Contamination of Horticultural Land in Canterbury – A Scoping Study

Prepared for

Environment Canterbury

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Executive Summary

Environment Canterbury (ECan) has a statutory duty to identify and monitor contaminated land. Horticultural activity is listed on the Ministry for the Environment's Hazardous Activities and Industries List (HAIL), and is therefore considered to be an activity that may potentially contaminate land. This report is intended to help ECan in scoping to what extent horticultural practices may have resulted in persistent soil residues from the use of horticultural pesticides in Canterbury.

A broad overview of current and historic horticultural land use in Canterbury is provided and the report considers the Canterbury region within a wider national and international context. The report gives guidance on the likely chemicals of concern, the fate and transport behaviour of these chemicals in soil, and typical concentrations of these chemicals within the soil resulting from horticultural land use.

The study found that some land within the Canterbury region has a long history of intensive horticultural land use, although generally the area has always had a smaller scale horticultural industry than most other regions. This use may have resulted in the accumulation of pesticide residues in the soil which, if at sufficiently high concentrations, could present a risk to the environment or to human health.

The more persistent chemicals such as arsenic, lead, copper, zinc, dieldrin and DDT, the use of which in New Zealand dates back to the early 1900s until the 1970s, have the potential to be present in soil for decades in the case of organic compounds and almost indefinitely for heavy metals. The study shows that these chemicals have been used historically in Canterbury and are, in common with other regions, the chemicals of concern for Canterbury.

All the contaminants of concern tend to bind strongly to soil and are therefore resistant to leaching, tending to stay within the surface soil. Investigations from overseas and other regions in New Zealand suggest the highest concentrations will be within the top 250 or 300 mm of soil, with concentrations commonly approaching background concentrations at depth of 450 mm. There is variation with soil type, with sandier soils tending to have greater depths of contamination, however, horticultural soils in Canterbury are expected to be similar to horticultural soils in other parts of New Zealand and the patterns of contamination observed elsewhere are expected to be applicable to Canterbury.

The main areas that have had historical horticultural land use are in and around Christchurch City, Rangiora and Loburn, Timaru, Ashburton, Geraldine and Waimate. The largest areas are in and around Christchurch. Many of the areas that have been historically cultivated in Christchurch City have already undergone redevelopment from horticulture to residential, business or industrial land uses. However, the Marshlands area is one of the major areas still under current horticultural cultivation in Christchurch, with smaller corners of glasshouse and orchard cultivation in the Port Hills valleys of Heathcote and Horotane.

Information from local growers indicates that spray regimes on Canterbury crops are and may have been less frequent and intense than those used in other areas of New Zealand, and therefore contaminant residues, if any, may be lower in Canterbury compared to other regions in the North Island. However analysis of results from soil measurements conducted as part of routine contaminated site assessments reports for former orchard and market garden land in the Christchurch area suggests that soil residue concentrations are consistent with other regions in New Zealand. Some samples from the Christchurch studies will fail human health guidelines for arsenic and possibly DDT, while glasshouse samples may fail human health guideline values for arsenic, lead and dieldrin. Some copper concentrations are also in excess of toxic concentrations for some plants.

The report recommends that, as a first priority, further investigation concentrates on the Christchurch area, being the location of greatest historic horticultural activity and also the area undergoing the most residential redevelopment of former horticultural land. While this report has identified general areas, specific areas need to be identified by examining historic aerial photographs, talking further to growers and talking to relevant territorial local authorities. Areas of existing or former horticultural land likely to undergo redevelopment, particularly residential redevelopment, in the next ten to twenty years should be identified, and a sampling strategy developed and implemented to determine soil residue concentrations and associated risks. Further investigation of other horticultural areas in Canterbury can follow, following a similar process and concentrating on areas most likely to be redeveloped in the next ten to twenty years.

1.0 Introduction

Some land within the Canterbury region has a history of intensive horticultural land use, including orcharding, market gardening and viticulture. This use may have resulted in the accumulation of pesticide residues in the soil. These residues, if at sufficiently high concentrations, could present a risk to the environment, or, if the land was subdivided for residential use, to human health.

Environment Canterbury (ECan) has a statutory duty to identify and monitor contaminated land. Horticultural activity is listed on the Ministry for the Environment's Hazardous Activities and Industries List (HAIL), and is therefore considered to be an activity with a potential to contaminate land. This report, prepared by Pattle Delamore Partners Limited (PDP), is intended to help ECan in scoping to what extent horticultural use may have contaminated land in Canterbury. It does this by providing a broad overview of current and historic horticultural use in Canterbury and, by drawing on local information and studies from elsewhere in New Zealand, provides guidance on the likely chemicals of concern and the possible concentrations within soil of these chemicals.

2.0 The Chemicals of Concern

2.1 General

In a general sense, chemicals of concern are those substances that may be present at sufficient concentrations in the soil as to present a risk to a receptor. This does not include chemicals that may be quite legitimately applied to a crop or the soil in order to eliminate some pest, rather than chemicals that are sufficiently persistent or bioaccumulative that, over time, they build up in sufficient concentrations that a risk may be presented.

Virtually all chemicals now being used on horticultural land, as well as the chemicals that have been used over the last three decades, degrade sufficiently quickly that they present no concern for land if applied at normal application rates. Degradation typically occurs over several weeks to several months since the time of last application. However, there may be a concern for these less persistent substances over limited areas such as storage sheds where concentrated chemicals may have spilled.

The more persistent chemicals, which were used in New Zealand from the early 1900s until the 1970s, have the potential to be present in soil for decades, in the case of synthetic organic compounds, and almost indefinitely for heavy metals. These are described in more detail in subsequent sections.

2.2 Commonly Used Pesticide Chemicals

A wide range of chemicals have been used as pesticides in New Zealand. Two broad ranges of substances need to be considered – pesticides that contain various forms of heavy metals, and the large number of synthetic organic compounds.

Metals and metalloids that have been used in pesticides in New Zealand include (ARC, 2002):

- arsenic – particularly as lead-arsenate insecticide formulations from the early 1900s until 1970s
- copper – as a fungicide in various forms such as copper sulphate in Bordeaux mixture, copper oxychloride and copper hydroxide from early 1900s to the present
- lead – as lead-arsenate (but also found in white lead-based paints that may have been used in glass-houses) from early 1900 until 1970s
- mercury – in fungicides and bactericides
- tin – organo-tin compounds to control mites and spiders
- zinc – in fungicides still in use

Some metals such as cadmium can also be associated with heavy fertiliser use.

The wide range of organic compounds used as pesticides fall into a number of major categories. These include:

- organochlorines, e.g. DDT[1], dieldrin, lindane from late 1940s until 1970s
- organophosphates, e.g. malathion, diazinon, currently used
- organonitrogen compounds, e.g. simazine, currently used
- carbamates, e.g. carbaryl, zineb, currently used
- synthetic pyrethroids, e.g. permethrin, currently used
- acid herbicides, e.g. 2,4,5-T; 2,4-D, many in current use

Only a few substances have proved to be sufficiently persistent in broad-scale applications to be detectable at significantly elevated concentrations in soil in New Zealand. Most modern chemicals break down sufficiently rapidly that they are not detectable after a few weeks or months, although these may present a concern if at very high concentrations associated with spills at mixing, storage or disposal locations. The substances that are most commonly detected at significantly elevated concentrations in soil on existing or former horticultural land in New Zealand are discussed in greater detail in Section 3.0 but, in summary, these are, for metals and metalloids, arsenic, copper, lead and zinc, and for organic substances, the organochlorine compounds dieldrin, DDT and the DDT metabolites DDD and DDE. Cadmium may be found in elevated concentrations as a result of fertiliser use, but is not considered here.

Of the substances that are most commonly detected, an even smaller number are sufficiently toxic to be a particular concern, principally arsenic, lead and DDT, and to a

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[1] DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene) and DDD (1,1-dichloro-2,2-bis(p-chloro-phenyl)ethane) are both present as contaminants in technical grade DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane). DDD was also a pesticide in its own right. DDE and DDD are also degradation and metabolic products of DDT. For the purposes of this report DDT, DDD and DDE are considered to have similar toxicities and, except where specifically identified, will be referred to collectively as DDT.

lesser extent dieldrin, for human health, and all of these plus copper, for the environment in general. These can be considered the chemicals of concern for broad-acre horticultural land.

2.3 Regulatory History and Status

Agricultural pesticides were first regulated in 1934 with the Poisons Act (Schedule 4), which provided general controls on registration and carriage of substances listed in the Act schedules. All agricultural and horticultural pesticides and weed killers were subsequently placed into the Poisons (General) Regulations (Schedule 3) under the Poisons Act 1934, providing for stronger controls on sales, importation, carriage and use (Buckland, et al, 1998).

The 1959 Agricultural Chemicals Act, which established the Agricultural Chemicals Board, introduced compulsory registration and regulation of all agricultural chemicals, including stringent requirements on labelling, packaging and sales. Registrations were able to be revoked for substances likely to prejudice health and safety of humans, stock or beneficial species.

The Toxic Substances Act 1979 and the Pesticides Act 1979 established the Toxic Substances Board and the Pesticides Board, respectively (Buckland, et al. 1998). These two bodies administered the use of pesticides, until the various acts and regulations controlling pesticide use were replaced by the Hazardous Substances and New Organisms Act 1996 (HSNO Act). Transitional provisions meant that the Toxic Substances and Pesticides boards continued in existence following the enactment of the HSNO Act, with hazardous substances being brought under the Act in 2001, with various classes of substances progressively transferred to the Environmental Risk Management Authority's (ERMA) control. Pesticides were transferred in July 2004.

A number of the organochlorine pesticides, including aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex and toxaphene are on a list of "Persistent Organic Pollutants" (POPs) subject to international control under the Stockholm Convention (see http://www.pops.int/). New Zealand became one of 90 signatories to this convention in 2001 and ratified the convention by an amendment to the HSNO Act in 2004.

The use of the persistent contaminants of concern for horticultural land in New Zealand was, with the exception of copper, progressively discontinued through the 1960s and 70s, due to concern about effects on the environment. Copper pesticides have been used since the late 1800s and that use continues, principally as fungicides. At present there are many pesticides containing copper registered with ERMA.

Lead arsenate was introduced for horticultural use in New Zealand in the early 1900s (and arsenicals were also used in sheep dips). However, a search of the ERMA database found no currently authorised lead-based pesticides and only one containing arsenic, a selective herbicide containing methylarsinic acid for the control of coarse grasses in turf. Lead arsenate is thought to have been discontinued in the 1970s (ARC, 2002).

Early trials were carried out for DDT use as a pesticide in 1945 and by 1951 its use was widespread in fertiliser for treatment of pasture. Aldrin and dieldrin were introduced in 1954 under the Stock Remedies Act 1934. In 1961 the first of increasing restrictions on the use of DDT, dieldrin, aldrin, BHC and other organochlorines were imposed by regulation under the Agricultural Chemicals Act. In 1970 DDT was banned from any use on agricultural land, except limited horticultural use where other products were ineffective. Aldrin and dieldrin were effectively banned for agricultural and horticultural use in 1975 and by that stage the Agricultural Chemicals Board had a policy of generally phasing out organochlorines. This policy was continued by the Pesticides Board from 1979, and the last remaining products containing DDT, dieldrin, aldrin, and lindane were deregistered or the products withdrawn between 1985 and 1990 (Buckland, et al, 1998).

The banning of importation, production or use of these organochlorine substances was confirmed by New Zealand's ratification of the Stockholm Convention in 2004.

2.4 Properties of Selected Substances

As noted previously, the substances that have been detected most often at concentrations of concern are the substances with the greatest persistence. For the metals and metalloids these tend to be the substances that bind most strongly to soil, and therefore resist leaching. Being elements they will not degrade, and can only be lost by leaching, or in the case of some arsenic compounds, volatilisation. Similar binding behaviour is also displayed by the persistent organic compounds, but the chlorinated pesticides also resist degradation, or their degradation products are also toxic and persistent (e.g. aldrin degrades to dieldrin and DDT into DDD and DDE). Some organic compounds (e.g. DDT) have the further adverse property of bioaccumulating in animals despite only low concentrations in the soil.

Brief summaries of the properties of arsenic, copper, lead, DDT and dieldrin are provided in the following sections.

2.4.1 Arsenic

Arsenic is a metalloid with a complex chemistry, being able to form many inorganic and organic compounds. Inorganic arsenic occurs in many minerals and is widely distributed in rocks, soils and sediments. It can exist in several oxidation states, the most common being the pentavalent (+5, arsenate) and trivalent (+3, arsenite) forms (Environment Agency, 2002). Arsenite is the thermodynamically stable oxidation state in reducing environments (e.g. anaerobic conditions), whereas arsenate is the thermodynamically stable oxidation state in oxygenated environments expected at and near the soil surface where contaminated soil is typically contacted (Yang, *et al*, 2002).

Arsenic species tend to bind to soil and resist leaching, and therefore tend not to be mobile. It is more strongly absorbed onto soils with higher organic or clay content and least strongly absorbed onto sandy soils. In strongly adsorbing soils, transport rate and speciation are influenced by organic carbon content and microbial population. The amount of arsenic sorbed from solution increases as the free iron oxide, magnesium oxide, aluminium oxide or clay content of the soil increases (WHO, 2001). Carbonate minerals are expected to adsorb in calcareous soils. In general, iron oxides/hydroxides are the most commonly involved in adsorption of arsenic in both acidic and alkaline soils.

The behaviour of arsenate and arsenite in soil differ considerably. Arsenate species adsorb more strongly than arsenite, although both arsenite and arsenate are transported at a slower rate in strongly adsorbing soils than in sandy soils (WHO, 2001). In a non-absorbing sandy loam, arsenite is five to eight times more mobile than arsenate.

Soil pH also influences arsenic mobility. At a pH of about 6 arsenate is slightly more mobile than arsenite, but when pH changes from acidic to neutral to basic, arsenite increasingly tends to become the more mobile species, though mobility of both arsenite and arsenate increases with increasing pH.

Phosphate suppresses arsenate adsorption by soil, and the use of phosphate fertilisers significantly increases the amount of arsenic leached from soil contaminated with lead arsenate pesticide residues (WHO, 2001). Liming also has the potential to mobilise arsenic (ATSDR, 2000), which is consistent with the pH dependence of sorption reactions of arsenic on iron oxide minerals.

Many soil organisms are capable of converting arsenate and arsenite to several reduced forms, largely methylated arsines, which are volatile WHO (2001).

Terrestrial plants may accumulate arsenic by root uptake from the soil or by adsorption of airborne arsenic deposited on the leaves, some plant species accumulating substantial levels (WHO, 2001).

2.4.2 Copper

Copper is a metallic element that occurs naturally as the free metal. Most copper compounds occur in +1 (cuprous) and +2 (cupric) valence states (ATSDR, 2002). The cupric ion is the most important oxidation state of copper.

Copper binds to soil much more strongly than other divalent cations. Most copper deposited in soil from agricultural use will be strongly adsorbed and will remain in the upper few centimetres of soil, except in sandy soils where the stability of bound copper is less (WHO, 1998). The half-life of copper in soil is between 310 and 1500 years, depending on soil properties (Noway and Ayres, 1997).

Copper's movement in soil is determined by many physical and chemical interactions of copper with the soil components. In general, copper will adsorb to organic matter, carbonate minerals, clay minerals, or hydrous iron and manganese oxides. The binding affinities with inorganic and organic matter in sediments and soils is dependent on pH, the oxidation-reduction potential in the local environment, and the presence of competing metal ions and inorganic anions (ATSDR, 2002a). Liming an acid soil increases the amount of copper adsorbed (Cornforth, *et al*, 2002).

Accumulation of copper from soil contamination may lead to exceptionally high burdens in terrestrial plants. At high soil levels copper can be extremely toxic to plants with generally visible symptoms being metal toxicity are small chlorotic (yellowing) leaves and early leaf fall. Growth is stunted and initiation of roots and development of root laterals is poor (WHO, 1998).

Toxic effects have been observed in laboratory studies of earthworms exposed to copper in soil, with significant adverse effects at 50 – 60 mg/kg.

2.4.3 Lead

The fate of lead compounds in water and soil depends on their chemical and physical form, as well as other factors such as pH, organic matter content and the presence of colloids and iron oxide. Most lead is strongly retained in soil, and little is transported into surface or ground waters. The bioavailability of lead in soil to plants and to young children who may ingest soils and dusts is generally low, but can be influenced by chemical form and the presence of other substances (Environment Agency, 2002b).

The fate of lead in soil is affected by the adsorption at mineral interfaces, the precipitation of sparingly soluble solid forms of the compound, and the formation of relatively stable organic-metal complexes or chelates with soil organic matter. Most lead is retained strongly in soil, and very little is transported through runoff to surface water or leaching to groundwater except under acidic conditions (EPA 1986a). The mobility of lead will increase in acid conditions due to greater solubility.

Lead may be taken up in edible plants from the soil via the root system, by direct foliar uptake and translocation within the plant, and by surface deposition of particulate matter. The amount of lead in soil that is bioavailable to a vegetable plant depends on factors such as cation exchange capacity, pH, amount of organic matter present, soil moisture content, and type of amendments added to the soil.

2.4.4 DDT

Technical grade DDT is a mixture of three isomers, p,p’-DDT (typically 85%), o,p’-DDT (15%), and o,o’-DDT (trace amounts), none of which occur naturally. Technical grade DDT may also contain DDE and DDD as contaminants. Both DDE and DDD are breakdown products of DDT (ATSDR, 2002b), with DDE being the primary aerobic metabolite and DDD being an anaerobic breakdown product. All three can persist in the environment for decades.

The persistence of DDT is in part a result of its inherent chemical stability, but also its very low aqueous solubility and vapour pressure. In addition, it is resistant to photo-degradation and microbial degradation (Boul, 1994). Results obtained by Boul, *et al.* (1994) for unirrigated mid-Canterbury soils found half-life values of around 10 years for DDT in the upper 75 mm soil layer and DDE had remained little change after 20 years.

When deposited on soil, DDT, DDD and DDE are strongly adsorbed, with all soils showing a strong adsorptive capacity. Adsorption is least in sandy loams, several times greater in clay soils and greatest in highly organic material (WHO, 1989).

However, DDT, DDD and DDE may also initially revolatilise into the air, although this is more likely to occur from moist soils than dry soils. Biodegradation becomes a more important loss mechanism with time (WHO, 1989).

As a result of their strong binding to soil, DDT, DDE and DDT mostly remain on the surface layers of soil with little leaching into the lower soil layers and groundwater. DDT may be taken up by plants that are then eaten by animals and may bioaccumulate to high levels, primarily in adipose tissue and milk of the animals ATSDR (2002b).

2.4.5 Aldrin/Dieldrin

Aldrin and dieldrin are the common names of two similar man-made compounds that were formerly used as insecticides. They do not occur naturally in the environment. Technical-grade aldrin and dieldrin contain not less than 85% aldrin or dieldrin, respectively (ATSDR, 2002c).

Aldrin readily changes into dieldrin once it enters the environment and its fate is therefore closely linked to dieldrin (ATSDR, 2002c; Ritter, *et al*. no date). Aldrin binds strongly to soil particles and is very resistant to leaching into groundwater. Volatilisation is an important mechanism of loss from the soil (Ritter, et al.). The half-life of aldrin in soil is estimated to be 50 – 120 days, with microbiological conversion to dieldrin.

Dieldrin is much more resistant to biodegradation than aldrin (Swann et al. 1983, reported in ATSDR 2002c). Dieldrin has a strong affinity for organic matter and sorbs tightly to soil particulates. The half-life of dieldrin in temperate soils is approximately 5 years. This persistence, combined with high lipid solubility, provides the necessary conditions for dieldrin to bioaccumulate in organisms (Ritter, *et al*.).

Movement of dieldrin through the soil solution is extremely slow, suggesting little potential for groundwater contamination (ATSDR, 2002).

Given aldrin's rapid change to dieldrin in the environment, the two are considered together in this report.

2.5 Soil Guideline Values

A large number of different guidelines are in use throughout the world for the various substances typically encountered as persistent contamination on former horticulture sites. Unfortunately there is a wide variation in guideline values for particular substances between different jurisdictions. This is because of different policy contexts, and hence different derivation methodologies, and also different toxicity values on which the derivations are based. Care is required when using the various guideline values that the differences in derivation methods are understood (particularly if guidelines for different substances are selected from different jurisdictions), and that values appropriate to the particular receptor of interest and exposure pathways are used. If values from overseas are used it is preferable that the derivation is similar to that used in New Zealand.

It is not possible to go into the detail of derivation methodologies in this scoping study, however, Cavanagh and O'Halloran (2002), and Cavanagh and Proffitt (2005), provide useful summaries of different human health-based guideline methodologies, and Cavanagh and O'Halloran (2006) guideline methodologies for ecological receptors.

Countries that use a combination of human health and ecological values (e.g. Canada and Netherlands) will tend to have lower guideline values than if based on human health alone. In addition, where cancer risk values are used for deriving guidelines for carcinogens (e.g. New Zealand and the United States), the selection of that risk value has a large effect on the final guideline. The United States typically selects a ten-fold more conservative risk value (1 in 1,000,000) than New Zealand (1 in 100,000) and consequently United States guideline values are ten times lower than would be adopted in New Zealand for otherwise the same derivation.

A summary of human health guidelines is set out in Table 1 for the substances most likely to be found at elevated concentrations on horticultural land. A similar summary is presented in Table 2 for ecological receptors. It should be noted that the listed copper guideline value in Table 1 from MoH/MfE (1997) is for protection of plants, not human health and that the derivation of the health-based copper value in those guidelines is generally accepted as being very conservative and requiring revision.

Table 1: Selected International Guideline Values for Standard Residential Exposure Scenario (mg/kg)

Country	Arsenic	Copper	Lead	DDT	Dieldrin	Source/Comments
New Zealand	30	130/ 370	-	-	-	MoH/MfE (1997) Soil ingestion, inhalation, 10% home-grown produce. Lower copper value based on phytotoxicty. Carcinogens (arsenic) calculated for 1 in 100,000 risk.
	30	-	-	28	2.6	MfE(2006) Soil ingestion, 10% home-grown produce consumption, dermal, allowance for dietary intake (threshold substances only)
	9	>10,000	270/ 460	-	-	Cavanagh and Proffitt (2004). Site-specific criteria from Sandilands based on soil ingestion, 10% home-grown produce, allowance for dietary intake where relevant. Lower and higher values for lead are for 60% and 100% bioavailability respectively.
Australia	100	1000	300	200	10	NEPC (1999a) Soil ingestion, dermal, allowance for dietary intake. Assumed to be suitable for up to 10% produce being home-grown.
United States	0.39	3128	400	1.7	0.03	US EPA (2004) Soil ingestion, dermal and inhalation. Carcinogens calculated for 1 in 1x 10^6 risk (arsenic, DDT, dieldrin).
	20	-	400	2	0.042	New Jersey clean-up criteria (HPCTF, 1999). Arsenic based on naturally occurring levels.
Canada	12	63	140	0.7	-	CCME (2004) Lowest of human health and ecological receptors. Human health based on equal apportionment of allowable intake between soil, water, air, food and consumer goods (CCME, 1996).
United Kingdom	20	-	450	-	-	(Environment Agency, 2002a, b) Soil ingestion, home-grown produce, allowance for dietary intake. Lead value based on soil – blood model.
Netherlands	55	190	530	4	4	(VROM, 2000) Combination of ecological and human health. DDT for ∑DDT, dieldrin includes aldrin

Table 2: Selected International Guideline Values for Ecological Receptors (mg/kg)

Country		Arsenic	Cadmium	Copper	Lead	Zinc	DDT	Dieldrin	Source/Comments
New Zealand	Minimal risk value	12	1	45	60	180	1.8	0.002	Cavanagh and O'Halloran (2006) Medium risk values adjusted for Auckland region background concentrations. May not be applicable to other regions.
	Serious risk value	22	12	135	100	200	13	0.5	
Australia (Urban EILs)		20	3	100	600	200	-	-	NEPC (1999b)
United States Eco-SSL	Plants	18	32	-	120	-	-	-	US EPA (2005a, b, c)
	Invertebrates	-	140	-	1700	-	-	-	
	Birds	43	0.77	-	11	-	-	-	
	Mammals	46	0.36	-	56	-	-	-	
Canada (Agricultural SQGe)		17	3.8	63	70	200	0.7	-	Environment Canada (1999a, b, c, d, e) The Canadian Soil Quality Guidelines use the lowest of ecological or human health guidelines (CCME, 1996). For all these substances except cadmium ecological guidelines were critical.

3.0 Patterns of Soil Contamination

3.1 Overseas Studies

Pesticide contamination of former orchard land has been the subject of a number of overseas studies, particularly within the fruit growing areas of the United States. These studies have concentrated on organochlorine and lead and arsenic residues, the latter a legacy of many decades of lead arsenate use.

Peryea (1998) reports lead arsenate was the most extensively used of the arsenical insecticides. It was first prepared as an insecticide in 1892 for use against gypsy moth in Massachusetts, USA, and was also used in Australia, Canada, New Zealand, England, France and North Africa. Use essentially ceased in the 1960s with the introduction of organochlorine pesticides.

A study of 13 old orchards in the State of New York (Merwin, *et al.* 1994) found concentrations of arsenic and lead in surface soils 0 – 150 mm) ranging from 1.60 to 141 mg/kg and 1.48 to 720 mg/kg, respectively. A study in New Jersey (HPCTF, 1999), which collated soil residues results from reports reviewed by the New Jersey Department of Environmental Protection, reported average concentrations of arsenic, lead, DDT, DDE, DDD and dieldrin from 18 orchard and field crop (understood to be vegetables) properties as shown in Table 3. Aldrin and other organochlorine pesticides were not detected. A similar collation of orchard and site assessment reports by the Department of Ecology in the State of Washington found concentrations of up to 800 mg/kg of arsenic and up 1000 mg/kg for lead (HPCTF, 1999).

Table 3: Soil Sampling Results for New Jersey Orchard and Cropping Properties (mg/kg)

Site type	Arsenic	Lead	DDT	DDE	DDD	Dieldrin
Field Crops (263 samples)	1.2 – 65.3	ND – 551	ND – 1.2	ND – 0.43	ND – 0.43	ND – 0.39
Orchard (157 samples)	4.2 – 231	8.9 – 924	0.01 – 26	0.002 – 8.8	ND – 6.8	ND – 0.27
Orchard and crops (38 samples)	4.8 – 310	66 – 350	0.06 – 3.0	0.1 – 2.6	ND	ND – 0.37

ND = non-detect – detection limits not given.

New Jersey surveyed the other states in the United States (HPCTF, 1999) to determine the extent of historic pesticide contamination. The survey found that 14 states consider the historic use of pesticides to be problematic with respect to site development and cleanup. For example, the states of Washington and Wisconsin have public information programmes providing guidance for dealing with lead and arsenic residues (see http://www.datcp.state.wi.us/arm/agriculture/pest-fert/pesticides/accp/lead_arsen.jsp and http://www.ecy.wa.gov/programs/tcp/area_wide/area_wide_hp.html).

In Australia, Merry, *et al.* (1983) analysed 98 surface soil samples (0 – 100 mm) from orchards in South Australia and Tasmania for copper, lead and arsenic. They found concentrations of copper ranging up to 320 mg/kg with a mean of 101 mg/kg; lead up to 600 mg/kg with a mean of 170 mg/kg and arsenic up to 120 mg/kg, with a mean of 29 mg/kg. They found a strong correlation between concentrations of each. Merry, *et al.* suggested annual accumulation rates of 1.25 and 5 μg for arsenic and lead respectively, equivalent to three applications of lead arsenate each year.

Merry, *et al.* (1983) also measured copper, arsenic and lead in six vertical profiles with a variety of soil types. Copper and lead generally remained in the top 300 mm, regardless of the soil type, with highest concentrations in the top 150 mm. Arsenic remained in the surface soil for soils rich in clay, organic material and iron, but leaching occurred in sandy soils, with peak concentrations occurring below the surface, adsorbed onto organic or clay-rich material, or prevented from travelling further by a hard pan.

A study of DDT contamination in a river catchment by the Washington Department of Ecology (Serdar & Era-Miller, 2004) included taking surface soil samples (0 – 50 mm) in 13 orchard properties. The sampling was part of gaining a better understanding of the reasons behind the presence of DDT in surface waters and bed sediments of streams draining the catchment. Three sub-catchments were sampled, with results as shown in the following table:

Table 4: DDT Soil Concentrations Lower Mission Creek Basin, USA

Sub-catchment	Mean Concentrations ± Range (mg/kg)			
	4,4’-DDE	4,4’-DDD	4,4’-DDT	∑DDT
Mission	4.6 ± 1	0.76 ±0.6	2.2 ±1.7	7.6 ± 2.0
Brender	4.2 ± 0.9	0.076 ± 0.002	4.0 ± 1.2	8.2 ± 0.4
Yaksum	6.6 ± 2.2	0.10 ± 0.03	8.0 ± 4.0	14.0 ± 7.0

Studies of aldrin and dieldrin in agricultural soils in the United States and Canada, reported in ATSDR (2002c), found dieldrin residues in higher concentrations and with greater frequency than residues of aldrin as a result of the rapid conversion of aldrin to dieldrin. The amount of dieldrin and aldrin residues in soils was monitored from 12 separate farm lands located in the Fraser Valley of British Columbia, Canada in 1989 (Szeto and Price, 1991). Each farm had a known history of at least 25 years of vegetable growing and use of various pesticides. Aldrin was detected on one farm with a mean concentration of 0.078 mg/kg, while dieldrin was detected on two farms at a mean concentration of 0.69 mg/kg, but ranging from 0.104 to 1.280 mg/kg.

3.2 Typical Broad-Acre Soil Concentrations in New Zealand

A number of soil sampling surveys have been carried out at a regional or sub-regional level in New Zealand. This sampling used 10-part composite samples over one-hectare areas, with each sub-sample in the composite being a 75 mm deep core of surface soil. Sampling carried out for the Auckland Regional Council (ARC, 2002), Environment Bay of Plenty (SEM, 2004), Tasman District Council (Gaw, 2003), Environment Waikato (Gaw *et al.* 2006), and in the Hawke's Bay (McCaskill, 2004; PDP, 2004; 2005) indicates only a narrow range of chemicals is likely to be detected at concentrations high enough to be of concern. In particular, only four substances are found at significantly elevated concentrations, being arsenic, copper, lead and DDT (including DDE and DDD).

The Auckland, Waikato, Bay of Plenty and Tasman studies indicate that a few other metals might be detected on some properties, but they are either not toxic enough or concentrations will not be high enough to be of concern for human health, but may be of general environmental concern. Zinc and cadmium (from fertiliser use) are examples, although Gaw, *et al.* (2006) reported no significant difference between grazing land and horticultural properties. Mercury was found to be of no particular concern on horticultural properties in New Zealand (Gaw, *et al.*, 2006), although mercury was not analysed in the Bay of Plenty or Hawke's Bay studies.

Some organochlorine compounds other than DDT might also be detected, including dieldrin, dicofol, lindane and endosulfan. Of these, only dieldrin (and its near relative, aldrin) is considered sufficiently persistent and toxic to be of concern, but testing in other regions has not detected dieldrin at high enough concentrations to suggest widespread routine testing is necessary on horticultural land. Dieldrin is most likely to be detected where some berry fruits were grown (ARC, 2002) and therefore should be considered on a case-by-case basis.

Typical concentrations of the major substances expected to be found in New Zealand are summarised by region in Table 5. If these are compared with the human health guideline values in Table 1, it can be seen that only arsenic consistently exceeds guideline values, while lead sometimes exceeds guidelines (but will generally accompany an arsenic exceedance).

Gaw *et al.* (2006) noted that arsenic concentrations for orchard soils were higher than for other horticultural uses (although glasshouse use was not included in this assessment), with higher concentrations for orchards in the Tasman District (mean 30 mg/kg, geometric mean 21 mg/kg) than for either Auckland (mean 15, geomean 11 mg/kg) or the Waikato regions (mean 18 mg/kg, geomean 10 mg/kg). PDP's experience of sampling orchards around Auckland suggests that arsenic concentrations in excess of that found in the ARC (2002) study (the same Auckland data as summarised in Gaw, *et al.*, 2006) is not uncommon, with concentrations in excess of 30 mg/kg quite often found (Keith Delamore, pers. comm).

Table 5: New Zealand Surface Soil Sampling Results by Region

Land use	10-part Composites of 75 mm deep cores (mg/kg)				
	Region	**Arsenic**	**Copper**	**Lead**	**Total DDT** [1]
Pip/Stone Orchard	Auckland (n=12)[2]	2 – 34	21 – 490	11.4 – 178	<0.03 – 24.4
	Waikato (n = 7)	4 – 58	242 – 523	14 – 251	0.73 – 34.5
	Bay of Plenty (n=17)	3 – 48	6 – 304	4.6 – 184	<0.03 – 6.09
	Hawke's Bay (n=18/10)[3]	4 – 73	28 – 542	16 – 341	0.02 – 15.3
	Tasman (n=5)	3 – 48	10 – 123	15 – 243	1.49 – 7.14
Glasshouses	Auckland (n=12)	<2 – 20	7 – 253	6.0 – 1250	<0.03 – 289
Market Gardens/Vegetable Cropping	Auckland (n=8)	4 – 11	21 – 137	14.4 – 45.7	0.08 – 0.91
	Waikato (n = 7)	6 – 11	26 – 112	21 – 48	0.04 – 1.68
	Bay of Plenty [4] (n=24)	<2 – 28	11 – 215	6.2 – 63.2	<0.03 – 4.37
	Hawke's Bay (n=6)	3 – 10	8 – 58	10 – 32	<0.01 – 0.12
	Tasman (n=5)	2 – 21	6 – 67	8 – 21	0.06 – 1.16
Vineyard	Auckland (n=11)	<2 – 14	16 – 152	2.7 – 87.6	<0.03 – 2.84
	Waikato	6 – 15	22 – 115	22 – 51	<0.03 – 1.26
	Hawke's Bay (n=5)	2 – 7	43 – 119	12 – 56	0.02 – 0.35
Pasture	Auckland (n = 6)	2 – 5	9 – 16	9 – 359	0.01 – 0.002
	Waikato (n = 7)	3 – 9	12 – 33	12 – 43	<0.03 – 0.75
	Bay of Plenty (n=24)	<2 – 15	4-50	1.4 – 25.2	<0.03 – 1.18
	Hawke's Bay (n=6)	2 – 13	9 – 24	8 – 30 [5]	0.01 – 0.21
	Tasman (n = 5)	<2 – 7	5 – 55	6 – 11	<0.03 – 1.3
Pasture to Orchard post 1975	Hawke's Bay	4 – 39	19 – 110	13 – 137	0.05 – 9.1

Notes:

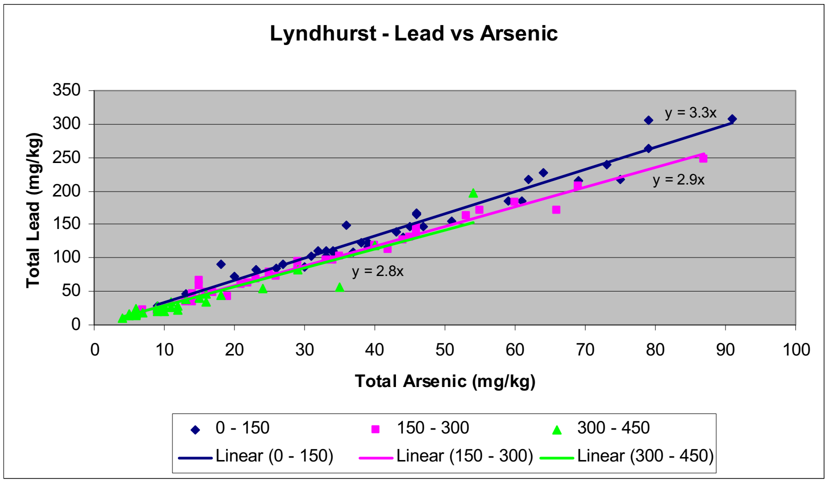
1. The sum of DDT, DDD and DDE.
2. n = number of samples
3. Arsenic and lead has 18 values from Macaskill (2004) and PDP (2005), whereas copper and DDT only 10 values from Macaskill (2005).
4. Glasshouses and market gardens lumped together in SEM (2005). No information as to how "horticulture" category differs from other apparent horticulture uses, and has therefore been combined with glasshouse/market garden in the table to be more consistent with other regions.
5. Anomalous high result of 359 mg/kg excluded as atypical.

For the Bay of Plenty region, SEM (2005) found slightly higher arsenic concentrations for “horticulture” (the distinction between this and market gardens or orchards is not clear) compared with orchards, although the maximum was higher for orchards. The reported arithmetic means for the Bay of Plenty were 11 mg/kg and 10 mg/kg for horticulture and orchards, respectively.

The sampling carried out by Macaskill (2004) in the Hawke’s Bay found intermediate arsenic concentrations compared with Tasman and Auckland, (mean 18 mg/kg, geomean 13 mg/kg), however, sampling by PDP (2005) in a long-term orchard area of the Hawke’s Bay, the Lyndhurst area on the outskirts of Hastings, found higher arsenic concentrations than the regional studies. For the eight Lyndhurst properties sampled the mean arsenic concentration was 36 mg/kg and the geometric mean was 40 mg/kg.

Except where paint may cause anomalous results in glasshouses, lead contamination closely mirrors that of arsenic. This is expected given that they were generally applied together as lead arsenate and they have similar resistance to leaching.

Gaw, *et al.* (2006) reported lead:arsenic ratios in the range 3.4 – 6.6 for orchard soils in the Auckland, Tasman and Waikato regions. The bottom end of this range is very close to the average lead:arsenic ratio of 3.3 found in 36 samples taken from the top 150 mm of soil from four orchard properties in the Lyndhurst area of Hastings (PDP, 2004), as shown in the following plot.



The ratio is lower for greater sampling depths, presumably reflecting a slightly smaller mobility for lead compared with arsenic in these particular soils (silt and clay loams), but in all cases the data fall on remarkably straight lines for each sampling depth. The variation of concentration with depth is discussed in greater detail in the next section.

Glasshouses were sampled as a separate use in ARC (2002), but were not sampled separately in any of the other studies. Glasshouses did not show particularly high arsenic concentrations, the mean concentration being below the means for orchards and market gardens. However, both lead and DDT returned extreme results. The single high lead concentration (1250 mg/kg) was attributed to lead paint flakes. Recalculating the lead mean without this extreme value results in a mean of 55 mg/kg, which is lower than the mean for market gardens and higher than the mean for orchards in the same study. Similarly, removing the extreme DDT value (289 mg/kg) from the glasshouse dataset reduces the mean from 25.2 mg/kg to 1.2 mg/kg. This recalculated mean again falls between market gardens and orchards.

These recalculations suggest that glasshouses will not generally return high concentrations of the contaminants of concern, but that routine sampling should be carried out because of the possibility of extreme results in some glasshouses. In addition, PDP's experience in sampling glasshouses in the Auckland area is at variance with the ARC (2002) study with respect to arsenic, with arsenic concentrations of 100 mg/kg not uncommon (Keith Delamore, pers. comm.), reinforcing the conclusion that glasshouses should be routinely sampled.

It is expected that the same narrow range of chemical residues as has been detected in other regions will be generally applicable to the Canterbury region, as similar chemicals will have been used during the same periods in the past. Thus, while acknowledging that there will be some differences in chemical types, application frequencies and timing due to climatic and cropping differences, the information available suggests these differences are not great enough to result in quite different groups of chemicals remaining as soil residues in one region compared with another.

The results of a small number of site-specific studies of horticultural land in Canterbury are discussed in Section 5.3.

3.3 Broad-Acre Soil-Residue Variability

There are a number of New Zealand studies available that provide confirmation that vertical migration of agrichemical residues is generally limited, however there are few studies available exploring the spatial variability of broad-acre (as distinct from hotspot) agrichemical residues within a particular property. Given the similarity of soil types and general similarity in horticultural practices, the patterns of soil residues observed elsewhere in New Zealand are expected to be generally applicable to Canterbury.

3.3.1 Vertical Variability

In a general sense, the strong affinity to be adsorbed onto soil particles or organic material displayed by arsenic, copper, lead and many of the organochlorine pesticides mean that chemicals applied as sprays will tend to remain within the surface soil layers. This has been observed in overseas studies, reported above, and has also been found in New Zealand studies.

Initial sampling of four cropping areas in the Auckland area reported in ARC (2002) found little difference between samples for nominal sample depths of 75 and 150 mm. This was attributed to the soil being ploughed or cultivated. Further sampling was carried out on two orchards with three soil cores taken to a depth of 1m. Across the three cores, copper concentrations were highest at the surface and tended to decrease with depth, with residues generally associated with the top 200 mm. DDT had a similar result. Arsenic concentrations tended to increase to a depth of approximately 150 to 170 mm and then decrease. Lead concentrations tended to increase slightly below the surface layer and then decrease, with no evidence of lead accumulation below the top 200 mm.

Three vertical soil profiles collected by Environment Waikato (EW) and Hamilton City Council on former orchard land found a rapid drop-off in concentrations of arsenic, copper, lead and DDT within the top 200 to 300 mm of soil (Nick Kim, EW, pers.comm). An exception was in one profile, where a substantial increase in arsenic was found between 300 and 600 mm compared with the 200 to 300 mm above. This was attributed to a sandy horizon overlying an iron-oxide-rich layer, the former promoting transport from the surface soil to a greater depth and the latter capturing the arsenic. This is consistent with the known ability of iron oxides to absorb arsenic.

PDP carried out sampling in another former orchard in Hamilton near the orchard described above. The orchard had commenced operation in the early 1900s. Several sample pairs were collected at the surface (0 – 75 mm) and at a depth of 200 – 275 mm. In general, there was a substantial reduction in concentrations between the surface and deeper sample of each pair, regardless of the analyte being considered, although concentrations were still clearly above background at the greater depth. Two deeper profiles were collected from an area that had been levelled, cultivated and grassed, as shown in the Table 6: Depth Profiles from a Former Hamilton Orchard.

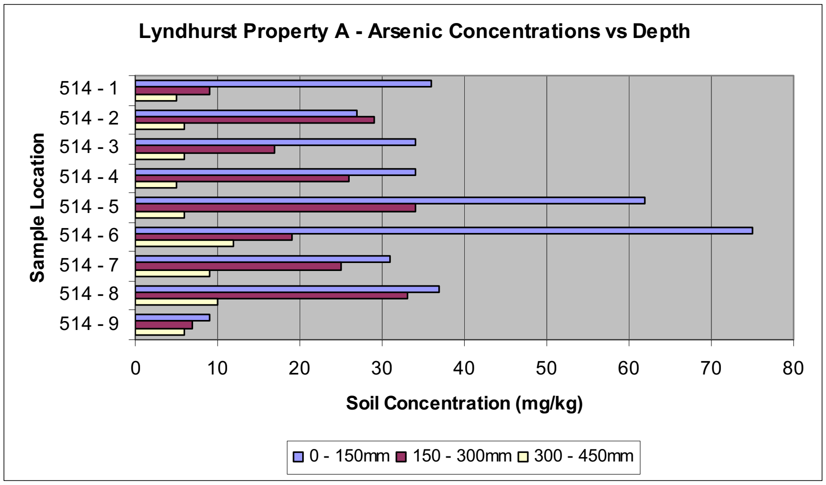
Table 6: Depth Profiles from a Former Hamilton Orchard

Sample	Depth (mm)	Arsenic	Copper	Lead	Total DDT
Profile A	0 – 37	109	547	490	20.9
	37 – 75	92	715	429	20
	150 – 225	153	548	829	19.3
	300 – 375	120	28	25.1	0.79
	450 – 525	17	13	22.9	0.23
Profile B	0 – 75	29	415	107	5.29
	150 – 225	23	369	72.7	2.52
	300 – 375	7	20	15.5	0.05
	450 – 525	6	8	14.5	<0.03

Of note are the generally high concentrations in one of the profiles and, in the same profile, arsenic concentrations still being substantially elevated at 375 mm. The deepest samples, starting at 450 mm, were typical of background concentrations.

In similar work carried out for the Hastings District Council in the Lyndhurst area, again an area of multiple orchards dating back to the early 1900s, PDP collected samples on four properties at 150 mm vertical intervals down to 450 mm. Up to nine profiles on each property were collected on a 60 m grid (PDP 2005). Samples were analysed for arsenic and lead. The soils were deep silt and clay loams overlying sand and gravel alluvium. A plot from one of these properties of the vertical distribution of arsenic, for each sample location, is shown below.

It is apparent that the arsenic concentration drops off rapidly within the top 300 mm, although in these particular soils many samples still had elevated concentrations in the 150 – 300 mm interval. With a few exceptions, concentrations were close to background in the interval 300 – 450 mm.



On another Lyndhurst property, a similar plot (see next section) showed concentrations were typically consistent for the top two 150 mm intervals (i.e. over the top 300 mm), although sometimes the second 150 mm interval was a little higher than the surface interval. On this property concentrations were still well above background for the 300 – 450 mm interval. Both properties were close together and the soils were similar. The differences between the properties was attributed to different spraying practices over extended periods of time and probably deep cultivation causing a relative consistent concentration for the top 250 – 300 mm, in the case of the second property.

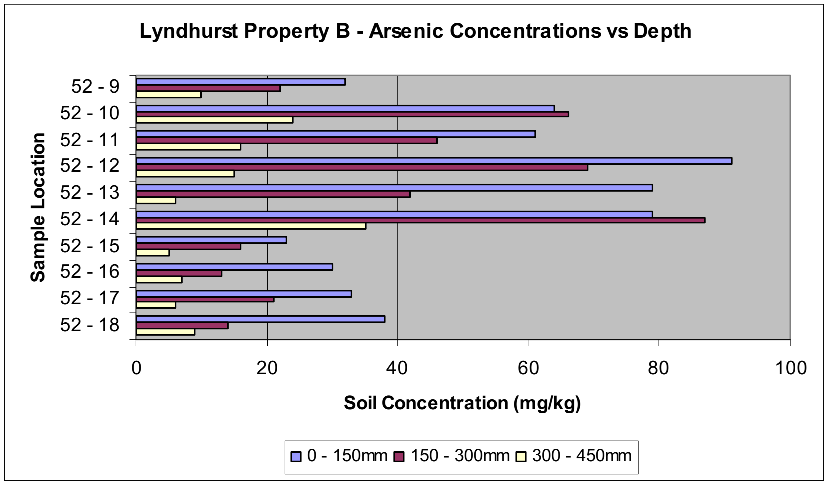
3.3.2 Spatial Variability

In a general sense, the methods of spray application, particular since the introduction of air-blast sprayers, should ensure a reasonably consistent application rate for a particular horticultural crop. Therefore variability of soil residues from place to place should not be as great as some other forms of contaminated site. However, earlier forms of spray application included knap-sack sprayers and hand-directed spray booms either attached to a vehicle-mounted pump and tank, or a reticulated system with a central, fixed tank and pump. These earlier systems would tend to result in greater spatial variability than air-blast methods. Reticulated systems were known to leak or even burst, resulting in the potential for hotspots where these systems were used.

A limited number of studies into the spatial variability of soil residues appear to be in the public domain in New Zealand. The study for the ARC (2002) examined the spatial variability between one-hectare 10-part composites for four properties; two orchards, a market garden and a vineyard. This, in effect, measures variability of the average concentration from one hectare to another in a particular property, and will reflect different crop types as well as unevenness of spray application and unevenness of subsequent leaching or degradation. The sample number was small for each property (either two or four samples), so only limited conclusion can be drawn. Greater variability was observed in orchards compared with market gardens or vineyards and DDT and lead was more variable than arsenic or copper. The data were presented as relative standard deviations (standard deviation/mean). Assuming normal distributions and a 95% confidence interval (±1.96 standard deviations), then the orchard results suggest that DDT concentrations in 10-part composites from a particular property could range from 0 to 220% of the mean of all the 10-part composites for that property. Similarly, the range would be from 67 to 133% of the mean for arsenic and 30 to 170% of the mean for lead. Assuming arsenic is the main contaminant of concern for horticultural properties, these results suggest that a two fold range in concentrations from one 10-part composite to another is possible, and the wider conclusion is that a number of 10-part one-hectare composites is required to properly represent the likely range of concentrations in a large property.

ARC (2002) also examined the smaller-scale variability of samples within a one-hectare orchard area by taking several different 10-part composites over the same area. The results demonstrated that the soil was reasonably homogeneous within the one hectare. For the 95% confidence interval, the mean for both arsenic and DDT for a particular sample was found to be within 25% of the overall mean.

A different approach to spatial variability was taken by PDP (2005), in which individual samples were taken on a 60 m grid to investigate both vertical and spatial variability for four properties in the Lyndhurst area of Hastings. A plot from one of those properties was presented in the previous section and a plot from another property is presented below.



Considering just the surface (0 – 150 mm) samples and ignoring samples that appear to be at background concentrations (one sample in Property A), it is apparent that up to a four-fold variation in arsenic concentrations occurred from place to place. However, there is a distinct bi-modal pattern in both properties, probably reflecting different blocks of trees and therefore spray regimes (the properties were mixed stone and pip fruit, with pip fruit tending to have more spray applications). When considering all four properties sampled, where group of results could be defined based on proximity to each other and similarity of concentrations, suggestive of particular blocks of trees (e.g. samples 52-10 to 52-14 in Property B), the highest result in the group was generally not more than 50% greater than the lowest result, and typically less.

When the calculated mean arsenic concentration from the nine or so grid surface samples from each property were compared with 10-part composite taken separately from each property in a “zig-zag” fashion, there was good agreement within each property, although the 10-part composite was typically 10 to 40% higher than the grid sample mean. This is probably partly a result of the 10-part composites being 75 mm deep cores, whereas the individual samples were 150 mm deep. Given the drop-off with depth the deeper samples could be expected to have lower concentrations.

Similar grid sampling results have been sighted by PDP when peer reviewing soil sampling reports. Typically the highest arsenic concentration within a set is 50 - 70% higher than the lowest, but on occasions there is a two-fold range.