Minimum	Maximum	Standard Deviation	95th Percentile	95% Students *t*-interval
Alluvium	30	1.7	1.5	1.4	0.6	4.4	0.9	3.9	1.4<μ<2.1
Alluvium (Taupo Pumice)	4	0.9	0.9	0.9	0.7	1.1	0.2	1.1	0.6<μ<1.2
Basalt	1	4.9*	-	-	-	-	-	-	-
Colluvium	4	4.0	3.6	3.8	1.9	6.4	1.9	6.4	0.9<μ<7.1
Greywacke	7	1.6	1.6	1.5	1.1	1.9	0.3	1.9	1.3<μ<1.8
Hamilton Ash	5	1.6	1.2	0.9	0.6	4.3	1.6	4.3	-0.3<μ<3.5
Hinuera	9	1.4	1.2	1.3	0.4	2.3	0.6	2.3	0.9<μ<1.9
Peat	9	1.0	0.9	0.9	0.2	1.6	0.5	1.6	0.7<μ<1.4
Sandstone/Siltstone	7	1.7	1.4	1.1	0.6	3.8	1.2	3.8	0.6<μ<2.9
Tephra	81	2.8	2.2	2.3	0.4	12.1	1.9	6.7	2.3<μ<3.2
Tephra (Taupo Pumice)	34	0.8	0.6	0.5	0.2	3.2	0.7	2.6	0.5<μ<1.0

All values in mg kg^{-1}.

*-Caution must be taken for the basalt value as it is based on only one sample. Therefore it is not a true mean value.