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Evaluating the potential of historic sheep dips as point sources of trace element and organochlorine pollutants

A thesis
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Abstract

Sheep dipping was a historic agricultural practice where sheep were immersed into insecticides to eradicate external parasites. Historical use of pesticides has caused localised soil contamination at former sheep dipping sites. There is limited information on offsite contamination such as in stream sediments, groundwater, and surface water. Predominant contaminants at historic sheep dipping sites are arsenic (As) and organochlorine (OC) compounds. There are estimated to be 50,000 former sheep dip sites in New Zealand, of which, over 10,000 are estimated to be in the Waikato Region. Contamination at historical sheep dip sites is potentially concerning for human and environmental health.

The objectives of this study were to (1) evaluate a range of historic sheep dips to identify sites that had the highest leaching potential; (2) characterise the selected study sites; (3) establish the extent of contamination in soil, sediments, and water; (4) evaluate the extent of offsite contamination; and (5) assess compliance to environmental guideline limits.

Soil samples from two former sheep dip sites were analysed for arsenic, copper, and organochlorines at depths of up to 20 cm. Further soil samples were analysed for arsenic at depths of up to 7.5 cm. Stream water and sediment samples were analysed for arsenic, copper, and organochlorines at upstream, downstream, and discharge point of a dip site located on a flood zone. Arsenic (0 - 2,839 mg/kg), dieldrin (0 - 8.60 mg/kg), lindane (including by-products) (0 - 0.560 mg/kg), DDT (including metabolites) (0 - 1.200 mg/kg), and endrin (0 - 0.127 mg/kg) were the main contaminants detected in soil samples. Concentrations of As (0.9 - 32 mg/kg), dieldrin (0 - 0.038 mg/kg), and benzene hexachloride (α -BHC and β -BHC) (0 - 0.0031 mg/kg) were detected in stream sediments. Organochlorine was not detected in surface water. As in surface water ranged from 0 to 0.0021 g/m³, which was well below the maximum acceptable value (MAV) of 0.01 g/m³ for potable drinking water supplies.

Arsenic concentrations in 142 soil samples were well above environmental guidelines for human habitation (30 mg/kg). Dieldrin recorded low to moderate contamination in soils with one sample exceeding the environmental guideline of 6 mg/kg. Arsenic in 4 of the 18 stream sediment samples were above the interim sediment quality low level guideline (ISQG-Low) of 20 mg/kg. Dieldrin concentrations in surface sediments up to 13 cm deep were well above the interim sediment quality high level guideline (ISQG-High) of 0.008 mg/kg. α -BHC and β -BHC had no ISQG guideline. The levels detected were above the lindane guideline (ISQG-High) of 0.001 mg/kg in surface sediments. Evidence of sheep dip chemicals moving away from a sheep dip site included arsenic, dieldrin, and DDT up to 100 m downhill from a dip site located on the margins of a steep slope with an adjacent gully. Elevated As was detected in stream sediments up to 40 m downstream of a dip site located on a flood zone. High level contamination from dieldrin, α -BHC, and β -BHC were recorded in downstream sediments.

This study recommends that sheep dips located within 15 m of a stream and margins of steep slopes with an adjacent gully should be regarded as priority sites for contaminated land investigations that should include a monitoring programme.

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List of Acronyms

AAS	Atomic Absorption Spectrophotometer
ANZECC	Australia and New Zealand Environment Conservation Council
BHC	Benzene Hexachloride
IANZ	International Accreditation New Zealand
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma with a Mass Spectrometry
GC-ECD	Gas Chromatography with an Electron Capture Detector
GPS	Global Positioning System
MAV	Maximum Acceptable Value
MfE	Ministry for the Environment (NZ)
MoH	Ministry of Health (NZ)
NES	National Environmental Standards
OPs	Organophosphates
PCBs	Polychlorinated biphenyls
POP	Persistent Organic Pollutant
RMA	Resource Management Act (1991) (NZ)
UK	United Kingdom
UN	United Nations
USEPA	United States Environmental Protection Agency

Chapter 1 - Introduction

Chapter One

Introduction

1.1 Background

Sheep make up the world's second largest livestock sector after cattle. In New Zealand, sheep are a vital part of the rural economy. Pests such as ectoparasites are a major concern to sheep farmers and are a drain on farming resources (Hooda *et al.*, 2000). Pests and diseases need to be controlled using pesticides to maintain acceptable standards of animal welfare. Chemicals applied on sheep ensure that sheep farming is sustainable in the long term. Insecticides are used to control external parasites on sheep. Insecticides also have the potential to have adverse effects on humans and the environment (Heath, 1994).

Sheep farmers have dipped sheep as a legal requirement by showering or full immersion into insecticides for over 150 years, using several dipping methods, depending on stock numbers. Historically for instance, a few hundred sheep would prefer a smaller dip such as a sheep shower or jetting. Sheep showers were built on the farm (Figure 1-1) or provided by a mobile unit. Farms with larger stock numbers had concrete structures built on the ground with a holding pen and a fenced drip area. Some sheep farms have, over the years, used a variety of shower jetting, plunge, and swim-through type dips, and footbaths. Due to the modern pour-on treatments for ectoparasites former dipping methods are no longer used (Gregory, 2013).



Figure 1-1 Remnants of a sheep shower, last used in about 1965. Showing the holding pens on the bottom right fenced area, drip zone uphill of the power sprayer and the old shearing shed. Photo taken 14 March 2013

Chemicals used and methods of dipping evolved over time as a result of the increasing efficiency of new chemicals to control ectoparasites (Table 1-1). Arsenic and organochlorine were important in sheep farming to control ectoparasites on sheep (Ministry for the Environment, 2006). Arsenic based insecticides were first used in 1849 before the invention of organochlorine in 1935. Arsenic based compounds such as lead and copper arsenate were first used before the introduction of organochlorine compounds; DDT, lindane, dieldrin, and aldrin. Organochlorines were succeeded by organophosphates (OPs) in the mid-1980s before being deregistered in New Zealand by the New Zealand government in 1989 (McBride, 2004). Organophosphates are less toxic for humans to handle compared to organochlorines and less persistent in the environment (Cook, 1992). Organophosphates do not bioaccumulate in high levels in fat (Hill, 2010). Organophosphates have high solubility therefore runoff easily in rainwater and percolate into groundwater contaminating surface and groundwater (Hill, 2010).

Table 1-1 Summary of chemicals used in New Zealand for treatment of sheep ectoparasites

Chemical	Period of usage
Arsenic	1840s -1961
Organochlorines:	
DDT	1945 – 1961
Lindane	1947 - 1961
Dieldrin	1955 - 1961
Aldrin	1955 -1961
Organophosphates	1960s - present
Synthetic pyrethroids	1970s - present

Management of historical sheep dip sites in New Zealand has improved since the recognition of contaminants on sheep dip sites in the mid-1990's (McBride, 1994). Subsequent studies have led to the development of national guidelines and standards. The Ministry for the Environment guidelines for the management of contaminated land sites of former sheep dip focuses on the identification, investigation and management of former sheep dip sites (Ministry for the Environment, 2006). Regional councils and territorial authorities are required by the Resource Management Act to identify, investigate, and manage disturbances on historic contaminated sites as a result of land use changes and expanding urban boundaries. Less expensive remediation options such as fencing off known sites and discharge monitoring to more expensive options like soil removal and replacement or incineration, are management options used to ensure the land is fit for the purpose of development. Management options used should ensure that levels of toxic and persistent contaminants such as arsenic and organochlorine compounds are within National Environmental Standards (NES). Horticulture, dairying, and urban development are examples of land use changes that have taken place at former sheep dip sites.

Chemicals formerly used as insecticides such as lead and copper arsenate, DDT and metabolites DDE & DDD, lindane, dieldrin, and aldrin are chemicals of concern due to toxicity, persistence, and tendency to bioaccumulate in the trophic levels of the food chain. However, chemicals used to treat animals for external parasites in New Zealand and worldwide have improved as a result of the

introduction of modern insecticides. Modern insecticides are hazardous at the time of use, but they generally degrade readily in the environment.

In the last 50 years at least three major groups of compounds have been widely approved for treatment of ectoparasites: organophosphate products (OP), synthetic pyrethroids (SP), and injectable macrocyclic lactones (Armstrong and Phillips, 1999; Cocker *et al.*, 2000). Alternative methods of pest control have also been developed in the last 20 years. Pour on products and preparations that generally apply onto the animal by spraying along the back and flanks using a special applicator (Armstrong and Phillips, 1999; Cocker *et al.*, 2002).

1.2 Thesis objectives

The primary aim of this thesis was to establish evidence of sheep dip contaminants moving away through land, sediments, and surface water at two historical sheep dip sites in the Waikato Region of New Zealand. This thesis was part of a wider review intended to provide additional information to Waikato Regional Council's proposed Contaminated Land Strategy developed in 2012. Evidence provided in this thesis was to assist the Regional Council's contaminated land management resources prioritisation.

Specific objectives included:

- i) Identify and investigate historical sheep dips sites located on land that has the potential to release contaminants into the local environment.
- ii) Characterise the study sites.
- iii) Determine the extent and distribution of sheep dip contaminants on soil, stream sediments, and surface water using judgemental and systematic sampling regimes.
- iv) Evaluate the extent of offsite contamination
- v) Assess compliance to environmental guideline limits.

1.3 Thesis content and layout

A literature review of the history of sheep dipping, chemicals used, health and environmental impacts, and management practices is reported in Chapter Two. Chapter Three describes the study sites such as site descriptions and histories. A description of the general methods which also includes sampling objectives, design, and strategies used throughout the study is included in Chapter Three. Chapter Four presents the preliminary sampling and experimental methods. Results gained through the judgemental sampling regime are also described in Chapter Four. Chapter Five describes the detailed investigation undertaken using the systematic sampling regime which included sampling design, methods, and results. A description of the sample analyses methods using the handheld X-Ray Fluorescence (XRF) is described in Chapter Five. A discussion of results, conclusions, and recommendations of the study are summarised in Chapter Six.

Chapter 2 - Literature Review

Chapter Two

Literature Review

2.1 Introduction

Since the introduction of sheep by missionaries in the 1840's (Bruce, 1978), much of the Waikato region continue to be used for sheep farming (Waikato Regional Council, 2014). Over 150 years of sheep dipping have left many former sheep dipping sites with soil, groundwater, and surface water contamination (Ministry for the Environment, 2006).

Land and water surrounding historical sheep dip sites have been contaminated with persistent chemicals mainly through the practices of disposing of dip solution, draining of the dip solution off the animals and dip solution leaking directly into watercourses (Hooda *et al.*, 2000). The area of contamination was not only limited to the clearly identified former sheep dip sites, but in some locations, pesticides have also migrated into surface water and groundwater (Hadfield and Smith, 1999; Crawley *et al.*, 2002; Gregory, 2013)

This chapter reviews the literature on historical sheep dipping practices and the associated legislation in New Zealand. A section is presented on pesticides and their fate and behaviour within the environment. Major chemicals of concern associated with sheep dipping are discussed including environmental impacts, health risks, and management strategies.

2.2 External parasite control

Several ectoparasites affect sheep. Six main ectoparasites in sheep populations are: scab (*Psoroptes ovis*), blowfly (*Lucilia sericata*), louse (*Bovicola ovis*), tick (*Ixodes ricinus*), headfly (*Hydrotea irritans*), and keds (*Melophagus ovinus*) (Taylor *et al.*, 2000; Cocker *et al.*, 2002).

Dipping is carried out to control ectoparasitic infestation of sheep. The five target parasites of concern in New Zealand are scab, blow-fly, lice, keds and ticks. Other parasitic mites such as louse and fleas are a problem in many parts of the world including New Zealand. Originally, sheep scab posed the most serious problem to the welfare of sheep in the UK (Armstrong and Phillips, 1999) and New Zealand. Parasites cause serious damage to the quality of wool and quantity of New Zealand meat (WaiPAC, 1995). Non-target organisms can be affected by sheep dip chemicals (Armstrong and Phillips, 1999).

For over 150 years chemicals used and methods of dipping have improved. Toxic and environmentally persistent arsenic and copper based compounds to organochlorines were preferred dipping chemicals as the chemicals were available, relatively cheap and effective in pest control. As a result, old-sheep dip sites have been contaminated with arsenic and organochlorine compounds.

The specific number and location of former sheep dips in New Zealand are largely unknown (McBride, 2004). There are estimates of more than 10,000 of historical sheep dip sites in the Waikato region alone and around 50,000 across New Zealand (McBride *et al.*, 1998). Estimates are derived from stocking numbers and the number of sheep farm properties that also include on-farm permanent structures, portable units, communal dip locations and spraying units (McBride *et al.*, 1998; Ministry for the Environment, 2006).

Sheep dipping methods have evolved from dipping animals in a chemical bath (a "sheep dip") through to the modern preferred pour-on methods. Ministry of the Environment guidelines for the management of contaminated land sites of historical sheep dips are intended to help local authorities address the potential risks to human health and the environment.

Increased demand for high-value crops and horticulture in New Zealand have led to the development of many pastoral farming land into more intensive cropping, horticultural, dairying and residential land uses. The change in land use of sites previously used for sheep dipping activities raises the risk for contaminant exposure to people (Ministry for Environment, 2006). Development activities can also increase the migration of any residual contaminants from a site (McBride, 2004; Ministry for Environment, 2006).

2.3 Sheep dip legislation

Pesticides are an important hazard in agriculture. In developed countries pesticide use is strictly regulated. The contamination of sheep dip sites arose through past practices, sanctioned and enforced by legislation. To eradicate sheep scab (*Psoroptes ovis*) in the United Kingdom (UK) the UK government enacted the Sheep Scab Order in 1938 under the 'Diseases of Animals Act' which introduced nationwide compulsory dipping (Cocker *et al.*, 2002). The order required farmers to dip their sheep flocks within six weeks of an appointed date each year, in the autumn months (Cocker *et al.*, 2002). In New Zealand however various statutes relating to sheep were enacted from 1849 until a major review resulted in The Sheep Act of 1908 (McBride, 2004). The Sheep Act 1908 was aimed at consolidating previous statutes while providing for the "eradication and prevention of parasitic and other diseases in sheep" (McBride *et al.*, 1998; McBride, 2004). Offences against the Sheep Act 1908 were "punishable by imprisonment with or without hard labour" (McBride, 2004).

The Stock Act was superseded by the Animals Act 1967. Over and above compulsory dipping, this act required that dipping be carried out with an effective

dip preparation for destroying parasites. The Biosecurity Act 1993 has superseded all previous pieces of legislation (McBride *et al.*, 1998).

The Resource Management Act 1991 is the primary legislation related contaminated sites in New Zealand. The Resource Management Act does not provide for the comprehensive management of contaminated sites (Wilson, 1998). The Ministry for the Environment (2006) comprehensive guide for local authorities focuses on identification, investigation and management of risks associated with former sheep dip sites.

2.4 Dipping methods

Plunge-type dips (Figure 2-1) were first introduced as a dipping technique in the early to mid-1800s before the introduction of "pot dips" for smaller stock numbers and swim-through dips on large stations (McBride, 2004; Ministry for the Environment, 2006).



Figure 2-1 Dipping in Levin on 2 March 1906. Photo showing the holding pens in the background and a solid built concrete structure containing dipping chemicals. Source: Adkin Collection, National Library, reproduced from Ministry for the Environment, 2006.

The power-spray machine, which made its way to New Zealand by the mid-1940s, allowed a new and much faster method of dipping. Tip spraying was used for a relatively short time from the introduction of dieldrin and aldrin in 1955 to their withdrawal in 1961. Jetting was, and is still, being used as additional protection against flystrike, and involves spraying the sheep through a handheld device with a highly concentrated insecticide.

Pour-on methods have become popular in controlling flies, keds and lice since the 1980s. The pour-on method uses an applicator to place insecticide directly along the back of the sheep. The chemical then diffuses through the wool grease of the sheep. Jetting and the pour-on method use chemicals such as synthetic pyrethroids or insect growth regulators that are of low toxicity for people and sheep. “They may, however, pose a risk to aquatic species if they get into waterways” (Armstrong and Phillips, 1999; McBride *et al.*, 1998; McBride, 2004; Ministry for the Environment, 2006).

2.5 Assessment of historic sheep dips

In New Zealand, a number of historic sheep dip studies were undertaken between 1994 and 2013. An initial scoping study by a Waikato farmer and founding member; and former chairman of the Waikato Pesticides Awareness Committee (WAIPAC), Graham McBride (1994) demonstrated that significant contamination of soil by arsenic and organochlorines had occurred at former sheep dip sites. Investigation on sheep dip sites in the Canterbury region (Environment Canterbury, 2003), the Waikato region (McBride *et al.*, 1998; Wilson, 1998; Hadfield and Smith, 1999; Dewar, 2005; and Prakash, 2005), Tasman District (Tasman District Council, 2013), and at Te Mahia (Gregory, 2013) determined the extent of soil contamination and evaluated risks to surface and groundwater, grazing animals, and human health. Although the research has determined the extent, fate, distribution, and management of contaminants at the studied sites, more information is needed to determine the extent of risks to human and environmental health (McBride, 2004; Dewar, 2005; Northcott, 2005) in New Zealand.

2.6 Environmental impacts of historical sheep dipping

The extent, fate and distribution of contaminants in a former sheep dipping site are largely dependent on the historical dipping approach. For instance, plunge-dip, pot dip and swim-through dip always had a large amount of residual dip solution left over during each dipping operation (McBride, 2004; Ministry for the Environment, 2006) (Figure 2-2). Dipping using power-spray technique was invented in the mid-1940s. Contamination on dip sites using the power-spray machine were not as severe compared to plunge or swim-through dips because very little dip is wasted. There was hardly any left-over dip to dispose of at the end of using a power-spray unit (Ministry for the Environment, 2006).

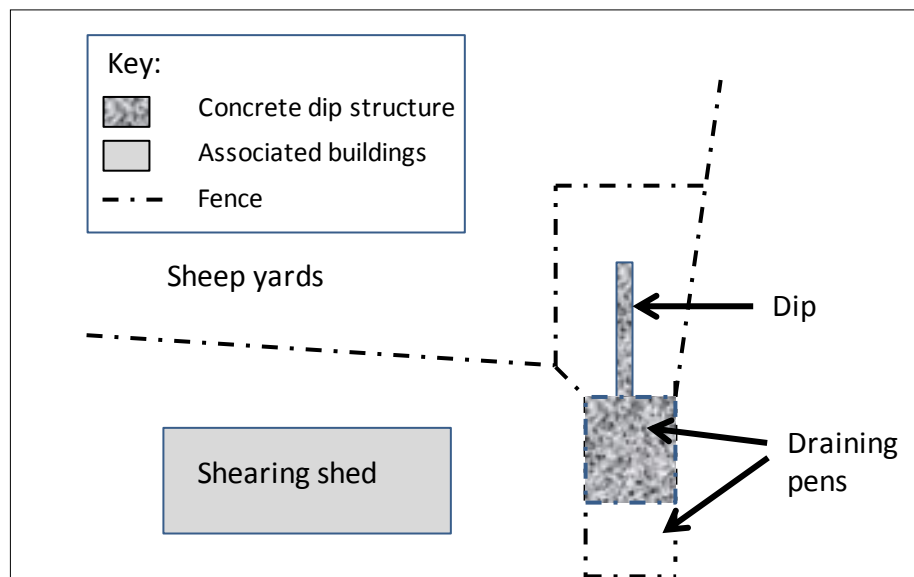


Figure 2-2 Typical layout of a plunge-type sheep dip. Schematic adapted from the Ministry for Environment, 2006.

Chemicals such as arsenic, dieldrin, and lindane are likely to remain in the sheep dip soil for several years after dipping operations have ceased (McBride, 1994; Hadfield and Smith, 1999; Ministry for the Environment, 2006; Hill, 2010). The detection of arsenic and organochlorines over 50 years, after their last use in the Waikato region, at concentrations that exceed the recommended human health or environmental criteria demonstrated environmental persistence. The highest levels

of arsenic are observed just below the surface layer of soil due to arsenic's slow migration over time (Ministry for the Environment, 2006). Generally, disused sheep dip sites contamination decreases with depth.

According to the Ministry for the Environment guidelines, the migration of sheep dip or footbath contaminants into aquatic environments may cause adverse effects to humans, animals, aquatic animals and plants, and the wider ecosystem (Armstrong and Phillips, 1999; Ministry for the Environment, 2006). Dip solutions were often emptied into a burial pit close by, discharged by a pipe over a bank, or pumped out of the bath onto the adjoining yards and allowed to soak into the ground. The sludge from the bottom of the sump, potentially high in accumulated arsenic and organochlorines was often shovelled out onto the ground alongside the dip (Ministry for the Environment, 2006).

The extent of environmental impacts also depends on local topography and drainage. For example, surface-water run-off and/or groundwater movement may affect areas down-gradient of the former sheep dip site (Hadfield and Smith, 1999; Ministry for the Environment, 2006).

2.7 Arsenic contamination

Arsenic is recognised as one of the most toxic naturally occurring elements (Piper and Kim, 2006). Due to its widespread use and frequent enrichment in soil As is considered as a priority pollutant in human and environmental exposure. Among the numerous industrial and agricultural sources of As inputs to the terrestrial environment, the widespread historical use of arsenical pesticides for treatment of livestock has left a legacy of impacted hot spots in New Zealand.

The United State Environmental Protection Agency (USEPA) has classified arsenic (As) as a class A carcinogen (Sarkar *et al.*, 2006 after Southworth, 1995). Ingestion of just 20 mg arsenic oxide (As_2O_3), one of the main components of the sheep dipping solution can be lethal (Andrews *et al.*, 2004; Sarkar *et al.*, 2007). Chronic exposure to As can result in skin and organ cancer, impaired nerve

function, as well as liver and kidney damage (Sarkar *et al.*, 2007; Piper and Kim, 2006). Historically, arsenical compounds have been used worldwide in cattle and sheep dipping for treating ticks in animals, resulting in significant As accumulation in soils (McBride, 1994; McLaren *et al.*, 1997; Wilson, 1998; McBride *et al.*, 1998; Hadfield and Smith, 1999; Cocker *et al.*, 2000; Dewar, 2005; Prakash, 2005).

2.8 Persistent organic pollutants

Persistent organic pollutants (POPs) are chemical substances that persist in the environment, bio-accumulate through the food chain, and pose a risk of causing adverse effects to human health and the environment (Hill, 2010). The Stockholm Convention on Persistent Organic Pollutants is an international agreement aimed at protecting human health and the environment by banning the production and use of some of the most toxic chemicals (McBride, 2004). The Stockholm Convention became international law in May 2004, and was ratified in September 2004 and enforced on 23 December 2004 by the New Zealand government. Persistent organic pollutants covered by the convention included nine pesticides; aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, hexachlorobenzene, and toxaphene, PCBs (polychlorinated biphenyls), dioxins, and furans (polychlorinated dibenzo-p-dioxins or PCDDs, and polychlorinated dibenzofurans or PCDFs) (McBride, 2004).

2.9 Organochlorine pesticides as POPs in New Zealand

Organochlorine (OC) pesticides were widely used in New Zealand from the mid-1940s until the 1970s (Buckland *et al.*, 1998) (Table 2-1). OCs including DDT, aldrin, dieldrin, and lindane were used as insecticides in agriculture for the control of lice on cattle, ectoparasites (lice, keds and blowflies) in sheep and grass grub in pasture (Buckland *et al.*, 1998). OCs were also used for insect control on vegetables and in orchards. Aldrin was used to control horticultural pests such as

wireworm, soldier fly and blackvine weevil, and in limited quantities to control household spiders (McBride, 2004). Dieldrin was used for controlling carrot rust fly, crickets and armyworm and was also used for timber preservation (mostly in plywood glues) and to mothproof carpets. The main areas of OC use were agriculture, horticulture, timber treatment and public health before the New Zealand Pesticides Board formally deregistered all organochlorine pesticides with the exception of endosulfan in late 1989 (Buckland *et al.*, 1998; McBride, 2004; Ministry for Environment, 2006).

Table 2-1 Summary of the historic usage of selected organochlorine pesticides in New Zealand. Adapted from Buckland et al (1998).

	Pesticide Application
DDT	Used as a pasture insecticide to control grass grub (<i>Costelytra ealandia</i>) and porina (<i>Wiseana</i> sp.) caterpillars. Frequently mixed with fertiliser or lime and applied particularly to agriculture pastures, as well as lawns, market gardens and parks.
Lindane (γ -HCH)	Used as an insecticide in agriculture for the control of lice on cattle, ectoparasites (lice, keds and blowflies) in sheep and grass grub in pasture. Also used for insect control on vegetables and in orchards. Household use: flyspray, flea control, and carpet moth. Commercial hexachlorocyclohexane (HCH) was not officially used in New Zealand, although many dip sites show evidence of the use of crude HCH.
Aldrin and Dieldrin	Introduced in 1954 for use as stock remedies in sheep sprays or dips for controlling sheep ectoparasites. Aldrin was used to control horticultural pests such as wireworm, soldier fly and blackvine weevil, and in limited quantities to control household spiders. Dieldrin was used for controlling carrot rust fly, crickets and armyworm and was also used for timber preservation (mostly in plywood glues) and to mothproof carpets.
Chlordane	Broad spectrum agricultural insecticide, also used in the timber industry as a treatment against termites and borer, and as an insecticide in glues used for the manufacture of plywood, finger jointed and laminated timber.
Hexachlorobenzene	Used experimentally between 1970 and 1972 as a seed dressing fungicide for cereal grain.
Heptachlor, Endrin and Toxaphene	Only small amounts of these pesticides were ever used in New Zealand.

2.10 Water pollution

Traditionally sheep dips have been sited close to watercourses which served as a ready supply of dilution water for the dip concentrate. Few incidents of discharge into waterways have been reported (Virtue and Clayton, 1997). Transfer of pesticides from agricultural soils to groundwater and surface water bodies can cause contamination of water resources in some parts of New Zealand (Cameron *et al.*, 2002). The extent of water contamination by pesticides varies significantly between regions and is strongly affected by land use practices, soil properties, and climatic conditions (Cameron *et al.*, 2002).

The disposal of spent dip solution into nearby watercourses was identified in a two year study in the UK to be a threat to the quality of groundwater aquifers (Blackmore and Clark, 1994). For instance, in the Grampian region of Scotland, organochloride insecticide analysis of samples taken during 1984-1985 from the River Ugie and its tributaries showed, by the timing and the nature of the compounds found, that sheep dips were likely sources of pollution of freshwaters in the region (Littlejohn and Melvin, 1991). However, the analysis showed no evidence of serious contamination of the waters by phenolic compounds that are present at high concentrations in sheep dip fluids.

The contamination of watercourses with sheep dip chemicals can have adverse effects on the aquatic ecosystem (Armstrong and Phillips, 1999; Hooda *et al.*, 2000). A review of the Scotland Purification Board's pragmatic approach in dealing with surface water pollution from sheep dip chemicals by Virtue and Clayton (1997) showed that sheep dip chemicals cause pollution resulting in fish kills and reduction in stream biota. There is a lack of information in the New Zealand sheep dip literature except assumptions regarding the pattern of historical dip chemical disposal by New Zealand farmers. Majority of farmers in the UK disposed of the spent dip either to a soakaway or direct disposal on the land close to the dipper without spreading (Hooda *et al.*, 2000). Littlejohn and Melvin (1991) monitoring the disposal of dip solution from a dip tank to a soakaway, situated 300 - 400 m from the nearest stream, found that dip-chemicals appeared in the

stream within 2 hrs of the dip solution being released (Hooda *et al.*, 2000 after Littlejohn, 1992). Results of the UK studies are consistent with results of investigations into pesticide contamination of groundwater in the Waikato region. Hadfield and Smith (1999) investigated the extent of groundwater contamination from pesticide use in the Waikato region and found two sites had dieldrin at concentrations (up to 0.18 ppb) in excess of the maximum acceptable value (MAV) for drinking water (0.01 ppb) (Table 2-2) (Ministry of Health, 1995). One of the sites was a potable water-supply well near Hamilton (Hadfield and Smith, 1999). The contamination at the water-supply well was from a plume of contaminated groundwater originating from a former sheep dip site located 14 m away. Dieldrin has persisted at this site for almost 40 years after the chemicals were last used (Hadfield and Smith, 1999). Similarly, investigations on private groundwater wells in the Kaikoura plain by Environment Canterbury (2003) revealed arsenic concentrations exceeding the New Zealand drinking water standards of 0.01 g/m³ (Ministry of Health, 1995; Environment Canterbury, 2003; Ministry for the Environment, 2006).

Table 2-2 Maximum acceptable values for pesticides.

Compound	Period used	MAV drinking water (mg/L)	MAV soil mg/kg	Oral LD50 (mg/kg)	Solubility (mg/L)	Koe (L/kg)	Half life (days)
Arsenic	1840 - 1980+	0.01	55	125	17,000	100,000	∞
Aldrin	1955-1961	0.00003	0.2	67	0.027	17,500	365
Dieldrin	1955-1961	0.00003	0.2	46	0.14	12,000	1000
DDT isomers	1945-1961	0.002	0.2	115	0.04	24,000	3,800
Diazinon	1962 -	0.01		350	60	1,520	39
Lindane	1947-1961	0.002	0.2	175	7	1,355	423
Cypermethrin	1979 -			240	0.004	61,000	36

Source: Prakash, 2005

Table 2-2 summarises the historical use of toxic dipping chemicals including period of use, maximum acceptable values (MAV) in New Zealand soil and water, solubility, and half-life of each chemical. Sheep dip sites in the Waikato and Canterbury regions have reported levels exceeding MAV in both soils and groundwater. Studies undertaken by the Scottish Environment Protection Agency at the catchments of the Tweed River, UK (Hooda *et al.*, 2000) and survey methods employed by Virtue and Clayton (1997) was useful in determining the extent and fate of contaminants on catchment water quality. Similar studies needed to be undertaken in New Zealand to determine the scale of sheep dip contamination on surface and groundwater quality on a catchment scale.

2.11 Stream sediment contamination

Majority of chemicals discharged into the aquatic systems eventually end up in sediments (Burton *et. al.*, 2001). A sediment toxicity evaluation needed to be conducted to evaluate the extent of sediment contamination at various depths and the adverse effect it may pose to stream ecology and water quality. The interim sediment quality guidelines (ISQG) used by Australia and New Zealand are a concern because it does not predict bioaccumulative effects that may affect higher trophic levels (Burton, 2002). Contaminants such as Mercury and some organochlorines such as PCBs and DDT have been linked through food web transfer with impacts on upper trophic levels (Burton, 2002). A study of 500 sites in 19 large hydrologic basins throughout the United States from 1992 to 1995 by the United States Geological Survey (USGS) found that nationally, persistent organochlorine compounds such as total DDT, total chlordane, dieldrin, and total PCBs had the highest detection frequencies in sediment and biota including frequent detection in whole fish. Organochlorine concentrations were relatively high in agricultural regions with histories of high use and in sediments and biota generally associated with urban areas (Wong *et. al.*, 2000).

2.12 Human health risks

Arsenic and organochlorines are considered carcinogens therefore prolonged exposure to sheep dip chemicals containing As and OCs can be problematic to humans, animals and the ecosystem. Potential risks arise through contact with contaminated soils, groundwater or surface water; eating food grown in or on contaminated soil; or eating animals that have ingested contaminated soil (Ministry for the Environment, 2006). The risk of exposure is due to toxicity, persistence, and the tendency to accumulate through the trophic levels of the food chain. Contaminated sheep dip sites present a health risk to humans depending on the pathways of human exposure.

Potential exposure pathways include the ingestion of small amounts of soil or dust. Significant exposure risk occurs through the consumption of home produce grown in contaminated soil, and the consumption of contaminated drinking water (Ministry for the Environment, 2006). Consumption of aquatic and wild foods may be at risk from contamination of waterways (Stewart *et al.*, 2011), including sediments (Ministry for the Environment, 2006). Farm bore-water supplies near old sheep dips have been documented on several occasions (McBride *et al.*, 1998; Hadfield and Smith, 1999; McBride, 2004; Environment Canterbury, 2003).

Young children may be at immediate risk from exposure to contaminants in soil when playing in and around an old sheep dip site. Concentrations of arsenic at old sheep dip sites can occasionally range from 40 mg/kg to 11,000 mg/kg exceeding background concentrations of arsenic in New Zealand soils which typically range from 2 to 30 mg/kg (Ministry for the Environment, 2006; Piper and Kim, 2006) and background levels in the Waikato region of 1 to 25 mg/kg (Taylor and Kim, 2009). Risks to young children are compounded by the fact that children have a lower body weight therefore lower tolerance to high concentrations than adults (Ministry for the Environment, 2006).

Additionally, disused sheep dips may also pose a physical risk for children if not fenced off. Accidental drowning has been recorded in New Zealand (Ministry for the Environment, 2006). Moreover, New Zealand export market for wool and meat could be impacted if levels of contaminants exceed limits set by importers of New Zealand wool and meat. Domestic producers and exporters must meet strict food safety regulations internally and externally (Table 2-3).

Table 2-3 Maximum residue limits for New Zealand meat products

Substance	Sample Tissue	MRL (mg/kg)
Arsenic	Liver and muscle	2.0
Lead	Liver and muscle	2.0
DDT (and metabolites)	Fat	5
Aldrin/dieldrin	fat	0.2

Source: New Zealand Food Regulations 1984, in Wilson 1998.

2.13 Livestock health risks

Despite the limited record of uptake and accumulation of heavy metals by livestock and correlations relating heavy metal concentrations in soil to those in livestock, the Ministry for the Environment and Ministry of Health (1997) derived a preliminary soil acceptance criterion for the protection of livestock health. Acceptance level for arsenic was 38 mg/kg and copper was between 38 mg/kg and 380 mg/kg (Ministry for the Environment and Ministry of Health, 1997).

Young livestock are vulnerable to acute poisoning from ingestion of high-to-moderate (≥ 38 mg/kg As) levels of sheep dip arsenic (McBride *et al.*, 1998; Ministry for the Environment, 2006). In 1993, two heifers died in the Waikato region from acute arsenic poisoning as a result of ingesting arsenic-contaminated soil within an old sheep dip, and others were chronically poisoned (McBride *et al.*, 1998; Ministry for the Environment, 2006). In the Kaikoura area, stock deaths have been reported from arsenic poisoning due to grazing near old sheep dips or footbaths (Environment Canterbury, 2003). The probability of livestock becoming poisoned depends mainly on whether:

- the soil associated with the old dip is high in arsenic (in particular), and the animal ingests a significant fraction of its daily soil from the area immediately around the old sheep dip site
- the bore water for livestock is contaminated, or contaminated groundwater flows into surface water used by stock, both from the property with the dip site and from off the property (Ministry for the Environment, 2006)

2.14 Ecological concerns

Arsenic and DDT bind strongly to soil, and so leaching into the groundwater is expected to be limited at old disused sheep dip sites (Ministry for the Environment, 2006). In some places, however, contaminants in the soil appeared

to be progressively increasing in the groundwater after 40 years (Hadfield and Smith, 1999). Depth migration of arsenic and OCs demonstrated that gradual leaching through the soil profile depends on the soil type at the site and the leachability of the contaminant (McBride, 2004; Ministry for the Environment, 2006; Sarkar *et al.*, 2007). It is rare for low-level discharge of sheep dip arsenic and organochlorine to have a significant adverse effect on the wider environment (Ministry for the Environment, 2006), however, fish kills and reduction in stream biota were reported in the UK sheep dip disposal studies and subsequent monitoring by Virtue and Clayton (1997). Assessment of the impacts of sheep dip chemicals on stream biota is yet to be undertaken at New Zealand sheep dip sites.

Despite the lack of environmental monitoring data on former sheep dip sites in New Zealand, risks to aquatic biota occur when contaminants are released into freshwaters or marine waters. Recent studies have shown that contamination of aquatic biota could be the result of multiple sources pollutants in freshwater systems. Dieldrin, Σ PCBs and p,p'-DDE in eels and arsenic in trout and flounder were at levels that were of concern to human health in South Canterbury (Stewart *et al.*, 2011). Concentrations of organochlorine and PCBs in freshwater mussels in the upper Waikato River were comparable with or exceeded those found in estuarine shellfish in urbanised or industrialised areas of Auckland (Hickey *et al.*, 1997).

Generally, contaminants are adsorbed to the sediment and gradually accumulate as the discharge continues. Surface run-off can also transport contaminated sediment to water in the vicinity of the site, resulting in aquatic flora and fauna being exposed to contaminated sediment (Ministry for the Environment, 2006). Dieldrin, Σ PCBs and p,p'-DDE in eels and arsenic in trout and flounder were primary contaminants of concern in South Canterbury (Stewart *et al.*, 2011).

Environmental concerns about organochlorine insecticide residues arise from their accumulation through the food chain (Hill, 2010). When animals ingest POPs they are partitioned into the organisms fat reserves which stores the compound in fats, excluding it from metabolism and excretion (Andrews, 2004; Hill, 2010). Plants in soils with increasing soil As concentrations are known to cause plant toxicity.

High arsenic content may show inhibition of growth, photosynthesis and reproduction. Phytotoxic responses typically occur at lower concentrations than toxic effects on soil organisms (McLaren *et al.*, 1998; Mojsilovic *et al.*, 2011). Organochlorine insecticides act on the central nervous system of animals and are acutely toxic to insects, while higher concentrations are required for acute poisoning of other invertebrates and vertebrates.

2.15 Environmental management

The management of New Zealand's natural resources is governed by the Resource Management Act that was passed into law in 1991. A number of measures such as guidelines and codes of practice have been put in place to regulate land application and disposal of manure, wastes, and pesticides (Cameron *et al.*, 2002). For example, the Ministry for the Environment (2006) guide for local authorities stated that territorial authorities must make sure that land intended for new land-use activities or subdivision is suitable for its intended purpose. Former sheep dip sites needed to be properly investigated and, if necessary, remediated as part of a resource consent approval. Residual concentrations of contaminants at sites subject to resource consent considerations should be equal to, or below, recommended guideline values for the proposed land use (Ministry for the Environment, 2006).

Regional councils are required to ensure that all risks associated with sheep dip sites are appropriately managed, including discharges to the environment including to groundwater or surface water, or discharges to air or soil associated with the removal or contouring of potentially contaminated soil during redevelopment. Medical officers of health and health protection officers at district health boards usually work closely with local government on contamination issues that cause a nuisance or need to be notified to protect the public. "Poisoning due to chemical contamination of the environment is required to be notified on reasonable suspicion" (Health Act, Schedule 2 in Ministry for the Environment, 2006).

2.16 Summary and conclusion

It can be concluded from this literature review of historical sheep dipping that:

- Sheep dipping in New Zealand was a necessary practice to combat pests and diseases.
- Agri-chemicals used as insecticides have improved over the last 30 years.
- Legitimate uses of toxic chemicals in the past have led to land and water contamination and possible adverse effects on human and environmental health.
- Contaminated sites needed to be identified, investigated and managed to limit adverse effects on the environment.

Chapter 3 - Study sites and general methods

Chapter Three

Study sites and general methods

3.1 Introduction

Investigations into historical sheep dip sites were carried out in two phases. Phase I involved the preliminary sampling of the study sites using professional and judgmental sampling strategies and methods. Phase II was the detailed investigation of the trace element arsenic using systematic sampling strategies and methods. Experimental design and methods for phase II are included in Chapter Five. This chapter describes phase I which included how the study sites were identified, the description of the selected study sites, and the general methods that were used. Characteristics of the study sites including field methods such as sampling strategies, design, and sample collection are described in this chapter.

3.2 Location of suitable sites

Identifying historic sheep dip sites initially involved a study of historical aerial photographs from 1930 to 1970 and archived government reports relating to historical sheep farming in the North Island of New Zealand. Enquiries were undertaken locally by asking local people. Anecdotal information from current and former landowners was also used in phase I. Possible locations of historical sheep dip sites were compiled and landowners were interviewed to confirm the locations. Sheep dip sites were identified in the field by structural evidence such as the presence of old concrete structures on the ground or in one case a sheep spray shower was onsite.

The preliminary study of sheep dip sites yielded seven sheep dips. A site had to be close to a watercourse and/or located on a >10 degree slope to be included in my study. Two sites met the selection criteria for my study. The two sites were identified as site A and site B. According to the current landowners, both sites A and B have not been previously studied. Site A was selected due to the dip being located on a flood plain and close to a small stream (Stream X). Stream X discharges into a larger stream (Stream Y), within 50 m of the dip. Site B was selected due to the dip's location on a steep (>10 degree) slope, and south facing, hill that leads to a gully, stream, and wetland. Surface water, soil, and stream sediments were sampled, to establish any contamination that may have occurred, at sites A and B.

3.3 Site descriptions

3.3.1 Introduction

Sites A and B are in a predominantly sheep farming hill country area, west of Hamilton within the Waikato region. Specific locations and names of properties cannot be disclosed because of the confidentiality agreements with the owners. Consequently, distinguishing features significant to each site are omitted. Global Positioning System (GPS) measurements were taken at each sampling point but remain in confidential records.

3.3.2 Study site A

Study site A was an old pot bath (Figure 3-1). The dip structure had a 2 metre diameter dip sump which was 1.5 metres deep, and 3 metre drain length. The dip lies east to west with the head facing west and drain exit to the east. The dip structure was solidly built and visible from the adjacent road. Remnants of the dip exit and drip area could be seen from the road though slightly obscured by mature trees growing beside the main drain, the drip area, and the area between the road and the dip.



Figure 3-1 Redundant pot bath sheep dip. Last used about 1965. Dip entrance in the foreground and draining pens at the far end of the dip.

The pot bath concrete structure was located 6 m from the road to the east and 8 m from the esplanade reserve to the west. The land in the vicinity of the dip was used to graze stock (Figure 3-2). The former landowner showed us the location of the dip and provided information regarding the dips historical use. The current landowner allowed the research to proceed within the terms of a signed confidentiality agreement.

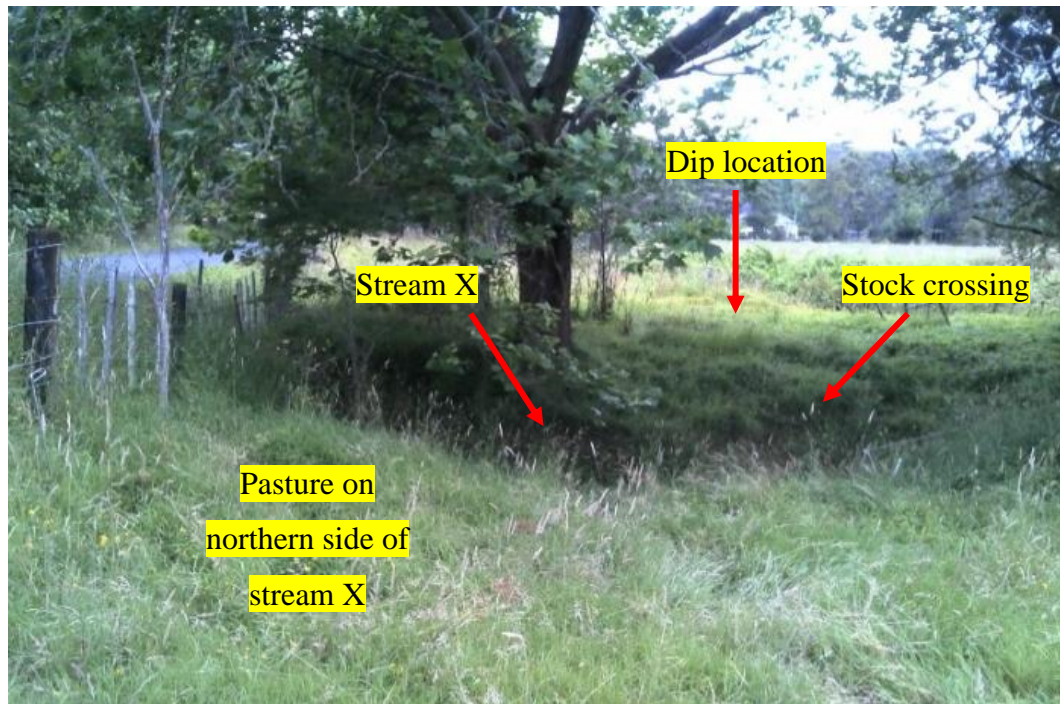


Figure 3-2 Photo taken from the northern paddock in the foreground looking south towards stream X and the dip location on the southern paddock behind the large tree

The former owner reported that he helped his father and elder brothers in the sheep farm dipping sheep when he was in his mid-teens, in the early 1960's. His recollection of the location of the redundant pot dip, the old holding yards, drip area, splash zone and spent chemical disposal patterns fit the physical evidence found onsite. Evidence onsite included the redundant dip superstructure, remnants of concrete, old fence posts, and bits and pieces of old timber lying in the vicinity of the dip. Some old pieces of timber were used to cover the dip to prevent stock falling in (Figure 3-1).

There were two streams flowing close to the old dip. The closest and smaller, stream X, was located 7 m north of the dip and flows east to west into the larger stream Y. Stream X had a stock crossing (Figure 3-3).



Figure 3-3 Stock crossing showing stream bank erosion extending to the runoff zone on the top right which is a likely source of sediments to stream X.

Stream X and the land adjacent to the dip site (to the right of the right of stream X in Figure 3-3), is where the dip solution was probably emptied. Either side of stream X continues to be grazed (Figure 3-2). River bank erosion had occurred on the edge of esplanade reserve fence line which is mid-way between the dip and stream Y and downstream of the confluence of stream X and stream Y. The eroded area cuts into the reserve.

3.3.3 Study site B

Study site B was an old plunge sheep dip. The main dip sump and draining platform were visible onsite (Figure 3-3). The old sheep dip was located on a 100 m elevation with a steep (>10 degree) south facing slope, currently used as a grazing area. The dip structure had a 2 m diameter sump which was 1.5 m deep. The dip was 8 m long with concrete lead out sides. The dip lies east to west with the main sump facing the downslope gully. The dip had not been filled in. There was a fenced hilltop area 5 m away from the dip exit which was used for grazing. Native bush borders either side of the paddock, east and west of the dip site. The native bush located on the eastern side was fenced off from stock.



Figure 3-4 Site B, showing the redundant plunge sheep dip with main dip sump in the foreground and draining platform to the left at the far end.

Land on which site B was located had been in the same ownership since the day the old plunge dip was last used in the early 1960's. The landowner showed us the location of the dip and provided information regarding the dips historical use. Site B had little historical information on chemical disposal patterns therefore professional judgement was used in determining the experimental design and sampling plan. The old dip has the potential to discharge contaminants onto land and gully (Figure 3-4).



Figure 3-5 Study site B showing the potential discharge pathway

Land and gully directly downslope of the dip site is where it is probable that the spent dip solution was emptied. The 5 m wide gully runs north to south on the west side the dip site and leads to a stock water supply and a small stream downhill. According to the landowner the gully was widened sometime before 1900 to be used as a track for cross country horse carts (Figure 3-5). The stock water supply was cut into the true left side of the gully 90 m downhill from the dip site. Adjacent to the stream was a wetland which has formed largely from a natural spring that leads into the stream.



**Figure 3-6 Site B, looking uphill from the end of the gully in the foreground.
Insert: Stock water supply**

3.4 Sampling objectives, design and strategy

3.4.1 Sampling objectives

The aim of the initial sampling of sites A and B was to identify the extent of the sheep dip contamination. Soil sampling was undertaken to establish the nature, degree, and extent of pesticide chemical contamination on land. Surface water and stream sediments were sampled to determine if there were any historic sheep dip chemicals in the receiving environment.

Shallow sampling from 0 to 10 cm depths was considered sufficient to determine the horizontal extent of contamination. Deeper samples, from 10 – 20 cm,

determine whether there was evidence for the materials migrating downwards in the soil profile.

The sheep dip structures at sites A and B were visible onsite. Soil samples were collected from a 5 m perimeter around the base of the sheep dip at both sites. The perimeter covers the main area around the dip. Soils of the splash and exit zones of the dip were sampled. Sampling also included the vicinity of the draining platform and from the area where the spent sheep dipping solution was possibly disposed.

Sampling was undertaken in two phases. Phase I included the screening of sites A and B for arsenic, copper and organochlorine pesticides. Phase I sampling provided screening information which assisted the scoping of more detailed arsenic sampling undertaken in Phase II.

3.4.2 Sampling design and strategy

Judgemental sampling strategies were used in phase I due to high analytical costs. Both sites had historical information to support site selection. The former landowner at site A and current landowner at site B had good knowledge of where and when the former sheep dip chemicals were used at each site. Results from phase I were used to justify a more detailed investigation using systematic sampling strategies in phase II.

Conceptual models of sites A and B were established using the location of the dip as source of contamination, the land as transport pathway, and the stream and gully as receiving environments (Figure 3-7). Both sites A and B were undisturbed in terms of the sites being previously excavated or buried. Visual inspection showed that the grazing land and a nearby reserve were transport pathways and streams X and Y were potential receptors for materials from site A. Grazing land and gully were identified as receiving environments at site B.

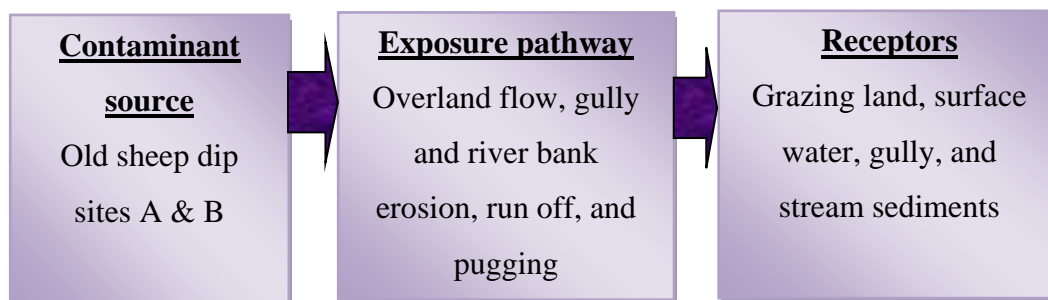


Figure 3-7 Conceptual model for sites A and B

Soil samples were taken from soils around the dip at both sites including the splash zone around the dip, soil in the disposal and run-off area where sludge and spent dipping chemicals may have been disposed off, and soil from the drip area. Site surface water and stream sediments were sampled upstream, downstream and at the discharge zone. Site B gully areas were also sampled.

3.4.3 Preparation for field work

Preparations before the field work commenced included seeking approval for financial support from Waikato Regional Council (WRC) and getting the confidentiality agreement between The University of Waikato and individual owners of sites A and B signed. Availability of suitably trained field assistants were also organised before the field days.

Sampling equipment, including a soil corer and a sediment corer were obtained. Glass jars and plastic sampling containers were obtained in a chilly bin from Hill Laboratories Ltd. Personal protective equipment (PPE) including a hi-vis vest, waders, steel capped gumboots, gloves and glasses from Waikato Regional Council (WRC) were sourced. WRC also provided field instruments, including a handheld GPS for logging site locations and a dissolved oxygen meter for surface water sampling.

3.4.4 Health and safety plan

A health, safety and environment plan (HSEP) was created and approved. The plan contains an assessment of the on-site hazards which includes:

- measures to eliminate, isolate or minimise these hazards for the tasks involved in soil, sediment and surface water sampling
- emergency response measures
- lists of measures such as a second person to assist with driving, sampling and any other work in case of an emergency
- approval given to use WRC personal protective equipment (high-vis vests, sun hats, sun screen, safety glasses and rubber gloves)

Directly handling soil with bare hands was avoided by wearing rubber gloves. Field work was carried out safely and delays were minimised due to adequate preparation prior to the field day.

3.4.5 Field notes and transport

All samples collected were inspected and information logged using a field sheet and GPS locations were recorded for all sample sites. General observations on the soil sampling locations, weather conditions, ground surface topography, and preferential pathways such as to the stream on site A and gully on site B for contaminant migration were recorded. The location and depth of samples collected was recorded at the time of sampling at sites A and B.

3.4.6 Sample locations and labels

Samples collected were clearly and uniquely labelled. Sample details were recorded in specifically prepared field sheets which included information such as:

- a unique sample reference number
- date, time, depth and location collected
- sampler's name
- site observations and weather conditions

Sampling records were kept in a field notebook, which identified the site, exact sampling location marked using the garmin handheld GPS, and any observations or measurements that could influence the interpretation of the results. Sample locations close to a feature that has the potential to influence results were documented by photographs with a reference location clearly marked. Sampling records were written with a waterproof pencil on waterproof paper, dated and signed.

3.4.7 Sample handling

Sample containers were supplied by Hill Laboratories Ltd. Sample containers used were adopted from the “Contaminated land management guidelines No.5: Site investigation and analysis of soils (revised 2011) (Ministry for the Environment, 2004). The sample containers were handled to maintain sample integrity during transportation and storage. Samples were in sealed containers away from sources of heat or light prior to laboratory analysis.

3.4.8 Documentation

Hill Laboratories chain of custody (COC) form was used to accompany the delivery of each batch of samples to the laboratory. The COC details the links in the transfer of samples from collection to arrival which included the time and date the samples are collected, name of person who delivered the samples, time and

date the samples are received at the laboratory, name of person receiving the samples, name and contact details of who to report to, urgency of analysis (routine turnaround), and the job reference number.

Each sample has a record of the unique identifier (which match those on the containers), the matrix (soil, sediment, or surface water), and the laboratory analyses quote Q53216 as reference number for pre-arranged work.

Chapter 4 - Preliminary sampling: methods & results (Phase I)

Chapter Four

Phase I - methods and results

4.1 Introduction

Two sampling strategies were used to determine spatial contamination from historic sheep dip sites. Phase I which was the preliminary sampling of sites A and B based on judgemental sampling strategies is described in this chapter. Systematic grid sampling was employed in phase II. This chapter describes the preliminary sampling methods used and reports the results of analyses to determine if trace element and organochlorine contamination have occurred at the sheep dip sites and at the offsite locations. Experimental methods such as trace element analysis and organochlorine analysis are also described. A summary and conclusions are included in this chapter. Discussions for this chapter are presented in Chapter 6.

Samples were analysed for arsenic, copper, and organochlorine pesticides and results were compared to New Zealand guideline limits based on the risks to human and environmental health. Arsenic guideline limit for agricultural and residential land uses was 30 mg/kg and (Ministry for the Environment and Ministry of Health, 1997) and maximum acceptable value (MAV) for drinking water was 0.01 g/m³ (Ministry of Health, 1995).

The guideline levels used for stream sediments were indicative interim values for freshwater systems which were drawn from the developed guidelines for marine and estuarine systems (Ministry for the Environment, 2006).

Interim freshwater sediment quality low level guideline (ISQG-Low) for the protection of ecological receptors was 20 mg/kg. No adverse effects are expected at levels below ISQG-Low. ISQG-High was 70 mg/kg, for which, significant adverse effects are expected in 50% of organisms (Ministry for the Environment, 2006). Background levels of arsenic in New Zealand soils ranged from 2 – 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997) and background As levels in the Waikato region ranged from 1 – 25 mg/kg (Taylor and Kim, 2009).

Guideline level for copper was 370 mg/kg (Cavanagh, 2004a). Dieldrin soil guideline value for human habitation was 2.7 mg/kg (Ministry for the Environment, 2006). Interim sediment quality guideline lower limit (ISQG-Low) for dieldrin was 0.00002 mg/kg and higher limit (ISQG-High) was 0.008 mg/kg.

4.2 Site and sampling plans

4.2.1 Introduction

Site plans for both sites A and B show the locations of the sample points in relation to the sheep dip and the surrounding landscape (Figure 4-1 and Figure 4-2). The site plans were sketched due to the confidentiality agreement. Sampling points for stream sediments and surface water were developed using the wastewater discharge monitoring model of upstream, downstream, and discharge point sampling. Soil sampling points were chosen to determine if any contamination had occurred at the vicinity of the dip site and on land downslope from the dip location.

4.2.2 Site plan for site A

The plan for site A shows the location of the old pot sheep dip, the rural road, streams X and Y, and sampling points for water (AW), sediment (ASED), and soil (AS) (Figure 4.1). Grazing is the main activity around the dip and upstream east of the road and on the western side of stream Y. Part of the area was unused land covered by blackberry and other weeds.

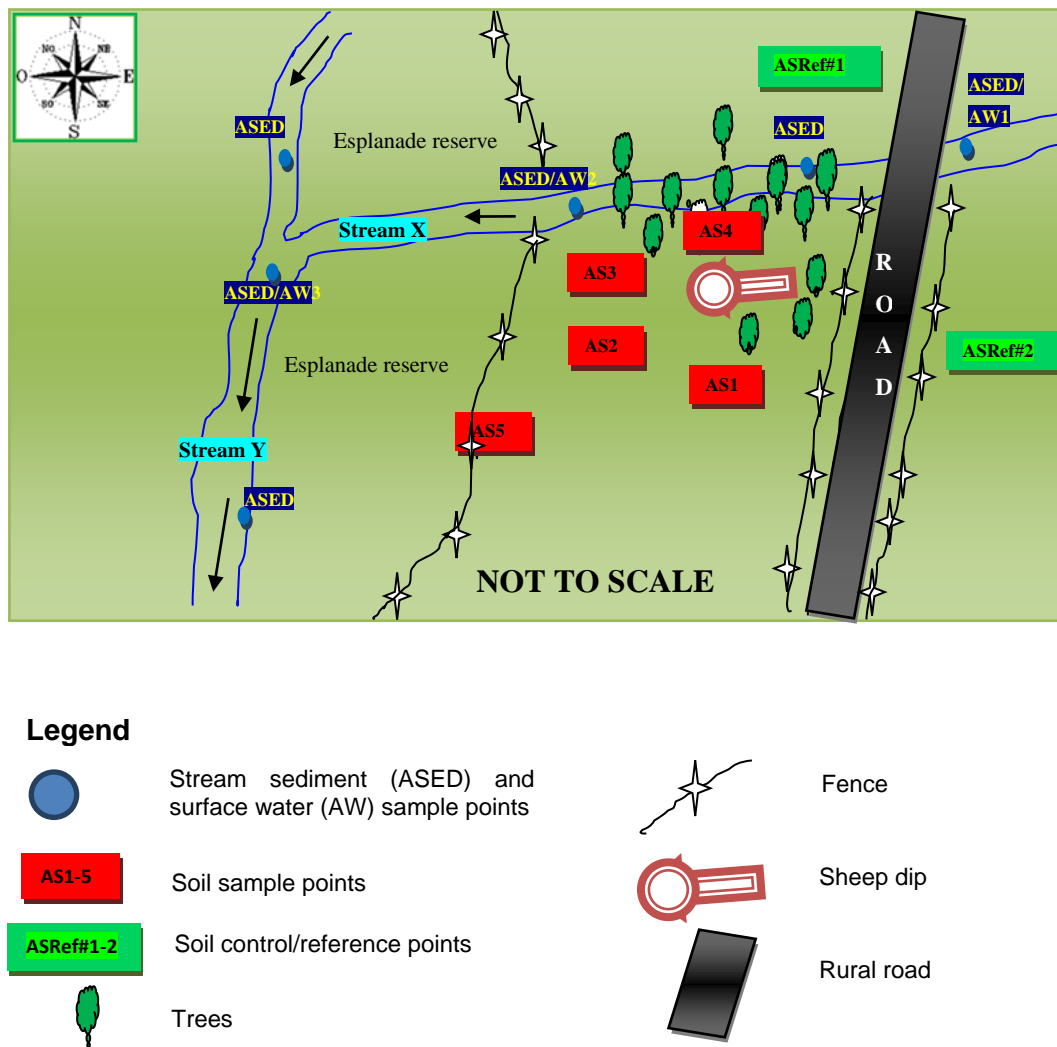


Figure 4-1 Site plan for site A.

The site plan (Figure 4.1) shows the proximity of the sheep dip to streams X and Y, the rural road and the fenced esplanade reserve between stream Y and the road. The reserve extends from the fence line east of the dip to the river bank of both stream X and Y. A west facing slope exists between the dip site and stream Y.

The slope dropped 1 m on the edge of the reserve creating a potential overland flow path to the direction of stream Y.

4.2.3 Sampling plan for site A

Soil sampling locations for site A (Figure 4-1) were selected to give a good indication of the extent of contamination around the dip site as previous work (McBride, 1994; Wilson, 1998; Environment Canterbury, 2003; Dewar, 2005; Prakash, 2005; Gregory, 2013; Tasman District Council, 2013) indicated that most contamination was limited to the immediate area around the dip site. A 5 m perimeter around the old dip was constructed with four sampling points selected. The four soil samples were labelled AS1- 4. Soil site selection based on the key areas of contaminant entry and exit of the dip which include AS1 - drip area, AS2 - stock holding yard, AS3 - plunge and splash area, and AS4 – the runoff zone.

A further soil sample labelled AS5 was taken 12 m downslope from the dip in the direction stream Y, along the reserve fence line. AS5 was on the edge of the old fence line separating the grazing area from the esplanade reserve on the dip side of stream X. AS5 was selected to provide evidence for surface migration down slope.

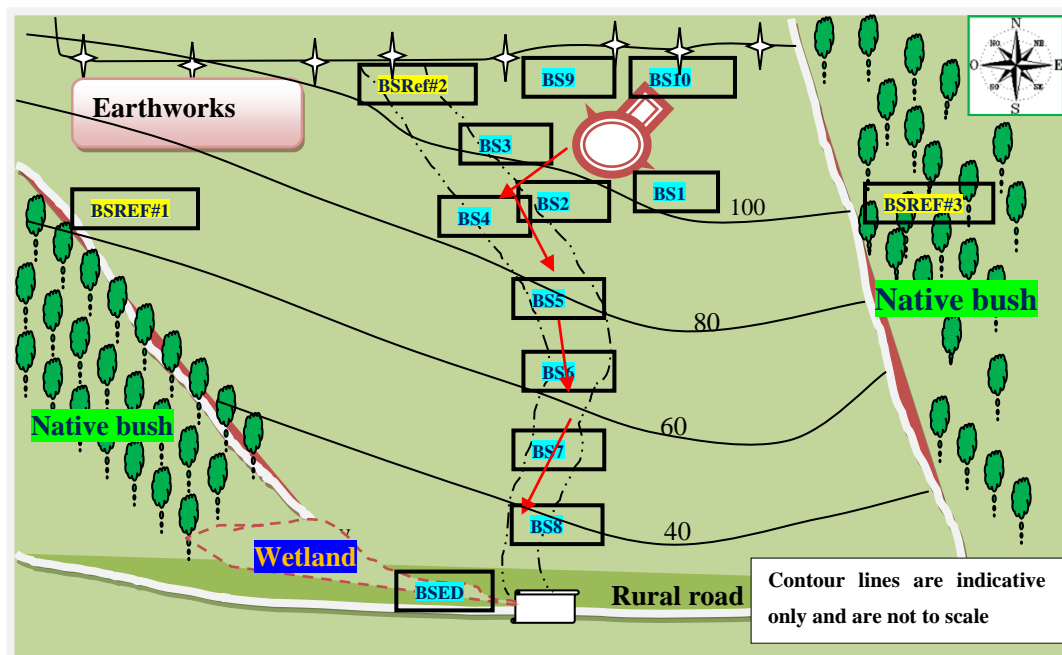
Two reference sites labelled ASRef#1 and 2 were established. Reference sample ASRef#1 was established 10 m north of the stock crossing, on the northern side of stream X. Reference sample ASRef#2 was established upstream, across the road, to the east of the dip.

Six sediment and three surface water points were selected and sampled. Sediment and surface water sample locations were chosen to show if contamination has occurred in stream sediments and surface water. Previous work on stream sediments indicated arsenic concentrations of 3 and 5 mg/kg (Environment Canterbury, 2003). Surface water below the dip site at Te Mahia indicated spiked arsenic levels (Gregory, 2013).

Sediment samples were labelled ASED1 - 6. Surface water samples were labelled AW1 - 3. Distance and direction of soil sample locations was determined by the likely contaminant distribution pathway. Evidence provided by identifying depressions caused by historical surface flow paths, slope factor, proximity to stream X which is indicative of potential spent dip disposal site, and recent flood deposits.

4.2.4 Site plan for site B

The main features of the site plan for site B included the location of the old plunge sheep dip on the hill top, the native bush on the east and west of the dip, grazing paddock downhill, earth works west of the dip, and gully that leads to the wetland, stream, and the rural road on the lowland area (Figure 4-2). The sampling plan shows the proximity of the sheep dip to the fenced native bush, the rural road, wetland, and the stream.



Legend

	Reference sites		Redundant plunge dip		Direction of flow downhill
	Soil sample		Sediment sample		

Figure 4-2 Site plan for site B

4.2.5 Sampling plan for site B

Soil sampling for site B was based on the site plan shown on Figure 4-2. Sampling locations were selected to give a good indication of the extent of contamination around the site. The focus was the immediate area around the dip and the gully from above the dip site to the stream. For soil sampling, a 5 m perimeter around the old dip was constructed with five sampling points, BS1-3 and BS9-10. Sampling points denoted by BS1-10 were for normal soil samples and BSREF1-3 for background reference samples. Potential contaminant entry and exit include BS1/2 - drip area, BS3 - runoff area, BS4/5 - discharge zone, BS9 - plunge and splash area, and BS10 - drain exit.

A single sediment sample was collected at the stream end of the gully to give an indication of the extent of contamination at the likely entry point into the stream. The sediment sample was labelled BSED and analysed for arsenic and copper.

Samples BS6-8 follows the discharge pathway along the gully line. Three reference sites labelled BSRef#1 - 3 were established. Reference sample BSRef#1 was sampled on the eastern paddock approximately 40 m south of the earthworks and on the edge the native bush. Reference sample BSRef#2 was taken up-gully, north of site BS4. Reference sample BSRef#3 was from the eastern native bush.

4.3 Sampling and experimental methods

4.3.1 Introduction

Soil, stream sediments, and surface water were sampled at site A. Soil was sampled at site B. All samples collected in phase I were analysed at Hill Laboratories Ltd, Hamilton. Phase I sampling was undertaken in June 2013. Phase II sampling was carried in January 2014. Phase II sampling for site B was undertaken in February 2014. Field days varied in terms of weather and field conditions.

4.3.2 Soil sampling

In phase I soil sampling, soil cores were collected using a 25 mm diameter soil corer. Two 20 cm cores were sampled at each sample point. The two replicate cores were combined to produce two composite samples; 1 – 10 cm and 10 – 20 cm deep. Fourteen samples were taken from site A and 26 samples from site B in phase I.

Each composite sample was immediately placed into a pre-labelled 250 ml lab prepared plastic container. Sample containers were then placed in a chilly bin and transported to Hill laboratories Ltd for analysis. All soil samples were air dried in a 35°C oven and ground for arsenic, copper and organochlorine analysis.

4.3.3 Stream sediment sampling

Sediment sampling was carried out on site A in both phase I and II sampling runs. Sediment cores were sampled using a 60 mm diameter sediment corer. A sledgehammer was used to drive the corer into the stream bed until it couldn't go

any further. Cores were then sectioned equally using a scalpel. The lengthiest core was 32 cm long and was divided into five equal sections. The shallowest core was 10 cm long and divided to two 5 cm sections. Each section was analysed as a separate sample. Samples from each core were placed in labelled plastic containers and transported to Hill Laboratories Ltd for the determination of arsenic, copper and organochlorine.

For stream X a reference 10 cm core labelled ASSED1 was sampled upstream of the road culvert. Two samples were taken from the core. ASSED1/1 was the 0 – 5 cm sample and ASSED1/2 the 5 – 10 cm sample. Similarly, a 10cm sediment core labelled ASSED2/1-2 was collected downstream of the road culvert. A 32 cm core (ASED3/1-5) sampled from the discharge zone was sectioned to 6.4 cm for each sample resulting in five sediment samples. The 32 cm core from the discharge zone and the reference 10 cm core from the upstream of culvert site were selected for the initial screen of sheep dip pesticides. Elevated dieldrin levels from the discharge zone core resulted in the screening of all remaining cores except the downstream of culvert core, which had a low detection probability.

Three sediment cores were taken from stream Y. A 12 cm core sectioned to 0 - 6 cm and 6 – 12 cm labelled ASSED4/1-2, from upstream of the confluence. Similarly, a 9 cm core labelled ASSED5/1-2 divided to 4.5 cm sections were sampled at the confluence. And a 32 cm core sectioned to 6.4 cm each section and labelled ASSED6/1-5 were sampled downstream of the confluence. The most upstream site was upstream of the road culvert on stream X. The lowest reach of the studied region was downstream of stream X and Y confluence.

4.3.4 Surface water sampling

Surface water was sampled at site A due to the close proximity of streams X and Y to the old sheep dip. There were six surface water sampling points with two samples collected at each sampling point, resulting in twelve samples. The sample bottle was submerged facing upstream of normal stream flow and sample collected at mid-stream and at mid-depth. Field measurements of dissolved

oxygen in milligrams per litre and percent dissolved oxygen (% saturation), and water temperature were taken at each sampling point using a Hach DO meter.

Water for total arsenic and total copper analysis was collected in a nitric preserved 100 ml plastic container. Samples for trace level pesticides in water were taken in a 500 ml brown glass bottle with no added preservative. All water samples were immediately stored in ice at $< 4^{\circ}\text{C}$ and transported to Hill Laboratories Ltd, Hamilton, for laboratory testing.

Three surface water samples labelled AW1-3 were taken. AW1 was taken upstream of the road culvert, AW2 from the discharge zone, and AW3 sampled at the confluence. All three samples were tested for trace level organochlorines in water. AW1 and AW2 were tested for total arsenic and total copper.

4.3.5 Experimental method

4.3.5.1 Trace element analysis

4.3.5.1.1 Introduction

Several methods can be used to analyse matrices such as soil, sediments, and surface water for trace elements. Acid digestion is a common extraction method for quantifying trace elements. Extracts are often measured by various analytical instruments such as Inductively Coupled Plasma (ICP), Atomic Adsorption Spectrometry (AAS), and chromatography. Detectors in the instrumentation can be different, for instance, ICP can be used in conjunction with either Optical Emission Spectrometry (OES) or Mass Spectrometry (MS).

4.3.5.1.2 Trace element analysis method

Phase I samples were sent to Hill Laboratories Ltd (Hamilton), an IANZ (International accreditation New Zealand) accredited laboratory, for laboratory analyses. Soil and sediments samples were air dried at 35°C overnight and then sieved using a 2 mm sieve. A sub-sample of the dried 2 mm fraction was then used in the determination of trace elements. Screen level, arsenic and copper, were extracted using a nitric/ hydrochloric acid digestion. Extracts then analysed on the inductively coupled plasma with a mass spectrometry (ICP-MS) using USEPA method 200.2 (United States Environmental Protection Agency, 1999). Detection limit for both arsenic and copper was 2 mg/kg dry wt.

Trace level analytes, arsenic and copper, in surface water samples were extracted using the boiling nitric acid digestion method. Extracts were analysed on the ICP-MS using USEPA method 200.8 (United States Environmental Protection Agency, 1999). Detection limit was 0.0011 g/m³ for trace level arsenic and 0.00053 g/m³ for trace level copper.

4.3.5.2 Organochlorine analysis

Soil, sediment, and water samples were analysed for organochlorine compounds. Dried 2 mm sieved fractions from both soil and sediment samples were subjected to sonication extraction, followed by a solid phase extraction cleanup (SPE), then extracts were analysed using gas chromatography (GC) which was fitted with a dual column electron capture detector (GC-ECD). Detection limits for each pesticide in both soil and sediment samples were varied (Table 4-1 and Table 4-2).

Table 4-1 Organochlorine pesticides trace in soil including methods and detection limits (DL).

Code	Parameter	DL	*Method	Code	Parameter	DL	*Method	Detection limits (mg/kg)
Aldrin	Aldrin	a	GC-ECD	Endosul	Endosulfan I	a	GC-ECD	
Alpha-BH	Alpha-BHC	a	GC-ECD	Endosull	Endosulfan II	a	GC-ECD	
Beta-BHC	Beta-BHC	a	GC-ECD	Endosulp	Endosulfan sulphate	a	GC-ECD	a 0.0010
Delta-BH	Delta-BHC	a	GC-ECD	Endrin	Endrin	a	GC-ECD	b 0.002
Gamma-BH	Gamma-BHC	a	GC-ECD	Endrin a	Endrin aldehyde	a	GC-ECD	
cis-Chlo	cis-Chlordane	a	GC-ECD	Endrin K	Endrin Ketone	a	GC-ECD	
trans-Ch	trans-Chlordane	a	GC-ECD	Heptachl	Heptachlor	a	GC-ECD	
2,4"-DDD	2,4"-DDD	a	GC-ECD	Heptaepo	Heptachlor epoxide	a	GC-ECD	
2,4"-DDE	2,4"-DDE	a	GC-ECD	Hexachlo	Hexachlorobenzene	a	GC-ECD	
2,4"-DDT	2,4"-DDT	a	GC-ECD	Methoxyc	Methoxychlor	a	GC-ECD	
4,4"-DDD	4,4"-DDD	a	GC-ECD	Total Ch	Total Chlordane	b	GC-ECD	
4,4"-DDE	4,4"-DDE	a	GC-ECD		(cis+trans)*100/42			
4,4"-DDT	4,4"-DDT	a	GC-ECD					
Dieldrin	Dieldrin	a	GC-ECD					

***Method**
GC-ECD: Sonication extraction, SPE cleanup, GPC cleanup (if required), dual column GC-ECD analysis. Tested on air dried at 35°C and sieved, <2mm fraction. Sample may contain a residual moisture content of 2-5%

Table 4-2 Organochlorine pesticides trace in sediments. Methods and detection limits (DL).

Code	Parameter	DL	*Method	Code	Parameter	DL	*Method	Detection limits (mg/kg)
Aldrin	Aldrin	a	GC-ECD	Endosul	Endosulfan I	a	GC-ECD	
Alpha-BH	Alpha-BHC	a	GC-ECD	Endosull	Endosulfan II	a	GC-ECD	
Beta-BHC	Beta-BHC	a	GC-ECD	Endosulp	Endosulfan sulphate	a	GC-ECD	a 0.0010
Delta-BH	Delta-BHC	a	GC-ECD	Endrin	Endrin	a	GC-ECD	b 0.002
Gamma-BH	Gamma-BHC	a	GC-ECD	Endrin a	Endrin aldehyde	a	GC-ECD	
cis-Chlo	cis-Chlordane	a	GC-ECD	Endrin K	Endrin Ketone	a	GC-ECD	
trans-Ch	trans-Chlordane	a	GC-ECD	Heptachl	Heptachlor	a	GC-ECD	
2,4"-DDD	2,4"-DDD	a	GC-ECD	Heptaepo	Heptachlor epoxide	a	GC-ECD	
2,4"-DDE	2,4"-DDE	a	GC-ECD	Hexachlo	Hexachlorobenzene	a	GC-ECD	
2,4"-DDT	2,4"-DDT	a	GC-ECD	Methoxyc	Methoxychlor	a	GC-ECD	
4,4"-DDD	4,4"-DDD	a	GC-ECD	Total Ch	Total Chlordane	b	GC-ECD	
4,4"-DDE	4,4"-DDE	a	GC-ECD		(cis+trans)*100/42			
4,4"-DDT	4,4"-DDT	a	GC-ECD					
Dieldrin	Dieldrin	a	GC-ECD					

***Method**
GC-ECD: Sonication extraction, SPE cleanup, GPC cleanup (if required), dual column GC-ECD analysis. Tested on air dried at 35°C and sieved, <2mm fraction. Sample may contain a residual moisture content of 2-5%

Surface water samples sent to Hill Laboratories initially undergo liquid / liquid extraction before the extracts were analysed on the gas chromatography, fitted with a dual column electron capture detector (GC-ECD. Detection limit for individual pesticides differ for trace level analysis of organochlorine pesticides in surface water (Table 4-3).

Table 4-3 Organochlorine compounds analysed on water samples including detection limits and methods used.

Code	Parameter	DL	*Method	Code	Parameter	DL	*Method	Detection limits (g/m ³)
Aldrin	Aldrin	a	GC-ECD	Endosul	Endosulfan I	b	GC-ECD	a 0.000005
Alpha-BH	Alpha-BHC	b	GC-ECD	Endosull	Endosulfan II	b	GC-ECD	b 0.000010
Beta-BHC	Beta-BHC	b	GC-ECD	Endosulp	Endosulfan sulphate	b	GC-ECD	c 0.00002
Delta-BH	Delta-BHC	b	GC-ECD	Endrin	Endrin	a	GC-ECD	d 0.00004
Gamma-BH	Gamma-BHC (Lindane)	b	GC-ECD	Endrin a	Endrin aldehyde	a	GC-ECD	
cis-Chlo	cis-Chlordane	a	GC-ECD	Endrin K	Endrin Ketone	b	GC-ECD	
trans-Ch	trans-Chlordane	a	GC-ECD	Heptachl	Heptachlor	a	GC-ECD	
2,4"-DDD	2,4"-DDD	b	GC-ECD	Heptaepo	Heptachlor epoxide	a	GC-ECD	
2,4"-DDE	2,4"-DDE	b	GC-ECD	Hexachlo	Hexachlorobenzene	d	GC-ECD	
2,4"-DDT	2,4"-DDT	b	GC-ECD	Methoxyc	Methoxychlor	a	GC-ECD	
4,4"-DDD	4,4"-DDD	b	GC-ECD	Total Ch	Total Chlordane	c	GC-ECD	
4,4"-DDE	4,4"-DDE	b	GC-ECD		(cis+trans)*100/42			
4,4"-DDT	4,4"-DDT	b	GC-ECD					
Dieldrin	Dieldrin	a	GC-ECD					

***Method**
GC-ECD: Liquid / liquid extraction, SPE (if required), dual column GC-ECD analysis

4.4 Results site A

4.4.1 Soil

4.4.1.1 Arsenic and copper residues in soil

Arsenic (As) concentrations in soil samples at Site A were varied in the top 0 – 10 cm and up to 20 cm deep (Table 4-4, Figure 4-3, Appendix I). Six out of the fourteen samples tested had levels well above the environmental guideline level of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997). Out of the six samples that had elevated As, four were surface samples (0 – 10 cm) and two 10 – 20 cm depth samples. The minimum value of arsenic was 5 mg/kg recorded at the reference site located 20 m across the road on the eastern side of the dip site (ASRef#2). The maximum value of 137 mg/kg was from the deep sample site AS4b which was immediately adjacent to the dip.

Table 4-4 Arsenic and copper concentrations in soil samples from Site A.

Sample number	Depth cm	Distance from dip m	AsTR mg/kg dry wt	CuTR mg/kg dry wt
AS1a	0-10	5	112	26
AS1b	10-20	5	26	24
AS2a	0-10	5	37	24
AS2b	10-20	5	9	23
AS3a	0-10	5	80	21
AS3b	10-20	5	21	21
AS4a	0-10	5	109	22
AS4b	10-20	5	137	35
AS5a	0-10	12	11	24
AS5b	10-20	12	11	27
ASRef1a	0-10	25	9	25
ASRef1b	10-20	25	72	27
ASRef2a	0-10	25	7	16
ASRef2b	10-20	25	5	12
Guideline/Standard			30	370
TR = Total recoverable				
Highlighted values are above MfE & MoH (1997) guideline of 30 mg/kg.				

Arsenic concentrations on the reference soil samples ranged from 5 to 72 mg/kg. Three reference samples were consistent with background levels of soil arsenic ranging from 1 – 25 mg/kg in the Waikato region (Taylor and Kim, 2009) and the environmental guideline level of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997) for agricultural land and land for lifestyle blocks. A 10 – 20 cm depth reference sample taken 20 m north of the dip site and across stream X (ASRef#1b) had 72 mg/kg As which is above the environmental guideline limit of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997).

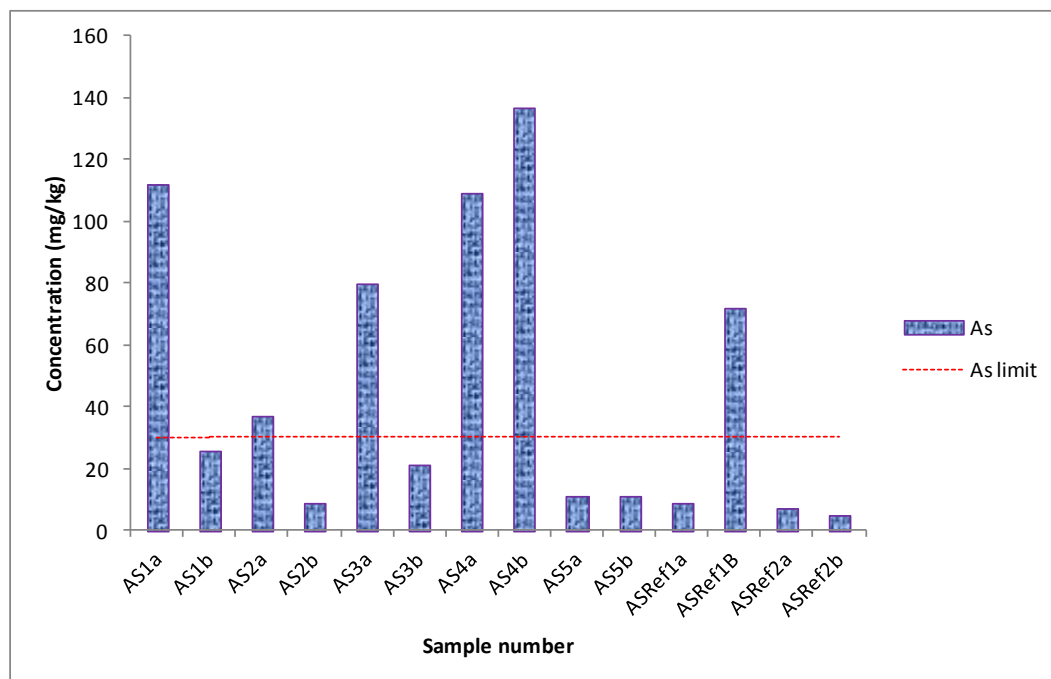


Figure 4-3 Arsenic concentration with respect to the Ministry for the Environment and Ministry of Health (1997) guideline value of 30 mg/kg for agriculture and residential land uses.

Copper concentrations ranged from 12 mg/kg to 30 mg/kg (Figure 4-4). Concentrations of copper were all below the soil acceptance level of 370 mg/kg (Cavanagh, 2004a) and background levels 38 to 380 mg/kg for the protection of livestock on agricultural land associated with contaminated sites (Ministry for the Environment and Ministry of Health, 1997). The lowest detected concentration of 12 mg/kg was the deep sample from a reference site located across the road (ASRef2b) and the highest detected concentration of 35 mg/kg was from the deep sample adjacent to the dip site (AS4b).

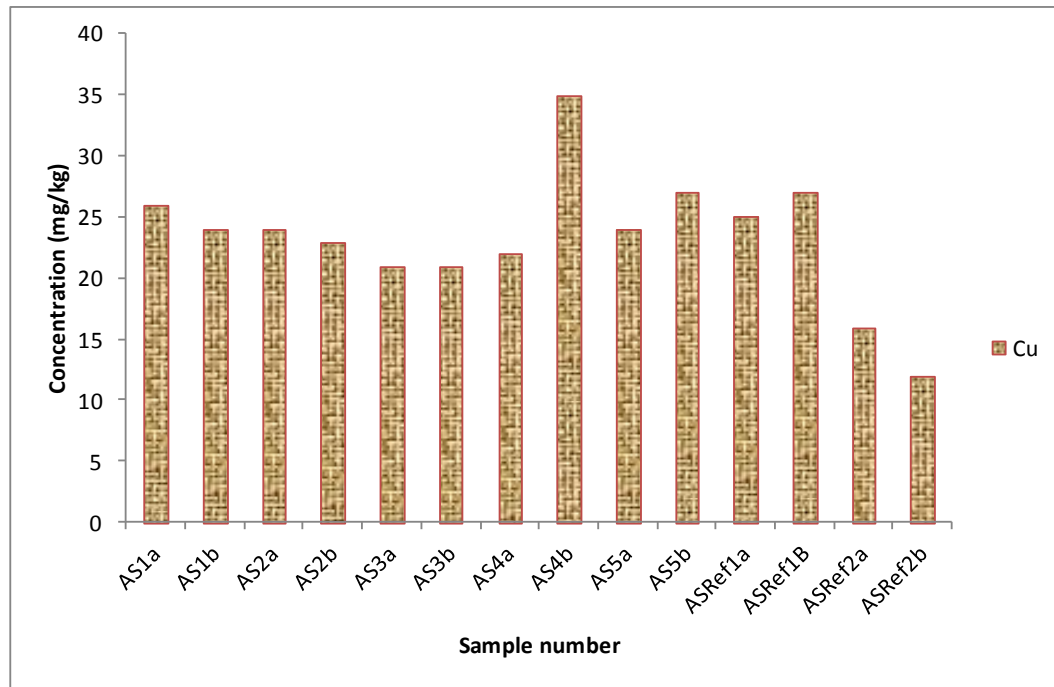


Figure 4-4 Copper concentrations showing levels well below the soil acceptance level of 370 mg/kg (Cavanagh, 2004a).

4.4.1.2 Organochlorine residues in soil

Three soil samples out of the fourteen analysed had detectable pesticides dieldrin and α -BHC (Table 4-5, Appendix I). Concentrations of dieldrin varied between samples. All three samples that contained dieldrin were below the soil guideline value of 0.7 mg/kg for human health at lifestyle blocks and 2.7 mg/kg for standard residential use on land associated with old sheep dip sites (Ministry for the Environment, 2006).

Table 4-5 Organochlorine pesticides residues in soil.

Site number	Distance from dip m	α -BHC mg/kg	Dieldrin mg/kg
AS1a	5	<0.0010	<0.0010
AS1b	5	-	-
AS2a	5	<0.0010	<0.0010
AS2b	5	-	-
AS3a	5	<0.0010	0.15
AS3b	5	<0.0010	<0.0010
AS4a	5	0.019	0.078
AS4b	5	0.033	0.104
AS5a	12	<0.0010	<0.0010
AS5b	12	-	-
ASRef1a	25	<0.0010	<0.0010
ASRef1b	25	-	-
ASRef2a	25	<0.0010	<0.0010
ASRef2b	25	-	-
Detection limit		<0.0010	<0.0010
Guideline/Standard		Lindane = 0.006	0.002
a = surface sample, 0 - 10 cm; b = deep sample, 10 - 20 cm			
Highlighted results are above the Ministry for the Environment (2006) guideline values.			

Two samples, one surface (0 – 10 cm) and the other from 10 – 20 cm depth, both from sample site AS4 which was adjacent to the sheep dip, had traces of α -BHC. Surface sample AS4a had 0.019 mg/kg α -BHC and the deep sample AS4b had 0.033 mg/kg α -BHC (Table 4-5). Both samples are above the lindane guideline value of 0.006 mg/kg for the protection of on-site ecological receptors on soils associated with historic sheep dip sites (Ministry for Environment, 2006).

Surface (0 – 10 cm) and deep (10 – 20 cm) samples AS4a and AS4b had both dieldrin and alpha-BHC. The surface AS4a sample had 0.019 mg/kg alpha-BHC and 0.078 mg/kg dieldrin. Deep sample AS4b had 0.033 mg/kg alpha-BHC and 0.104 mg/kg dieldrin. All other organochlorine pesticides tested were below detection levels.

4.4.2 Stream sediments

Analytical cost limited the number of samples analysed. Sixteen sediment samples were analysed for organochlorine pesticides and seven samples for total recoverable arsenic and copper (Appendix I). Two sediment samples upstream of the road culvert (ASED1/1-2) and five sediment samples from downstream of the probable dip discharge site (ASED3/1-5) were analysed for total recoverable arsenic and copper.

4.4.2.1 Arsenic and copper residues in sediments

Reference sediment core ASED1/1-2, which was upstream of the dip site, in stream X, had 0.9 mg/kg As in the surface (0 – 5 cm) sample and 7.5 mg/kg As in the 5 – 10 cm sample (Table 4-6). The discharge zone or the zone that is sometimes referred to as the seepage zone which is the area between the stock crossing and the confluence of streams X and Y, where sheep dip chemicals are likely to enter the receiving environment, causing off-site contamination, had arsenic concentrations of 18 to 32 mg/kg (Table 4-6).

Table 4-6 Arsenic and copper in stream sediments.

Site location	Sample number	Core depth cm	Distance from dip m	AsTR mg/kg dry wt	CuTR
Upstream of road culvert	ASED1/1	0 - 5	20	0.9	46
Upstream of road culvert	ASED1/2	5 - 10	20	7.5	28
Discharge zone	ASED3/1	0 - 6	10	32	18
Discharge zone	ASED3/2	6 - 13	10	25	22
Discharge zone	ASED3/3	13 - 19	10	19	19
Discharge zone	ASED3/4	19 - 26	10	20	19
Discharge zone	ASED3/5	26 - 32	10	18	20
Guideline/Standard				20	-
TR = total recoverable					
- = not available					
Highlighted values for arsenic are above the interim sediment quality guideline (ISQG-Low) limit of 20 mg/kg for freshwater sediments associated sheep-dip sites (MfE & MoH, 1997).					

Three out of five samples from the discharge zone had arsenic concentrations above the interim sediment quality guideline lower limit (ISQG-Low) of 20 mg/kg, below which, adverse effects are not expected in freshwater sediments (Ministry for the Environment, 2006). The mean arsenic concentration of the five samples was 22.8 mg/kg which was 37 percent higher than the reference site located upstream of the road culvert (ASED1/1-2). Arsenic levels decreased with increasing core depth. Copper levels at the discharge zone were 50 percent lower than the upstream control site surface sample concentration of 46 mg/kg.

Extent and distribution of arsenic and copper residues in the discharge samples are shown on Figure 4-5. Arsenic levels were highest near the surface. On the other hand copper levels were uniform in the entire sediment core.

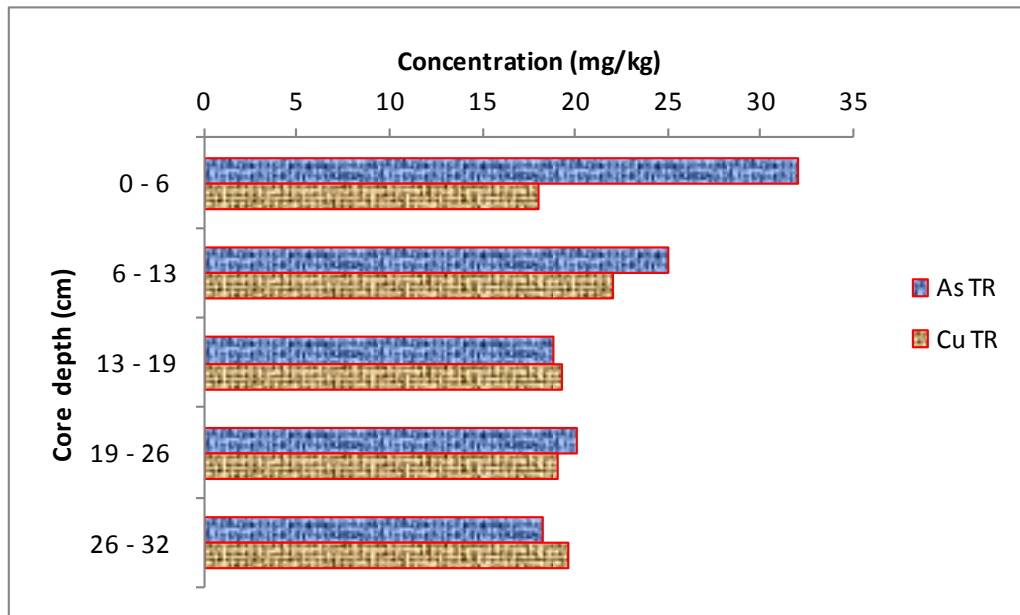


Figure 4-5 Total recoverable As and Cu in discharge zone sediment core ASSED3.

4.4.2.2 Organochlorine residues in sediments

Three organochlorine pesticides were detected in all the five discharge zone sediment samples located downstream of the dip site (ASED3). All remaining samples were below detection limit. Dieldrin concentrations ranged from 0.0017 mg/kg to 0.038 mg/kg. All five sediment samples were well above the interim sediment quality guideline low (ISQG-Low) limit of 0.00002 mg/kg for dieldrin (Ministry for the Environment, 2006). Dieldrin concentrations on the surface samples down to 13 cm core depth were well above the interim sediment quality guideline higher limit (ISQG-High) of 0.008 mg/kg (Ministry for the Environment, 2006). The levels of dieldrin depict a decreasing trend with increasing core depth (Figure 4.6).

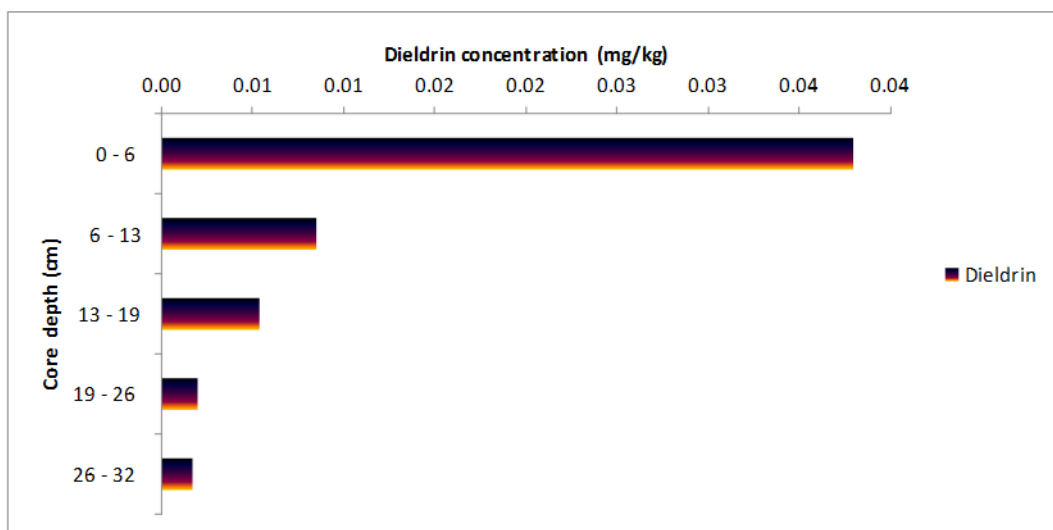


Figure 4-6 Extent and distribution of dieldrin in stream sediment core ASED3. Other cores had no detectable organochlorines.

Alpha-BHC and beta-BHC were detected on the same core as dieldrin but only in the surface sample (ASED3/1). The shallow 6.4 cm sample ASED3/1 had 0.0011 mg/kg alpha-BHC and 0.0031 mg/kg beta-BHC; both are by-products of the widely used sheep dip chemical lindane. There was an absence of sediment quality guideline limits for alpha and beta BHC for freshwater sediments therefore lindane limits were used to assess compliance to environmental standards. Both alpha and beta BHC results were above the interim sediment quality guideline high (ISQG-High) value of 0.00032 mg/kg for lindane (Ministry for the Environment, 2006).

4.4.3 Surface water

Surface water samples from upstream of dip site (AW1), the discharge zone (AW3), and downstream of the dip site (AW5) were analysed for pesticide residues in surface water. All three samples (AW1, AW3, and AW5) were analysed for trace level organochlorine pesticides. No Organochlorine pesticides were detected in surface water samples in either stream X or stream Y (Table 4-7).

Table 4-7 Surface water field (DO and temperature) and lab (As, Cu, and organochlorine results.

Sample name	Date dd/mm/yy	Time hh:mm	DO g/m ³	DO saturation PDO (%)	Wtemp °C	As g/m ³	Cu g/m ³	Organochlorine trace in water
Guideline/standard			-	>80	-	<0.01	<2	-
AW1	15/06/13	11:57am	9.5	87.3	11.7	<0.0011	0.0010	ND
AW3	15/06/13	13:02pm	9.4	85.7	11.7	0.0021	0.0021	ND
AW5	15/06/13	14:10pm	9.9	89.7	11.0	NT	NT	ND
- = not available								
ND = not detected								
NT = not tested								

Two surface water samples, AW1 and AW3 were analysed for total arsenic and total copper. Total arsenic was not detected on the upstream sample. The discharge sample had detectable As however the concentration was well below the Ministry of Health (1995) guideline limit of 0.01 g/m³ and was also below the ANZECC trigger value of 0.024 g/m³ for a 95 percent level of protection for freshwater (ANZECC and ARMCANZ, 2000; in Ministry for the Environment, 2006). Both samples (AW1 and ASW3) had trace levels of copper.

4.5 Results site B

4.5.1 Arsenic and copper residues

All soil samples tested at Site B had arsenic levels above the environmental guideline of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997) except the three reference sites, BS5b and BS8 (a&b) (Figure 4-7, Table 4-8, Appendix I). The minimum value for arsenic was <2 mg/kg, recorded at site BS8, located 115 m downhill from the dip site. The maximum value was 640 mg/kg from the 10 – 20 cm sample at BS10b which was located on the 5 m perimeter of dip site. Two samples at site BS7, located 96 m downhill from the dip site, had a mean concentration of 76 mg/kg arsenic. Reference sample concentrations ranged between 3 mg/kg and 8 mg/kg, well below the

environmental guideline of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997).

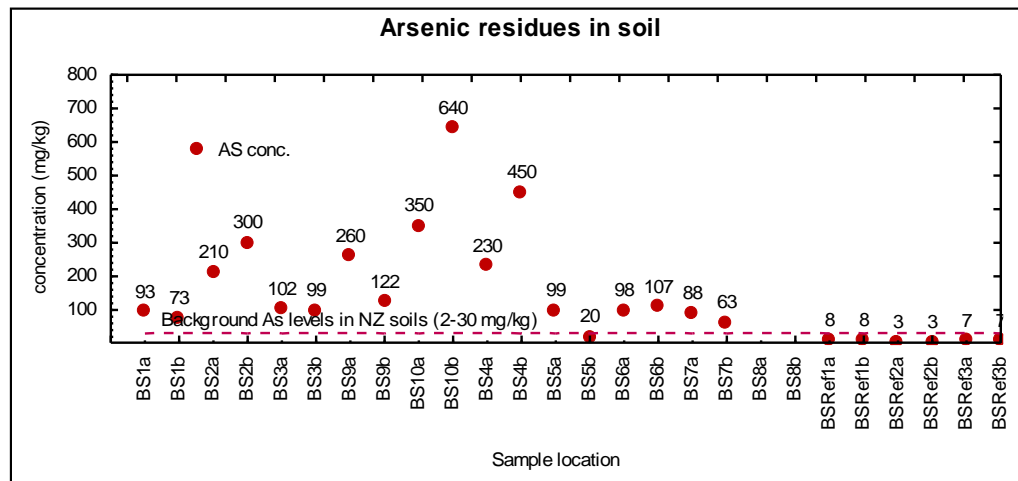


Figure 4-7 Residual arsenic concentrations in soil showing the extent and distribution relative to the environmental guideline limit of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997).

Copper concentrations ranged from 21 mg/kg to 102 mg/kg. The minimum value was recorded at reference site BSRef3b located in the native bush, 47 m east of the dip site. The maximum was recorded at BS5b located 35 m downhill, south the dip site (Table 4-8). Reference concentrations for copper ranged from 21 mg/kg to 33 mg/kg, well within the background levels in New Zealand soils and the national guidelines for contaminated sites.

Table 4-8 Arsenic and copper concentration in soil samples at Site B.

Sample number	Depth cm	Distance m	AsTR mg/kg dry wt	CuTR mg/kg dry wt
BS1a	0 - 10	5	93	73
BS1b	10 - 20	5	73	31
BS2a	0 - 10	5	210	31
BS2b	10 - 20	5	300	32
BS3a	0 - 10	5	102	38
BS3b	10 - 20	5	99	34
BS9a	0 - 10	5	260	52
BS9b	10 - 20	5	122	60
BS10a	0 - 10	5	350	64
BS10b	10 - 20	5	640	57
BS4a	0 - 10	19	230	64
BS4b	10 - 20	19	450	79
BS5a	0 - 10	39	99	91
BS5b	10 - 20	39	20	102
BS6a	0 - 10	62	98	53
BS6b	10 - 20	62	107	61
BS7a	0 - 10	96	88	42
BS7b	10 - 20	96	63	42
BS8a	0 - 10	115	<2	58
BS8b	10 - 20	115	<2	55
BSRef1a	0 - 10	111	8	33
BSRef1b	10 - 20	111	8	32
BSRef2a	0 - 10	33	3	25
BSRef2b	10 - 20	33	3	38
BSRef3a	0 - 10	47	7	24
BSRef3b	10 - 20	47	7	21
Soil Guideline			30	370
TR = total recoverable				
Highlighted values are above the soil guideline of 30 mg/kg As (MfE & MoH, 1997)				

Concentrations of copper and arsenic had a statistical regression r^2 value of 0.0811, ($P = 0.158$) indicative of low precision which means that there were no relationship in terms of the extent of contamination at Site B (Figure 4-8).

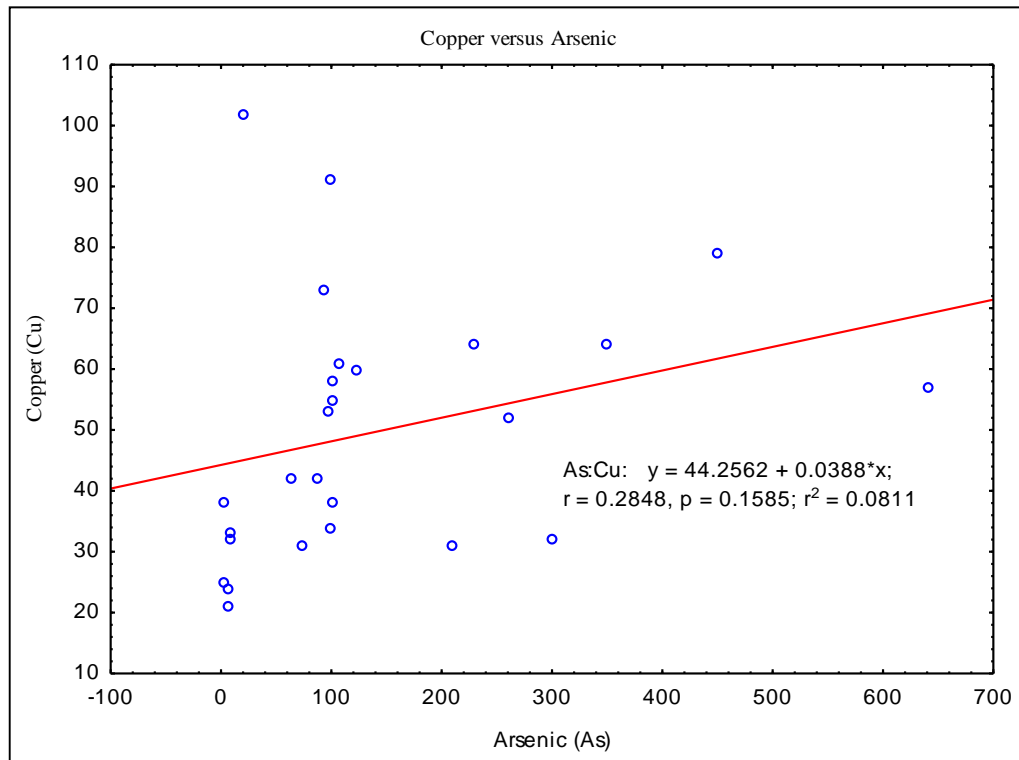


Figure 4-8 Plot showing the extent of copper and arsenic concentrations at Site B.

Despite the difference in the extent of concentrations between copper and arsenic at Site B, a relationship between arsenic and copper in terms distribution patterns was observed. Copper appeared to be trending higher with high arsenic or low with low to moderate arsenic concentration (Figure 4-9). This relationship may suggest that a likely dipping chemical used at Site B was copper arsenate which was a widely used sheep dipping chemical in New Zealand.

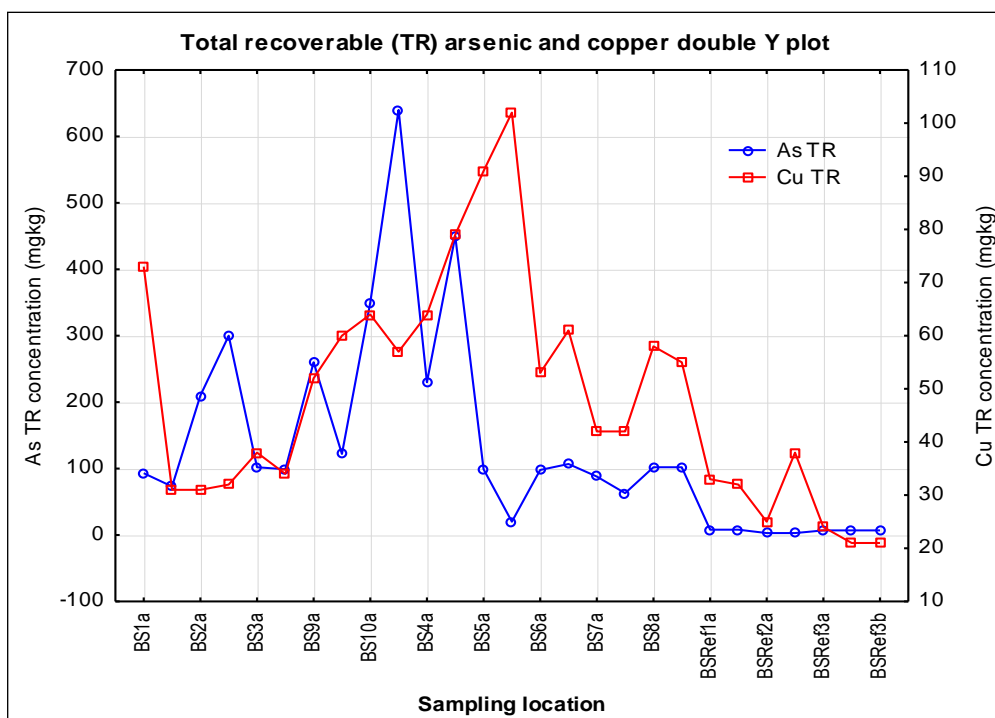


Figure 4-9 Arsenic and copper based dipping chemical.

4.5.2 Organochlorine residues

Sixteen samples were analysed for organochlorines in soil at Site B. Thirteen organochlorine compounds were detected in ten soil samples (Table 4-9). Other sheep dip organochlorine pesticides were not detected. All reference samples had no detectable organochlorine pesticide.

Four of the detected compounds were by-products of lindane; DDT (including metabolites), two endrin compounds, and dieldrin. Dieldrin had the highest concentration at 8.60 mg/kg which was from the 10 – 20 cm sample at site BS10b located close to the exit of the draining platform. The lowest detected organochlorine was delta-BHC (δ -BHC) at 0.010 mg/kg from site BS2b which was the site located on the splash area adjacent to the sheep dip site.

Table 4-9 Thirteen detectable organochlorine residues.

Sample number	Site location	Distance from dip (m)	α -BHC mg/kg	β -BHC mg/kg	δ -BHC mg/kg	γ -BHC (Lindane) mg/kg	2,4'-DDD mg/kg	4,4'-DDD mg/kg	2,4'-DDE mg/kg	4,4'-DDE mg/kg	2,4'-DDT mg/kg	4,4'-DDT mg/kg	Endrin mg/kg	Endrin ketone mg/kg	Dieldrin mg/kg
BS2a	Splash/run off zone	5	<u>0.053</u>	<u>0.073</u>	<0.0010	<u>0.016</u>	<0.0010	<u>0.017</u>	<0.0010	<u>0.104</u>	<0.0010	<u>0.032</u>	<0.0010	<0.0010	<u>0.450</u>
BS2b	Splash/run off zone	5	<u>0.059</u>	<u>0.138</u>	<u>0.010</u>	<u>0.021</u>	<0.0010	<u>0.021</u>	<0.0010	<u>0.140</u>	<0.0010	<u>0.044</u>	<0.0010	<0.0010	<u>0.510</u>
BS9a	beside of draining pen	5	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<u>0.033</u>	<0.0010	<u>0.018</u>	<0.0010	<0.0010	<u>0.054</u>
BS10b	drain exit and drip zone	5	<u>0.027</u>	<u>0.560</u>	<u>0.039</u>	<u>0.061</u>	<u>0.055</u>	<u>0.108</u>	<0.0010	<u>0.490</u>	<u>0.210</u>	<u>0.880</u>	<u>0.127</u>	<u>0.039</u>	<u>8.60</u>
BS4a	dicharge entry into gully	19	<u>0.077</u>	<u>0.113</u>	<u>0.013</u>	<u>0.016</u>	<u>0.067</u>	<u>0.045</u>	<0.0010	<u>0.440</u>	<u>0.029</u>	<u>0.122</u>	<0.0010	<0.0010	<u>1.62</u>
BS4b	dicharge entry into gully	19	<u>0.136</u>	<u>0.220</u>	<u>0.028</u>	<u>0.040</u>	<u>0.145</u>	<u>0.123</u>	<u>0.016</u>	<u>1.200</u>	<u>0.165</u>	<u>0.740</u>	<0.0010	<0.0010	<u>3.500</u>
BS5a	dow nhill gully	39	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<u>0.077</u>	<0.0010	<u>0.018</u>	<0.0010	<0.0010	<u>0.035</u>
BS6a	dow nhill gully	62	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<u>0.127</u>	<0.0010	<u>0.023</u>	<0.0010	<0.0010	<u>0.027</u>
BS6b	dow nhill gully	62	<u>0.029</u>	<u>0.011</u>	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<u>0.220</u>	<0.0010	<u>0.037</u>	<0.0010	<0.0010	<u>0.021</u>
BS7a	dow nhill gully	96	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<u>0.129</u>	<0.0010	<u>0.030</u>	<0.0010	<0.0010	<0.010
BSRef1a	Reference - west side	111	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.010
BSRef1b	Reference - west side	111	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.010
BSRef2a	Reference - north	33	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.010
BSRef2b	Reference - north	33	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.010
BSRef3a	Reference - east side	47	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.010
BSRef3b	Reference - east side	47	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.0010	<0.010
Detection limit			<0.0010	<0.0010	<0.0010	<0.0010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Soil guideline/standards			Lindane = 0.006				Σ DDT = 8.4						-		6.0

a= surface, 0 - 10 cm; b = deep, 10 - 20 cm

Highlighted/underlined results are above environmental guideline values in Ministry for the Environment and Ministry of Health (1997) and Ministry for the Environment (2006).

Lindane compounds were found in varying concentrations between surface and 10 – 20 cm deep samples. α -BHC was in two surface and four deep samples with concentrations ranging from 0.027 to 0.136 mg/kg. β -BHC was found in the same samples as α -BHC however the levels range from 0.011 to 0.560 mg/kg. One surface and three deep samples had δ -BHC with levels from 0.010 to 0.028 mg/kg. γ -BHC found in two surface samples and three deep samples with concentrations ranging between 0.016 and 0.061 mg/kg.

DDT including DDT metabolites (DDE and DDD) was found in both surface and deep samples at varying concentrations. 2,4'-DDD and 4,4'-DDD had 0.017 to 0.145 mg/kg from sites around the dip and gully. 2,4'-DDE and 4,4'-DDE had 0.016 to 1.200 mg/kg. All ten samples had 4,4'-DDE. Only BS4b had 2,4'-DDE. 2,4'-DDT and 4,4'-DDT with levels ranging from 0.018 to 0.880 mg/kg. 4,4'-DDT was present on all samples analysed. 2,4'-DDT was detected on three samples. Pesticide endrin and endrin ketone was detected on sample BS10b at 0.127 mg/kg and 0.039 mg/kg concentrations respectively. Dieldrin was detected on all ten samples except BS7a. Concentrations of dieldrin range from 0.021 to 8.60 mg/kg. Organochlorine residues detected had non-formal distribution patterns around and away from the sheep dip. Elevated residues levels were found at the splash, the drip area, and the discharge zone along the gully line (Figure 4-10).

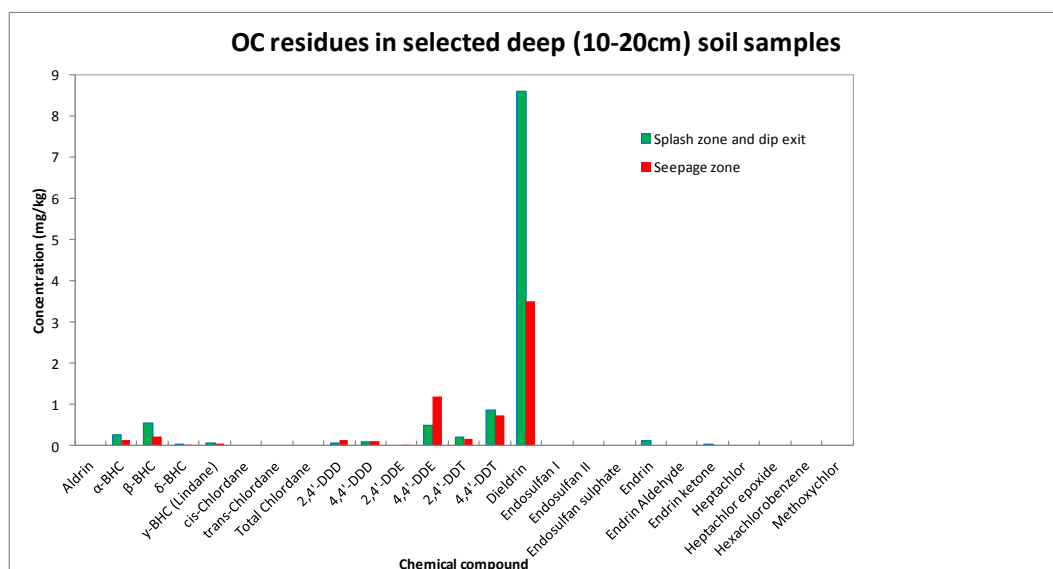


Figure 4-10 Detectable organochlorine pesticides in soil samples BS10b and BS4b.

4.6 Summary and conclusions

- Two sites (A & B) were investigated for sheep dip chemicals by sampling soils up to 20 cm depth in selected areas around the sheep dips.
- Stream sediment core sampling and surface water sampling were carried out in stream X at Site A.
- Soil, sediment, and surface water samples were analysed for sheep dip arsenic, copper, and organochlorines at Hill Laboratories Ltd (Hamilton).
- Soils showed arsenic concentrations above environmental guideline levels at both sites A and B (up to 640 mg/kg). Maximum value at Site A was 137 mg/kg from the 10 – 20 cm sample site AS4b which was adjacent to the dip site. Despite the maximum value at Site A being detected in the deeper (10 – 20 cm) sample, 4 out of 7 samples with elevated As were from 0 – 10 cm depth.
- The maximum arsenic concentration at Site B was 640 mg/kg, from the 10 – 20 cm sample adjacent to the dip site (BS10b).
- Two samples with a mean concentration of 76 mg/kg arsenic were recorded 96 m downhill from the dip site, at Site B. Detailed study of the extent and distribution of arsenic in surface soil samples (up to 7.5 cm depth) along the gully to 100 m downhill was recommended for Site B in Phase II.
- Contaminants arsenic, dieldrin, lindane (including by-products), DDT (including metabolites), and Endrin were present at Site B.
- DDT (including DDT metabolites) was detected in a wide area at Site B (up to 96 m downhill). DDT was undetected on the reference samples. The maximum concentration recorded for DDT was on the 10 – 20 cm sample

at the runoff entry point into the gully ($\Sigma\text{DDTs} = 2.389 \text{ mg/kg}$) which was well below the guideline for human habitation ($\Sigma\text{DDTs} = 8.4 \text{ mg/kg}$).

- Phase I sampling at Site B showed low to moderate dieldrin contamination with one sample having 8.60 mg/kg dieldrin, exceeding the guideline levels of 6 mg/kg for agriculture, (Ministry for the Environment and Ministry of Health, 1997). Three samples from Site B were above the guideline for human habitation of 2.7 mg/kg . Dieldrin concentrations were highest in the immediate vicinity of the sheep dip at both sites A and B (up to 8.60 mg/kg). The gully at Site B had low to moderate dieldrin contamination with concentrations ranging from not detected to 3.5 mg/kg dieldrin. Elevated levels of dieldrin were found up to 62 m downhill at Site B.
- Copper were generally within background levels therefore does not have a contamination problem at sites A and B. The maximum values of arsenic and copper were from the same location at Site A. While arsenic was above the environmental guideline, copper on the other hand was well below guideline levels. Copper and arsenic at Site B had a likely relationship in terms of the pattern of distribution and the extent of concentrations which imply that copper arsenate was likely to be one of the many dipping chemicals used at Site B.
- Preliminary sampling showed co-contamination of arsenic and dieldrin in soils around the dip site at sites A and B. Similar pattern of co-contamination emerged at the discharge zone stream sediments on stream X at Site A and the discharge entry point into the gully at Site B.
- Preliminary sampling confirmed the presence of contaminated sites regardless of being a statistically deficient method.
- Stream sediments downstream of the dip site at site A were contaminated with arsenic (up to 32 mg/kg), dieldrin (up to 0.038 mg/kg), $\alpha\text{-BHC}$ (0.0011 mg/kg), and $\beta\text{-BHC}$ (0.0031 mg/kg).

- Contamination on the surface sediment sample taken downstream from the dip site at Site A was above the environmental guideline levels for the detected pesticides; As, dieldrin, α -BHC, and β -BHC . Significant dieldrin contamination has occurred in the surface sediments up to 13 cm, breaching the interim sediment quality guideline limit (ISQG-High) of 0.008 mg/kg (Ministry for the Environment, 2006). Arsenic, dieldrin, and benzene hexachlorides (α -BHC and β -BHC) levels were either detected on surface samples only or at highest levels near the surface which could suggest that surface depositions are likely to be the result of recent events and not the result of accumulations during the dipping period. High arsenic concentration may be inhibiting organochlorine degradation particularly dieldrin, although co-contamination would be difficult to assess in stream sediments.
- Elevated arsenic (0.0021 g/m³) were detected in surface water downstream of the dip site compared to the upstream site however the detected levels were well below the maximum acceptable value (MAV) of 0.01 g/m³ for potable drinking water supplies (Ministry of Health, 1995).
- Organochlorine pesticides were undetected in surface water samples.

Chapter 5 - Systematic sampling: methods and results (Phase II)

Chapter Five

Methods and results – phase II

5.1 Introduction

Systematic sampling provides current best practice for assessing contamination at old sheep dip sites in New Zealand (Ministry of the Environment 2006). Phase II was the detailed sampling of sites A and B using systematic sampling strategies. The objective of phase II was to determine the spatial extent and distribution of arsenic on soil around the sheep dip and the wider area beyond the 5 m perimeter of the dip site. The extent of arsenic contamination on stream X sediments was also investigated, given the high results in Phase I. Systematic grid sampling strategies were used for soil sampling. A 40 m transect was used on stream sediments grab sampling. Systematic sampling was generally a good method for assessing variability of contamination and is statistically sound, however high analytical cost would be a drawback for many landowners.

This chapter describes the systematic sampling design, methods, and results. Experimental methods using the XRF instrument in a lab setup are also described. A summary and conclusions are included in this chapter however discussions for this chapter are included in Chapter 6.

Soil samples were taken on the surface up to 7.5 cm. Sediment samples were taken from the surface sediments up to 10 cm deep. Sample analyses were carried out using the XRF elemental analyser at the University of Waikato X-Ray Diffraction (XRD) laboratory.

5.2 Sampling design and methods

5.2.1 Soil sampling design

Sampling plans for phase II were based on the knowledge gained in phase I related to arsenic levels and distribution. The plan for site A was to begin sampling from the edge of the fenced area where the dip was located then move north 10 m across stream X and then sample 20 m upstream, east of the road reserve. Soil samples for site A were collected from a 2 x 2 m grid constructed to 32 m long and 16 m wide. Width varied depending on the distance between the road reserve fence line and remnants of a fence line separating the dip area and the esplanade reserve. Total area sampled at site A was 172 m² which produced a total of 129 soil samples (Figure 5-1).

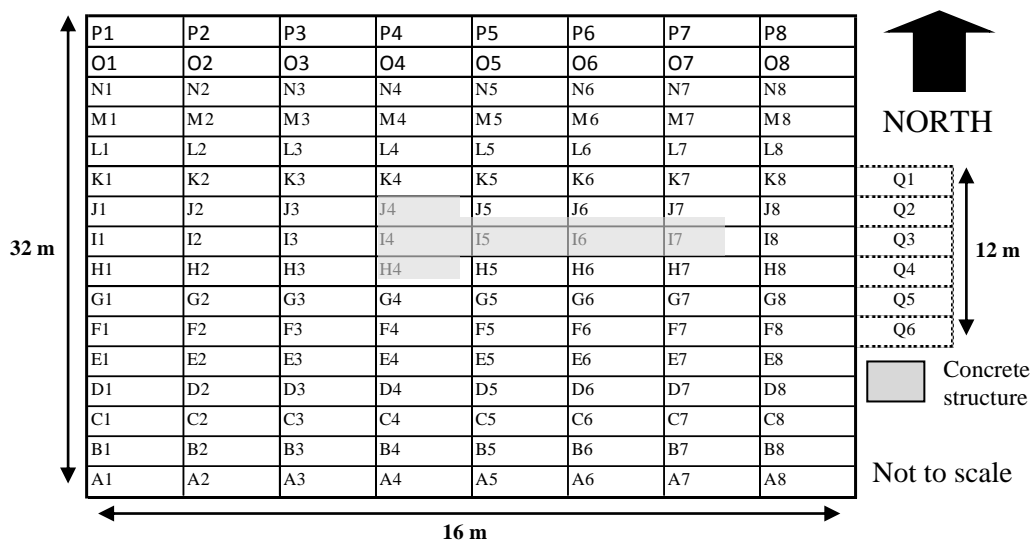


Figure 5-1 Layout of grid for systematic sampling at Site A showing sample locations. Samples Q1 – Q6 were from the grid on the east side of the road.

The sampling plan for site B was divided into two parts. The first part covered the dip location and the top of the gully that leads into the parking area at the top of the hill. Grid lines run east to west for the first part. Sampling for the first part commenced from the top of the hill which is 15 m east of the dip site and then moved into the dip location, down into the gully and across to the other side of the gully.

The second part of the site B sampling plan covered the area at the top of the gully which is west of the dip site and downhill to the end of the gully. Grid lines ran north to south. Sampling for the second part commenced at the top of the gully from the southern end of part one and completed at the bottom of the hill, 112 m from the dip site. Soil samples for site B were collected using a 5 x 5 m grid. The total area sampled was 1500 m² which produced 120 soil samples.

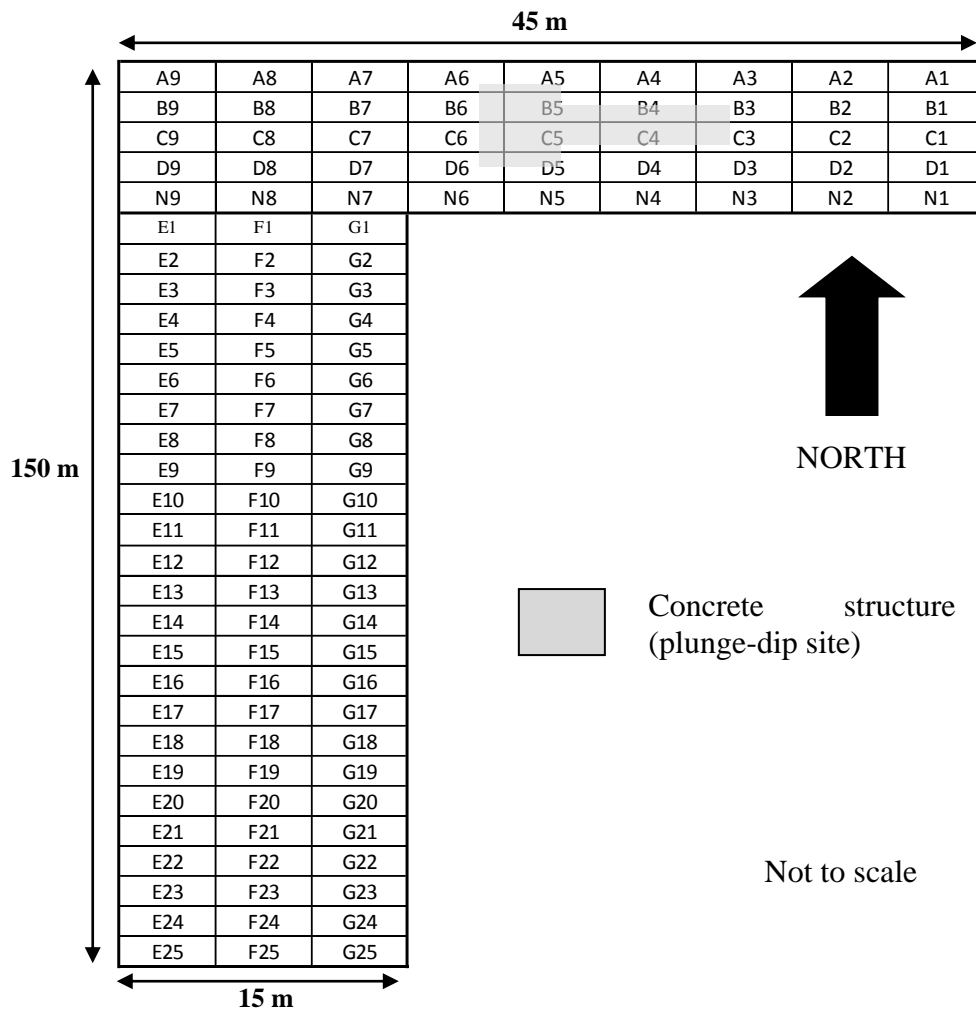


Figure 5-2 Grid layout for systematic sampling at Site B showing sample locations.

5.2.2 Soil sampling method

Surface soil samples from 0 – 10 cm depth were the focus of the phase II sampling plan. Soils were sampled with a surface soil core sampler. Two core

samples were collected from each grid, combined into a pre-labelled zip lock bag to form a composite sample, and transported to the lab for air-drying in a 35°C oven prior to analyses. Every grid sample location and transect sample points were recorded on a garmin handheld GPS. Grid locations and arsenic concentrations of each grid were used to create contour plots of residual arsenic. Plots were produced using a 3D map gridding software package ‘SURFER’.

5.2.3 Sediment sampling design

The sampling plan for stream X sediments was to capture the distribution of arsenic along the discharge zone which is an area from the stock crossing on stream X to the confluence of stream X and Stream Y. Sampling began upstream of the stock crossing and completed at the confluence at equal intervals. A 36 m transect was constructed starting from the culvert to the confluence of stream X with stream Y with 3 m sampling intervals established. Twelve stream sediment grab samples were collected from the sediment transect.

5.2.4 Sediment sampling method

Surface sediment samples were collected using a 130 mm diameter sediment corer to a depth of 10 cm. Samples were immediately placed into a large zip lock plastic bag and transported to Hill Laboratories Ltd for air drying at 35°C and 2 mm sieving prior to analysis.

5.2.5 Experimental method

5.2.5.1 Introduction

Phase II samples were analysed using a laboratory setup of the handheld Olympus Innov-X-Ray fluorescence (XRF) elemental analyser. XRF is a method used for elemental analysis of a range of media such as soils, plant material, and chemical,

biological and geological material. The handheld XRF elemental analyser is a relatively new onsite analytical instrument that could be used in contaminated land investigations such as the investigation of old sheep dip sites in New Zealand as a screening tool.

Previous sheep dip investigation using the XRF showed that the portable XRF can be used with a great deal of accuracy, quickly and onsite (Dewar and Rajendram, 2005). However, comparative analysis work on laboratory versus XRF data indicated that moisture content has some bearing on the XRF results, if used onsite (Tasman District Council, 2013). Better results could be achieved by sieving and rapid drying of soil samples rather than using field moist samples (Dewar and Rajendram, 2005).

Soil and sediment samples collected in phase II were treated the same way as phase I sample preparation before the analyses were performed. All 261 samples collected in phase II were analysed. All samples were transported from the sheep dip site to Hill Laboratories Ltd for air drying and sieving prior to lab analysis.

5.2.5.2 Laboratory analysis

The first step in preparation of soil and sediment analysis was for all samples to be dried and sieved. Soil and sediment samples were air dried in a 35°C oven and 2 mm sieved at Hill Laboratories Ltd (Figure 5-3).



Figure 5-3 Air dried (2 - 5% moisture content) and 2 mm sieved samples for XRF analysis.

A homogenous sub-sample of the < 2 mm fraction was placed into a white plastic sample container (Figure 5-4) to which a thin layer of membrane film cover the bottom and the top covered with a thin layer of paper, cotton wool, and capped. Sample labels were transferred onto the sub-sample containers. Prepared batches were then transferred to the instrument room for testing on the XRF. Detection limit for arsenic on the XRF was < 5 mg/kg dry weight (Appendix II).



Figure 5-4 Sub-sampled 2 mm fraction is prepared into an XRF sample container for elemental analysis.

Laboratory setup of the pXRF instrument was undertaken where a bench-top stand was used to minimise radiation exposure to the operator and supervising lab staff (Figure 5-5). Operating the pXRF safely and effectively was paramount in the lab analysis method.



Figure 5-5 Laboratory setup of the handheld XRF showing the standard operational setup of the four main components (laptop, samples, bench-top, and XRF).

Under the supervision of a certified laboratory staff member, the following operating procedures (SOP) were used to safely operate the instrument:

- to begin, the bench-top was unfolded and the bench-top adapter screwed in to the pXRF, making sure the contact points between the adapter and the pXRF were positioned correctly
- safety warning selected as the power source was switched on
- “Innov-X Delta Advanced PC Software” installed into the laptop computer, switched on, and connected via USB to the back of the bench-top to start up the device then;
- a pre-set username and password was entered to access start up menu, then
- a calibration check using the supplied 316 stainless steel “coin” was undertaken

Using the start menu the following specifications were programmed into the device and used to analyse soil and sediment samples:

- soil method for matrix option
- 50 KV X-Ray beam emissions at 30 seconds acquisition time per beam
- three beams emitted for every sample load which resulted in 1.5 minutes of each sample analysis time
- each sample was labelled according to sample identification on the sample container then;
- samples were placed into the space provided in the bench-top before the lid was closed and start button selected on the computer for the sample analysis to begin

Data from each batch of samples analysed were exported onto the computer for data analysis and archiving. The XRF instrument detection limit was 5 mg/kg (Appendix II).

5.3 Results

5.3.1 Data validation and quality assurance

Quality of data is essential in evaluating contaminated sites. In this study, samples in Phase II were analysed using an instrument that was different to the analysis of Phase I samples. Sample preparations prior to analysis were similar therefore validating new data by retesting previously tested samples were important in the comparative analysis of experimental methods.

Data quality assurance was undertaken in this study by repeating samples already analysed by Hill Laboratories (Hamilton), an IANZ (International Accreditation New Zealand) accredited laboratory. Samples were retested to assess differences between the trace element method used at Hill Laboratories and the XRF instrument.

There were 12 retested samples, of which 9 were sheep dip samples and 3 reference samples, all from site B.

5.3.2 Validation data results

Results for the validation samples had a linear correlation value of 0.92 on 95% confidence limit which was indicative of high precision and high accuracy (Figure 5-6; Table 5-1). Validation data confirmed the validity of methods performed from sample preparation to through sample analysis. The dataset also indicated that the p-XRF analyser can be a reliable lab testing instrument in sheep dip investigations.

Table 5-1 Data validation run result.

Sample ID	Elevation m	Date dd/mm/yy	Hills lab As mg/kg dry wt	XRF As (Uni)
BS1a	106 m	22/06/2013	93	97
BS2a	104 m	22/06/2013	210	196
BS9a	106 m	22/06/2013	260	248
BS10a	106 m	22/06/2013	350	298
BS4a	100 m	22/06/2013	230	220
BS5a	95 m	22/06/2013	99	88
BS6a	89 m	22/06/2013	98	98
BS7a	84 m	22/06/2013	88	96
BS8a	81 m	22/06/2013	<2	ND
BSRef1a	106 m	22/06/2013	8	9.8
BSRef2a	92 m	22/06/2013	3	ND
BSRef3a	96 m	22/06/2013	7	8.5
ND - not detected				

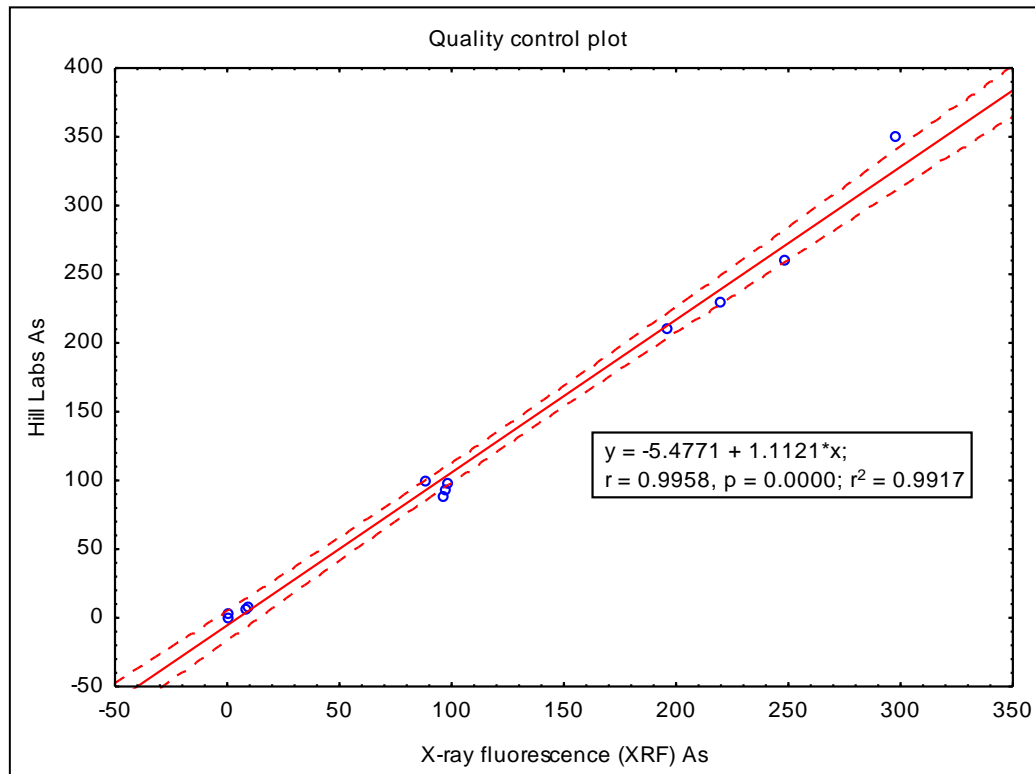


Figure 5-6 Comparative data analysis showing high precision and accuracy in sample preparation and experimental methods.

5.3.3 Site A results

5.3.3.1 Soil

From the 129 soil samples analysed from Site A 76 had concentrations above background levels of arsenic in New Zealand soils, 30 mg/kg. The minimum arsenic concentration was 7 mg/kg and the maximum 2,839 mg/kg. Samples closer to the dip had elevated levels compared to samples from across stream X on the northern paddock and across the road to the east and uphill (Figure 5-7).

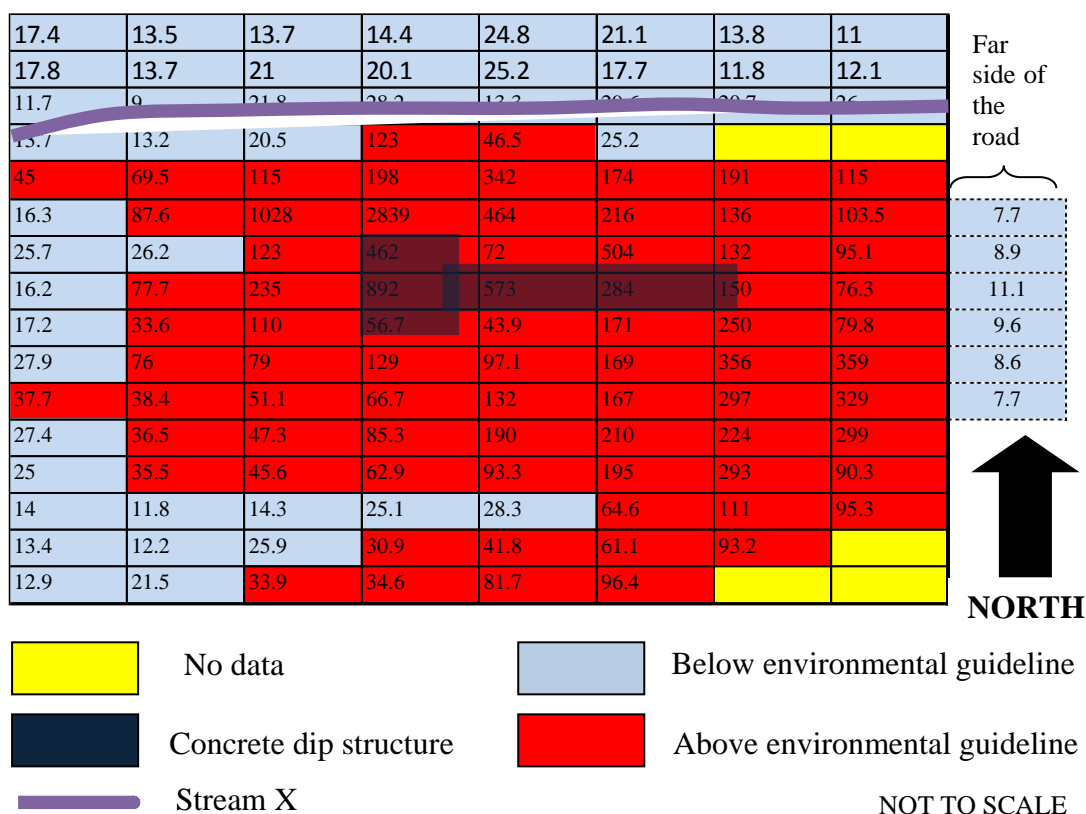


Figure 5-7 Phase II arsenic concentrations within the grid at Site A (in mg/kg).

5.3.3.2 Stream sediments

Concentrations of arsenic in stream sediments ranged from 8.2 mg/kg to 29.9 mg/kg. Sample Sed#3 had 29.9 mg/kg arsenic which is the only sample above the interim sediment quality guideline (ISQG-Low) of 20 mg/kg (Ministry for the Environment, 2006). All other sediment grab samples had elevated arsenic however the levels were below the ISQG-Low level guideline.

5.3.4 Site B results

Site B's 120 samples had a minimum of 4 mg/kg As and maximum of 579 mg/kg As. From the total 120 samples analysed 42 had concentrations above arsenic guideline level, of 30 mg/kg. Samples from the vicinity of the dip had elevated levels compared to samples directly downslope of the dip and samples taken from the true left and true right of the mid-gully line.

The minimum value sample site was located mid-way between the sheep dip and the stock water supply. The maximum value was recorded at sample site E4, located in the adjacent gully, 13 m west of the sheep dip. The area where the maximum was sampled was the likely discharge area from the dip site.

Elevated arsenic was detected at sample site G9 (30.1 mg/kg) which was the site that was furthest from the sheep dip at Site B. In phase I the average concentration around this sample point was 56.5 mg/kg. Sample site G9 was on a 91 m elevation, mid-gully, and 100 m downhill from the sheep dip, and 10 m uphill from the stock water supply.

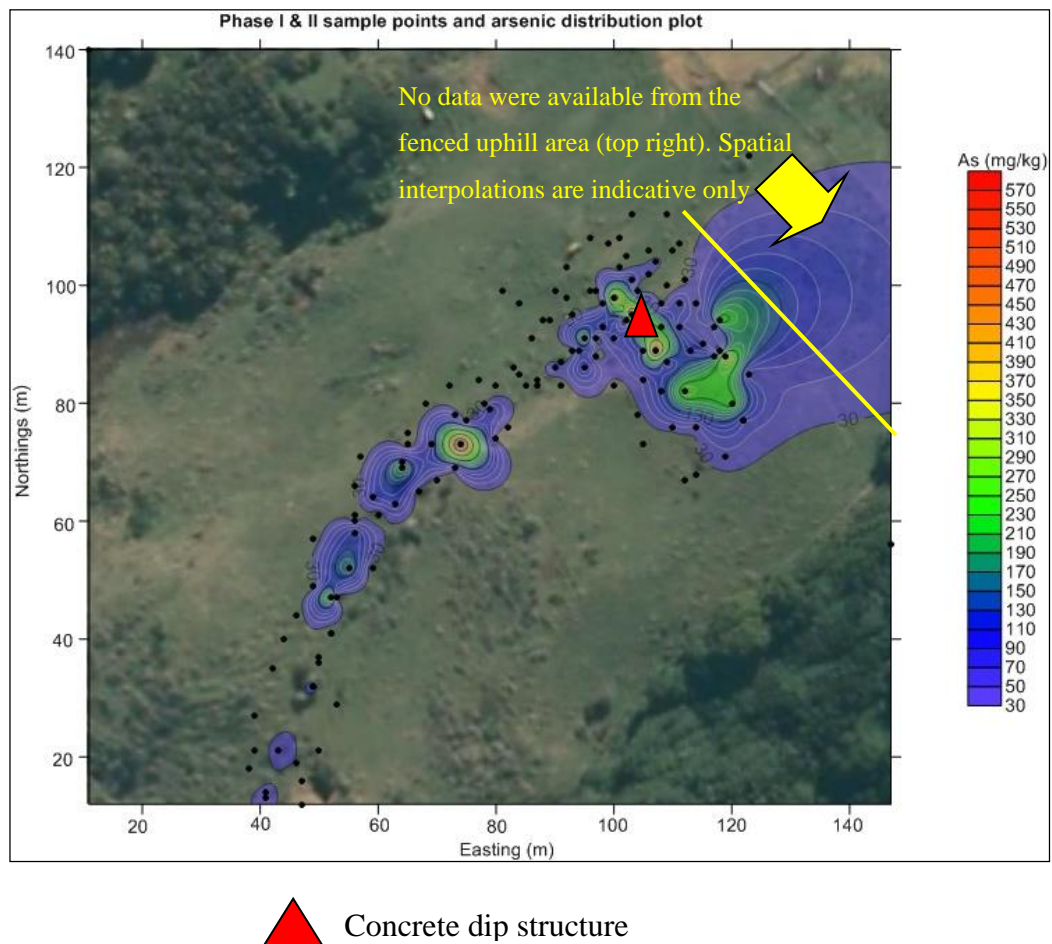


Figure 5-8 Phase I & II spatial plot showing the distribution of arsenic in relation to samples above and below guideline (not included in colour overlay level of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997)).

5.4 Summary and conclusions

- At site A, arsenic concentrations ranged from 7 to 2,839 mg/kg As.
- At Site B, arsenic concentrations were between 4 mg/kg and 579 mg/kg.
- Site A soils had arsenic concentrations above the environmental guideline of 30 mg/kg, up to 25 m south of the dip site.
- Site B had arsenic concentrations above the environmental guidelines up to 100 m downhill, with the maximum value recorded 13 m down-gully from the dip site.
- Stream sediments had concentrations between 8.2 mg/kg As and 29.9 mg/kg As, with one sediment sample taken downstream of the dip site, having concentration above the interim sediment quality low level guideline (ISQG-Low) of 20 mg/kg As.
- Phase II sampling in stream sediments showed arsenic migration 40 m downstream in stream X.

Chapter 6 - Discussion and conclusions

Chapter Six

Discussion and conclusion

6.1 Introduction

Historic sheep dipping practices have contributed to environmental pollution. This study was designed to provide further information and understanding on the extent and impacts of historic sheep dip chemicals on soil, sediment, and surface water quality in the Waikato region.

Establishing evidence of offsite impacts has implications for further work at sheep dip sites as there are over 10,000 sheep dip sites in the Waikato region that may need to be identified and assessed for contamination. Historic sheep dip sites that have the potential to cause offsite contamination through contaminant leaching into stream sediments and surface waters were investigated with evidence presented and discussed in this chapter. A summary of the findings, limitations of the study, concluding remarks, and recommendations are also presented.

6.2 Extent of contamination

6.2.1 Soil

Land at Site A contained pesticides arsenic, dieldrin, and α -BHC that are associated with sheep dips. Soil arsenic dominates with concentrations of up to 2,839 mg/kg, well above the environmental guidelines for agriculture and human habitation of 30 mg/kg (Ministry for the Environment and Ministry of Health,

1997). There was evidence that the spread of sheep dip arsenic was restricted by natural barriers such as the esplanade reserve on the western side of the dip site and human invention such as road works on the eastern side of the dip site. Arsenic contamination of soil at site A extended up to 25 m from the dip site.

A reference sample from 10 – 20 cm depth, located on the northern side of stream X, had 72 mg/kg arsenic, higher than the environmental guideline which regrettably was not a good reference site. The high arsenic concentration was likely to be the result of draining from stock after dipping. The reference sample site has been overlaid with 10 cm of new material which could be the result of either floods since the 1960s or land disturbances from road works.

There was little evidence of recent flood events at the dip site at Site A. Apart from the reference sample that had elevated arsenic, there was no further evidence of elevated arsenic concentration on the northern side of stream X. Moreover, there was no evidence of elevated arsenic on soils on the upstream side of the dip. There was no elevated arsenic on the upstream side the road. The road reserve appeared to have restricted dipped animals from crossing the road. Samples taken from the roadside fence line had high levels of sheep dip arsenic whereas the other side of the road had no elevated arsenic.

Most soil arsenic on site A was in the immediate vicinity of dip site. The southern side of Site A had elevated levels up to 25 m from the dip site. Arsenic above the guideline levels on the northern side of the dip was limited to 7 m due to stream X. Stream X appeared to be a barrier restricting pesticide chemical mobility northwards.

Samples located along the stream bank, on the dip side, had greater than 30 mg/kg As. The small area (7 m) between stream X and the dip site was potentially the contaminant entry point for pesticide chemicals discharge zone into the stream. There was evidence of stream bank erosion on the dip side of stream X. Erosion is by natural causes but more prominent was erosion from the stock crossing. Contaminated eroded soil had potential to be transported into stream X by gravity and stock.

Proximity of stream X to the dip site, high concentrations of pesticide chemicals on the river bank, and river bank erosion assumed that the old sheep dip at site A was the likely source of pesticide contaminants, overland flow, and river bank erosion the exposure pathway of arsenic, dieldrin, α -BHC, and β -BHC pesticides into stream X. Data showed that the area on the stream X side of the dip is potentially the run off zone. Soil samples from the splash zone, the run off area, and the drip area had mean As concentrations of 66 mg/kg. The area inside the 5 m perimeter of the dip site had concentrations of arsenic of up to 2,839 mg/kg. Outside of the 5 m perimeter, the drip zone was the most contaminated area with mean arsenic concentrations of 221 mg/kg.

Generally, Site A arsenic and organochlorine contamination of soil was mostly elevated in the immediate vicinity of the sheep dip which is consistent with previous studies in the Canterbury region (Environment Canterbury, 2003), Marlborough region (Tasman District Council, 2013), Te Mahia (Gregory, 2013), and the Waikato region (McBride, 1994; Wilson *et al.*, 1998; Dewar, 2005; and Prakash, 2005). The extent (up to 2,839 mg/kg) and distribution of contaminants arsenic and organochlorines at Site A poses risks to animal health and elevated risks to stream health due to leaching from runoff and stock access. Removing the contaminated soil from its current location could remedy immediate and long term health and environmental risks however the exercise would be costly and difficult. Immediate risks to animal health can be remedied by fencing off the dip site and stream X by constructing a fence which extends from the road reserve to the esplanade reserve along the northern side of stream X.

In terms of depth migration at Site A, arsenic (up to 137 mg/kg) and dieldrin (up to 0.104 mg/kg) were detected in soils from 10 – 20 cm depth. Further testing of deeper (>20 cm) core samples would have provided information on depth migration and the potential for groundwater contamination at Site A. Higher number of soil samples with elevated As, coupled with, the objective look at surface migration and discharge potential from sheep dips in this thesis resulted in the detailed investigation of surface samples (up to 7.5 cm) at Site A.

Site B was contaminated with arsenic, dieldrin, DDT, lindane, and endrin. Arsenic, DDT (including metabolites), and dieldrin contamination were found to be the most widespread downhill from the dip site.

Arsenic concentrations of up to 640 mg/kg were recorded at Site B with levels above the environmental guideline of 30 mg/kg present in soil 100m downhill from the dip site. From the 129 samples collected from the grid sampling 42 had As concentration above the environmental guideline of 30 mg/kg (Ministry for the Environment and Ministry of Health, 1997). Systematic sampling provided good spatial coverage of contamination distribution at sites A and B however the total extent of contamination on the uphill side and the grazing area on either side of the gully line at site B was not fully covered because the grid was not large enough. A larger size grid would have given more information on the extent and spatial distribution, uphill of the dip site at Site B. Site A sampling grid appears to be inadequate for the size of the sheep dip and coverage of the immediate vicinity. The esplanade reserve and the area north of stream X had insufficient data to extrapolate spatial distribution in the wider area of Site A.

The maximum arsenic concentration on phase I sampling, at Site B, was 640 mg/kg which was from the 10 – 20 cm sample a site adjacent to the dip site (BS10b). Arsenic concentration on the surface sample was 350 mg/kg at the same location. A similar scenario of deeper sample having higher value than the surface sample emerged at sample site BS4 (a&b), a site located at the likely entry point of contaminants into the gully below the dip site. From the total number of samples with elevated arsenic at Site B, 44% had higher concentrations in the 10 – 20 cm samples which indicated that vertical migration through the soil profile has occurred however the extent of vertical migration is unknown. The same scenario emerged at Site A where the highest arsenic concentration was from the 10 – 20 cm sample at a site adjacent to the dip site (AS4b). The pattern of low arsenic concentration on the surface (0 – 10 cm) soil sample compared to the deep (10 – 20 cm) soil sample, indicating vertical migration, appeared to be associated with soil sample sites that has significant arsenic contamination (>100 mg/kg As).

Dieldrin residues above guideline levels were measured in the immediate vicinity of the sheep dip, in the gully, and up to 62 m downhill of Site B. Elevated levels dieldrin were widespread, however only one sample was above the environmental guidelines of 6 mg/kg for agriculture and human habitation (Ministry for the Environment, 2006).

DDT including metabolites was widespread (up to 96 m downhill of Site B) however the levels were well below the environmental guideline of 8.4 mg/kg (Ministry for the Environment, 2006). DDT was a sheep dipping chemical however its use was more widespread compared to other organochlorines. DDT was not detected on reference samples and the distribution pattern at Site B was similar to dieldrin which implied that the DDT was likely to have been used as a dipping chemical at Site B. The maximum concentration recorded for DDT was on the 10 – 20 cm sample at the runoff entry point into the gully (Σ DDTs = 2.389 mg/kg) which was well below the guideline for human habitation (Σ DDTs = 8.4 mg/kg).

Arsenic appears is potentially of concern to grazing livestock, due to the uptake of contaminated soils and pasture. Pasture from the area adjacent to the dip site and up to 25 m away on the southern side of the dip site at Site A needed to be investigated for sheep dip chemical contamination. Similarly, pasture at Site B, from the area within the 5 m perimeter and the gully up to 100 m downhill from the dip site should to be tested for sheep dip chemicals.

Compared to Site A, slope factor (>10 degrees), the adjacent gully, and stock access were probable reasons for the elevated concentrations away from the dip site at Site B. Remediation options such as phytoextraction can be effective on arsenic and organochlorines such as lindane and DDT (Gregory, 2013). Remediating the dip site, at Site B, and offsite contamination up to 100 m downhill using biochar amendment and phytoextraction technologies could be costly and difficult for the property owner. Cost effective mitigation options such as fencing off the dip site and the gully up to 100 m downhill to restrict stock access would remedy immediate and long term risks from further contamination at the dip site and the gully downhill. Fencing, together with, phytoextraction such

as planting ryegrass and willow trees in the fenced area can be effective in removing contaminants, if the ryegrass and willows are eventually removed (Gregory, 2013).

At Site B, the extent and distribution of arsenic (up to 100 m), dieldrin (up to 62 m), and DDT (up to 96 m) from the dip site potentially increases the risk of arsenic and organochlorines (dieldrin and DDT) contaminating the stock water supply located in the gully, 110 m downhill from the dip site. The stock water supply should be tested for sheep dip chemicals. Relocating the stock water supply away from the gully could potentially reduce the risks of surface water contamination.

Copper contamination at the studied historical sheep dip sites did not appear to a problem with all concentrations from the preliminary samplings was well within the acceptance level of 370 mg/kg (Cavanagh, 2004a).

6.2.2 Stream sediments

Arsenic concentrations in stream sediments at Site A ranged between 0.9 mg/kg and 7.5 mg/kg upstream of the dip site. Concentrations of arsenic in stream sediments downstream of the dip site ranged from 8.2 mg/kg to 32 mg/kg in the surface sediments and up to 20 mg/kg in deep samples (up to 26 cm deep). Three stream sediments from phase I and one from phase II sampling had concentrations of arsenic above the interim sediment quality guideline (ISQG-low) of 20 mg/kg dry wt (Ministry for the Environment, 2006). The elevated arsenic was taken from the discharge zone, an area between the dip site and the confluence of streams X & Y. The extent (up to 32 mg/kg) and distribution, up to 40 m, downstream from the dip site was probably indicative of a widespread low to moderate stream sediment arsenic contamination.

In addition to arsenic contamination, the discharge zone sediment core had detectable organochlorine compounds dieldrin (0.0017 mg/kg to 0.038 mg/kg), α -BHC (0.0011 mg/kg), and β -BHC (0.0031 mg/kg). Alpha-BHC (α -BHC) and β -

BHC were detected at concentrations above the guideline (for lindane) in surface sediments (up to 6.4 cm deep). Dieldrin contamination was up to 32 cm depth. Dieldrin levels in the surface sediments (up to 13 cm) were well above the interim sediment quality guideline higher limit (ISQG-High) of 0.008 mg/kg. Dieldrin levels decreased with increasing sediment core depth. There was no evidence of sheep dip pesticides upstream of dip site at Site A.

High concentrations of arsenic and organochlorines (dieldrin, α -BHC, and β -BHC) in surface sediments were most likely due to recent sediment erosion and deposition. Arsenic and dieldrin may have had a longer period of sediment transport and deposition on stream X because they were the only pesticide found in the deep (32 cm) sediment core sample. The extent and pattern of contaminant distribution in surface sediments suggests that the pollutants may have originated from the historic sheep dip at Site A however attached to new materials on surface sediments. Contaminated sediments from the 1960's may have been removed earlier by natural causes of sediment migration downstream.

Surface migration due to natural causes such as sediment runoff and deposition are most likely to have occurred at Site A however exacerbated by stock access to the dip site and stream X. Stock access appeared to have accelerated the movement of contaminants into stream X by causing stream bank erosion at the stock crossing. Remediating stream sediment contamination would be difficult and costly for the landowner. Restricting stock access by fencing off stream X would potentially reduce the rate of erosion at the stock crossing and therefore decelerate sheep dip chemicals leaching into stream X.

The combination of moderate to significant contamination from Arsenic, dieldrin, α -BHC, and β -BHC in stream sediments downstream of a dip site located on a flood zone is of concern given the absence of such data in New Zealand's known historic sheep dip sites. Elevated stream sediment arsenic and dieldrin levels above 0.008 mg/kg are likely to cause significant adverse effects in sediments and biota with cumulative risks from dieldrin to the trophic levels of the food chain (Wong *et. al.*, 2000).

Dieldrin was not considered in the detailed study undertaken in Phase II due to analytical cost however the co-contamination pattern captured in the stream sediments may signal that dieldrin contamination is likely to be less widespread.

Assessing the risks of sediment contamination to human and environmental health can be difficult. Data collected from Site A showed that elevated arsenic was present in all (13) discharge zone sediment samples however one sample had 29.9 mg/kg which was the same area where the sediment core was taken in the preliminary sampling phase. The distribution pattern of arsenic from the discharge zone sediments suggests that stream sediments potentially have more widespread areas of low-level contamination along stream X and a small area of relatively higher-level contamination.

A sediment toxicity evaluation needed to be conducted on the area of relatively high level contamination from arsenic, dieldrin, α -BHC, and β -BHC to evaluate the extent of sediment contamination at various depths and the adverse effect it may pose to stream ecology and water quality. The interim sediment quality guidelines (ISQG) used by Australia and New Zealand do not predict bioaccumulative effects of organochlorines that may affect higher trophic levels (Burton, 2002).

The Ministry for the Environment (2006) guide for local authorities is effective for onsite assessment of historic sheep dips. The guide however lacked strategies for offsite contamination such as risk management strategies for sediment contamination. This study showed that the discharge monitoring model of upstream, downstream, and discharge point monitoring was an effective screening method of assessing sediment contamination at a sheep dip site located near a water source. The model however was not sufficient in determining the full extent and distribution patterns of contaminants along the stream channel whilst not sufficient for assessing risks to human and environmental health. This study has shown that there were low to moderate contamination however there were also areas of relatively high-level contamination which could have been easily missed. A sediment transect with equal sampling intervals should be used in combination with the monitoring method to produce a more detailed evaluation of the impacts

of contaminants on stream sediments. Grab sampling along a 40 m sediment transect was a useful method of assessing the spread of arsenic on surface sediments in this study.

6.2.3 Surface water

There was no evidence of trace element contamination of surface waters at site A. Surface water at the discharge zone had detectable concentration of total arsenic (0.0021 g/m^3) however the level is below the maximum acceptable value (MAV) of 0.01 g/m^3 for potable drinking water standards. There was no detectable arsenic in surface water upstream of the dip site. Copper was detected upstream and in the discharge zone. The levels of copper were below the drinking water standards. Organochlorine pesticides were not detected in surface waters. Low detection levels in this project were limited to a period of high flow and river level as the samples were collected in June during winter. Given the extent of sediment contamination, surface water monitoring to determine seasonal variations would potentially be valuable.

6.3 Limitations of the study

- High analytical cost was a limiting factor. More samples for organochlorine analysis on Sites A and B would have given a better understanding on the extent and spatial distribution of organochlorine contamination at Sites A.
- Systematic sampling grid was not large enough at Site B. A larger size grid would have given more information on the extent and spatial distribution in the area uphill of the dip site and the grazing area located on either side of the gully.
- Site A sampling grid was inadequate for the size of the sheep dip and coverage of the immediate vicinity. The esplanade reserve and the area north of stream X had insufficient data to extrapolate spatial distribution in the wider area.
- Insufficient surface water samples were collected due to the high analytical cost. Regular (monthly) surface water monitoring to cover winter and summer stream flows would have given more information on the impacts of discrete point source discharge on surface water quality.
- Insufficient deep soil and sediment samples were collected at both sites A and B which was limiting to information on depth migration. Further testing of deeper (>20 cm) core samples would have provided good information on depth migration and the potential for groundwater contamination at Site A.

6.4 Summary and conclusions

- Two historical sheep dips were investigated. Site A was a 6 m long pot bath with superstructure still largely in place. Site A was located on a flood plain within 7 m of a small stream (X) which leads into a larger stream (Y). Site B was an 8 m long plunge dip with the main sump and draining platform largely in place. Site B was located on a >10 degree south facing slope, adjacent to a steep gully. Sites A and B were both grazing areas. Both sites were sampled in the preliminary investigation and both sites were also investigated in detail.
- Sheep dip chemicals arsenic, benzene hexachloride, and dieldrin were present in concentrations above the interim sediment quality guidelines at site A. Similarly, elevated levels of arsenic, dieldrin, DDT (including DDT metabolites), lindane (including its by-products), and endrin were present at site B. Results varied depending on the sample locations in relation to the sheep dip. However, both sites A and B were contaminated with historic sheep dip chemicals.
- Copper contamination at the studied historical sheep dip sites did not appear to be a problem with all concentrations from the preliminary samplings was well within the acceptance level of 370 mg/kg (Cavanagh, 2004a).
- At Site A, no sheep dip contaminants were detected in adjacent surface waters during winter flows. Surface water monitoring should be undertaken all year round for better understanding of seasonal variations in contaminant discharge.
- There was no evidence of sheep dip arsenic in stream sediments upstream of the dip site at Site A.

- Downstream of Site A, sediments contained sheep dip arsenic, dieldrin, α -BHC, and β -BHC. Deposition of sediments containing sheep dip chemicals was most likely due to recent erosion and runoff events.
- There was elevated arsenic (up to 32 mg/kg) in stream sediments (up to 40 m) downstream from the dip site. Levels of arsenic at the discharge zone which is the area between the stock crossing and the confluence of stream X and stream Y, were above the interim sediment quality guideline lower limit (ISQG-Low) of 20 mg/kg.
- Dieldrin concentrations in the discharge zone sediments ranged between 0.0017 mg/kg and 0.038 mg/kg. Concentrations of dieldrin in the surface sediments (up to 13 cm) were well above the interim sediment quality guideline higher limit (ISQG-High) of 0.008 mg/kg. Dieldrin levels in the surface sediments could cause adverse effects to stream health (Wong *et al.*, 2000; Ministry for Environment, 2006).
- Stream sediments appeared to have limited areas of relatively higher-level contamination however more widespread areas of low-level contamination along stream X was likely to be a typical pattern of contamination resulting from historical sheep dip site at Site A.
- There was strong evidence of sheep dip chemicals migrating away from the sheep dip at both sites A and B. Migration downhill (up to 100 m) at site B and 40 m into stream X at site A.
- Pasture needed to be investigated for sheep dip chemical contamination.
- There is potential to further investigate the impacts of contaminated sheep dip sediments on stream health.

6.5 Recommendations

- Sheep dips located within 15 m of a stream should be regarded as a priority contaminated site for soil, sediment, and surface water investigation.
- Sheep dips located on the margins of steep slopes with an adjacent gully should be regarded as a priority site for contaminated land investigation.
- Further research needed to be undertaken on contaminated stream sediments associated with sheep dip sites to provide more information on the extent of offsite contamination, given that there are estimated to be over 10,000 sites in the Waikato region.
- A sediment toxicity evaluation needed to be conducted at sheep dip sites that have the potential to leach contaminants, such as Site A in this study, to evaluate the extent of sediment contamination at various depths and the adverse effect it may pose to stream ecology and water quality.

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Appendices

Appendix I – Preliminary Sampling Results



Hill Laboratories
BETTER TESTING BETTER RESULTS

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ANALYSIS REPORT

Page 1 of 3

Client:	Waikato Regional Council	Lab No:	1146280	SPV2
Contact:	Asaeli Tulagi	Date Registered:	17-Jun-2013	
	C/- Waikato Regional Council	Date Reported:	02-Jul-2013	
	Private Bag 3038	Quote No:	53216	
	Waikato Mail Centre	Order No:	W1601-20	
	HAMILTON 3240	Client Reference:	Sheep Dips MSc	
		Submitted By:	Asaeli Tulagi	

Amended Report

This report replaces an earlier report issued on the 25 Jun 2013 at 2:41 pm
At the client's request, OCP analyses have been added to samples AS3b & AS4b.

Sample Type: Soil						
Sample Name:	AS1a 15-Jun-2013	AS1b 15-Jun-2013	AS2a 15-Jun-2013	AS2b 15-Jun-2013	AS3a 15-Jun-2013	
Lab Number:	1146280.1	1146280.2	1146280.3	1146280.4	1146280.5	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	112	26	37	9	80
Total Recoverable Copper	mg/kg dry wt	26	24	24	23	21
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
alpha-BHC	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
beta-BHC	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
delta-BHC	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
gamma-BHC (Lindane)	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
cis-Chlordane	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
trans-Chlordane	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.04	-	< 0.04	-	< 0.04
2,4'-DDD	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
4,4'-DDD	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
2,4'-DDE	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
4,4'-DDE	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
2,4'-DDT	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
4,4'-DDT	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Dieldrin	mg/kg dry wt	< 0.010	-	< 0.010	-	0.015
Endosulfan I	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Endosulfan II	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Endosulfan sulphate	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Endrin	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Endrin Aldehyde	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Endrin ketone	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Heptachlor	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Heptachlor epoxide	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Hexachlorobenzene	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Methoxychlor	mg/kg dry wt	< 0.010	-	< 0.010	-	< 0.010
Sample Name:	AS3b 15-Jun-2013	AS4a 15-Jun-2013	AS4b 15-Jun-2013	AS5a 15-Jun-2013	AS5b 15-Jun-2013	
Lab Number:	1146280.6	1146280.7	1146280.8	1146280.9	1146280.10	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	21	109	137	11	11
Total Recoverable Copper	mg/kg dry wt	21	22	35	24	27



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The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Appendix I – Preliminary Sampling Lab Results

Sample Type: Soil						
Sample Name:	AS3b 15-Jun-2013 1146280.6	AS4a 15-Jun-2013 1146280.7	AS4b 15-Jun-2013 1146280.8	AS5a 15-Jun-2013 1146280.9	AS5b 15-Jun-2013 1146280.10	
Lab Number:						
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
alpha-BHC	mg/kg dry wt	< 0.010	0.019	0.033	< 0.010	-
beta-BHC	mg/kg dry wt	< 0.010	< 0.010	0.014	< 0.010	-
delta-BHC	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
gamma-BHC (Lindane)	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
cis-Chlordane	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
trans-Chlordane	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.04	< 0.04	< 0.04	< 0.04	-
2,4'-DDD	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
4,4'-DDD	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
2,4'-DDE	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
4,4'-DDE	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
2,4'-DDT	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
4,4'-DDT	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Dieldrin	mg/kg dry wt	< 0.010	0.078	0.104	< 0.010	-
Endosulfan I	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Endosulfan II	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Endosulfan sulphate	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Endrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Endrin Aldehyde	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Endrin ketone	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Heptachlor	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Heptachlor epoxide	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Hexachlorobenzene	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Methoxychlor	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	-
Sample Name:	ASRef1a 15-Jun-2013 1146280.11	ASRef1b 15-Jun-2013 1146280.12	ASRef2a 15-Jun-2013 1146280.13	ASRef2b 15-Jun-2013 1146280.14		
Lab Number:						
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	9	72	7	5	-
Total Recoverable Copper	mg/kg dry wt	25	27	16	12	-
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	< 0.010	-	< 0.010	-	-
alpha-BHC	mg/kg dry wt	< 0.010	-	< 0.010	-	-
beta-BHC	mg/kg dry wt	< 0.010	-	< 0.010	-	-
delta-BHC	mg/kg dry wt	< 0.010	-	< 0.010	-	-
gamma-BHC (Lindane)	mg/kg dry wt	< 0.010	-	< 0.010	-	-
cis-Chlordane	mg/kg dry wt	< 0.010	-	< 0.010	-	-
trans-Chlordane	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.04	-	< 0.04	-	-
2,4'-DDD	mg/kg dry wt	< 0.010	-	< 0.010	-	-
4,4'-DDD	mg/kg dry wt	< 0.010	-	< 0.010	-	-
2,4'-DDE	mg/kg dry wt	< 0.010	-	< 0.010	-	-
4,4'-DDE	mg/kg dry wt	< 0.010	-	< 0.010	-	-
2,4'-DDT	mg/kg dry wt	< 0.010	-	< 0.010	-	-
4,4'-DDT	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Dieldrin	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Endosulfan I	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Endosulfan II	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Endosulfan sulphate	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Endrin	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Endrin Aldehyde	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Endrin ketone	mg/kg dry wt	< 0.010	-	< 0.010	-	-

Appendix I – Preliminary Sampling Lab Results

Sample Type: Soil						
Sample Name:		ASRef1a 15-Jun-2013	ASRef1b 15-Jun-2013	ASRef2a 15-Jun-2013	ASRef2b 15-Jun-2013	
Lab Number:		1146280.11	1146280.12	1146280.13	1146280.14	
Organochlorine Pesticides Screening in Soil						
Heptachlor	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Heptachlor epoxide	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Hexachlorobenzene	mg/kg dry wt	< 0.010	-	< 0.010	-	-
Methoxychlor	mg/kg dry wt	< 0.010	-	< 0.010	-	-

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Soil			
Test	Method Description	Default Detection Limit	Samples
Environmental Solids Sample Preparation	Air dried at 35°C and sieved, <2mm fraction. Used for sample preparation. May contain a residual moisture content of 2-5%.	-	1-14
Organochlorine Pesticides Screening in Soil	Sonication extraction, SPE cleanup, dual column GC-ECD analysis (modified US EPA 8082). Tested on dried sample	-	1, 3, 5-9, 11, 13
Total Recoverable digestion	Nitric / hydrochloric acid digestion, US EPA 200.2.	-	1-14
Total Recoverable Arsenic	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, screen level. US EPA 200.2.	2 mg/kg dry wt	1-14
Total Recoverable Copper	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, screen level. US EPA 200.2.	2 mg/kg dry wt	1-14

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

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Ara Heron BSc (Tech)
Client Services Manager - Environmental Division



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ANALYSIS REPORT

Page 1 of 3

Client:	Waikato Regional Council	Lab No:	1146273	SPV2
Contact:	Asaeli Tulagi C/- Waikato Regional Council Private Bag 3038 Waikato Mail Centre HAMILTON 3240	Date Registered:	17-Jun-2013	
		Date Reported:	01-Jul-2013	
		Quote No:	53216	
		Order No:	W1601-20	
		Client Reference:	Sheep Dips MSc	
		Submitted By:	Asaeli Tulagi	

Amended Report This report replaces an earlier report issued on the 26 Jun 2013 at 4:20 pm
At the client's request, an OCP analysis has been added to sample ASW5.

Sample Type: Sediment						
Sample Name:	ASED 1/1 15-Jun-2013	ASED 1/2 15-Jun-2013	ASED 3/1 15-Jun-2013	ASED 3/2 15-Jun-2013	ASED 3/3 15-Jun-2013	
Lab Number:	1146273.1	1146273.2	1146273.5	1146273.6	1146273.7	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	0.9	7.5	32	25	18.8
Total Recoverable Copper	mg/kg dry wt	46	28	18.0	22	19.3
Organochlorine Pesticides Trace in Soil						
Aldrin	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
alpha-BHC	mg/kg dry wt	< 0.0010	< 0.0010	0.0011	< 0.0010	< 0.0010
beta-BHC	mg/kg dry wt	< 0.0010	< 0.0010	0.0031	< 0.0010	< 0.0010
delta-BHC	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
gamma-BHC (Lindane)	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
cis-Chlordane	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
trans-Chlordane	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
2,4'-DDD	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
4,4'-DDD	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
2,4'-DDE	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
4,4'-DDE	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
2,4'-DDT	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
4,4'-DDT	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Dieldrin	mg/kg dry wt	< 0.0010	< 0.0010	0.038	0.0085	0.0054
Endosulfan I	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Endosulfan II	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Endosulfan sulphate	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Endrin	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Endrin Aldehyde	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Endrin ketone	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Heptachlor	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Heptachlor epoxide	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Hexachlorobenzene	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Methoxychlor	mg/kg dry wt	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002
Sample Name:	ASED 3/4 15-Jun-2013	ASED 3/5 15-Jun-2013				
Lab Number:	1146273.8	1146273.9				
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	20	18.2	-	-	-
Total Recoverable Copper	mg/kg dry wt	19.0	19.6	-	-	-



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The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Appendix I – Preliminary Sampling Lab Results

Sample Type: Sediment						
Sample Name:		ASED 3/4 15-Jun-2013	ASED 3/5 15-Jun-2013			
Lab Number:		1146273.8	1146273.9			
Organochlorine Pesticides Trace In Soil						
Aldrin	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
alpha-BHC	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
beta-BHC	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
delta-BHC	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
gamma-BHC (Lindane)	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
cis-Chlordane	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
trans-Chlordane	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
2,4'-DDD	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
4,4'-DDD	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
2,4'-DDE	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
4,4'-DDE	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
2,4'-DDT	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
4,4'-DDT	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Dieldrin	mg/kg dry wt	0.0020	0.0017	-	-	-
Endosulfan I	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Endosulfan II	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Endosulfan sulphate	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Endrin	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Endrin Aldehyde	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Endrin ketone	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Heptachlor	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Heptachlor epoxide	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Hexachlorobenzene	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Methoxychlor	mg/kg dry wt	< 0.0010	< 0.0010	-	-	-
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.002	< 0.002	-	-	-
Sample Type: Aqueous						
Sample Name:		ASW 1 15-Jun-2013	ASW 3 15-Jun-2013	ASW 5 15-Jun-2013		
Lab Number:		1146273.19	1146273.21	1146273.23		
Individual Tests						
Total Arsenic	g/m³	< 0.0011	0.0021	-	-	-
Total Copper	g/m³	0.00098	0.00169	-	-	-
Organochlorine Pesticides Trace in water, By Liq/Liq						
Aldrin	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-
alpha-BHC	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
beta-BHC	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
delta-BHC	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
gamma-BHC (Lindane)	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
cis-Chlordane	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-
trans-Chlordane	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-
2,4'-DDD	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
4,4'-DDD	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
2,4'-DDE	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
4,4'-DDE	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
2,4'-DDT	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
4,4'-DDT	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
Dieldrin	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-
Endosulfan I	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
Endosulfan II	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
Endosulfan sulfate	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
Endrin	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-
Endrin aldehyde	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-
Endrin ketone	g/m³	< 0.000010	< 0.000010	< 0.000010	-	-
Heptachlor	g/m³	< 0.000005	< 0.000005	< 0.000005	-	-

Appendix I – Preliminary Sampling Lab Results

Sample Type: Aqueous						
Sample Name:		ASW 1 15-Jun-2013	ASW 3 15-Jun-2013	ASW 5 15-Jun-2013		
Lab Number:		1146273.19	1146273.21	1146273.23		
Organochlorine Pesticides Trace in water, By Liq/Liq						
Heptachlor epoxide	g/m ³	< 0.000005	< 0.000005	< 0.000005	-	-
Hexachlorobenzene	g/m ³	< 0.000004	< 0.000004	< 0.000004	-	-
Methoxychlor	g/m ³	< 0.000005	< 0.000005	< 0.000005	-	-
Total Chlordane [(cis+trans)*100/42]	g/m ³	< 0.000002	< 0.000002	< 0.000002	-	-

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Sediment			
Test	Method Description	Default Detection Limit	Samples
Environmental Solids Sample Preparation	Air dried at 35°C and sieved, <2mm fraction. Used for sample preparation. May contain a residual moisture content of 2-5%.	-	1-2, 5-9
Organochlorine Pesticides Trace in Soil	Sonication extraction, SPE cleanup, GPC cleanup (if required), dual column GC-ECD analysis. Tested on dried sample	-	1-2, 5-9
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2.	-	1-2, 5-9
Total Recoverable Arsenic	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.2 mg/kg dry wt	1-2, 5-9
Total Recoverable Copper	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.2 mg/kg dry wt	1-2, 5-9

Sample Type: Aqueous			
Test	Method Description	Default Detection Limit	Samples
Organochlorine Pesticides Trace in water, By Liq/Liq	Liquid / liquid extraction, SPE (if required), dual column GC-ECD analysis	-	19, 21, 23
Total Digestion	Boiling nitric acid digestion. APHA 3030 E 22 nd ed. 2012 (modified).	-	19, 21
Total Arsenic	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 21 st ed. 2005 / US EPA 200.8.	0.0011 g/m ³	19, 21
Total Copper	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 21 st ed. 2005 / US EPA 200.8.	0.00053 g/m ³	19, 21

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

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Ara Heron BSc (Tech)
Client Services Manager - Environmental Division



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ANALYSIS REPORT

Page 1 of 5

Client:	Waikato Regional Council	Lab No:	1148415	SPv4
Contact:	Asaeli Tulagi	Date Registered:	24-Jun-2013	
	C/- Waikato Regional Council	Date Reported:	05-Nov-2013	
	Private Bag 3038	Quote No:	53216	
	Waikato Mail Centre	Order No:		
	HAMILTON 3240	Client Reference:	Sheep Dips MSc	
		Submitted By:	Asaeli Tulagi	

Amended Report

This report replaces an earlier report issued on the 01 Oct 2013 at 3:02 pm
OCP analyses have been added to samples 1148415.21 to .26 at the
request of the client.

Sample Type: Soil						
Sample Name:	BS1a 22-Jun-2013	BS1b 22-Jun-2013	BS2a 22-Jun-2013	BS2b 22-Jun-2013	BS3a 22-Jun-2013	
Lab Number:	1148415.1	1148415.2	1148415.3	1148415.4	1148415.5	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	93	73	210	300	102
Total Recoverable Copper	mg/kg dry wt	73	31	31	32	38
Organochlorine Pesticides Screening In Soil						
Aldrin	mg/kg dry wt	-	-	< 0.010	< 0.010	-
alpha-BHC	mg/kg dry wt	-	-	0.053	0.059	-
beta-BHC	mg/kg dry wt	-	-	0.073	0.138	-
delta-BHC	mg/kg dry wt	-	-	< 0.010	0.010	-
gamma-BHC (Lindane)	mg/kg dry wt	-	-	0.016	0.021	-
cis-Chlordane	mg/kg dry wt	-	-	< 0.010	< 0.010	-
trans-Chlordane	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Total Chlordane [(cis+trans) 100/42]	mg/kg dry wt	-	-	< 0.04	< 0.04	-
2,4'-DDD	mg/kg dry wt	-	-	< 0.010	< 0.010	-
4,4'-DDD	mg/kg dry wt	-	-	0.017	0.021	-
2,4'-DDE	mg/kg dry wt	-	-	< 0.010	< 0.010	-
4,4'-DDE	mg/kg dry wt	-	-	0.104	0.140	-
2,4'-DDT	mg/kg dry wt	-	-	< 0.010	< 0.010	-
4,4'-DDT	mg/kg dry wt	-	-	0.032	0.044	-
Dieldrin	mg/kg dry wt	-	-	0.45	0.51	-
Endosulfan I	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Endosulfan II	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Endosulfan sulphate	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Endrin	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Endrin Aldehyde	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Endrin ketone	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Heptachlor	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Heptachlor epoxide	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Hexachlorobenzene	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Methoxychlor	mg/kg dry wt	-	-	< 0.010	< 0.010	-
Sample Name:	BS3b 22-Jun-2013	BS4a 22-Jun-2013	BS4b 22-Jun-2013	BS5a 22-Jun-2013	BS5b 22-Jun-2013	
Lab Number:	1148415.6	1148415.7	1148415.8	1148415.9	1148415.10	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	99	230	450	99	20
Total Recoverable Copper	mg/kg dry wt	34	64	79	91	102



This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised.
The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Appendix I – Preliminary Sampling Lab Results

Sample Type: Soil						
Sample Name:		BS3b 22-Jun-2013	BS4a 22-Jun-2013	BS4b 22-Jun-2013	BS5a 22-Jun-2013	BS5b 22-Jun-2013
Lab Number:		1148415.6	1148415.7	1148415.8	1148415.9	1148415.10
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
alpha-BHC	mg/kg dry wt	-	0.077	0.136	< 0.010	-
beta-BHC	mg/kg dry wt	-	0.113	0.22	< 0.010	-
delta-BHC	mg/kg dry wt	-	0.013	0.028	< 0.010	-
gamma-BHC (Lindane)	mg/kg dry wt	-	0.016	0.040	< 0.010	-
cis-Chlordane	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
trans-Chlordane	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	-	< 0.04	< 0.04	< 0.04	-
2,4'-DDD	mg/kg dry wt	-	0.067	0.145	< 0.010	-
4,4'-DDD	mg/kg dry wt	-	0.045	0.123	< 0.010	-
2,4'-DDE	mg/kg dry wt	-	< 0.010	0.016	< 0.010	-
4,4'-DDE	mg/kg dry wt	-	0.44	1.20	0.077	-
2,4'-DDT	mg/kg dry wt	-	0.029	0.165	< 0.010	-
4,4'-DDT	mg/kg dry wt	-	0.122	0.74	0.018	-
Dieldrin	mg/kg dry wt	-	1.62	3.5	0.035	-
Endosulfan I	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Endosulfan II	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Endosulfan sulphate	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Endrin	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Endrin Aldehyde	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Endrin ketone	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Heptachlor	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Heptachlor epoxide	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Hexachlorobenzene	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Methoxychlor	mg/kg dry wt	-	< 0.010	< 0.010	< 0.010	-
Sample Name:		BS6a 22-Jun-2013	BS6b 22-Jun-2013	BS7a 22-Jun-2013	BS7b 22-Jun-2013	BS8a 22-Jun-2013
Lab Number:		1148415.11	1148415.12	1148415.13	1148415.14	1148415.15
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	98	107	88	63	< 2
Total Recoverable Copper	mg/kg dry wt	53	61	42	42	58
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
alpha-BHC	mg/kg dry wt	< 0.010	0.029	< 0.010	-	-
beta-BHC	mg/kg dry wt	< 0.010	0.011	< 0.010	-	-
delta-BHC	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
gamma-BHC (Lindane)	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
cis-Chlordane	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
trans-Chlordane	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.04	< 0.04	< 0.04	-	-
2,4'-DDD	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
4,4'-DDD	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
2,4'-DDE	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
4,4'-DDE	mg/kg dry wt	0.127	0.22	0.129	-	-
2,4'-DDT	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
4,4'-DDT	mg/kg dry wt	0.023	0.037	0.030	-	-
Dieldrin	mg/kg dry wt	0.027	0.021	< 0.010	-	-
Endosulfan I	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Endosulfan II	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Endosulfan sulphate	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Endrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Endrin Aldehyde	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Endrin ketone	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-

Appendix I – Preliminary Sampling Lab Results

Sample Type: Soil						
Sample Name:	BS6a 22-Jun-2013	BS6b 22-Jun-2013	BS7a 22-Jun-2013	BS7b 22-Jun-2013	BS8a 22-Jun-2013	
Lab Number:	1148415.11	1148415.12	1148415.13	1148415.14	1148415.15	
Organochlorine Pesticides Screening in Soil						
Heptachlor	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Heptachlor epoxide	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Hexachlorobenzene	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Methoxychlor	mg/kg dry wt	< 0.010	< 0.010	< 0.010	-	-
Sample Name:	BS8b 22-Jun-2013	BS9a 22-Jun-2013	BS9b 22-Jun-2013	BS10a 22-Jun-2013	BS10b 22-Jun-2013	
Lab Number:	1148415.16	1148415.17	1148415.18	1148415.19	1148415.20	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	< 2	260	122	350	640
Total Recoverable Copper	mg/kg dry wt	55	52	60	64	57
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	-	< 0.010	-	-	< 0.010
alpha-BHC	mg/kg dry wt	-	< 0.010	-	-	0.27
beta-BHC	mg/kg dry wt	-	< 0.010	-	-	0.56
delta-BHC	mg/kg dry wt	-	< 0.010	-	-	0.039
gamma-BHC (Lindane)	mg/kg dry wt	-	< 0.010	-	-	0.061
cis-Chlordane	mg/kg dry wt	-	< 0.010	-	-	< 0.010
trans-Chlordane	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	-	< 0.04	-	-	< 0.04
2,4'-DDD	mg/kg dry wt	-	< 0.010	-	-	0.055
4,4'-DDD	mg/kg dry wt	-	< 0.010	-	-	0.108
2,4'-DDE	mg/kg dry wt	-	< 0.010	-	-	< 0.010
4,4'-DDE	mg/kg dry wt	-	0.033	-	-	0.49
2,4'-DDT	mg/kg dry wt	-	< 0.010	-	-	0.21
4,4'-DDT	mg/kg dry wt	-	0.018	-	-	0.88
Dieldrin	mg/kg dry wt	-	0.054	-	-	8.6
Endosulfan I	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Endosulfan II	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Endosulfan sulphate	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Endrin	mg/kg dry wt	-	< 0.010	-	-	0.127
Endrin Aldehyde	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Endrin ketone	mg/kg dry wt	-	< 0.010	-	-	0.039
Heptachlor	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Heptachlor epoxide	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Hexachlorobenzene	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Methoxychlor	mg/kg dry wt	-	< 0.010	-	-	< 0.010
Sample Name:	BSRef1a 22-Jun-2013	BSRef1b 22-Jun-2013	BSRef2a 22-Jun-2013	BSRef2b 22-Jun-2013	BSRef3a 22-Jun-2013	
Lab Number:	1148415.21	1148415.22	1148415.23	1148415.24	1148415.25	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	8	8	3	3	7
Total Recoverable Copper	mg/kg dry wt	33	32	25	38	24
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
alpha-BHC	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
beta-BHC	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
delta-BHC	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
gamma-BHC (Lindane)	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
cis-Chlordane	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
trans-Chlordane	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
2,4'-DDD	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
4,4'-DDD	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010

Appendix I – Preliminary Sampling Lab Results

Sample Type: Soil						
Sample Name:		BSRef1a 22-Jun-2013	BSRef1b 22-Jun-2013	BSRef2a 22-Jun-2013	BSRef2b 22-Jun-2013	BSRef3a 22-Jun-2013
Lab Number:		1148415.21	1148415.22	1148415.23	1148415.24	1148415.25
Organochlorine Pesticides Screening in Soil						
2,4'-DDE	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
4,4'-DDE	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
2,4'-DDT	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
4,4'-DDT	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Dieldrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Endosulfan I	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Endosulfan II	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Endosulfan sulphate	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Endrin	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Endrin Aldehyde	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Endrin ketone	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Heptachlor	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Heptachlor epoxide	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Hexachlorobenzene	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Methoxychlor	mg/kg dry wt	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
Sample Name:		BSRef3b 22-Jun-2013				
Lab Number:		1148415.26				
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	7	-	-	-	-
Total Recoverable Copper	mg/kg dry wt	21	-	-	-	-
Organochlorine Pesticides Screening in Soil						
Aldrin	mg/kg dry wt	< 0.010	-	-	-	-
alpha-BHC	mg/kg dry wt	< 0.010	-	-	-	-
beta-BHC	mg/kg dry wt	< 0.010	-	-	-	-
delta-BHC	mg/kg dry wt	< 0.010	-	-	-	-
gamma-BHC (Lindane)	mg/kg dry wt	< 0.010	-	-	-	-
cis-Chlordane	mg/kg dry wt	< 0.010	-	-	-	-
trans-Chlordane	mg/kg dry wt	< 0.010	-	-	-	-
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.04	-	-	-	-
2,4'-DDD	mg/kg dry wt	< 0.010	-	-	-	-
4,4'-DDD	mg/kg dry wt	< 0.010	-	-	-	-
2,4'-DDE	mg/kg dry wt	< 0.010	-	-	-	-
4,4'-DDE	mg/kg dry wt	< 0.010	-	-	-	-
2,4'-DDT	mg/kg dry wt	< 0.010	-	-	-	-
4,4'-DDT	mg/kg dry wt	< 0.010	-	-	-	-
Dieldrin	mg/kg dry wt	< 0.010	-	-	-	-
Endosulfan I	mg/kg dry wt	< 0.010	-	-	-	-
Endosulfan II	mg/kg dry wt	< 0.010	-	-	-	-
Endosulfan sulphate	mg/kg dry wt	< 0.010	-	-	-	-
Endrin	mg/kg dry wt	< 0.010	-	-	-	-
Endrin Aldehyde	mg/kg dry wt	< 0.010	-	-	-	-
Endrin ketone	mg/kg dry wt	< 0.010	-	-	-	-
Heptachlor	mg/kg dry wt	< 0.010	-	-	-	-
Heptachlor epoxide	mg/kg dry wt	< 0.010	-	-	-	-
Hexachlorobenzene	mg/kg dry wt	< 0.010	-	-	-	-
Methoxychlor	mg/kg dry wt	< 0.010	-	-	-	-
Sample Type: Sediment						
Sample Name:		BSed1/1 22-Jun-2013	BSed1/2 22-Jun-2013	BSed1/3 22-Jun-2013	BSed1/4 22-Jun-2013	
Lab Number:		1148415.27	1148415.28	1148415.29	1148415.30	
Individual Tests						
Total Recoverable Arsenic	mg/kg dry wt	4	5	5	5	-

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Soil			
Test	Method Description	Default Detection Limit	Samples
Environmental Solids Sample Preparation	Air dried at 35°C and sieved, <2mm fraction. Used for sample preparation. May contain a residual moisture content of 2-5%.	-	1-30
Organochlorine Pesticides Screening in Soil	Sonication extraction, SPE cleanup, dual column GC-ECD analysis (modified US EPA 8082). Tested on dried sample	-	3-4, 7-9, 11-13, 17, 20-26
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2.	-	1-30
Total Recoverable Arsenic	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, screen level. US EPA 200.2.	2 mg/kg dry wt	1-30
Total Recoverable Copper	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, screen level. US EPA 200.2.	2 mg/kg dry wt	1-26

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

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Graham Corban MSc Tech (Hons)
Client Services Manager - Environmental Division

Appendix II – XRF Detection Limits

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HANDHELD XRF ANALYZERS

Limits of Detection

Low-Density Sample Types — (soils, powders, liquids)																					
<div><div>Not Measured</div><div><1 %</div><div><0.5 %</div><div><200 ppm</div><div><50 ppm</div><div><20 ppm</div><div><10 ppm</div><div><5 ppm</div></div>																					
H 1																		He 2			
IIA																IIIA	IVA	VA	VIA	VIIA	
0.05 Li 3	0.11 Be 4															0.18 B 5	0.26 C 6	0.39 N 7	0.52 O 8	0.68 F 9	0.85 Ne 10
1.04 Na 11	1.07 Mg 12															1.48 Al 13	1.58 Si 14	1.74 P 15	1.84 S 16	2.01 Cl 17	2.14 Ar 18
3.31 K 19	3.52 Ca 20	3.69 Sc 21	4.01 Ti 22	4.46 V 23	4.91 Cr 24	5.41 Mn 25	5.96 Fe 26	6.49 Co 27	7.08 Ni 28	7.68 Cu 29	8.26 Zn 30	8.91 Ga 31	9.57 Ge 32	10.36 As 33	11.22 Se 34	12.16 Br 35	13.13 Kr 36				
3.64 Rb 37	3.92 Sr 38	4.04 Y 39	4.36 Zr 40	4.74 Nb 41	5.14 Mo 42	5.59 Tc 43	6.09 Ru 44	6.61 Rh 45	7.16 Pd 46	7.76 Ag 47	8.37 Cd 48	9.01 In 49	9.68 Sn 50	10.37 Sb 51	11.10 Te 52	11.87 I 53	12.68 Xe 54				
3.89 Cs 55	4.15 Ba 56	4.29 La 57	4.64 Ce 58	5.04 Pr 59	5.48 Nd 60	5.96 Pm 61	6.48 Sm 62	7.03 Eu 63	7.62 Gd 64	8.23 Tb 65	8.87 Dy 66	9.54 Ho 67	10.24 Er 68	10.97 Tm 69	11.74 Yb 70	12.54 Lu 71					
8.81 Fr 87	9.47 Ra 88															10.56 At 85	11.22 Rn 86				
12.01 Lanthanides 57-71																					
12.01 La 57	13.44 Ce 58	14.72 Pr 59	15.73 Nd 60	16.89 Pm 61	18.07 Sm 62	19.36 Eu 63	20.72 Gd 64	22.17 Tb 65	23.72 Dy 66	25.38 Ho 67	27.10 Er 68	28.93 Tm 69	30.94 Yb 70	33.12 Lu 71							
13.29 Ac 89	13.89 Th 90	14.51 Pa 91	15.21 U 92	15.91 Np 93	16.69 Pu 94	17.50 Am 95	18.42 Cm 96	19.36 Bk 97	20.33 Cf 98	21.33 Es 99	22.36 Fm 100	23.42 Md 101	24.51 No 102	25.62 Lr 103							
Actinides 89-103																					

Alloy Analysis:
Elements detected: Magnesium (Mg, Z=12) through Sulfur (S, Z=16) and Titanium (Ti, Z=22) through Plutonium (Pu, Z=94).

Please see separate Alloy Analysis LOD Specifications.



Detection limits are a function of testing time, sample matrix and presence of interfering elements. Detection limits are estimates based on 1-2 minutes test times and detection confidence of 3σ (99.7% confidence). Interference-free detection limits are intended as guidelines; please contact Olympus Innov-X to discuss your specific application.

PHOTON ENERGIES, IN ELECTRON VOLTS, OF PRINCIPAL K- AND L-SHELL EMISSION LINES

Element	Symbol	Atomic #	K _{α1}	K _{β1}	L _{α1}	L _{β1}
Actinium	Ac	89	90.88	102.85	12.65	15.71
Aluminum	Al	13	1.49	1.56	0	0
Antimony	Sb	51	26.36	29.73	3.6	3.84
Argon	Ar	18	2.96	3.19	0	0
Arsenic	As	33	10.54	11.73	1.28	1.32
Astatine	At	85	81.52	92.3	11.43	13.88
Barium	Ba	56	32.19	36.38	4.47	4.83
Beryllium	Be	4	0.11	0	0	0
Bismuth	Bi	83	77.11	87.34	10.84	13.02
Boron	B	5	0.18	0	0	0
Bromine	Br	35	11.92	13.29	1.48	1.53
Cadmium	Cd	48	23.17	26.1	3.13	3.32
Calcium	Ca	20	3.69	4.01	0.34	0.34
Carbon	C	6	0.28	0	0	0
Cerium	Ce	58	34.72	39.26	4.84	5.26
Cesium	Cs	55	30.97	34.99	4.29	4.62
Chlorine	Cl	17	2.62	2.82	0	0
Chromium	Cr	24	5.41	5.95	0.57	0.58
Cobalt	Co	27	6.93	7.65	0.78	0.79
Copper	Cu	29	8.05	8.91	0.93	0.95
Dysprosium	Dy	66	46	52.12	6.5	7.25
Erbium	Er	68	49.13	55.68	6.95	7.81
Europium	Eu	63	41.54	47.04	5.85	6.46
Fluorine	F	9	0.68	0	0	0
Francium	Fr	87	86.1	97.47	12.03	14.77
Gadolinium	Gd	64	43	48.7	6.06	6.71
Gallium	Ga	31	9.25	10.26	1.1	1.12
Germanium	Ge	32	9.89	10.98	1.19	1.22
Gold	Au	79	68.8	77.98	9.71	11.44
Hafnium	Hf	72	55.79	63.23	7.9	9.02
Holmium	Ho	67	47.55	53.88	6.72	7.53
Indium	In	49	24.21	27.28	3.29	3.49
Iodine	I	53	28.61	32.29	3.94	4.22
Iridium	Ir	77	64.9	73.56	9.18	10.71
Iron	Fe	26	6.4	7.06	0.71	0.72
Krypton	Kr	36	12.65	14.11	1.59	1.64
Lanthanum	La	57	33.44	37.8	4.65	5.04
Lead	Pb	82	74.97	84.94	10.55	12.61
Lithium	Li	3	0.05	0	0	0
Lutetium	Lu	71	54.07	61.28	7.66	8.71
Magnesium	Mg	12	1.25	1.3	0	0
Manganese	Mn	25	5.9	6.49	0.64	0.65
Mercury	Hg	80	70.82	80.25	9.99	11.82
Molybdenum	Mo	42	17.48	19.61	2.29	2.39
Neodymium	Nd	60	37.36	42.27	5.23	5.72

Element	Symbol	Atomic #	K _{α1}	K _{β1}	L _{α1}	L _{β1}
Neon	Ne	10	0.85	0	0	0
Nickel	Ni	28	7.48	8.26	0.85	0.87
Niobium	Nb	41	16.62	18.62	2.17	2.26
Nitrogen	N	7	0.39	0	0	0
Osmium	Os	76	63	71.41	8.91	10.36
Oxygen	O	8	0.52	0	0	0
Palladium	Pd	46	21.18	23.82	2.84	2.99
Phosphorus	P	15	2.01	2.14	0	0
Platinum	Pt	78	66.83	75.75	9.44	11.07
Polonium	Po	84	79.29	89.8	11.13	13.45
Potassium	K	19	3.31	3.59	0	0
Praseodymium	Pr	59	36.03	40.75	5.03	5.49
Promethium	Pm	61	38.72	43.83	5.43	5.96
Protactinium	Pa	91	95.87	108.43	13.29	16.7
Radium	Ra	88	88.47	100.13	12.34	15.24
Radon	Rn	86	83.78	94.87	11.73	14.32
Rhenium	Re	75	61.14	69.31	8.65	10.01
Rhodium	Rh	45	20.22	22.72	2.7	2.83
Rubidium	Rb	37	13.4	14.96	1.69	1.75
Ruthenium	Ru	44	19.28	21.66	2.56	2.68
Samarium	Sm	62	40.12	45.41	5.64	6.21
Scandium	Sc	21	4.09	4.46	0.4	0.4
Selenium	Se	34	11.22	12.5	1.38	1.42
Silicon	Si	14	1.74	1.84	0	0
Silver	Ag	47	22.16	24.94	2.98	3.15
Sodium	Na	11	1.04	1.07	0	0
Strontium	Sr	38	14.17	15.84	1.81	1.87
Sulfur	S	16	2.31	2.46	0	0
Tantalum	Ta	73	57.53	65.22	8.15	9.34
Technetium	Tc	43	18.37	20.62	2.42	2.54
Tellurium	Te	52	27.47	31	3.77	4.03
Terbium	Tb	65	44.48	50.38	6.27	6.98
Thallium	Tl	81	72.87	82.58	10.27	12.21
Thorium	Th	90	93.35	105.61	12.97	16.2
Thulium	Tm	69	50.74	57.52	7.18	8.1
Tin	Sn	50	25.27	28.49	3.44	3.66
Titanium	Ti	22	4.51	4.93	0.45	0.46
Tungsten	W	74	59.32	67.24	8.4	9.67
Uranium	U	92	98.44	111.3	13.61	17.22
Vanadium	V	23	4.95	5.43	0.51	0.52
Xenon	Xe	54	29.78	33.62	4.11	4.42
Ytterbium	Yb	70	52.39	59.37	7.42	8.4
Yttrium	Y	39	14.96	16.74	1.92	2
Zinc	Zn	30	8.64	9.57	1.01	1.03
Zirconium	Zr	40	15.78	17.67	2.04	2.12

