PATTLE DELAMORE PARTNERS LTD

DIOXIN CONCENTRATIONS IN RESIDENTIAL SOIL, PARITUTU, NEW PLYMOUTH

Dioxin Concentrations in Residential Soil, Paritutu, New Plymouth

Prepared for
The Ministry for the Environment
and
The Institute of Environmental Science and Research Limited

26 September 2002

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Quality Control Sheet

TITLE **Dioxin Concentrations in Residential Soil, Paritutu, New Plymouth**

CLIENT The Ministry for the Environment
And
The Institute of Environmental Science and Research Limited

VERSION Final

DATE 26 September 2002

JOB REFERENCE WJ366

SOURCE FILE(S) WJ366 Report Final.doc

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Limitations: This report has been prepared on the basis of visual observations, and the testing of 47 samples for 2,3,7,8-TCDD and full dioxin profiles. This information has been used to comment on the soil conditions, but these conditions cannot be guaranteed. The information applies to the times of sampling (28 May to 5 June 2002). With time the site conditions could change so that the reported assessment and conclusions are no longer valid.

The report has been prepared for the Ministry for the Environment and the Institute of Environmental Science and Research Limited, according to their instructions, for the particular objectives described in the report. Any reliance on this report by any other party shall be at such party's sole risk.

Table of Contents

SECTION PAGE

Tables

Figures

Appendices:

Ministry for the Environment
Manatu Mo Te Taiao

MINISTRY OF HEALTH
MANATU HAUORA

Environment and Health Statement

Low Levels of Dioxin in Residential Soils at Paritutu in New Plymouth

- **Soils from residences at Paritutu contained less than thirty million millionths of a part of dioxin. The Ministry for the Environment and the Ministry of Health see the risk for current and future residents to be so low as to be negligible.**
- **No clean up of people's lawns, gardens or public use areas is necessary.**
- **This study is a comprehensive assessment of dioxin levels in soil, and no further study of this type is needed.**

Introduction

Pattle Delamore Partners Limited has released a report of a study of the levels of dioxin (more correctly 2,3,7,8-tetrachlorodibenzo-p-dioxin) in soil at residential properties in the New Plymouth suburb of Paritutu.

This Environment and Health Statement explains what the measurements mean for people living in the area.

Background to the study

There have been longstanding community issues with the history of dioxin emissions from the former Ivon Watkins-Dow, now Dow AgroSciences, chemical plant located in Paritutu. There was uncertainty over dioxin levels in the environment.

An initiative to measure the level of dioxin in residential soil was presented to community groups at a meeting of the Paritutu Community Health Liaison Group on 7 March 2002. This proposal received universal support from those present.

How the study was carried out

In February 2002, the Ministry for the Environment appointed the Institute of Environmental Science and Research Limited and Pattle Delamore Partners to carry out the soil study. During April and May, consultation was held with the community over how best to undertake the study. A study proposal was then prepared incorporating, as far as practicable, the views of the community expressed during this consultation. This included the collection of additional soil samples at specific locations identified by the Dioxin Investigation Network.

Sampling was carried out in the last week of May and the first week of June. Forty seven samples were collected from 35 residential properties and public areas. Samples were taken from lawns (at two different depths for some sites), gardens and open spaces. A representative from the Dioxin Investigation Network accompanied Pattle Delamore Partners for all but one of the sites sampled. A second set of samples were taken from each site and provided to the Dioxin Investigation Network.

Chemical analysis was carried out by AgriQuality New Zealand Limited, using a method approved by the United States Environmental Protection Agency for measuring dioxin in soil. Two samples were also analysed by Pace Analytical Services Inc., an independent laboratory in the United States, following discussions and agreement with the Dioxin Investigation Network.

What the study found

This comprehensive study found that there were detectable levels of dioxin in the soils at all sites investigated. The low levels measured mean that any risk to a person's health is negligible.

Concentrations tend to be highest close to the Dow AgroSciences plant, and drop off rapidly within 800 to 1000 metres from the plant. Concentrations to the east of the Dow plant, towards Mount Moturoa Domain, are higher than to the south of the plant. This is consistent with the prevailing winds in the area.

Dioxin was present in concentrations measured in nanograms per kilogram (ng/kg). One nanogram per kilogram means one gram of dioxin in every million tonnes of soil.

On residential properties nearest to the Dow plant, soil dioxin concentrations were typically in the range 5 to 15 ng/kg of soil, falling to a range of 1 to 5 ng/kg further out. One sample had a concentration of 27 ng/kg. There was 92 ng/kg measured at a non-residential site, on the west-facing slope of Mount Moturoa Domain.

Generally there was little difference between soil dioxin levels in lawn areas compared with gardens on the same property. Typically lawn areas tended to be marginally higher. Similarly, there was little difference in soil dioxin levels between surface soils (that is, between 0 and 7.5 cm deep) and soils sampled at a depth between 7.5 and 15 cm.

A summary of results for the 47 soil samples is shown in Figure 1.

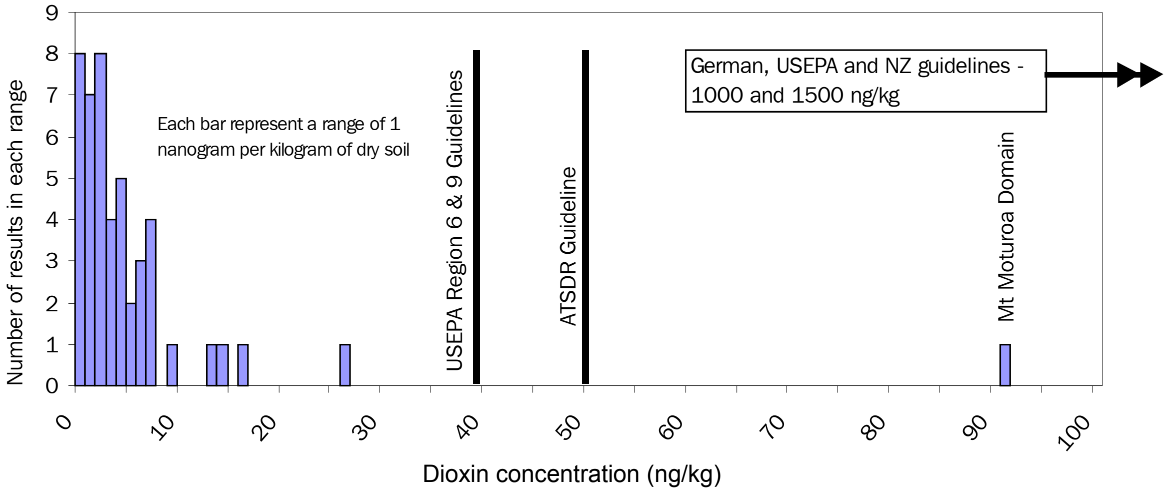

Figure 1. Soil dioxin concentrations, with New Zealand and international guidelines

This figure shows the number of soil samples that had dioxin concentrations within a certain range. For example, there were seven soil samples having a concentration within the range 1–2 ng/kg, and one soil sample having a concentration within the range 9–10 ng/kg. The black vertical lines represent the adjusted (see text) United States Environmental Protection Agency (USEPA) Region 6 and Region 9 guidelines, and the Agency for Toxic Substances and Disease Registry (ATSDR) guideline value for dioxin in residential soil. The guideline values from New Zealand, Germany and the federal United States Environmental Protection Agency are off the scale to the extreme right hand side.

A previous study by the Ministry for the Environment, published in 1998, did not find dioxin in urban soils in any other parts of the country. Although the current study of residential soils consistently measured low levels of dioxin in Paritutu, these levels are not considered to be a health concern.

Our assessment of the results

Guidelines designed to protect people's health from dioxin in residential soil have been developed in New Zealand, Germany, the United States, and in other countries.

In all cases, the levels of dioxin in residential soil in Paritutu are below the New Zealand and German criteria, and are below the guidelines set by the United States Environmental Protection Agency and the United States Agency for Toxic Substances and Disease Registry. These levels are also below guidelines set by local United States Environmental Protection Agency offices (when adjusted to account for differences in their method of derivation compared to the New Zealand guidelines), including those set by United States Environmental Protection Agency Region 6 and Region 9.

Consequently, the levels of dioxin measured in soil in residences at Paritutu are not considered to be a health concern.

The comparison of the dioxin levels measured in this study with these guidelines is illustrated in Figure 1.

The result for Mount Motorua Domain is above the “trigger” level of the United States Environmental Protection Agency (Region 6 and Region 9) and the United States Agency for Toxic Substances and Disease Registry guidelines. “Trigger” levels, if exceeded, trigger a more detailed assessment, rather than being a level at which health effects will occur. When the result for the Domain is considered in the context of how a person may be exposed to dioxin (for example, how long a person may spend on the Domain on any day), it is concluded that, at the level of dioxin measured in this study, there is a negligible health risk to recreational users of the Domain.

We can be confident with the results

There are several ways in which the quality of the data from this study can be measured. One way is to compare the results from the New Zealand laboratory with those obtained from the United States laboratory. Here we find that the levels of 2,3,7,8-TCDD measured by these two independent laboratories are very similar. This, and other quality assurance procedures that were implemented throughout the sampling and analytical work, tells us that we can be very confident about the quality of the information and the findings of this study.

Is health at risk and is a clean-up necessary?

The Ministry for the Environment and the Ministry of Health consider that the concentration of dioxin in the soil is so low that there is negligible health risk to current and future Paritutu residents.

Dioxin contaminated land can only present a health risk if there is actual exposure to the contaminant. People can be exposed by eating contaminated soil or foods (such as meat, milk or eggs) from animals raised on the contaminated land and, to a lesser extent, by eating homegrown vegetables, breathing in dust, and skin contact with contaminated soil. If exposure does occur, many factors, such as how much dioxin the person is exposed to and for how long, influence whether this actually affects health.

Given the study design and the consistency of the results, the Ministry for the Environment and the Ministry of Health believe that these soil results are representative of residential properties in Paritutu. Therefore, we consider that the risk to the health of current and future Paritutu residents from dioxin contaminated soil is negligible.

Because dioxin is very stable in the environment, levels measured now are considered to be an accurate reflection of historical levels when the Dow plant was manufacturing pesticides.

The community has many criteria for deciding if a clean up is required. If the levels of dioxin found in the soil are used as the yardstick, these levels do not indicate a requirement for clean up.

Do further studies need to be undertaken?

The current study covered a broad cross-section of residential properties in Paritutu. It is the single largest environmental study for dioxin of residential properties undertaken anywhere in New Zealand. We consider that this study provides comprehensive information on dioxin soil levels throughout Paritutu. The findings of this study support the results of earlier measurements of dioxin in residential soils in Paritutu, which have been made over the past decade. No further study of this type is warranted.

The Government continues to fund other studies on dioxin exposure and possible health effects in New Plymouth. A serum survey to determine the current amount of dioxin stored in the body of potentially highly exposed Paritutu residents is in the planning phases. Planning has taken longer than anticipated, but it is important that the methodology for this serum study is as robust as available information permit. Completion of the planning for the serum study has also been dependent on publication of the results of the Ministry for the Environment's soil study, so that these results can be used to assist in deciding how best the serum study should be carried out.

How to obtain more information

Further information on this study is available to all members of the public.

From libraries and councils: A copy of the Pattle Delamore Partners report and of this Environment and Health Statement has been provided to local libraries in Paritutu, and to the central New Plymouth library. In addition, a copy of the report has been provided to the Taranaki District Health Board's public health service, the New Plymouth District Council and the Taranaki Regional Council.

From the internet: A copy of the Pattle Delamore Partners report, the Environment and Health Statement and all other relevant documents (for example, the initial study design) are available from the Ministry for the Environment's web site at www.mfe.govt.nz.

If you seek further information, please write to:

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Executive Summary

Introduction

Agricultural chemicals, including the herbicide 2,4,5-trichlorphenoxyacetic acid (2,4,5-T), were historically manufactured in a plant, currently owned by Dow AgroSciences Ltd (Dow), located in the New Plymouth suburb of Paritutu. Dioxin, or more precisely 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), was a manufacturing contaminant of 2,4,5-T. 2,3,7,8-TCDD is recognised as a human carcinogen, and may cause a variety of other adverse health effects.

Concern has been expressed within the community that dioxin may be present in the soil within residential areas of Paritutu, as a result of air emissions from the Dow plant during the manufacture of 2,4,5-T, between 1960 and 1987. 2,3,7,8-TCDD is a very stable compound and could be expected to remain in the soil for many decades. Earlier soil studies have shown 2,3,7,8-TCDD in and around the plant, but a comprehensive survey of residential soils had not been carried out prior to this study.

Pattle Delamore Partners Limited (PDP) was engaged to carry out soil sampling and analysis for dioxin in residential areas of Paritutu, on behalf of the Ministry for the Environment (MfE). The objective of the work was to measure dioxin concentrations in residential properties close to the Dow plant, establishing soil concentrations both laterally and with distance from the plant. The assumptions of the study were that:

- The former IWD plant was the principal source of 2,3,7,8-TCDD present in the soil in the area.
- Contamination occurred via discharges to air with subsequent deposition over the residential neighbourhood.

This report sets out the background to the study, describes the study design, sampling protocols and fieldwork, and presents the concentrations of dioxins measured. The results are compared with previous soil sampling carried out in the area, with studies elsewhere in New Zealand, and with New Zealand and overseas guidelines for 2,3,7,8-TCDD in soil.

Community Consultation

Community consultation was an important part of this study. During the preparation of the study design, the Paritutu Community Health Liaison Group was consulted, and a draft version of the study design was provided to local action groups and central and local government agencies. The Dioxin Investigation Network (DIN) was consulted at key stages of the laboratory analysis programme.

Property owners and/or occupiers were approached individually to obtain information about their property, to explain the sampling and obtain their consent.

Property occupiers and owners received a copy of their individual results prior to the release of this report. Simultaneous with the release of this report a further letter drop was made to all Paritutu residents, providing a summary of findings and a copy of the Environment and Health statement (also bound into this report), jointly prepared by the Ministry for the Environment and the Ministry of Health. Copies of the report have been deposited in public libraries in the area.

Study Design and Sampling

The study focused on residential properties to the east and south of the Dow plant, but a small number of residential properties to the north-east of the factory were also sampled. The study design considered areas of likely maximum dioxin deposition through a review of meteorological data, topography, age and location of residential areas and results of the earlier soil investigations. However, given the considerable community interest in Paritutu, it was important that the study considered not just the likely areas of maximum deposition, but also the broader residential areas around the plant.

The primary study area is the arc of residential properties running from Maui Place and Rangitake Drive to the south-west of the Dow plant, to the residential properties in Findlay and Catherine streets and Ngamotu Road, adjacent to the industrial land to the east. A limited number of samples were taken from residential areas up to 2.5 km in the predominant downwind (eastward) direction, and from within or close to four residential, or former, residential properties within the industrial area close to the plant.

The study was to measure 2,3,7,8-TCDD concentration trends within surface soil (defined as 0 – 75mm) within the residential area. It was recognised that there could be local variations arising from particular wind conditions or topography, but it was not the intention of the study to establish the fine detail of localised concentration “highs” or “lows”. Secondary aims were to determine the 2,3,7,8-TCDD concentration within a further depth increment (75 – 100 mm) immediately below the surface sample locations, in selected properties, and also 2,3,7,8-TCDD concentrations in soil from a number of gardens.

The sampling was carried out on a curved grid, centred about the Dow plant. Sites were selected as close as possible to each pre-defined grid point based on:

- The occupant having lived there for as long as possible, preferably since 1960;
- Sampling soil that had not been disturbed since the Dow plant was established (lawn areas were considered the best targets);
- Sample locations were away from obstructions (buildings, high fences, large trees);
- Wood that may have been treated with pentachlorophenol (PCP) was avoided, because dioxin is known to be associated with PCP chemicals;
- The sampling area was large enough to allow a number of sub-samples to be taken.

The fieldwork was carried out in late May and early June 2002, with a total of 35 sites sampled. From these, 35 surface-soil samples, six deeper samples and six garden samples were collected. Both the deeper and garden samples were collected from sites distributed across the study area. The sampling was carried out in accordance with rigorous sampling protocols to avoid any possibility of contamination between samples. Samples were collected as composites of six soil cores from each site to ensure they were representative of the site. A DIN representative observed the sampling and was provided with a duplicate set of samples, to store or analyse as they saw fit.

Laboratory analysis was carried out in accordance with the United States Environmental Protection Agency (USEPA) Method 1613, by AgriQuality New Zealand Limited, Lower Hutt. A total of 47 soil samples were analysed for 2,3,7,8-TCDD from the 35 sites. Eight of these samples, distributed across the study area, were analysed for full dioxin profiles, including the sample with the maximum concentration of 2,3,7,8-TCDD. The full profiles allowed the calculation of toxic equivalents (TEQ), a method of representing the toxicity of the dioxin congener mixture relative to 2,3,7,8-TCDD. Two samples were selected for independent analysis for 2,3,7,8-TCDD by Pace Analytical Services Inc., Minneapolis, USA, for confirmatory analysis. The results of the independent verification were excellent.

Dioxin Concentration Results

Surface Soil Samples

2,3,7,8-TCDD was detected in all 35 surface soil samples at concentrations ranging from 0.71 to 92 ng/kg (parts per trillion). The majority (31 out of 35) had 2,3,7,8-TCDD concentrations less than 10 ng/kg and 23 results were less than 5 ng/kg. TEQ concentrations for the eight full profiles ranged from 2.6 to 79 ng/kg. The TEQ value calculated from the congener profile is dominated by the 2,3,7,8-TCDD concentration.

The eight full dioxin profiles showed a close similarity with profiles obtained in earlier MfE soil studies of other urban areas in New Zealand, except for the presence of 2,3,7,8-TCDD in the current study. 2,3,7,8-TCDD was not detected in any of the 22 MfE urban soil samples from other centres, but was detected in the two New Plymouth samples. The dioxin profiles from this study and the two early New Plymouth samples (and Paritutu) results are typical of other towns and cities in New Zealand except there is an “overlay” of 2,3,7,8-TCDD and to a lesser extent 1,2,3,7,8-pentachlorodinenzo-p-dioxin.

The spatial distribution of 2,3,7,8-TCDD in surface soils reflects the prevailing wind direction, from the west, and the topography. Concentrations to the east of the Dow plant, towards and beyond Mount Moturoa, are higher than to the south of the plant. In addition, land that slopes towards the plant, in particular Mount Moturoa, shows higher concentrations relative to flat or away-sloping areas. The steep-sided valley running between Ngamotu and Pioneer roads shows distinctly lower concentrations. Concentrations are higher at the plant boundary and drop off rapidly within 800 – 1000 m from the plant. To the east, 2,3,7,8-TCDD can still be detected 2.5 km from the plant.

Deeper Samples

The concentration of 2,3,7,8-TCDD in deeper samples (75 – 150 mm) ranged from 0.71 to 17 ng/kg. There is a good relationship between the surface and corresponding deeper samples, with the 2,3,7,8-TCDD concentration in the deeper samples being about 70% of the surface samples. A rapid drop-off in TCDD concentration with depth is expected, as TCDD binds very strongly to soil and has a low solubility. However, the results indicate vertical migration has occurred to at least 150 mm. The extent of deeper migration is not clear from this study.

Garden Samples

Concentrations of 2,3,7,8-TCDD in six soil samples taken from gardens ranged from 2 to 7.3 ng/kg. The garden samples also show a good relationship with the corresponding surface samples, with one exception, averaging approximately 80% of the corresponding lawn-soil samples. The garden soil concentrations are higher than would be expected to result from garden cultivation mixing in deeper “clean” soil. Possible factors include:

- Soil mixing has been relatively shallow, perhaps less than 200 mm.
- 2,3,7,8-TCDD has reached deeper in the soil column than expected.
- Deposition of 2,3,7,8-TCDD onto lawns has been added to gardens as grass clippings, either directly or as compost.

Comparison with Previous Paritutu Studies

A number of less extensive studies have previously been carried out in Paritutu. Comparing the results of the earlier studies with the current studies is problematic, because of uncertainties in sampling techniques, locations and basis for reporting, and differences in analytical techniques. However, sampling carried out by Taranaki Regional Council in 2001 and by MfE in 1996 appears to be consistent with the current study. Two samples analysed on behalf of a community group in 2001 are within the range of concentrations measured in this study, although the precise locations of these samples are not known.

Making comparison with samples taken in 1985 and 1986, by Dow and the then Department of Health is of uncertain validity, because of the uncertainties associated with these data. Overall, samples from residential areas are the same order of magnitude as the current study, but some results are higher than the current study.

While the earlier studies provide additional confidence in the results of the current study, they do not allow a definitive assessment of whether residents may, in the past, have been exposed to higher average concentrations. However, based on a half life for 2,3,7,8-TCDD of the order of 25 – 100 years for soil below the top few millimetres, it is not expected that soil concentrations in residential areas would have been markedly higher than those currently measured.

Comparison with International Guidelines

A variety of international soil criteria have been developed against which the results of this study may be compared. In this study, guidelines for a soil in residential areas from New Zealand (1,500 ng TEQ/kg), Germany (1000 ng TEQ/kg) and three different guidelines from the United States have been used. The most conservative criteria are from the United States; 39 ng /kg (2,3,7,8-TCDD) derived from guidelines issued by the Region 6 and Region 9 offices of the USEPA and 50 ng TEQ/kg by the United Sates Agency for Toxic Substances and Disease Registry (ATSDR). These US criteria are "screening levels" which if exceeded trigger further investigation at a site. Exceeding a screening level does not immediately imply there is a health risk. Any risk will be relative to the exposure assumed in the derivation of the guideline and the exposure likely in the actual situation.

All but one of the results for the samples collected fell within the most conservative residential guidelines used for comparison in this study (the USEPA Region 6 and 9 and ATSDR screening levels). All values fell within the higher New Zealand and German criteria by large margins. The single result that fell outside the USEPA Region 6 and 9, and ATSDR values, is the 2,3,7,8-TCDD concentration of 92 ng/kg in the sample collected from the west-facing slope of Mount Moturoa Domain.

It is concluded that residential properties of Paritutu, with the possible exception of a few properties backing onto the north-west slopes of Mount Moturoa, will have 2,3,7,8-TCDD soil concentrations (and TEQ values) less than the most conservative of the international risk-based residential guidelines currently in force. This is on the assumption that soil concentrations will not be markedly different between sample locations.

Within Mount Moturoa Domain, and on the north-west slopes of Mount Moturoa, 2,3,7,8-TCDD concentrations could be between about 20 and 90 ng/kg. Concentrations will be lowest on the lower slopes. Considering the likely exposure of recreational users of the Domain, a screening level of at least an order of magnitude greater than the residential guideline is considered appropriate. Similarly, the standard residential guideline is not appropriate for the high-density residential properties on the north-west side of Mount Moturoa, given the amount of paving on these properties. A screening level of at least twice the residential value is appropriate.

Conclusion

The results demonstrate that 2,3,7,8-TCDD is present at detectable but generally low concentrations in surface soil over the complete study area. The soil concentrations generally reflect distance from the Dow plant and the prevailing wind directions, with some variation apparent as a result of the topography. Comparatively higher concentrations were found on and around Mount Moturoa, immediately to the east of the Dow plant.

All soil sample results were below the New Zealand soil guideline for 2,3,7,8-TCDD, and with one exception, complied with all risk-based international guidelines. The exception, in Mount Moturoa Domain, is considered acceptable for the expected recreational use of that land. The results indicate further investigation of soil in residential areas of Paritutu is not warranted.

Previous studies have not found 2,3,7,8-TCDD in other urban areas elsewhere in New Zealand. The profile of dioxin contamination in Paritutu, and in particular the detection of 2,3,7,8-TCDD, is consistent with the nature of contamination associated with 2,4,5-T production. The findings of this study corroborate earlier investigations of the Dow plant being the source of 2,3,7,8-TCDD in the area.

Acknowledgements

The authors wish to acknowledge the assistance of Dr Simon Buckland of the Ministry for the Environment and Virginia Baker of the Institute of Environmental Science and Research Limited. In particular, Dr Buckland contributed to appendices on background information on dioxins, historical soil investigations and international soil guidelines.

Taranaki Regional Council (Brian Calkin and Gary Bedford) assisted with the site selection process by carrying out preliminary site inspections and interviewing owners. New Plymouth District Council (René Laan) assisted with providing aerial photographs and mapping information.

Initial drafts of this report were provided to the Ministry for the Environment, the Institute of Environmental Science and Research, Ministry of Health, Taranaki District Health Board and Taranaki Regional Council. Their assistance is also acknowledged.

The contributions of the various community groups is acknowledged, in particular the members of the Paritutu Community Health Liaison Group, Andrew Gibbs of the Dioxin Investigation Network and Paddy Burt of the Dioxin Action Group.

Finally, the assistance of the individual property owners and occupiers is acknowledged. This study would not have been possible without the information they provided about their properties and their co-operation during the sampling. The permission of the majority to publish the results with their properties identified is particularly appreciated.

1.0 Introduction

Agricultural chemicals have been historically manufactured in a plant, currently owned by Dow AgroSciences Ltd, located in the Paritutu area of New Plymouth. Products manufactured at the plant included the phenoxy herbicide 2,4,5 trichlorophenoxyacetic acid (2,4,5-T). Dioxins[2] (in particular 2,3,7,8-tetrachlorodibenzo-p-dioxin or 2,3,7,8-TCDD) were a manufacturing contaminant of 2,4,5-T. 2,3,7,8-TCDD is recognised as a human carcinogen, and may cause a variety of other adverse health effects, including effects on the immune system, reproduction and development (Smith and Lopipero, 2001).

Some people within the New Plymouth community, and in particular those living in the suburb of Paritutu, have expressed concern that dioxin may be present in the soils in the area. Pattle Delamore Partners Limited (PDP) has been engaged to carry out soil sampling and analysis for dioxin from residential properties in Paritutu, on behalf of the Ministry for the Environment. This work is part of wider government activity on dioxins, both in New Plymouth and nationally. The Institute of Environmental Science and Research (ESR) are managing the project, in conjunction with other government studies.

The objective of the work, as set out in the study brief (appended to the Study Design and Sampling Protocol, PDP 2002) was to:

> *Measure dioxin concentrations in residential properties close to the Dow AgroSciences (formerly Ivon Watkins-Dow [IWD]) site in Paritutu, New Plymouth, establishing soil concentrations both laterally and with distance from the factory source.*

The study was carried out in such a manner that the findings could contribute to subsequent studies for:

i) the identification of individuals who may have been maximally exposed to dioxins when resident in New Plymouth, and

ii) the assessment of human health risks to the population from exposure to dioxin.

The assumption is that long-stay residents, or residents in the area during the period of 2,4,5-T manufacturing at the Dow plant, will have been exposed to higher levels of dioxin in the soil, derived from emissions and discharges from the plant, than short-stay or more recent residents. However, it is not the intent of this study to undertake a health risk assessment, or to identify actual maximally exposed individuals. It was also not the intent of the study to establish the exact source or period of discharges from the plant.

The study is intended to integrate with a study to measure dioxin in blood serum being carried out by ESR on behalf of the Ministry of Health. This study, described in Baker

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[2] The collective term for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). 2,3,7,8-TCDD is also commonly referred to as dioxin.

et al., (2002, in prep.), is intended to identify a group of long-term, most likely highly exposed, Paritutu residents, obtain blood serum samples and compare the dioxin levels in the blood fats with a New Zealand population group from an earlier Ministry for the Environment study (Buckland *et al.*, 2001).

This report sets out the background to the current study, describes the study design, sampling protocols and fieldwork, and then presents the concentrations of dioxins measured. The results are compared with previous sampling carried out in the area, with studies elsewhere in New Zealand and with New Zealand and overseas guidelines for 2,3,7,8-TCDD in soil.

2.0 Background

2.1 Structure and Properties of PCDDs and PCDFs

A description of the structure and properties of PCDDs and PCDFs is contained in Appendix A. Appendix A has been compiled from a number of MfE reports (Buckland *et al.*, 2001, Buckland *et al.*, 1998, Smith and Lopipero, 2001). A summary is given below.

2.1.1 Structure and Toxicity

PCDDs and PCDFs are two groups of chlorinated aromatic[3] compounds. Both groups of chemicals may have up to eight chlorine atoms attached. Each individual compound is referred to as a congener, with each specific congener identified by the number and position of chlorine atoms around the aromatic nucleus. There are 75 possible PCDD congeners and 135 possible PCDF congeners. Groups of congeners with the same number of chlorine atoms are known as homologues.

Most PCDD and PCDF congeners are thought to be of no toxicological significance, however, the 17 congeners with chlorine atoms substituted in the 2,3,7,8-positions are thought to pose a risk to human and environmental health. Of the 17 congeners, the most toxic, and widely studied, is 2,3,7,8-TCDD.

2.1.2 Toxic Equivalents

PCDDs and PCDFs occur as complex mixtures of congeners in the environment. To represent the toxicity of a mixture as a single number, a system of toxic equivalents (TEQs) has been developed, based on a set of weighting factors, each of which expresses the toxicity of a particular congener in terms of an equivalent amount of 2,3,7,8-TCDD.

Multiplication of the concentration of a PCDD or PCDF congener by its toxic equivalency factor (TEF) gives an equivalent 2,3,7,8-TCDD TEQ concentration. The toxicity of a mixture of PCDDs and PCDFs is then derived by summing the individual TEQ concentrations to obtain the ‘Total TEQ’ for the mixture. This approach assigns a TEF to each of the 17 toxic 2,3,7,8- PCDDs and PCDFs. The remaining non-2,3,7,8-chlorinated congeners are considered biologically inactive and are assigned a TEF of zero.

The latest internationally accepted TEFs for the PCDDs and PCDFs, as agreed at a 1997 World Health Organization (WHO) consultation (Van den Berg *et al*., 1998), are shown in Appendix A. Earlier TEF schemes for the PCDDs and PCDFs, such as the international TEQ scheme (I-TEQ) (Ahlborg, 1989; Kutz *et al*., 1990), have been widely used to assess the combined toxicity of these compounds.

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[3] Aromatic compounds contain one or more benzene molecules, which consist of six carbon atoms arranged in a hexagonal ring. PCDDs and PCDFs both have two benzene rings connected by oxygen atoms.

The WHO-TEF values are used to calculate TEQ values in this study (i.e. WHO-TEQs, henceforth referred to simply as TEQs). As will be seen later, given the dominance of the 2,3,7,8-TCDD congener in the dioxin contamination of 2,4,5-T, these values are little different from the previously widely used International-TEQ (I-TEQ) values, and for the purposes of this study the two schemes are effectively interchangeable.

2.1.3 Sources

PCDDs and PCDFs are not produced intentionally, but are released to the environment from a variety of industrial discharges, combustion processes and as a result of their occurrence as unwanted by-products in various chlorinated chemical formulations. Historically, the manufacture and use of chlorinated aromatic chemicals have been major sources of PCDDs and PCDFs in the environment. Notable examples include the wood preservative and biocide pentachlorophenol (PCP) and 2,4,5-T.

Combustion processes are a particularly important source of PCDDs and PCDFs. Most thermal reactions involving the burning of chlorinated organic or inorganic compounds appear to result in the formation of these substances. PCDDs and PCDFs have been detected in emissions from the incineration of various types of wastes, from the production of iron and steel and other metals, from fossil fuel plants, domestic coal and wood fires, backyard burning, and from automobile engines as well as from accidental fires.

2.1.4 Physical and Chemical Properties and Environmental Fate

In general, PCDDs and PCDFs have low water solubility, high octanol-water partition coefficients[4] and low vapour pressure, and are resistant to chemical degradation under normal environmental conditions. These properties mean that they are extremely persistent in the environment, and their highly lipophilic[5] nature results in bio-concentration into biota and biomagnification through the food chain.

In soil, sediment, water and (to a lesser extent) ambient air, PCDDs and PCDFs are primarily associated with particulate and organic matter. Once adsorbed to particulate matter, PCDDs and PCDFs exhibit little potential for significant leaching or volatilisation. PCDDs and PCDFs are extremely stable compounds with environmental persistence measured in decades.

The only environmentally significant transformation process in soil is photodegradation[6] at the soil–air interface (ground surface). Although some volatilisation of PCDDs and PCDFs on soil does occur, the predominant fate of these chemicals adsorbed to soil is to remain in place near the surface of undisturbed soil, or to move to water bodies with soil erosion.

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[4] Measure of affinity to be absorbed to organic material

[5] Fat-loving – tendency to dissolve into and remain in (body) fat

[6] Destruction by the effects of sunlight

The wind erosion of surface-soil may also lead to the re-suspension of particle-bound PCDDs and PCDFs into the atmosphere.

2.2 The Dow Plant

The former Ivon Watkins Ltd (later Ivon Watkins-Dow (IWD), now Dow AgroSciences (NZ) Ltd) agricultural chemical manufacturing and formulating plant was established on its current Paritutu site in 1960. The plant manufactured a number of chemicals, including the selective herbicide 2,4,5-T. 2,4,5-T was once widely used for control of woody weeds such as gorse. The manufacture of 2,4,5-T in New Zealand ceased in 1987, although some stocks remained that were likely to have been used after this date.

At the time the plant was built on the Paritutu site (having moved from a site in Buller Street in central New Plymouth) the surrounding area was largely sand dunes and rural land. The area has subsequently been developed, with residential areas now to the south and south east of the site (Photograph 1, Figure 1).

A key intermediate in the manufacture of 2,4,5-T was trichlorophenol (TCP). Formation of 2,3,7,8-TCDD occurred during the TCP manufacturing process and remained as a contaminant in 2,4,5-T. No additional TCDD[7] is produced in the 2,4,5-T manufacturing process in the phenoxy plant. Until 1969 IWD used imported TCP, but from 1969 sodium trichlorophenate (Na-TCP) was manufactured on the Paritutu site (Pilgrim, 1986). During the first eight years of manufacturing Na-TCP, a xylene and trichloroanisole waste stream was significantly contaminated with 2,3,7,8-TCDD. This waste was initially stored, but was subsequently incinerated on site between late 1975 and April 1979.

Photograph 1: Panoramic view of sample area from Paritutu, overlooking the Dow plant and residential areas beyond

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[7] Where the context is clear, TCDD is used interchangeably with 2,3,7,8-TCDD in this report.

Figure 1: Location of study area

Modifications to the TCP production process in 1977 significantly reduced the production of 2,3,7,8-TCDD and eliminated the xylene/trichloroanisole waste stream. While 2,3,7,8-TCDD was still produced in the TCP process, from 1982 this was further reduced, using an improved solvent (xylene) extraction/purification. The resultant contaminated xylene was then recovered by distillation, with the residues being incinerated. Manufacturing of 2,4,5-T ceased at the Paritutu plant in late 1987.

The liquid waste incinerator was established in 1975 and operated for 3½ years. Pilgrim (1986) calculated an overall destruction efficiency of TCDD for the period 1975 to 1979 of better than 99.98%. The incinerator was not used between 1979 and 1985, but with the commissioning of the solvent distillation unit in the phenoxy plant in 1982, the incinerator was again used to destroy accumulated distillation residues in 1985 and 1988 (Pilgrim *et al.*, 1990). The liquid waste incinerator is no longer in operation and has been removed.

A solid waste incinerator was established in 1981 for destroying an accumulated backlog of chemical wastes and chemically contaminated packaging. This incinerator is still in use[8]. Monitoring of dioxin emissions from the solid waste incinerator suggest negligible amounts are being emitted (Pilgrim *et al.*, 1990; G Bedford, TRC, 2002, pers comm.).

It is presumed that 2,3,7,8-TCDD (and possibly other PCDDs and PCDFs) has been released into the atmosphere to varying degrees as fugitive emissions from the TCP and phenoxy herbicide processes, from plant ventilation stacks and from the burning of liquid and solid wastes in the two incinerators on the site. It is further assumed that the majority of 2,3,7,8-TCDD emissions occurred over the period of TCP use (and later production) and 2,4,5-T production, from 1960 until 1987.

During the time 2,4,5-T was manufactured, a number of changes occurred in processes at the plant and in regulatory requirements, with distinct reductions in 2,3,7,8-TCDD contamination in the TCP and also in the 2,4,5-T produced. Fugitive emission of 2,3,7,8-TCDD (whether from the TCP process or the phenoxy plant) presumably also reduced to reflect these changes.

Chemical release incidents have also occurred at the plant. At least two incidents are known. These were an explosion in the 4-(4-chloro-2-methylphenoxy) butanoic acid (MCPB) plant in November 1972 and a venting accident in the TCP plant in April 1986. The latter incident is known to have released TCDD (Pilgrim, 1986), but there is no information as to whether the earlier incident did. Dioxin is not a manufacturing contaminant of MCPB.

2.3 Previous Soil Studies

Over the years there have been a number of investigations into the manufacture of 2,4,5-T in New Plymouth and potential impacts on the local community and environment.

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[8] In later years this incinerator was modified to allow it to incinerate waste sludges.

These include a ministerial committee of inquiry (Brinkman *et al.*, 1986, 1987) and a report into the use of 2,4,5-T in New Zealand (Coster *et al.*, 1986). More recently, the TRC have investigated alleged incidents of waste disposal (TRC, 2001) and the local Medical Officer of Health has investigated rates of illness, including cancers and birth defects (O'Connor, 2001, 2002).

A summary of soil dioxin concentrations from previous studies in Paritutu is included in Appendix B. Sampling has been carried out on five occasions. They are:

- A study carried out on 17 April 1985 by the Regional Air Pollution Group, Department of Health (Pilgrim, 1986);
- Two sets of soil samples taken in April 1986 by the Department of Health following the TCP accident (Pilgrim, 1986);
- Samples collected in New Plymouth in 1996 as part of the MfE national environmental survey (Buckland *et al*, 1998);
- Investigation of alleged dump sites carried out by the Taranaki Regional Council in 2001 (TRC, 2001);
- Sampling carried out on behalf of the Community Residents Action Group in 2001 by Kingett Mitchell and Associates (The Daily News, 2001).

These studies are of variable quality. It is not clear from the reports of some of the early studies whether the results given are total TCDD or 2,3,7,8-TCDD, and it is also not clear whether reporting is wet or dry weight. It would be normal to report dry weights. Also, some of the 1985 and 1986 sample locations are rather vague, being shown as large crosses or areas over which composites were taken on sampling diagrams accompanying the results. This makes it difficult to compare these results with the specific locations of this study. Finally, detection limits for the early results were rather high, typically 20 – 30 ng/kg [9], which considerably reduces their usefulness in comparing with the current study.

The sample locations for the sampling carried out by Kingett Mitchell and Associates are also not known, nor, with any certainty, whether the results are 2,3,7,8-TCDD or TEQ values. The results are only known through a newspaper article and have not been formally released. Attempts to obtain the full results have been unsuccessful. In the absence of specific information, this study is of limited value to the current investigation, with the two quoted results only useful for comparison in a general way.

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[9] ng/kg = nanogram per kilogram, or one part per trillion. A nanogram is one billionth of a gram. To give a sense of scale, a part per trillion is equivalent to a teaspoonful distributed through 5,000,000 m^3 of soil, which is the same as a teaspoon within the top 1 metre of soil over a thousand rugby fields, each 100 m x 50 m.

3.0 Study Design and Site Investigation

3.1 Study Design

The detail of the study design is set out in Appendix C, which is in turn based on the Study Design and Sampling Protocol prepared for the investigation (PDP, 2002).

The study brief required the basic target of the study to be 2,3,7,8-TCDD, and assumed that its presence would be an indication of escape from the manufacturing process, whether through fugitive emissions, the 1986 incident or release of TCDD from the incineration of waste (this release may be from breakthrough of TCDD contaminated waste or from TCDD formation and release during incineration). The study design was therefore based on the assumptions that:

1. The former IWD plant was the principal source of 2,3,7,8-TCDD present in the soil in the area;
2. Contamination occurred via discharges to air with subsequent deposition over the residential neighbourhood, and
3. Sampling was to be focused on residential properties, specifically, properties to the east and south of the factory. The industrial or reserve land to the north or west of the factory were not to be sampled unless residential properties were identified within the industrial areas, in which case sampling of those properties would be considered.

The intent of the study was to measure general 2,3,7,8-TCDD concentration trends within surface soil (defined as 0 – 75mm) within the residential area. The general expectation was for a trend of decreasing concentration further from the site, and higher concentrations to the east of the site than to the south as a result of the prevailing wind direction. It was recognised that there could also be local concentration variations as a result of particular wind conditions or topographic variations. However, it was not the intention of the study to establish the fine detail of localised concentration “highs” or “lows”, which would have required a much higher density of sampling. In addition, high-concentration “hotspots” from aerial discharge and deposition over particular small areas were not expected, and there was no information to suggest that particular locations should be targeted.

Secondary aims were to determine 2,3,7,8-TCDD concentrations within a further depth increment (75 – 100 mm) immediately below the surface sample locations in selected properties and also 2,3,7,8-TCDD concentrations in soil from a number of vegetable gardens within properties from which surface soil samples had been taken. Both the deeper and garden samples were to be collected from sites distributed about the study area. A further aim was to examine the relationship between 2,3,7,8-TCDD and the full dioxin profile, by analysing some samples for the full profile.

The study design considered areas of likely maximum deposition through a review of meteorological data, topography, age and location of residential areas and results of the earlier dioxin soil investigations. However, given the considerable community interest in Paritutu, it was important that the study considered not just the likely areas of maximum dioxin deposition, but also the broader residential areas around the plant.

The primary study area was defined as the arc of residential properties running from Maui Place and Rangitake Drive to the south-west of the Dow plant, to the residential properties in Findlay and Catherine streets and Ngamotu Road, adjacent to the industrial land to the east (Figure 1). In addition, following community consultation, it was decided to take samples from residential areas up to 2.5 km in the predominant downwind directions, and from within or close to any residential land to the north or north east of the plant.

In developing the study design, no attempt was made to calculate dioxin emission rates or to differentiate between the various sources over time. It was considered that the current dioxin concentration in soil would represent the majority of the dioxin deposited over the period of manufacture, given its slow degradation in soil (half-life of 25 – 100 years (Paustenbach *et al.*, 1992, as reported in Buckland *et al.*, 2000)). Further, it was assumed that the measured concentrations would be typical of concentrations that occupants may have been exposed to over at least the last 15 years, since 2,4,5-T manufacturing stopped at the plant.

3.2 Site Selection

It was decided to sample on a curved grid (Figure 2). The detail of the grid design is given in Appendix C. Sites were then selected as close as possible to each grid point based on a set of selection criteria;

- The occupant had lived there for as long as possible, preferably since 1960;
- The samples were to be from areas of soil that had not been excavated, filled, or otherwise disturbed, since the Dow plant was established (lawn areas were considered the best targets);
- Sample locations were away from the lee of buildings or large trees, and at least 5 m from obstructions (buildings, high fences, large trees);
- Sample locations were at least 5 m away from wooden structures that may have been treated with pentachlorophenol, e.g. poles, fences and sleepers used for landscaping;
- The sampling area was large enough to allow a number of sub-samples to be taken over a several square metre area so that the resulting composite would be representative of the location.

✚ 01 Predetermined grid point location and site number

○ 32 Additional site - actual sampling location and site number. Site 34 not shown

Figure 2: Predetermined sampling grid and additional sampling sites

The sites to be sampled as part of the main sampling grid (labelled 01 to 27 on Figure 2) were first identified as a desktop exercise. The information used to determine the suitability of the sites included reference to aerial photos, a topographical map overlay, drainage plans and building permit dates. This information was then passed onto the TRC, who visited each of the properties with a checklist of desirable attributes, with this information subsequently used by PDP to determine the optimum sites. The TRC visit included questioning occupants on their duration of residence.

The final sites sampled were largely as identified by the TRC, with a few exceptions, where occupants could not be contacted, information was incomplete or it was considered that a more suitable site was required.

As a result of community consultation on the study design, additional sites at nominal distances of 1 km, 1.5 km and 2 km east of the Dow plant, were sampled. These sites (labelled 28 to 31 on Figure 2) were given nominal grid locations prior to the fieldwork, but were finally selected in the field. These sites were to meet the general site-selection criteria, except they were to be on public land where possible (to avoid having to get permission from private owners at short notice) and road reserves were also to be avoided. The actual sites were between 80 m and 130 m from the nominal pre-defined grid locations because of a lack of suitable public land closer to the grid points.

During the community consultation, the Dioxin Investigation Network (DIN) identified several residential properties, or former residential properties, within the nearby industrial area north-east of the plant. In addition to the normal selection criteria, there was a preference for these sites to be on public land, although two of the four sites that eventuated (labelled 32 to 35 on Figure 2) were on private properties.

Given that the Paritutu area had been progressively developed over a number of years, there was a range of property ages and length of time since the properties had possibly remained undisturbed. The newest areas were developed in the 1970s in the vicinity of Herekawe Drive. Marama Crescent and the streets off Marama Crescent, close to the southern boundary of the Dow Plant, were developed in the mid to late 1960s as worker housing for the construction of the New Plymouth Power Station. The oldest areas were generally along Paritutu Road, Ngamotu Street and around Mount Moturoa.

Most residents had not occupied their properties for as long as was desirable (i.e. 30 to 40 years). This was particularly true of the predominantly rental housing made up of former construction housing in and around Marama Crescent. Few occupants in this area had been there for more than two years.

There was also a general absence of vegetable gardens over the study area, particularly within areas of rental housing close to the Dow plant southern boundary. The garden samples were therefore collected from whatever gardens were available, generally ornamental gardens.

Other departures from the site selection criteria and sampling brief are outlined in the individual property summaries. Such departures were mainly where fences or high obstacles were closer than 5 m to the sampling location. In such cases, the obstacles were to either side of the sampling location. Other cases were where it was not possible to entirely avoid tree canopies.

3.3 Fieldwork

The fieldwork was carried out on 27 to 31 May 2002, and 4 and 5 June 2002. Weather during the initial sampling period was squally, with periods of heavy rain. The weather during the subsequent period was calmer, with relatively light winds and rain showers.

At least one representative of DIN observed all sampling, with the exception of Site 14 due to a misunderstanding. At each site the optimum sampling location was generally identified in accordance with the sampling brief, but also in agreement with the DIN representative. In some instances it was agreed that, although a site did not comply with all the desired criteria, it was sampled because it was the best option available.

3.3.1 Sampling Equipment

AgriQuality New Zealand Ltd (AgriQuality), Lower Hutt, the primary testing laboratory, supplied the sample jars, acetone, hexane, and Teflon squeeze bottles for the acetone and hexane. The sample jars were 280 ml glass, pre-cleaned, and the lids were supplied pre-lined with cleaned aluminium foil. The analyte free water was supplied in glass bottles by R J Hill Laboratories Limited, Hamilton.

The soil sample corers were new, and had a slightly tapered 75 mm long stainless steel barrel with an inside diameter of 25 mm. The scissors used to cut any long grass, and the tamping rod used to push the samples out of the corer, were made of stainless steel.

3.3.2 Sampling Protocol

Samples were collected as composites of six soil cores from each site, with the soil cores collected on a grid defined by the vertices and mid-points of a 2m equilateral triangle. All samples were collected in duplicate – the duplicate core being taken from within 50 mm of the initial core. The duplicate composite-samples were passed to the DIN representative at the end of each day.

The work at each site followed the pattern:

- Occupant/owner permission obtained, generally at least a day in advance.
- Discussions with the occupant regarding the past history of the site, and any site activities that might affect the choice of sampling locations.
- An appropriate sampling location was selected.
- The grid was paced out with the six sample points marked using flags on wire stems, one at each vertex, and one midway along each side.

- The sampling equipment, being the soil corer, the tamping rod for sample-core removal, and the grass trimming scissors (if needed), were decontaminated. The decontamination process stepped through: cleaning in tap water; scrubbing using phosphate free detergent; rinsing in tap water; rinsing in analyte free water; rinsing with acetone; and rinsing with hexane (the waste acetone and hexane were collected and returned to AgriQuality). Following decontamination, the tamping rod was normally stored within the corer barrel until needed.
- Where necessary, the grass on either side of the marker flags was trimmed to ground level, taking care not to touch the sampling area with anything but the scissors.
- Two 280-mL sample jars were labelled – both on the side and lid. The jars were then placed in the sampling area, or, where wind or rain caused problems, within some nearby shelter.
- The soil corer was used to collect the sample cores. All six sample cores at each location were collected into a single jar. The six sample cores for the duplicate sample (for DIN) were collected into a separate jar. Both the main and the duplicate sample cores were collected from each of the six coring locations at the same time. The sample cores were eased into the sample jars using the tamping rod to push the core up and out of the tapered corer, ensuring minimal soil residue remained in the corer following sample removal. The first sample core in each jar was normally laid on the tinfoil lined lid to prevent the tinfoil blowing away; the remainder were placed directly into the jars. In cases where the core compressed in the corer resulting in an ill-defined sampling depth, or where little core was recovered, the core was discarded and another core was collected.
- The main sample jar was placed into a resealable plastic bag and placed into an ice filled chilly bin. The duplicate sample jar was either placed into the DIN representative’s chilly bin, or the PDP chilly bin pending later collection by the DIN representative.
- If a deeper sample core was to be taken, a spade was used to break out a 200 mm square, 75 mm thick, turf at each of the six shallower core locations. Care was taken to not let the blade of the spade touch the exposed base of the hole left by removing the turf. The procedure for collecting the deeper sample core then followed that outlined above.
- If a suitable garden was observed, a set of garden-sample cores was collected. The procedure followed that outlined above, but no specific location was marked for the cores, with the cores being collected randomly from throughout the garden.
- If a rinsate blank was to be collected, the equipment was cleaned as described, then analyte free water was poured over the corer, and collected into a sample jar.
- If a trip/field blank was to be collected, the jar of analyte-free water was opened for the duration of the sampling at the particular location.

Following the completion of sampling, a plug of new turf was placed in the core holes. The turf was obtained from a commercial turf supplier in Waitara. Photographs were taken, a site sketch made, other sampling details noted, the occupant notified of the completion of sampling, and the site was then vacated. The sampling details for each property are recorded in property information sheets in Appendix E.

3.4 Laboratory Analysis

The laboratory analysis is detailed in Appendix F. The analysis followed United States Environmental Protection Agency (USEPA) Method 1613.

Samples were dried and homogenised prior to analysis. A sample was then taken from each primary sample to be analysed. The primary samples included all surface (0-75 mm) samples collected, a selection of deeper (75-150 mm) samples collected, distributed across the sampling area and a selection of samples taken from gardens, also distributed across the sampling area. All these samples were subjected to analysis for 2,3,7,8-TCDD.

When the results were received eight surface-samples were selected, in consultation with MfE and DIN, for full dioxin profile analysis (the 17 PCDD and PCDF congeners with chlorines at the 2,3,7 and 8 positions and totals for the tetra, penta, hexa and hepta homologue groups). The samples selected for full profile analysis were:

- The sample with the highest TCDD concentration (sample SS#05);
- A sample some distance from the Dow plant that was unexpectedly high (sample SS#27);
- Six other samples distributed across the sampling area to give both a good range of 2,3,7,8-TCDD concentrations and a good spatial distribution (samples SS#04, SS#06, SS#11, SS#13, SS#22 and SS#24).

Two samples were also selected for independent analysis for 2,3,7,8-TCDD on the basis of the initial 2,3,7,8-TCDD results from AgriQuality. These were the sample with the highest concentration (SS#27) and a sample with low, but detectable, 2,3,7,8-TCDD from close to the Dow plant (SS#02). MfE and DIN were consulted on the sample selection.

The two samples selected for independent analysis were split from the previously homogenised samples by AgriQuality and sent to Pace Analytical Services Inc., Minneapolis, USA. Pace was not aware of the original results nor did they have any communication with AgriQuality, other than confirmation that the samples had been received. PDP requested Pace analyse the samples in accordance with USEPA Method 1613, and received the report of the results direct from Pace.

The laboratory analytical certificates are included in Appendix F. In these certificates surface soil samples are identified in the form SS#nn, where nn is the site number. Garden samples have the letter G as a suffix, i.e. SS#nn-G. Deeper soil samples are identified with a suffix 75mm, i.e. SS#nn-75mm.

Note that the laboratory certificates refer to a sample SS#37. This is actually sample SS#27 and was mislabelled in the field. There is no SS#37 and the date of sampling and other information provides certainty that the sample labelled as SS#37 was actually SS#27. No other samples were mislabelled. The sample is referred to as sample SS#27 in all other references in this report.

A summary of all samples taken and analyses carried out is given in Table 1.

3.5 Community Consultation

Community consultation was carried out throughout the preparation of the study design, the carrying out of the fieldwork and the subsequent laboratory analysis and reporting.

As part of preparing the study design, the Paritutu community was consulted, with the draft and final versions of the sampling brief being distributed, and comments incorporated into the study design, as appropriate. A PDP representative attended a meeting of the Paritutu Community Health Liaison Group in New Plymouth in March to explain the proposed study. The opportunity was also taken to visit the Dow plant to be briefed by the general manager of Dow AgroSciences (NZ) Ltd on the operation and layout of the plant, and a meeting was held with DIN and Dioxin Action Group (DIAG) members.

Prior to the fieldwork commencing, a letter drop was carried out in Paritutu, explaining the purpose of the study and providing brief details of the proposed sampling. A copy of the letter may be found appended to the Study Design and Sampling Protocol (PDP, 2002).

A draft study design and sampling protocol was provided to MfE, ESR, MoH, TRC, and DIN and DIAG for their comment prior to finalising the document. The final document was provided to all these organisations, as well as the New Plymouth District Council, the Taranaki District Health Board and Dow AgroSciences (NZ) Ltd.

Individual property occupiers were approached prior to the commencement of the fieldwork to obtain information about their properties and to explain the sampling. The occupiers were again telephoned just prior to the sampling. At each property, the occupant was requested to sign a consent form. The consent form authorised the collection of the soil samples, and the reporting of the site's address in this report. The resident could grant the former authorisation, but the owner's consent was required for the latter permission where the site was a rental property. A copy of the consent form may be found in the Study Design and Sampling Protocol (PDP, 2002). Where permission to report the address was not given, an alternative site was selected if possible. Property occupiers and owners received a copy of their individual results prior to the release of this report.

Table 1: Samples collected [1] and analyses carried out [2, 3, 4]

Site no.	Address	Date Sampled	Surface (0-75 mm)	Deeper (75-150)	Garden	Rinsate Blank	Trip Blank
01	36 Marama Crescent	31 May	✓❖		✓		
02	12A Tahora Place	28 May	✓❖ P	✓❖			
03	42 Paritutu Road	4 June	✓❖		✓❖	✓	
04	11 Simons Street	30 May	✓❖✪	✓❖	✓❖		
05	Mt Moturoa Domain	30 May	✓❖✪P				
06	52A Marama Crescent	31 May	✓❖✪				
07	28A Simons Street	29 May	✓❖				
08	29 Scott Street	28 May	✓❖				
09	19 Port View Road	29 May	✓❖	✓❖	✓❖		
10	12 Tohu Place	30 May	✓❖				
11	8 Tumai Place	31 May	✓❖✪	✓❖			
12	12A Paritutu Road	28 May	✓❖		✓❖		
13	36 Simons Street	30 May	✓❖✪		✓		
14	7 Findlay Place	31 May	✓❖		✓❖		
15	19 Rangitake Place	31 May	✓❖				
16	79 Ngamotu Road	29 May	✓❖	✓❖	✓		
17	58 Ngamotu Road	30 May	✓❖		✓		
18	9 Catherine Crescent	31 May	✓❖		✓	✓❖	✓
19	Onuku Taipari Domain	29 May	✓❖				
20	133 Ngamotu Road	4 June	✓❖				
21	20 Rospeath Crescent	29 May	✓❖				
22	55A Ngamotu Road	30 May	✓❖✪				
23	37 Ngamotu Road	30 May	✓❖	✓❖	✓❖		
24	108 Pioneer Road	5 June	✓❖✪				
25	Ngamotu Domain – 81 Pioneer Road	4 June	✓❖				
26	Ngamotu Domain – 53 Pioneer Road	4 June	✓❖				
27	AW [5]	5 June	✓❖✪				
28	81 South Road	4 June	✓❖				
29	cnr Whiteley & Breakwater	4 June	✓❖				
30	70 Banks Street	4 June	✓❖				
31	St Josephs School, Calvert Road	4 June	✓❖				
32	105 Centennial Drive	5 June	✓❖				
33	151 Breakwater Road	5 June	✓❖				
34	AW [5]	5 June	✓❖			✓	✓
35	100 Centennial Drive – NPDC Domain	5 June	✓❖			✓	

1. ✓ = sample collected
2. ❖ = sample analysed for 2,3,7,8-TCDD by AgriQuality Ltd.
3. ✪ = sample analysed for dioxin congener profile by AgriQuality Ltd.
4. P = sample independently analysed for 2,3,7,8-TCDD by Pace Analytical.
5. AW = Address withheld. Permission to release address refused

As noted in Section 3.3, above, a DIN representative observed the sampling and received duplicate samples.

Following receipt of the 2,3,7,8-TCDD results from AgriQuality, DIN was consulted on the samples to be selected for full profile analysis, as required by the MfE study brief. DIN was also consulted on the two samples selected for confirmatory analysis by Pace Analytical Services, USA.

Simultaneous with the release of this report, a further letter drop was made to all Paritutu residents, providing a summary of the findings. This letter drop included a copy of the Environmental Health statement that has been released by the MfE and MoH. Copies of this report will be deposited in public libraries in the area.

4.0 Dioxin Concentration Results

4.1 Introduction

This section discusses the dioxin concentrations measured in residential soils in Paritutu. Within this report, the address of most sites is given, but, for two sites, consent to report the address was not granted. For these sites the location is identified in only a general way on various maps. The aerial photograph showing sampling sites (Figure 2 in both the Study Design and Sampling Protocol (PDP, 2002) and this report) shows the design grid, not the actual sampling sites, and should not be used to identify particular site locations. No occupant or owner names are listed in this report.

The results are presented and analysed in a variety of ways, both in tabulated and graphical form. Firstly, the results for all the samples are summarised against each property location in Table 2, and their spatial relationship presented in map form in Figure 3. Table 2 also shows samples that were collected but not analysed. The results for each property are also presented in the property information sheets in Appendix E.

This section initially examines the range of 2,3,7,8-TCDD concentrations. The differences between the surface and deeper samples, and surface and garden samples, are then examined. Next, TEQ values are calculated from the eight samples for which full profiles were analysed and the relationship between TEQ and 2,3,7,8-TCDD is established. From this relationship, TEQ equivalent concentrations are predicted for those samples that were not analysed for a full dioxin profile. Congener profiles are then plotted and compared with profiles obtained from previous studies in New Zealand.

Finally, the spatial distribution of the results is examined, and TCDD contours plotted. TCDD concentrations from previous studies are compared with the current results.

The data interpretation in this section is dependent on the quality of the data obtained from the sampling and laboratory analysis. The data quality, which the various quality checks showed to be satisfactory, is discussed at the end of this section.

Table 2: Concentration of 2,3,7,80-TCDD in Paritutu soils (ng/kg, dry weight basis)

Site Number	Address	Date Sampled[1]	Surface (0-75 mm)	Deeper (75-150 mm)	Garden	Rinsate Blank	Trip Blank
01	36 Marama Crescent	31 May	5.9		NT[2]		
02	12A Tahora Place	28 May	4.8	3.2			
03	42 Paritutu Road	4 June	5.8		4.5	NT	
04	11 Simons Street	30 May	7.4	2.2	4.9		
05	Mt Moturoa Domain	30 May	92				
06	52A Marama Crescent	31 May	15				
07	28A Simons Street	29 May	3.4				
08	29 Scott Street	28 May	6.1				
09	19 Port View Road	29 May	17	14	2.8		
10	12 Tohu Place	30 May	3.6				
11	8 Tumai Place	31 May	2.0	1.6			
12	12A Paritutu Road	28 May	2.9		2		
13	36 Simons Street	30 May	6.2		NT		
14	7 Findlay Place	31 May	8.0		7.3		
15	19 Rangitake Place	31 May	1.9				
16	79 Ngamotu Road	29 May	1.8	1.2	NT		
17	58 Ngamotu Road	30 May	0.93		NT		
18	9 Catherine Crescent	31 May	4.5		NT	ND[3]	NT
19	Onuku Taipari Domain	29 May	1.0				
20	133 Ngamotu Road	4 June	4.8				
21	20 Rospeath Crescent	29 May	0.75				
22	55A Ngamotu Road	30 May	0.76				
23	37 Ngamotu Road	30 May	0.71	0.61	1.3		
24	108 Pioneer Road	5 June	2.7				
25	Ngamotu Domain – 81 Pioneer Road	4 June	2.2				
26	Ngamotu Domain – 53 Pioneer Road	4 June	3.0				
27	AW[4,5]	5 June	27				
28	81 South Road	4 June	0.88				
29	cnr Whiteley & Breakwater	4 June	3.3				
30	70 Banks Street	4 June	2.4				
31	St Josephs School, Calvert Road	4 June	0.81				
32	105 Centennial Drive	5 June	6.1				
33	151 Breakwater Road	5 June	10				
34	AW[4]	5 June	7.3			NT	NT
35	100 Centennial Drive – NPDC Domain	5 June	2.3			NT	

1. All samples collected between 28 May and 5 June 2002
2. NT = sample collected, but not analysed
3. ND = non detect (LOD = 0.01 ng/L)
4. AW = Address withheld. Permission to release address not given.
5. incorrectly labelled as SS#37 in the laboratory report

Figure 3: Sampling locations and 2,3,7,8-TCDD concentrations

4.2 Range of Concentrations of 2,3,7,8-TCDD in Paritutu Soils

The concentrations of 2,3,7,8-TCDD presented in Table 2 are plotted as a histogram in Figure 4 to show the range of concentrations obtained. The histogram is broken down into the three sample sources, that is, surface (0 – 75 mm), deeper (75 – 150 mm) and garden samples. It can be seen that the great majority of the 47 results are less than 10 ng/kg, with only four results, of which two are surface and deeper samples from the same location, above that value. There is one much higher result, 92 ng/kg, from the west-facing slope of Mount Moturoa Domain.

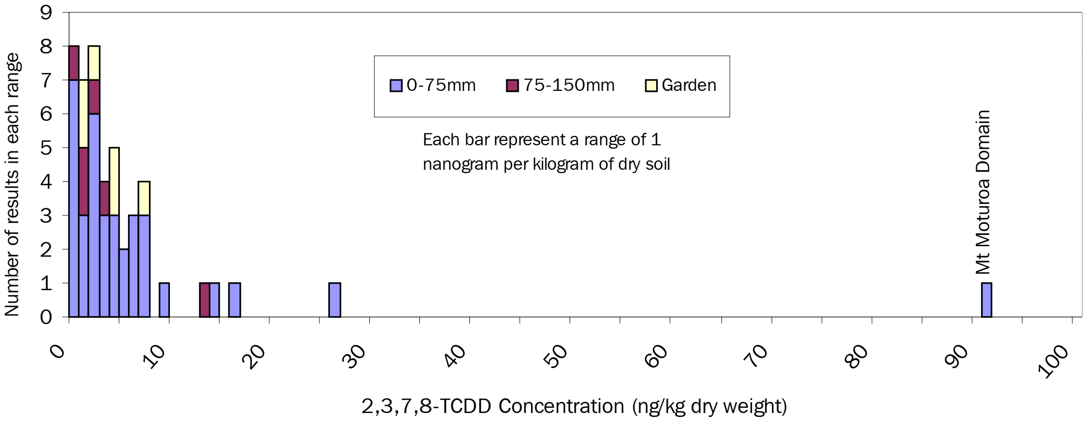


Figure 4: Histogram of surface, deeper and garden 2,3,7,8-TCDD results

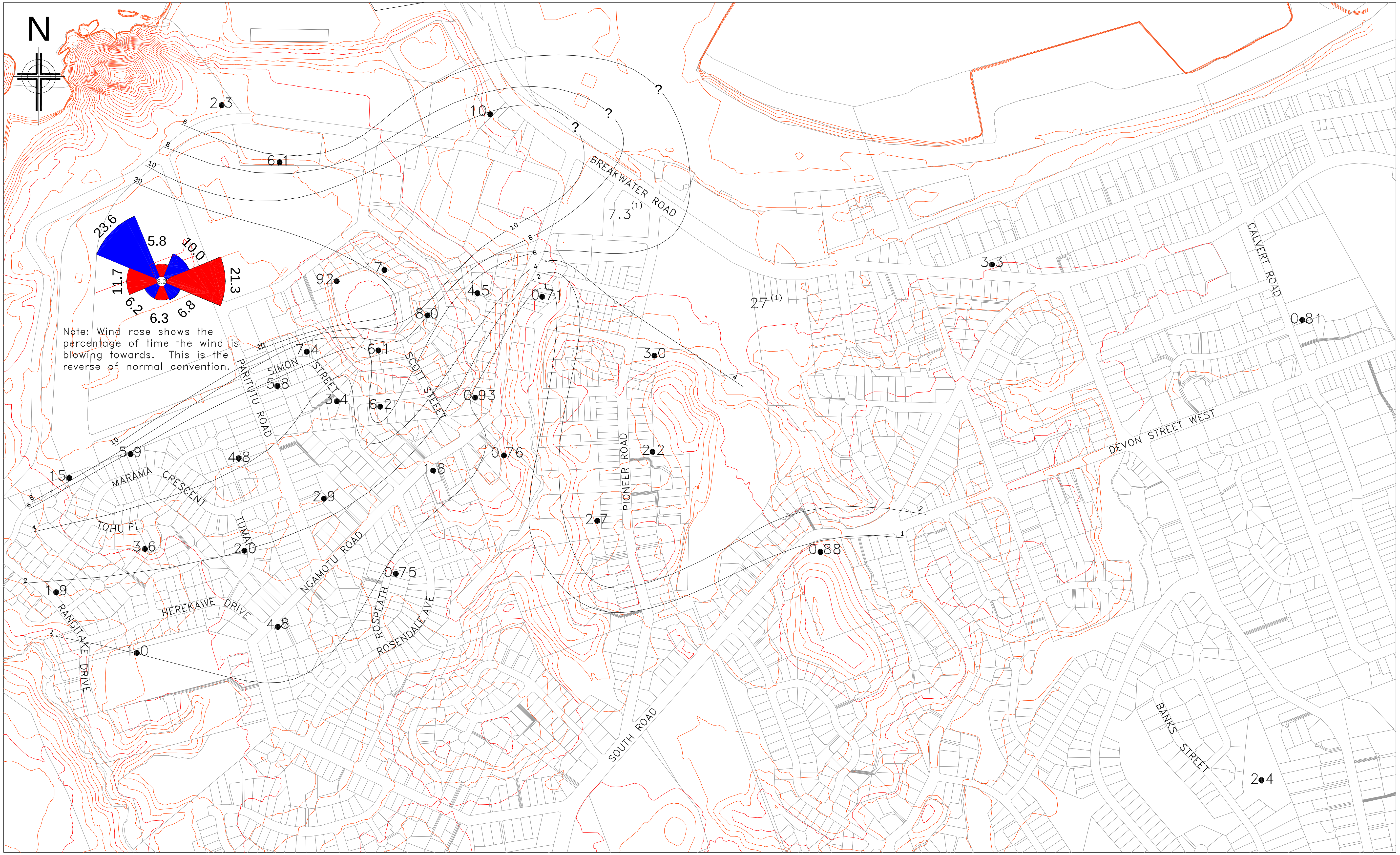
4.3 Spatial Distribution of 2,3,7,8-TCDD in Surface Samples

The spatial distribution of 2,3,7,8-TCDD in surface soils is shown in Figure 5. Concentration contours have been drawn, although some anomalous results make contouring uncertain at a number of locations. Figure 5 also shows the predominant wind directions in a wind rose, but note that the wind rose has been plotted in the reverse of the normal convention, to show the direction the wind is blowing in, rather than the direction the wind is coming from. Several things are apparent in Figure 5:

- Concentrations to the east of the Dow plant, towards Mount Moturoa are higher than to the south of the plant. This is consistent with winds from the westerly quadrant being more frequent (about 30% of the time) than northerly winds (13% of the time). Mount Moturoa falls in the 45° sector directly east of the plant, with winds blowing in this direction more than 20% of the time.
- There is an influence of topography on the concentration distribution. Faces that slope towards the plant (in particular Mount Moturoa) show higher concentrations relative to flat or away-sloping areas. The steep-sided valley running between Ngamotu and Pioneer roads shows distinctly lower concentrations.

- Concentrations are higher at the plant boundary and drop off rapidly within 800 – 1000 m from the plant, with some anomalies. However, to the east and east-south-east, 2,3,7,8-TCDD can still be detected 2.5 km from the plant, with 2.4 ng/kg being detected on a Banks Street property (Site 30) and 0.81 ng/kg on a Calvert Street property (Site 31).
- There is conflicting evidence as to whether there is a significant drop in concentration between 1.5 and 2.5 km from the plant, with the two results at 1.5 km (3.3 and 0.88 ng/kg) being similar to the two results at 2.5 km (0.81 and 2.4 ng/kg). It would appear that concentrations of the order of 1 to 3 ng/kg might be typical at these distances, noting that the MfE national environmental survey (Buckland *et al.*, 1998) detected 2,3,7,8-TCDD at a concentration of 0.53 ng/kg in a composite from three locations several kilometres further east (see Appendix B, Section B.3).
- There is insufficient data from the study to draw firm conclusions with regard to the industrial area to the east-north-east of the plant. There is some suggestion of greater carry towards the port, possibly a result of wind funnelling between the higher land of Paritutu and Mount Moturoa. However, TCDD concentrations further north in Centennial Drive (Site 32; 6.1 ng/kg and Site 35; 2.3 ng/kg) are typical of the results to the south of the plant, closest to the plant boundary, consistent with the wind blowing from the south at a similar frequency to that from the north.
- There are several anomalous results. The concentration of 15 ng/kg measured at the surface at Site 06 is somewhat higher than that expected from concentrations measured on nearby properties. However, it is consistent with the deeper sample taken from the same location. The sample at Site 06 was taken from close to the boundary of the plant and may represent the southern extremity of higher concentrations measured within the plant in earlier studies – as discussed in Section 4.8.
- Surface sample SS#20 from Site 20 in Ngamotu Road returned a concentration of 4.8 ng/kg, more in keeping with concentrations several hundred metres closer to the plant boundary. Neither prevailing wind direction nor topography provide an explanation for this higher than expected result. However, it should be noted that the concentration, while relatively higher than surrounding concentrations, is, in absolute terms, only 3 or 4 ng/kg higher than its neighbours. The TCDD measured in this property is probably of very limited extent and is considered to be of no particular consequence.
- Sample SS#27 at Site 27 has a considerably higher concentration than its neighbours, with no obvious reason from topographic or wind considerations. Unfortunately little further can be said about this site, as the owner has requested that its location not be published. The site, like many other urban properties in New Zealand, may have used 2,4,5-T for the control of weeds. However, the 2,3,7,8-TCDD concentration detected is markedly higher than that expected from "normal" application of 2,4,5-T, even if the 2,4,5-T contained 2,3,7,8-TCDD at

PARATUTU SOIL SAMPLING



Height contours - 5m intervals
Height contours - 20m intervals
2,3,7,8-TCDD concentration contours
1.0 2,3,7,8-TCDD concentration (ng/kg).
The decimal point denotes sampling location

(1) Sample result obtained from general area, as permission has not received from the site owner to show the exact location.

? Indicates estimated location of concentration contours

0m 200m 400m
SCALE

Figure 5: 2,3,7,8-TCDD concentration contours for surface soils

1 mg/kg as occurred prior to 1972 (Coster *et al.*, 1986). The concentration measured in sample SS#27 is not expected to be generally representative of the area.

In summary, the sampling suggests that residential properties in Paritutu within 1000 m of the Dow plant are likely to have 2,3,7,8-TCDD concentrations in the range 1 to 8 ng/kg. Properties further afield may have TCDD concentrations in the range 0.5 to 3 ng/kg.

4.4 Comparison of Surface Soils with Deeper Soils

Deeper soil samples, from 75 mm to 150 mm, were taken immediately below the surface samples at six locations. This was to determine whether there was a significant change with depth in 2,3,7,8-TCDD concentration. In general terms, TCDD concentration would be expected to reduce rapidly with depth at a location that has not been disturbed, because TCDD binds very strongly to soil and therefore would not be expected to be transported deeper by leaching. The results are shown in Table 3, and the locations and concentrations are also shown in Figure 6 (see also Figures 3 and 5).

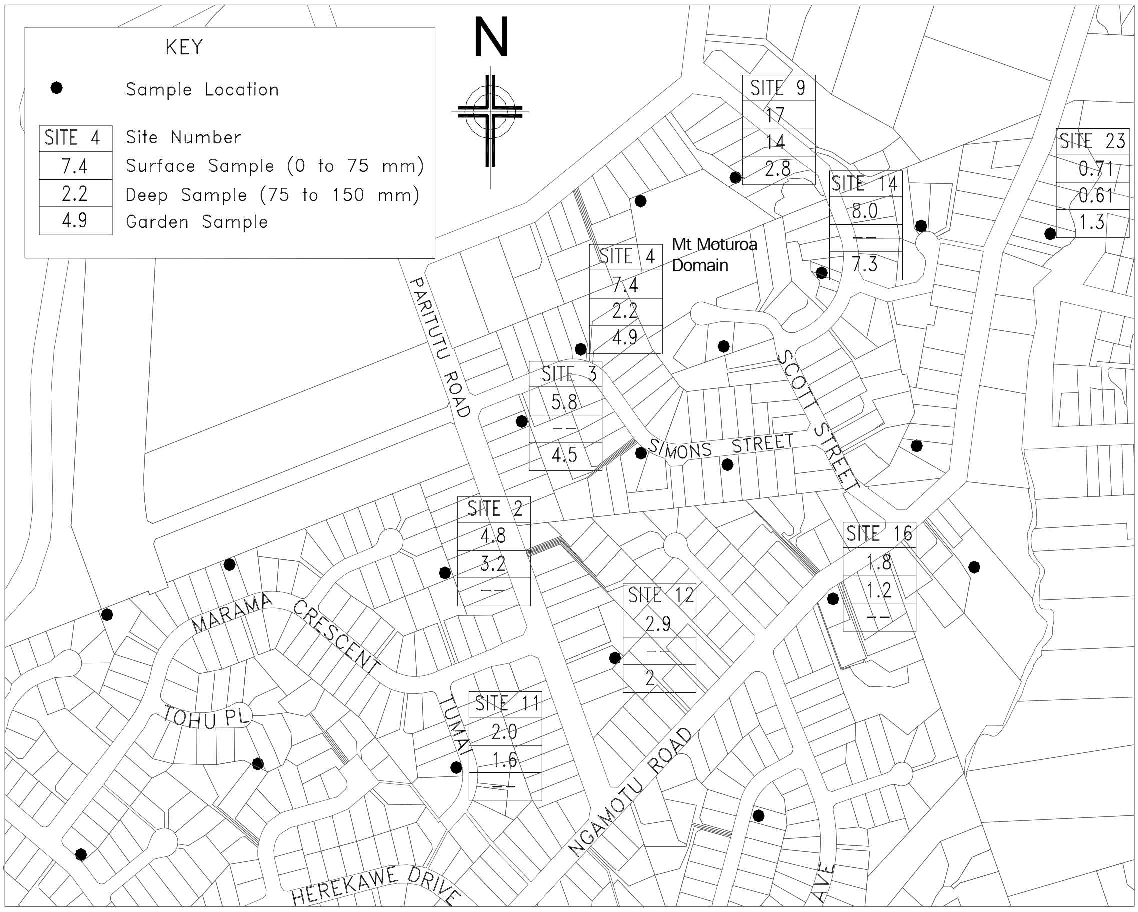


Figure 6: Comparison of garden and surface sample concentrations (ng/kg dry weight)

Table 3: Concentration of 2,3,7,8-TCDD (ng/kg dry weight) in surface and deeper soils

Site Number	Surface (0 – 75 mm)	Deeper (75 – 150 mm)
02	4.8	3.2
04	7.4	2.2
09	17	14
11	2.0	1.6
16	1.8	1.2
23	0.71	0.61

There is a good relationship between the surface and deeper soils, as shown in Figure 7, which plots the surface sample TCDD concentration (the x or horizontal axis) against the TCCD concentration of the deeper samples (the y or vertical axis), at the same location. A linear least-squares regression[10] has been performed to fit a line through the data. The slope of the line (0.735) shows that the TCDD concentration in the deeper soil concentration is, on average, roughly 70% of the surface soil concentration.

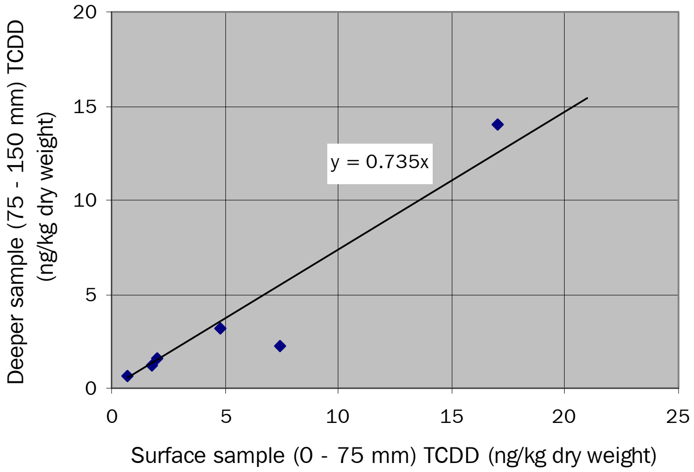


Figure 7: Correlation of 2,3,7,8-TCDD concentrations between surface and deeper samples

A drop-off in TCDD concentration with depth is expected, as TCDD binds very strongly to soil and has a low solubility, therefore little leaching to greater depth is expected.

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[10] Least squares regression line is a mathematical technique to obtain a best-fit line to a data set by minimising the square of the deviations of the data points from the line. In this case the line has been forced to pass through zero, and the slope of the line gives the relationship between the two sets of data, ie. deeper concentration (y-axis) = slope x surface concentration (x-axis).

However, some vertical migration would be expected, including the physical movement of soil by soil biota, and the flushing of small soil particles and fine sediment through soil pores and cracks. It is not clear from this study at what depth 2,3,7,8-TCDD would no longer be detected. A deeper vertical profile of samples would be required to assess this.

4.5 Comparison of Surface Soils with Garden Soils

Eleven samples were taken from gardens from a number of properties, and of these, six samples were analysed for 2,3,7,8-TCDD. The locations and TCDD concentrations are shown in Figure 6. Garden samples were taken to:

- Determine whether there were any significant differences in TCDD concentrations between areas that were supposed to be undisturbed soil (i.e. lawn areas) with areas that were clearly cultivated.
- Better understand the potential for human exposure to TCDD for people who are consumers of home-grown vegetables.

Garden cultivation might be expected to result in lower TCDD concentrations, as deeper soil (with presumably less contamination) would be mixed with the shallower more contaminated soil. The amount of dilution would depend on the depth of cultivation and the extent to which TCDD penetrates otherwise undisturbed soil. Further, adding imported soil or compost to gardens could result in additional dilution.

On the other hand, gardening activities might deposit additional TCDD in gardens. Much of the TCDD will initially be deposited on the leaves of grass making up lawn areas rather than be deposited directly on the soil surface. TCDD attached to the grass may undergo transformation (e.g. photodegradation on the leaf surface) or drop or be washed to the soil surface attached to particulate matter. However, if the lawn is cut before transformation or loss to the soil occurs, some of the TCDD attached to the grass would be removed as lawn cuttings. Depending on the gardening practices of the particular household, the lawn clippings could then be spread on gardens, either directly or after composting. This could result in a total mass of TCDD deposited per square metre being greater than for undisturbed soil, with the soil concentrations then being dependent on the amount of vertical mixing (and dilution) that occurred during gardening activities.

The results of the garden samples compared with the surface samples from the same properties are shown below in Table 4 and on Figure 8. A least squares regression has been performed in a similar manner to that performed between the surface and deeper samples (see previous section).

Apart from the garden result from Site 09, a good correlation exists between the surface and garden samples. Ignoring Site 09, the slope of the line shows that the garden TCDD concentration averaged approximately 80% of the concentration of the nearby surface lawn-soil concentration.

Table 4: Concentration of 2,3,7,8-TCDD (ng/kg dry weight) in surface and garden samples

Site no.	Surface (0 – 75 mm)	Garden	Garden Type
03	5.8	4.5	Vegetable garden
04	7.4	4.9	Ornamental, raised, old
09	17	2.8	Terraced, ornamental, from filled area.
12	2.9	2	Ornamental lawn border.
14	8.0	7.3	Terraced, from natural ground level.
23	0.71	1.3	Ornamental lawn border, slightly raised.

The garden sample results are somewhat higher than expected if substantial mixing in of "clean" deeper soil occurs during garden cultivation. Three reasons are suggested for the lack of apparent dilution:

- Garden cultivation has been relatively shallow, perhaps less than 200 mm, with the result that minimal deeper soil has been brought to the surface. The nature of some of the gardens suggests this is a possibility. Many of the sampled properties do not have gardens and, of those that did, most had only ornamental gardens. Ornamental gardens would generally be cultivated to a shallower depth than vegetable gardens, but also, of the properties that did have gardens, few had the appearance of being the work of "keen" gardeners, who might cultivate to greater depths.
- TCDD has reached deeper in the soil column than expected, certainly more than 150mm in the sites where deeper samples were taken from lawn areas, and presumably other similar locations.
- Addition of grass clippings to gardens has indeed resulted in greater accumulation of TCDD in the soil.

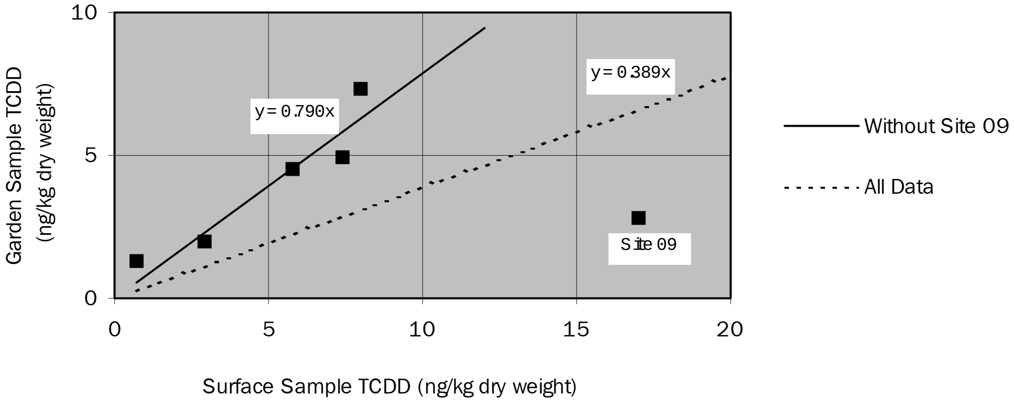

Figure 8: Correlation between surface and garden samples.

The garden sample from Site 09 is thought to be anomalous, as it was taken from the built-up part of a terraced garden. The appearance of the garden suggests that the terraces have been formed by cutting into the slope and the excavated soil used to fill the slope below the cut section. Imported soil may also have been used as terrace-fill. The resultant garden may therefore have undergone greater mixing and dilution than the other gardens sampled.

4.6 Calculation of TEQ Values

Toxic equivalent concentrations have been calculated for the eight samples analysed for full dioxin profiles using both the World Health Organization (WHO) and International TEFs. The results are presented in Table 5. It can be seen that, in absolute terms, the WHO-TEQ concentrations are typically less than 1 ng/kg higher than the corresponding I-TEQ concentrations, and 1 – 10% higher, in relative terms. For these particular samples, the difference is mainly a result of there being sufficient 1,2,3,7,8-PeCDD to have an effect because of the difference in the 1,2,3,7,8-PeCDD TEF between the two schemes (1 in the WHO scheme versus 0.5 for the International scheme). As discussed previously, in practical terms the difference is small, as the TEQ is dominated by the contribution of 2,3,7,8-TCDD, which has the same TEF in both the WHO and International schemes.

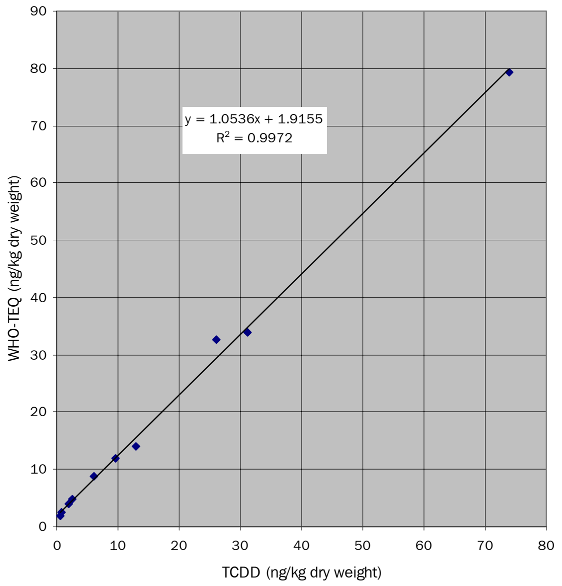

Figure 9: Correlation of WHO-TEQ with 2,3,7,8-TCDD concentrations

The full dioxin profile analyses also present the opportunity to compare 2,3,7,8-TCDD concentrations with TEQ values. Figure 9 is a plot of 2,3,7,8-TCDD versus TEQ. The plot includes concentration data from the two New Plymouth samples collected by MfE as part of their national environmental survey (see Appendix B, Section B.3). A least squares regression line has been calculated.

Table 5: 2,3,7,8-PCDD and PCDF concentrations and TEQ values (ng/kg, dry weight basis)

	I-TEFs	WHO-TEFs	SS#04	SS#05	SS#06	SS#11	SS#13	SS#22	SS#24	SS#27
2,3,7,8-TCDD	1	1	9.7	74	13	2	6.1	0.8	2.5	26
1,2,3,7,8-PeCDD	0.5	1	1.2	4.1	0.53	1.2	1.2	<0.7	1	3.8
1,2,3,4,7,8-HxCDD	0.1	0.1	0.64	1.4	<0.2	0.51	0.67	<1	0.64	1.6
1,2,3,6,7,8-HxCDD	0.1	0.1	1.3	2.1	0.55	1.3	1.3	1.1	1.6	2.6
1,2,3,7,8,9-HxCDD	0.1	0.1	0.86	1.3	0.54	0.91	1.6	1.3	1.2	1.7
1,2,3,4,6,7,8-HpCDD	0.01	0.01	30	20	10	16	15	25	25	34
OCDD	0.001	0.0001	300	160	80	100	110	180	220	230
2,3,7,8-TCDF	0.1	0.1	0.28	1	0.23	<0.6	0.95	0.64	0.95	3.1
1,2,3,7,8-PeCDF	0.05	0.05	0.23	0.35	0.16	0.64	0.64	0.54	0.85	1.5
2,3,4,7,8-PeCDF	0.5	0.5	<0.7	<0.8	<0.4	<0.5	1	0.8	0.59	1.8
1,2,3,4,7,8-HxCDF	0.1	0.1	<0.6	0.45	<0.6	<0.6	0.87	0.88	0.77	1.4
1,2,3,6,7,8-HxCDF	0.1	0.1	<0.8	<1	<0.4	<0.5	0.64	0.7	0.6	<1
2,3,4,6,7,8-HxCDF	0.1	0.1	0.39	0.56	0.34	<0.7	0.89	0.9	1	1.6
1,2,3,7,8,9-HxCDF	0.1	0.1	<0.3	<0.3	<0.2	<0.2	<0.4	<0.5	<0.2	<0.8
1,2,3,4,6,7,8-HpCDF	0.01	0.01	7.4	5.4	2.8	4.3	5	8.5	9.7	13
1,2,3,4,7,8,9-HpCDF	0.01	0.01	<0.8	<0.6	<0.3	<0.6	<0.4	<0.7	<0.4	0.6
OCDF	0.001	0.0001	24	14	6.5	2	5	12	17	16
I-TEQ[1]			11.6	77.4	13.8	3.47	8.26	2.56	4.6	30.9
WHO-TEQ[1]			11.9	79.3	14.0	3.98	8.76	2.56	4.90	32.6
WHO-TEQ / I-TEQ (%)			103%	102%	101%	115%	106%	100%	106%	105%

Notes:

1. TEQ values calculated using half the limit of detection where a congener was not detected and a detection limit was reported.

There is a close correlation[11] between the 2,3,7,8-TCDD concentration and the TEQ value, with the regression equation being:

TEQ concentration = 1.92 + 1.053 x (2,3,7,8-TCDD concentration)

In simple terms, the TEQ value is approximately 5% higher than the TCDD concentration plus about 2 ng/kg. Clearly, the TCDD dominates the TEQ for the results considered.

The regression equation can be used to estimate TEQ values from the 2,3,7,8-TCDD concentrations for the other samples from this study which were not analysed for a full dioxin profile, but for which specific 2,3,7,8-TCDD analysis was carried out. This prediction assumes that there is a common source of the dioxin contaminants (and hence similar dioxin profiles) for all samples. The estimated TEQ values are shown in Table 6. In general, the differences are sufficiently minor that the TCDD concentration can be used to approximate the TEQ value for most purposes.

4.7 PCDD and PCDF Congener Profiles

PCDD and PCDF congener profiles can display characteristic signatures typical of particular sources. For example, dioxins produced from the incineration of waste will have a different signature to a chemical process source (Cleverly *et al.*, 1997). There are a number of ways of presenting congener profiles. One method is to present the concentrations of each of the seventeen 2,3,7,8-substituted PCDD and PCDF congeners as a percentage of the total ($Cl_4 – Cl_8$) PCDD and PCDF[12] concentration.

This procedure has been performed for the eight samples analysed for full profiles in this study, and also on profile data from eight provincial towns and cities and from industrial and residential areas in Auckland city from the 1996 MfE national environmental survey study (Buckland *et al.*, 1998). A similar procedure could also have been carried out for data from Christchurch. The provincial centre profiles include the two New Plymouth results mentioned previously. The profiles are presented in Figure 10. (Note that the MfE study also has data for Christchurch, which, when plotted as congener profiles, shows a similar pattern to the Auckland profiles and therefore has not been presented here.)

There are some remarkable similarities but also some significant differences in the profiles. All profiles are dominated by OCDD, with lesser contributions from OCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,7,8,9-HpCDF. However, there are significant differences in the detection of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD in samples from the current study and in the samples collected for the MfE national environmental study in New Zealand urban areas other than New Plymouth. In the MfE national environmental

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[11] The R^2 value of 0.997 from the regression indicates good correlation. R^2 = 1 signifies perfect correlation.

[12] The sum of PCDD and PCDF congeners with four to eight chlorine atoms attached.

Table 6: 2,3,7,8-TCDD concentrations and TEQ values compared with guidelines (ng/kg)

New Zealand guideline (MfE/MoH, 1997)	1,500	I-TEQ
Germany (BMU, 1999)	1,000	I-TEQ
USEPA (Fields, 1998)	1,000	TEQ
EPA Region 6 (2001) & Region 9 (2000)	39	2,3,7,8-TCDD
US ATSDR (ATSDR, 1998)	50 1,000	TEQ - Screening Level TEQ - Action Level

Sample ID	Address	2,3,7,8-TCDD [1]	TEQ [2]	TEQ [3] Estimated
SS#01	36 Marama Crescent	5.9		8.1
SS#02	12A Tahora Place	4.8		7.0
SS#03	42 Paritutu Road	5.8		8.0
SS#04	11 Simons Street	7.4 (9.7)	11.9	9.7
SS#05	Mt Moturoa Domain	92 (74)	79.3	99
SS#06	52A Marama Crescent	15 (13)	14.0	18
SS#07	28A Simons Street	3.4		5.5
SS#08	29 Scott Street	6.1		8.3
SS#09	19 Port View Road	17		20
SS#10	12 Tohu Place	3.6		5.7
SS#11	8 Tumai Place	2.0 (2.0)	3.98	4.0
SS#12	12A Paritutu Road	2.9		5.0
SS#13	36 Simons Street	6.2 (6.1)	8.76	8.4
SS#14	7 Findlay Place	8.0		10
SS#15	19 Rangitake Place	1.9		3.9
SS#16	79 Ngamotu Road	1.8		3.8
SS#17	58 Ngamotu Road	0.93		2.9
SS#18	9 Catherine Crescent	4.5		6.7
SS#19	Onuku Taipari Domain	1.0		3.0
SS#20	133 Ngamotu Road	4.8		7.0
SS#21	20 Rospeath Crescent	0.75		2.7
SS#22	55A Ngamotu Road	0.76 (0.8)	2.56	2.7
SS#23	37 Ngamotu Road	0.71		2.7
SS#24	108 Pioneer Road	2.7 (2.5)	4.90	4.8
SS#25	Ngamotu Domain	2.2		4.2
SS#26	Ngamotu Domain	3.0		5.1
SS#27	AW [4]	27 (26)	32.6	30
SS#28	81 South Road	0.88		2.8
SS#29	cnr Whiteley & Breakwater roads	3.3		5.4
SS#30	70 Banks Street	2.4		4.4
SS#31	St Josephs School, Calvert Road	0.81		2.8
SS#32	105 Centennial Drive	6.1		8.3
SS#33	151 Breakwater Road	10		13
SS#34	AW [4]	7.3		9.6
SS#35	100 Centennial Drive	2.3		4.3
Geometric means [5]		3.7	11.6	6.5

1. 2,3,7,8-TCDD Concentrations from specific analysis, with concentration from full profile analysis in brackets.
2. TEQ values from Table 5.
3. Estimated TEQ value using least squares regression (see Section 4.6).
4. AW = Address withheld. Permission to release address not given.
5. Geometric mean is a better estimate than arithmetic mean for data that appear to be log-normally distributed.

survey (Buckland *et al.*, 1998), 24 samples were collected from urban areas in Auckland, Christchurch and provincial centres, including two samples in New Plymouth. 2,3,7,8-TCDD was not detected in any of the samples (detection limit range 0.1 – 1 ng/kg, median 0.4 ng/kg), except the two New Plymouth samples. In the same 24 samples, 1,2,3,7,8-PeCDD was also not detected, except in a single New Plymouth sample (detection limit range 0.1 – 3 ng/kg, median 0.6 ng/kg).

In the current study, 2,3,7,8-TCDD was detected in all 47 samples for which 2,3,7,8-TCDD analysis was carried out (minimum concentration 0.81 ng/kg) and 1,2,3,7,8-PeCDD was detected in all but one of the eight full dioxin profile analyses that were carried out (detection limit 0.7 ng/kg).

Further comparisons may be made with TEQ values calculated from the full dioxin profiles from the MfE national environmental survey and the current study. The MfE study reported I-TEQ values. The MfE TEQ values have therefore been recalculated using the WHO TEFs, assuming values for non-detects of half the analytical detection limit. The range of TEQ values is shown in Table 7, compared with the data from the current study. The two New Plymouth results have been left out of the provincial centre dataset on the assumption that the New Plymouth results are not typical of other provincial towns and cities in New Zealand. The differences in congener profiles between the New Plymouth dataset and other urban areas in New Zealand, as discussed earlier and illustrated in Figure 10, supports this assumption.

Table 7: Comparison of TEQ results from this study with the MfE national environmental survey (ng/kg)

Dataset	No of Results	TEQ Range	Mean TEQ	TCDD & PeCDD Detection Limit Range
Current study	8	2.56 – 77.4	19.8 [1]	-
Current study recalculated [2]	8	0.98 – 3.20	1.86	0.5 (assumed)
Provincial towns and cities [3, 4]	7	0.77 – 3.15	1.29	0.1 – 0.3 TCDD (actual) 0.3 – 0.8 PeCDD (actual)
Auckland [4]	9	1.09 – 4.97	2.16	0.3 – 1 TCDD (actual) 0.3 – 3 PeCDD (actual)

Notes

1. This arithmetic mean is biased by samples SS#05 and SS#27 and should not be taken as representing the TEQ for the study area. It is given for completeness to compare with the other mean values. A better estimate for the mean TEQ of the study area is the geometric mean of 6.5 ng/kg from Table 6.
2. Recalculated with 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD at an assumed limit of detection and taking half the limit of detection in the TEQ calculation.
3. Excluding two New Plymouth results.
4. Data from the national environmental survey (Buckland *et al.*, 1998)

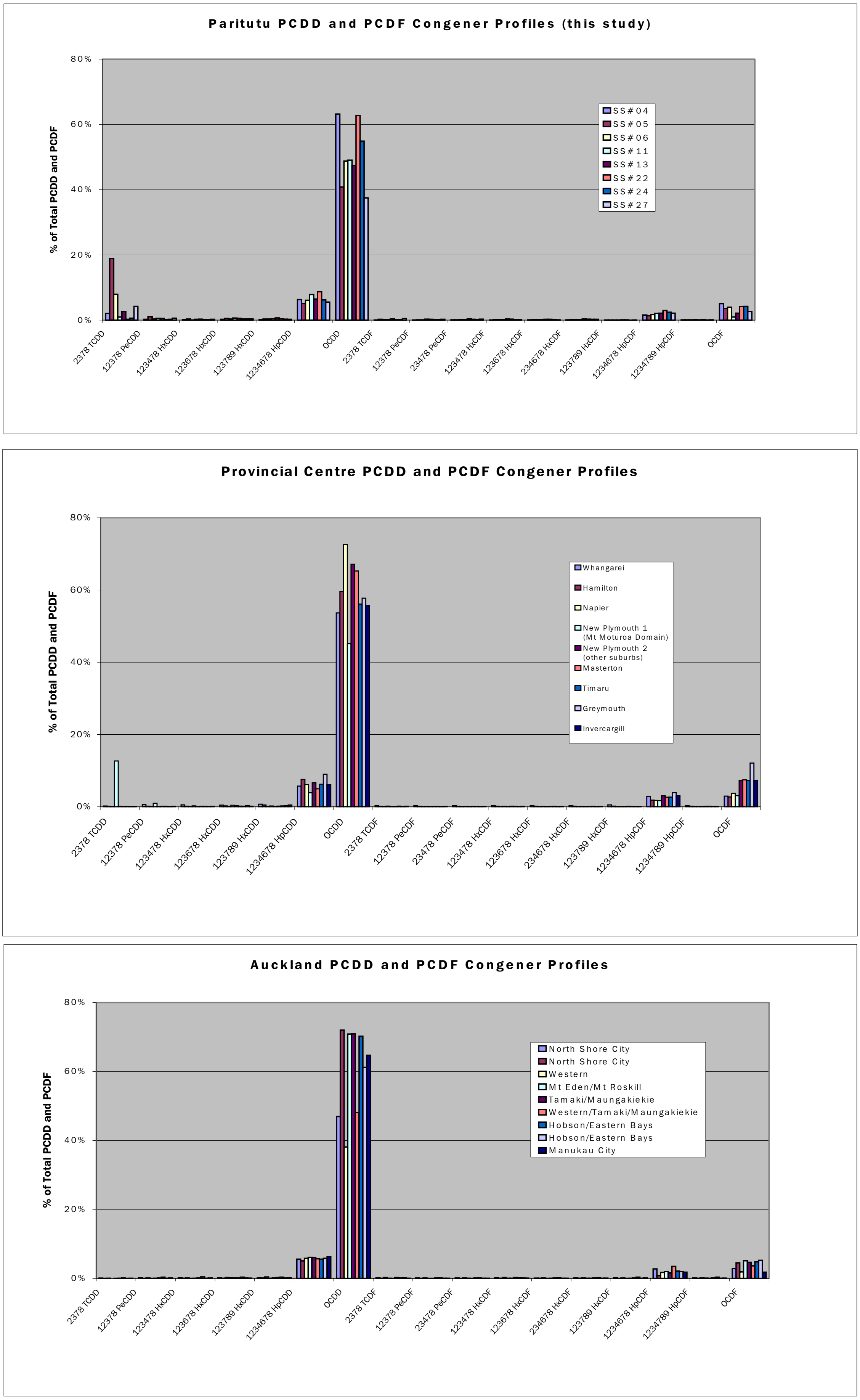

Figure 10: PCDD and PCDF congener profile comparisons

Table 7 also shows the TEQ value for the current study recalculated with the concentration for 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD set to 0.25 ng/kg, to simulate non-detects at a detection limit of 0.5 ng/kg, roughly the mean detection limit in the MfE national environmental survey (Buckland *et al.*, 1998) for these congeners.

It can be seen that the range and mean TEQ value for Auckland, the provincial centres (excluding New Plymouth) and the recalculated current study values (where TCDD and PeCDD have been set to a simulated detection limit) are all similar. In interpreting these values, it should be noted that typically 0.5 – 0.8 ng/kg of the TEQ is a mathematical artefact of setting non-detect values at half the detection limit. As has already been pointed out, the majority of the TEQ from the current study is from 2,3,7,8-TCDD. What the recalculation also shows is that without this contribution, and to a lesser extent the contribution of 1,2,3,7,8-PeCDD, the TEQ is similar to other urban centres in New Zealand.

In summary, it would appear that the New Plymouth (and Paritutu) results are typical of other towns and cities in New Zealand except there is an “overlay” of 2,3,7,8-TCDD and to a lesser extent 1,2,3,7,8-PeCDD.

4.8 Comparison with Previous Paritutu Studies

Results from earlier studies of dioxin concentrations in the Paritutu area (Appendix B), where the sampling locations are known, have been added to the contour plot from the current study in Figure 11.

It is difficult to relate many of these historical studies to the current study, particularly those carried out in 1985 and 1986 (as reported in Pilgrim, 1986), as the precise sample locations are not known and many of the samples were taken as composites collected over distances of several hundred metres. There are also uncertainties with the reporting basis of these earlier studies, but for the purposes of comparison it is assumed that all results are concentrations of 2,3,7,8-TCDD, dry weight. Because of these uncertainties, no attempt has been made to modify the concentration contours to take account of the earlier data. The contours are presented merely to facilitate comparison of the earlier data with the current study results.

Looking firstly at the more recent studies, of particular interest is the MfE national environmental survey (Buckland, *et al.*, 1998). This study included a sample from Mount Moturoa Domain, which returned a concentration of 31.2 ng/kg 2,3,7,8-TCDD. The sample was taken from the flat top of Mt Moturoa, and fits in well with values obtained in the current study.

Three samples were collected by TRC (2001) within residential properties (two were in the same property), but none reported quantified concentrations of TCDD. Detection limits were up to 6 ng/kg for these samples. However, assuming concentrations lie somewhere in the range 0 to 6 ng/kg, the results are consistent with the current study.

Soil samples recently collected and analysed on behalf of the Community Residents Action Group returned concentrations of 0.7 and 19 ng/kg. As previously discussed it is not known where the samples were collected nor whether the results are for 2,3,7,8-TCDD or TEQ, although the distinction is not expected to be important in this case. The lower concentration is consistent with the lower concentrations from the current study. The higher result is higher than that generally found within the residential areas, although it is consistent with what might be expected on the west and north facing slopes of Mount Moturoa, along the western and possibly southern boundaries of the Dow plant, or within industrial land to the east and reserve land to the north-west of the plant.

The 1985 and 1986 studies (pilgrim, 1986) tend to conflict with some of the results of the more recent studies. Results from the April 1986 study in Marama Crescent, Simons Street/Paritutu Road, Port View Road/Mt Moturoa and Centennial Drive north-east of the plant can all be compared to varying degrees with the current results. The Simons Street/Paritutu Road composite sample returned a non-detect, with a limit of detection of 10 ng/kg, which is not inconsistent with the current study. The Port View Road/Mt Moturoa composite (110 ng/kg) is also consistent with the current study, being similar to the 92 ng/kg recorded in this study on Mt Moturoa. However, the measured concentrations for the composites from Marama Crescent (20 ng/kg) and Centennial Drive (100 ng/kg) are higher than the current study by about four and 20 times, respectively.

The TRC soil samples at pylons 3 and 4, adjacent to Centennial Drive to the west of the plant (TRC, 2001), may be compared with composite samples taken in April 1986 immediately after the TCP plant incident (Pilgrim, 1986). The samples taken in 2001 returned concentrations of 2,3,7,8-TCDD eight to 40 times lower than the 1986 values.

There are several reasons why earlier concentrations may be higher than those measured in the current study or the TRC study from 2001:

- Soil concentrations may vary considerably over relatively short distances. However, the mode of deposition and the earlier and current results suggest that this is not generally the case.
- Differences in sampling technique, in particular the shallower sampling depth of some of the earlier studies, may result in higher concentrations. This is likely to be an important factor, accounting for some of the differences in observed concentrations.
- Differences in analytical techniques and the analytical standards used to quantify TCDD concentrations. It is reasonable to expect that the current methods and standards are more reliable than those used in the past due to significant improvements that have occurred over the last 15 years.
- Attenuation has occurred through volatilisation, degradation, leaching, and dust and soil removal. As discussed previously, 2,3,7,8-TCDD is particularly persistent and is generally not susceptible to degradation or leaching once it is bound to soil

- ● PDP - May/June 2002
- ⊕ TRC - June 2001
- ♦ MfE - 8 March 1996
- ▼ DoH - 16 April 1986
- ⊘ DoH - 15 April 1986
- × RAPCO - 17 April 1985

Height contours - 5m intervals
Height contours - 20m intervals
2,3,7,8-TCDD concentration contours for PDP results

0m SCALE 200m 400m

Note that the DoH (⊘) results are reported as TCDD and are assumed to be 2,3,7,8-TCDD for the purposes of this figure.

All concentrations reported as ng/kg

Figure 11: 2,3,7,8-TCDD results from current and earlier investigations

active deposition, and, in particular, the 1986 samples were taken immediately after the TCP incident. The samples may be biased by 2,3,7,8-TCDD that is at high concentrations at the very surface, which may have subsequently been removed or degraded to some extent. There is evidence that at the very surface (top few millimetres) the half life of TCDD may be 9 – 15 years (Paustenbach *et al*., 1992) as reported in Buckland *et al*., 2000). This may account for a reduction to perhaps 25% of the original value at the very surface. However, it is unlikely to account for any significant reduction below the first few millimetres of soil, where half-lives of 25 – 100 years in sub-surface soil have been reported (Paustenbach *et al*., 1992).

- The areas have been subjected to soil disturbance or soil build-up, such that, in effect, a different soil profile was sampled.

It is not possible to assess the relative importance of these potential causes for the differences observed between the earlier and more recent studies. Nor is it possible to definitively assess whether residents may, in the past, have been exposed to somewhat higher average concentrations in soil than are currently observed. However, on the basis of a 2,3,7,8-TCDD half-life in soil measured in decades, it is not expected that soil concentrations in residential areas would have been markedly higher than those measured in the current study.

4.9 Data Quality

A variety of data are available to assess the quality of the results of this study. Equipment rinsate blanks and trip blanks were collected during the sampling. One rinsate blank was analysed and returned a non-detect for 2,3,7,8-TCDD, at a detection limit of 0.01 ng/L. In the absence of obvious errors in the primary results, no further rinsate and no trip blanks were analysed.

Laboratory quality control is reported on the analytical certificates (Appendix F). The analytical procedure is also summarised in Appendix F. The primary laboratory (AgriQuality) processed a laboratory blank with each batch of samples (typically 8 – 10 samples per batch). All blanks were reported as non-detects. The AgriQuality method statement reports an on-going performance and recovery standard was analysed with each batch of samples to assess method precision. Recoveries of all isotopically labelled surrogate standards (reported on each analytical certificate) were also within the required limits specified by USEPA Method 1613.

As discussed previously, eight samples were reanalysed for a full dioxin profile to enable TEQ concentrations to be determined. This provides the opportunity to compare the 2,3,7,8-TCDD concentration from the full profile analysis with the result from the 2,3,7,8-TCDD specific analysis. In addition, two split samples were analysed for 2,3,7,8-TCDD by Pace Analytical to provide an independent check of the primary analytical laboratory. These results are presented in Table 8.

The majority of the full profile 2,3,7,8-TCDD concentrations were generally close (typically within 20%) to 2,3,7,8-TCDD specific analysis. The largest discrepancy was for sample SS#05. Differences may arise for two main reasons. Firstly, separate sub-sample were analysed for the 2,3,7,8-TCDD specific and full profile analyses, and while the two sub-samples were taken from the same homogenised sample and should have been identical, inhomogenities in the sample may result in different concentrations for 2,3,7,8-TCDD. Secondly, during the 2,3,7,8-TCDD specific analysis, the GC-MS equipment is specifically calibrated to detect 2,3,7,8-TCDD. However, for the analysis for the full congener profile, a compromise calibration has to be used to accommodate the measurement of a wide range of ion[13] masses. This compromise can result in a different concentration being quantified for the two analyses. Overall the comparison between the two sets of results is considered excellent.

Similarly, there was a good agreement (Table 8) in the results from the analysis of two cross-check samples by AgriQuality and Pace Analytical. The good agreement provides confidence that the primary analytical laboratory results are reliable.

Table 8: 2,3,7,8-TCDD concentration quality assessment

Sample ID	TCDD specific [1]	Full profile [1]	Independent [2]
SS#02	4.8	-	3.9
SS#04	7.4	9.7	
SS#05	92	74	94
SS#06	15	13	
SS#11	2	2	
SS#13	6.2	6.1	
SS#22	0.76	0.8	
SS#24	2.7	2.5	
SS#27	27	26	

1. Analysed by AgriQuality, Lower Hutt
2. Analysed by Pace Analytical Services, USA

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[13] An ion is an atom or group of atoms carrying an electrical charge. During the analytical process the dioxin compounds are ionised to enable them to be separated out for identification and quantification.

5.0 Comparison with International Guidelines

5.1 Introduction

A variety of international soil criteria exist for dioxin against which the results of this study may be compared. Several soil criteria and their basis are set out in Appendix C.

Most of the soil criteria do not have statutory force, but are issued as guidelines in recognition that:

- The science is not definitive.
- The assumed exposure scenarios are conservative assumptions of what might occur in reality.
- Exposure on a site will vary on a case by case basis depending on the land use and the receptors present on the site.
- The measurement of contaminant concentrations in soil is not an absolute process, with, for some situations, concentrations potentially varying over short distances.

While a result in excess of a guideline criteria may indicate a potential for a health risk to occur, it should be not be immediately assumed that a health risk will eventuate. Any risk will be relative to the exposure assumed in the derivation of the guideline and the exposure likely in the actual situation. The guidelines set out in Appendix C are for a residential (and in some cases parkland) scenario in which long-term frequent exposure through soil ingestion, and in some cases ingestion of produce grown on site, inhalation of dust and dermal contact with soil, is assumed. Exposure as a child is factored in. Residential exposure scenarios will result in lower guideline values than an industrial exposure scenario, where only adults are considered, the exposure duration and frequency is restricted to working hours and the opportunity for and degree of exposure to soil is less.

Some guidelines assume an tolerable daily intake (TDI), based on animal studies in which a “no observable adverse effects level” (NOAEL) in the animals concerned is factored down, generally by several orders of magnitude, to take account of experimental and interspecies uncertainty.

For human carcinogens, some guidelines assume there is no threshold TDI below which no effects will occur, but adopt the approach that there is some low frequency of cancer end points that is “acceptable”. The USEPA uses this approach for carcinogens, adopting a incremental cancer risk in a lifetime of 10^{-6} (1 in 1,000,000) on the basis that this will result in a cancer risk of 10^{-4} to 10^{-6} for exposure to the mixtures of chemicals typically found on Superfund sites (USEPA, 1996a). Superfund sites are major, federally listed contaminated sites in the US.

In New Zealand, for setting soil guidelines the Ministry for the Environment and the Ministry of Health have adopted a similar approach to the USEPA with respect to carcinogens (MfE/MoH, 1997, MfE, 1997, 1999), but have assumed a cancer risk of 10^{-5} (1 in 100,000). The MoH have also used a cancer risk of 10^{-5} in setting drinking-water standards. This cancer risk is in the middle of the range that the USEPA considers acceptable.

Many soil criteria documents use terms such as “screening level” and “action level”, which may or may not be tied into local regulatory practices. Typically a screening level is a trigger to carry out further investigation at a hazardous waste site (ATSDR, 1998, USEPA R9, 2000), but it is not considered a remediation level. An action level would typically trigger some sort of intervention, but not necessarily remediation. Other intervention could include site-specific exposure assessments, behaviour modification for occupants or institutional controls to prevent sensitive site uses. This is consistent with the concept of the soil criteria being guidelines, rather than regulatory numbers.

5.2 Guidelines Used for this Study

Five different guidelines have been chosen for comparison with the results of this study, as set out in Table 9 below.

Table 9: Residential soil guidelines (ng/kg)

Country	**Guideline**	**Comment**
New Zealand guideline (MfE/MoH, 1997)	1,500	I-TEQ – Interim guideline currently under review
Germany (BMU, 1999)	1,000	I-TEQ - Action level
USEPA (Fields, 1998)	1,000	TEQ
EPA Region 6 (2001) & Region 9 (2000)	39[1]	2,3,7,8-TCDD
US ATSDR (ATSDR, 1998)	50 1000	TEQ – Screening Level TEQ – Action Level

1. Set at 3.9 ng/kg for a one in a million cancer risk. Figure of 39 ng/kg is adjusted value for 1 in 100,000 cancer risk, consistent with other NZ guideline values.

The United States has a number of different guidelines promulgated by both state and federal agencies. The Federal EPA, the primary agency for developing regulations for soil in the US, has a preliminary remediation goal (PRG) of 1,000 ng TEQ/kg for residential soil. In response to a number of EPA regions setting their own criteria, the Office of Solid Waste and Emergency Response has issued a directive stating that this level (i.e. 1000 ng TEQ/kg) is to be generally used as a PRG for dioxin in surface soil at residential sites (Fields, 1998).

Two USEPA regional offices have issued their own, very much lower, risk-based guidelines for 2,3,7,8-TCDD - Region 6 and Region 9. Both these guidelines have similar derivations, being consistent with the Soil Screening Guidance: User's Guide and Technical Background Document (USEPA 1996a,b), and combine exposure from ingestion, dermal contact and inhalation of dust. To make the values consistent with the

New Zealand approach of using a cancer risk of 1 in 100,000 the USEPA Region 6 and 9 guideline values have been multiplied by 10 in Table 9 (see Appendix C). The Region 6 and 9 values are considered to be screening values which, if exceeded, indicate further investigation, rather than remediation, is required.

Canada has recently issued a revised residential/parkland soil guideline to replace the interim soil quality criterion set in 1991. The new value of 4 ng TEQ/kg (CCME, 2001) is not an effects-based value, but is based on a policy decision to classify dioxin as “toxic” under the Canadian Environmental Protection Act. As such, dioxin is slated for virtual elimination and the guideline has been set at a value considered to be representative of the mean background concentration of dioxins in Canadian soils. The same value also applies to agricultural, commercial and industrial land. The supporting documentation notes that the soil quality guidelines for dioxins are considered to be management levels, rather than levels that are protective of human or environmental health, because the guideline is not effects based. Accordingly, it is not considered appropriate to compare the results of the current study with the Canadian guideline, as the guideline does not provide a measure of the health risk posed by a value exceeding the guideline.

5.3 Guideline Comparison and Risk Assessment

The results reported in Section 4 are compared with the five guideline values in Table 6. A comparison is also made in histogram form in Figure 12.

The histogram shows all but one of the results fall below both the USEPA Region 6 and Region 9 guidelines and the ATSDR guideline. All values fall below the New Zealand, German and Federal USEPA criteria by large margins.

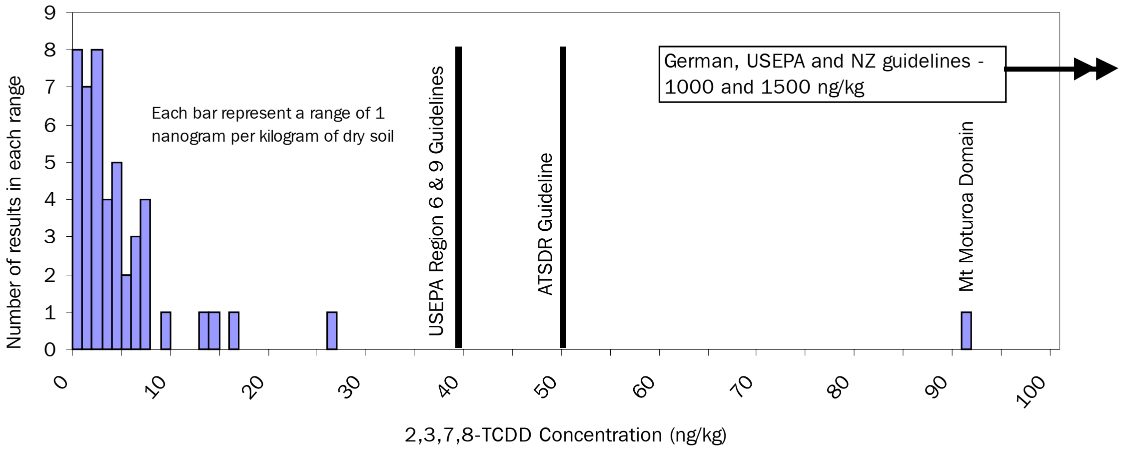


Figure 12: Histogram of 2,3,7,8-TCDD results showing guideline values

The single result (92 ng/kg) that falls outside the USEPA Region 6 and 9, and ATSDR guidelines is the sample from the west-facing slope of Mount Moturoa Domain, a recreational reserve. The MfE result (Buckland *et al.*, 1998) from elsewhere on the Domain (31.2 ng/kg TCDD,) complies with these guidelines. The dioxin concentration collected for the community action group (as reported in the Daily News, Appendix B), and all the TRC samples collected on residential and reserve land, are also below the Region 6 and 9 and ATSDR screening guidelines.

Examining the spatial distribution of the results from the current study (Figure 12), it is reasonable to conclude that, for the residential area of Paritutu, apart from part of the west-facing slopes of Mount Moturoa Domain, the surface soil can be expected to have 2,3,7,8-TCDD (and TEQ) values less than the USEPA Region 6 and 9 screening values.

The land immediately to the west, and below Mount Moturoa, towards the Dow plant is in industrial use (see Figure 2), for which the residential criteria does not apply. The USEPA Region 6 screening values for indoor and outdoor industrial workers are 200 and 540 ng TCDD/kg, respectively (adjusted for the New Zealand cancer risk of 1 in 100,000). All the earlier sampling (Appendix B) of industrial land, whether within or outside the Dow property, gave 2,3,7,8-TCDD concentrations that were below the upper value and all but one result were below the lower value.

Within Mount Moturoa Domain there is likely to be an area with 2,3,7,8-TCDD concentrations in excess of the USEPA Region 6 and 9 and ATSDR guidelines. The extent of this area is not known. It is considered that the concentration at Site 05 (Sample SS#05; 92 ng TCDD/kg) will be close to the maximum expected, given that the sample was taken from the highest and most westerly point of Mount Moturoa. The “leading edge” of Mount Moturoa is expected to intercept an air-borne plume travelling from the Dow Plant to a greater degree than any other point to the east of the plant. Previous sampling on Mount Moturoa measured a 2,3,7,8-TCDD concentration markedly lower than that recorded in the current study (Buckland, *et al.*, 1998).

It is appropriate to consider the likely exposure to soil of users of the Domain, in considering whether concentrations in the order of 100 ng TEQ/kg present a risk to recreational users (noting that only part of the Domain will have concentrations of that magnitude, as demonstrated by the markedly lower MfE sample (Buckland *et al.*, 1998)). The Domain has little if any exposed soil, being well covered by grass. Thus the opportunity for exposure to soil will be less than a residential situation with exposed soil in gardens. Further, the residential exposure scenario used in the derivation of the USEPA Region 6 and 9 guideline assumes exposure for a large part of each day for 350 days over a 30 year duration, in a 70 year lifetime.

While it is conceivable that an individual might visit the Domain every day for many years, the duration of daily exposure is likely to be at least an order of magnitude less than the residential situation. The lower opportunity for soil exposure afforded by the grass cover reduces the probability of exposure further. It is therefore considered that a reasonable screening level for a recreational user of Mount Moturoa Domain would be at least an order of magnitude higher than the residential scenario, that is, 390 ng 2,3,7,8-TCDD/kg, and possible higher. On this basis, the likelihood of an area on Mount Moturoa Domain having 2,3,7,8-TCDD concentrations (or TEQ) in excess of this level is considered to be extremely remote, and consequently there is no need to investigate the Domain further.

The concentrations measured around the western edge of the Domain suggest the possibility of 2,3,7,8-TCDD concentrations being somewhere in the range between 90 ng/kg and about 20 ng/kg (i.e. falling within the concentrations measured in samples SS#05 and SS#09) in the three or four residential properties on the north-west side of Mount Moturoa, in Port View Road. Concentrations are likely to be lowest at the base of the hill, and increase with elevation and more westerly aspect.

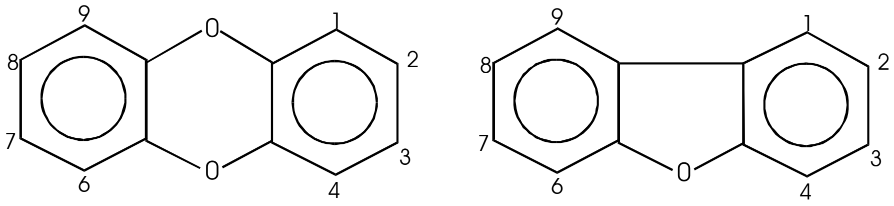
Considering the site-specific characteristics of the Port View Road properties, there appears to be little opportunity for exposure to soil, as these properties have multi-unit flats surrounded by mostly paved surfaces. A high-density residential exposure scenario would therefore be more appropriate than the standard residential scenario, with an appropriate guideline being at least a factor of two higher (the Australian soil guidelines suggests a factor of four, NEPC 1999) than for the standard residential guideline. On that basis, there is no need to investigate these properties further.

Appendix A Background Information on PCDDs and PCDFs

This appendix has been compiled from a number of MfE reports (Buckland *et al.*, 2001, Buckland *et al.*, 1998, Smith and Lopipero, 2001).

A.1 Chemical Structure and Toxicity

The PCDDs and PCDFs are chemically classified as halogenated hydrocarbons. They are tricyclic aromatic compounds, comprising two benzene rings joined via either one or two oxygen atoms at adjacent carbons on each of the benzene rings, as shown in Figure A-1, below.



Dibenzo-p-dioxin

Dibenzofuran

Figure A-1: Structures of dibenzo-p-dioxin and dibenzofuran

Both groups of chemicals may have up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9. Each individual compound resulting from this is referred to as a congener. Each specific congener is distinguished by the number and position of chlorine atoms around the aromatic nuclei. In total, there are 75 possible PCDD congeners and 135 possible PCDF congeners. Groups of congeners with the same number of chlorine atoms are known as homologues. The number of congeners in each homologue group is shown in Table A-1. The most widely studied of the PCDDs and PCDFs is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). This congener is often generically referred to as ‘dioxin’, and is the reference compound for this class of chemicals.

Congeners containing one, two or three chlorine atoms are thought to be of no toxicological significance. However, 17 congeners with chlorine atoms substituted in the 2, 3, 7 and 8- positions are thought to pose a risk to human and environmental health. Toxic responses include dermal toxicity, immunotoxicity, carcinogenicity and adverse effects on reproduction, development and endocrine functions. Increasing substitution from four to eight chlorine atoms generally results in a marked decrease in potency.

Table A-1: Homologues and congeners of PCDDs and PCDFs

Abbreviation	Homologue name	No. of possible congeners	No. of possible 2,3,7,8-chlorinated congeners
MCDD	Monochlorodibenzo-p-dioxin	2	0
DiCDD	Dichlorodibenzo-p-dioxin	10	0
TrCDD	Trichlorodibenzo-p-dioxin	14	0
TCDD	Tetrachlorodibenzo-p-dioxin	22	1
PeCDD	Pentachlorodibenzo-p-dioxin	14	1
HxCDD	Hexachlorodibenzo-p-dioxin	10	3
HpCDD	Heptachlorodibenzo-p-dioxin	2	1
OCDD	Octachlorodibenzo-p-dioxin	1	1
MCDF	Monochlorodibenzofuran	4	0
DiCDF	Dichlorodibenzofuran	16	0
TrCDF	Trichlorodibenzofuran	28	0
TCDF	Tetrachlorodibenzofuran	38	1
PeCDF	Pentachlorodibenzofuran	28	2
HxCDF	Hexachlorodibenzofuran	16	4
HpCDF	Heptachlorodibenzofuran	4	2
OCDF	Octachlorodibenzofuran	1	1

A.2 Toxic Equivalency Factors and Toxic Equivalents

In environmental media, PCDDs and PCDFs occur as complex mixtures of congeners, which therefore complicates any environmental or human health risk evaluation. However, because it is widely accepted that the toxicological action of PCDDs and PCDFs is via a common mechanism of action (in the initial stages, at least), these compounds have been assigned individual toxic equivalency factors (TEF) values, as agreed by international convention (see, for example, Kutz *et al*., 1990; Van den Berg *et al*., 1998). This mechanism of action is believed to involve the binding of a congener to a cellular protein known as the ‘Ah receptor’. The importance of the TEF approach is that it allows the combined toxicity of a complex mixture of congeners to be represented in terms of a single numerical value, or ‘toxic equivalents’ (TEQ). The TEQ contribution of each congener is calculated by multiplying its concentration by the TEF for that congener. This approach facilitates risk assessment and regulatory control of exposure to these mixtures.

The TEQ method is based on toxicological and in vitro biological data, and knowledge of structural similarities among this group of chemicals. In essence, TEFs are estimates of the relative toxicities of individual PCDD and PCDF congeners compared to the toxicity of 2,3,7,8-TCDD, which, as the reference compound for this group of chemicals, is assigned a TEF of 1. All 2,3,7,8-PCDDs and PCDFs have been assigned TEF values, which are generally less than 1, reflecting their lower toxic potency. Periodically, these TEFs are revised based on new toxicological data. The latest internationally accepted TEFs for the PCDDs and PCDFs, as agreed at a 1997 World Health Organization (WHO) consultation (Van den Berg *et al.*, 1998), are shown in Table A-2. The earlier "International" TEF (Kutz *et al.*, 1990) scheme (I-TEF) is also shown in Table A-2.

The use of TEFs assumes that the toxicity of the various congeners acts in an additive fashion. The toxic potency of a mixture of PCDDs and PCDFs (i.e. the TEQ) is the sum of the products of the concentration of each congener present in the mixture and that congener's TEF. Thus, the TEQ represents 2,3,7,8-TCDD toxic equivalents for mixtures of PCDDs and PCDFs.

Table A-2: Toxic equivalency factors for PCDDs and PCDFs

PCDD and PCDF congener	WHO-TEF (Van den Berg *et al.*, 1998)	I-TEF (Kutz *et al.*, 1990)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	0.5
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.001

A.3 Sources

PCDDs and PCDFs are not produced intentionally, but are released to the environment from a variety of industrial discharges, combustion processes and as a result of their occurrence as unwanted by-products in various chlorinated chemical formulations. Historically the manufacture and use of chlorinated aromatic chemicals have been major sources of PCDDs and PCDFs in the environment. Most notable examples include the wood preservative and biocide pentachlorophenol (PCP), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and the polychlorinated biphenyls (PCBs). Other processes, such as the production of chlorine-bleached pulp, have led to environmental contamination by PCDDs and PCDFs, as well as the trace contamination of pulp and paper products.

Combustion processes are recognised as being another important source of PCDDs and PCDFs. Most thermal reactions which involve the burning of chlorinated organic or inorganic compounds appear to result in the formation of these substances. PCDDs and PCDFs have been detected in emissions from the incineration of various types of wastes, particularly municipal, medical and hazardous wastes, from the production of iron and steel and other metals, including scrap metal reclamation, from fossil fuel plants, domestic coal and wood fires, and automobile engines (especially when using leaded fuels) as well as accidental fires. An extensive review of PCDD and PCDF sources has been published by Fiedler *et al*. (1990), and more recently by the United States Environmental Protection Agency (USEPA, 1998). Although natural, non-anthropogenic, combustion sources (like forest fires) have probably always been a source of PCDDs and PCDFs, the background levels associated with the pre-industrial processes (before the 1930s/1940s) are found to be negligible when compared to those resulting from more recent industrial activities (Kjeller *et al*., 1991; Beurskens *et al*., 1993; Jones and Alcock, 1996).

An inventory of dioxin emissions to air, land and water in New Zealand has been published (Buckland *et al.*, 2000)

A.4 Physical and Chemical Properties and Environmental Fate

In general, PCDDs and PCDFs have low water solubility, high octanol-water partition coefficients, low vapour pressure and are resistant to chemical degradation under normal environmental conditions. These properties mean that dioxin-like compounds are extremely persistent in the environment, and their highly lipophilic nature results in bio-concentration into biota and biomagnification through the food chain.

In soil, sediment, water and (to a lesser extent) ambient air, PCDDs and PCDFs are primarily associated with particulate and organic matter because of their high lipophilicity and low water solubility. The lower chlorinated congeners have a relatively higher vapour pressure, and more readily partition into the gaseous phase. Once adsorbed to particulate matter, PCDDs and PCDFs exhibit little potential for significant leaching or volatilisation. The available data indicate that these are extremely stable compounds under most environmental conditions, with environmental persistence measured in decades.

The only environmentally significant transformation process for PCDD/F congeners is considered to be photodegradation in the gaseous phase and at the soil–air or water–air interface. PCDDs and PCDFs entering the atmosphere are removed either by photodegradation or by wet or dry deposition. Although some volatilisation of PCDDs and PCDFs on soil does occur, the predominant fate of these chemicals adsorbed to soil is to remain in place near the surface of undisturbed soil, or to move to water bodies with soil erosion. The scouring of surface soil through wind erosion may also lead to the re-suspension of particle-bound PCDDs and PCDFs into the atmosphere. PCDDs and PCDFs entering the water column primarily undergo sedimentation and burial. The ultimate environmental sink of these PCDDs and PCDFs is believed to be aquatic sediments.

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Appendix B New Plymouth Historical Soil Investigations

Information on historical soil investigations of dioxin concentrations in soil in New Plymouth is presented in this Appendix. The summary focuses on studies undertaken in the suburb of Paritutu, where the Dow AgroSciences (formerly Ivon Watkins Dow, or IWD) chemical manufacturing plant is located.

Since 1985, five separate investigations have been undertaken. These studies, and their findings, are described below. Care must be taken when comparing the dioxin results from these historical studies with the findings of the current investigation, because:

- For many of the historical investigations, especially those from the 1980s, little information was provided in the study reports on either analytical methods or data quality assurance. In addition, in a number of cases, the precise location of the sampling site was not clearly reported. When such information is lacking, the accuracy, completeness and representativeness of the results cannot be assumed.
- The sampling programmes used in the various studies were not necessarily the same, varying particularly in the depth to which soils were taken. For example, one study took soil scrapes to a depth of 150 mm, whereas other studies took soil cores to depths of 50 mm and 100 mm.

B.1 Regional Air Pollution Control Group Investigation, 1985

The first study to measure dioxin soil levels was undertaken by the Regional Air Pollution Control Group (RAPCO), Department of Health, on 17 April 1985. The results were reported in a submission to the ministerial committee of inquiry set up to investigate possible health effects of manufacture of 2,4,5-T in New Plymouth (Pilgrim, 1986).

RAPCO and IWD personnel collected soil samples inside and outside IWD's boundary. Ten sample sets were obtained, each comprising seven to nine 25 mm diameter by 50 mm deep soil cores. Samples were divided into two groups; sets A being from within IWD's premises, and sets B outside their premises, generally being 300 to 800 metres from the centre of the manufacturing complex. The area sampled covered all wind directions. The locations are given in Figure B-1. Samples were analysed by the Department of Scientific and Industrial Research (DSIR), Lower Hutt, for 2,3,7,8-TCDD using gas chromatography mass spectrometry. The concentrations measured are reported in Table B-1.

The submission to the committee of enquiry notes "*the highest results were from sample sets North West B (140 ng/kg) and from East A (170 ng/kg), followed by East B (110 ng/kg). These results are consistent with the prevailing wind directions*[14] *– south-easterly at about 22% of the time and westerly at about 22% of the time. The results from North East B (100 ng/kg) also corresponds well to the south westerly wind direction*

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[14] Wind data from the Waireka meteorological station.

at about 14% of the time, and South A (90 ng/kg) corresponds with the north and north easterly wind directions (5% and 7% respectively)" (Pilgrim, 1986).

Table B-1: TCDD in soils within and around the IWD plant[1]

Sample number[2]	**Sample description**	**2,3,7,8-TCDD (ng/kg)[3]**
IWD 1	North B	50
IWD 2	North West B	140
IWD 3 (composite sample)	West B	No result reported
IWD 4 (composite sample)	North East B	100
HD 5	South A	90
HD 6 (composite sample)	South B	20
HD 7	South East A	60
HD 8 (composite sample)	South East B	nd (< 10)[4]
HD 9 (composite sample)	East A	170
HD 10 (composite sample)	East B	110

1. Source: Pilgrim, 1986
2. IWD sample numbers are results provided by IWD. HD sample numbers are results provided by DSIR, Lower Hutt
3. Not specified whether results are reported on a dry weight or wet weight basis
4. nd = not detected at 10 ng/kg

For samples taken from inside and outside the IWD perimeter (sample sets A and B respectively), higher 2,3,7,8-TCDD concentrations were consistently measured in the samples taken from within the IWD premises than from outside when considered along the same compass direction.

B.2 Department of Health Investigations, 1986

Following the trichlorophenol (TCP) process chemical release at the IWD plant on 15 April 1986, sampling was undertaken by the Department of Health that day, with further sampling the following day.

B.2.1 Sampling – 15 April 1986

Soil samples were collected during the morning of 15 April 1986 immediately following the TCP process chemical release (Pilgrim, 1986). These samples consisted of "*bulked*

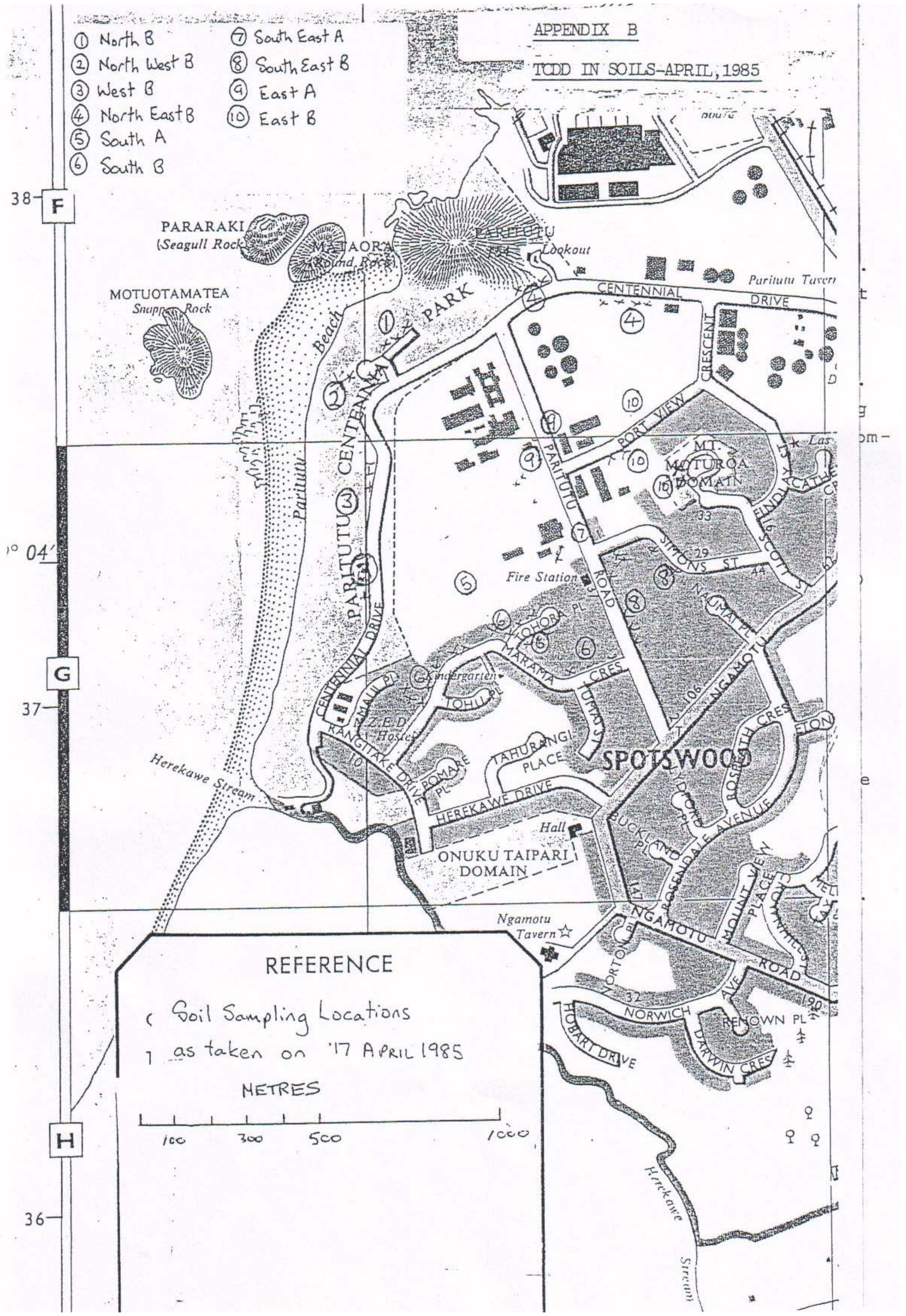

Figure B-1: Sampling locations for RAPCO investigations. Source: Pilgrim, 1986 [Appendix B] *scrapes 10 to 15 mm in depth from several areas in close proximity*"[15]. Samples were analysed by the DSIR for TCDD. The data reported (Pilgrim, 1996) are given in Table B-2.

Table B-2: Department of Health soil scrapes (collected 15/04/86)[1]

Sample number	**TCDD (ng/kg)**[2]
S8	nd (< 30)[3]
S9	40
S10	nd (< 30)

1. Source: Pilgrim, 1986
2. Not specified whether results are reported on a dry weight or wet weight basis. Similarly, not specified whether data are for 2,3,7,8-TCDD or for total TCDD congeners
3. nd = not detected at 30 ng/kg

Only one sample (S9) had a measurable TCDD concentration (40 ng/kg) above the limit of detection (30 ng/kg). This sample also had the highest TCP concentration at 500 μg/kg. The soil from which sample S9 was taken (adjacent to the Shell Todd driveway) was described as having an "*oily deposit*" (Pilgrim, 1996).

Wipe tests were also undertaken during the morning of 15 April. The locations of the wipe and soil samples are given in Figure B-2.

B.2.2 Sampling – 16 April 1986

Additional soil scrapes (together with grass samples) were collected by the Department of Health from all areas adjacent to IWD's perimeter on 16 April (Pilgrim, 1986). These composite samples comprised 10 to 15 random samples taken over a defined sector. The location of these samples is given in Figure B-3. Samples were analysed by the DSIR for 2,3,7,8-TCDD. The concentrations measured in the soil scrapes are reported in Table B-3.

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[15] Unclear whether "*in close proximity*" refers to the proximity of the sampling sites to the process plant, or, the proximity of the areas from where soil scrapes were taken relative to each other.

Table B-3: Department of Health soil scrapes (collected 16/04/86)[1]

Sample number	Sample description		2,3,7,8-TCDD (ng/kg)[2]
DEM 16/4/86/1	Sector E –	Inside IWD western boundary fence, from north to south	310
DEM 16/4/86/2	Sector A –	Grass embankment at the front (west side) of Shell BP and Todd tank farm. Across road from IWD	100
DEM 16/4/86/4	Sector B –	Centennial Park across Centennial Drive from IWD. From Paritutu Road to car park	nd (< 20)[3]
DEM 16/4/86/6	Sector C –	West of IWD on west side of Centennial Drive	60

1. Source: Pilgrim, 1986
2. Not specified whether results are reported on a dry weight or wet weight basis
3. nd = not detected at 20 ng/kg

B.3 Ministry for the Environment National Environmental Survey, 1996

The Ministry for the Environment has reported on a national environmental survey for organochlorine chemicals, including dioxin. This survey included the investigation of dioxin soil levels from parks and reserves in eight provincial towns (Whangarei, Hamilton, Napier, New Plymouth, Masterton, Timaru, Greymouth, Invercargill) (Buckland *et al.*, 1998). The New Plymouth samples were collected on 8 March 1996 from:

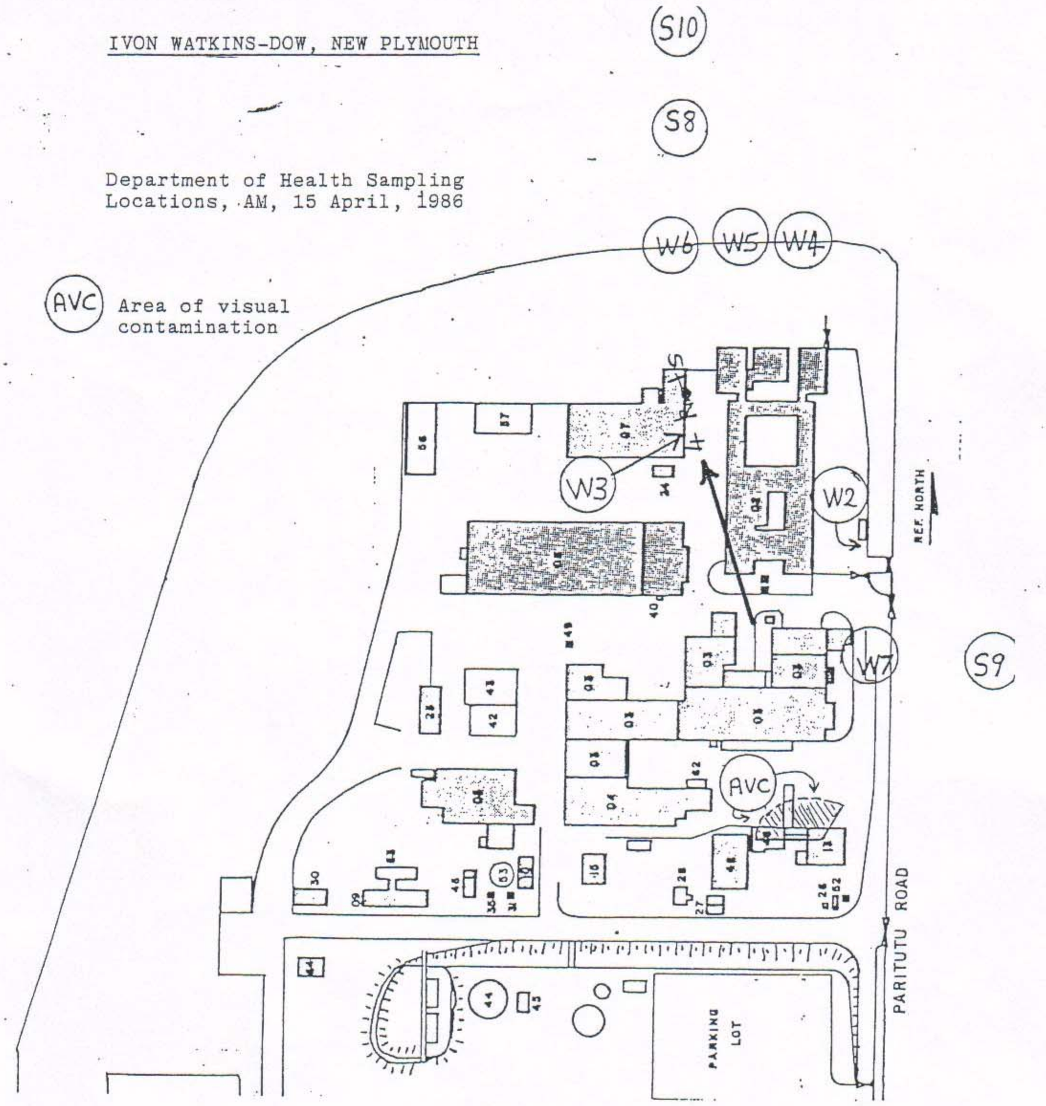
- Mt Moturoa Domain (map reference: NZMS 260 P19/992,374)
- Churchill Heights, Western Park (NZMS 260 P19/021,373)
- Marsland Hill (NZMS 260 P19/376,029)
- Brooklands Park (NZMS 260 P19/037,365).

Mt Moturoa Domain is located less than 1 km from the Dow AgroSciences plant in an easterly direction. Churchill Heights, Marsland Hill and Brooklands Park are located approximately 3.5 km, 4 km and 5 km from the plant respectively, also in an easterly direction.

Nine soil cores, taken to a depth of 100 mm, were collected from each site. A composite sample was prepared with the soil cores from Mt Moturoa Domain, and a second composite sample was prepared from the 27 cores taken from Churchill Heights, Marsland Hill and Brooklands Park. Both composite samples were analysed for PCDDs and PCDFs. Analysis was undertaken by high-resolution mass spectrometry (isotope dilution). Concentrations of 2,3,7,8-TCDD, PCDDs and PCDFs are reported in Table B-4. The full results for New Plymouth and the other provincial centres are given in Figure B-4.

IVON WATKINS-DOW, NEW PLYMOUTH

Department of Health Sampling Locations, AM, 15 April, 1986



DEPARTMENT OF HEALTH WIPE TESTS AND SOIL SCRAPES
(Analyses by DSIR, Lower Hutt)

SAMPLE	WIPE AREA(m²)	TCA(ng)	(ng/m²)	TCP(ng)	(ng/m²)	TCDD(ng)	(ng/m²)
Wipe (Blank)	----	90		40		6	
W 2	0.248	290	1170	70	280	N.D. at 3	
W 3	0.093	50	540	360	3870	N.D. at 3	
W 4	0.065	20	310	100	1540	8	123
W 5	0.070	20	290	110	1570	N.D. at 2	
W 6	0.062	50	810	230	3700	N.D. at 2	
W 7	0.310	40	130	1120	3600	N.D. at 3	
Soils		TCA(µg/Kg)		TCP(µg/Kg)		TCDD(ng/Kg)	
S 8	---	N.D.at 50		20		N.D. at 30	
S 9	---	120		500		40	
S 10	---	N.D. at 50		30		N.D. at 30	

N.D.= Not detected at ---
µg/Kg= Parts per billion (ppb)
ng/Kg= Parts per trillion (ppt)

ng = nanogram

ug = microgram

Figure B-2: Sampling locations for Department of Health investigations, 15/04/86. Source: Pilgrim, 1986 [Appendix 6]

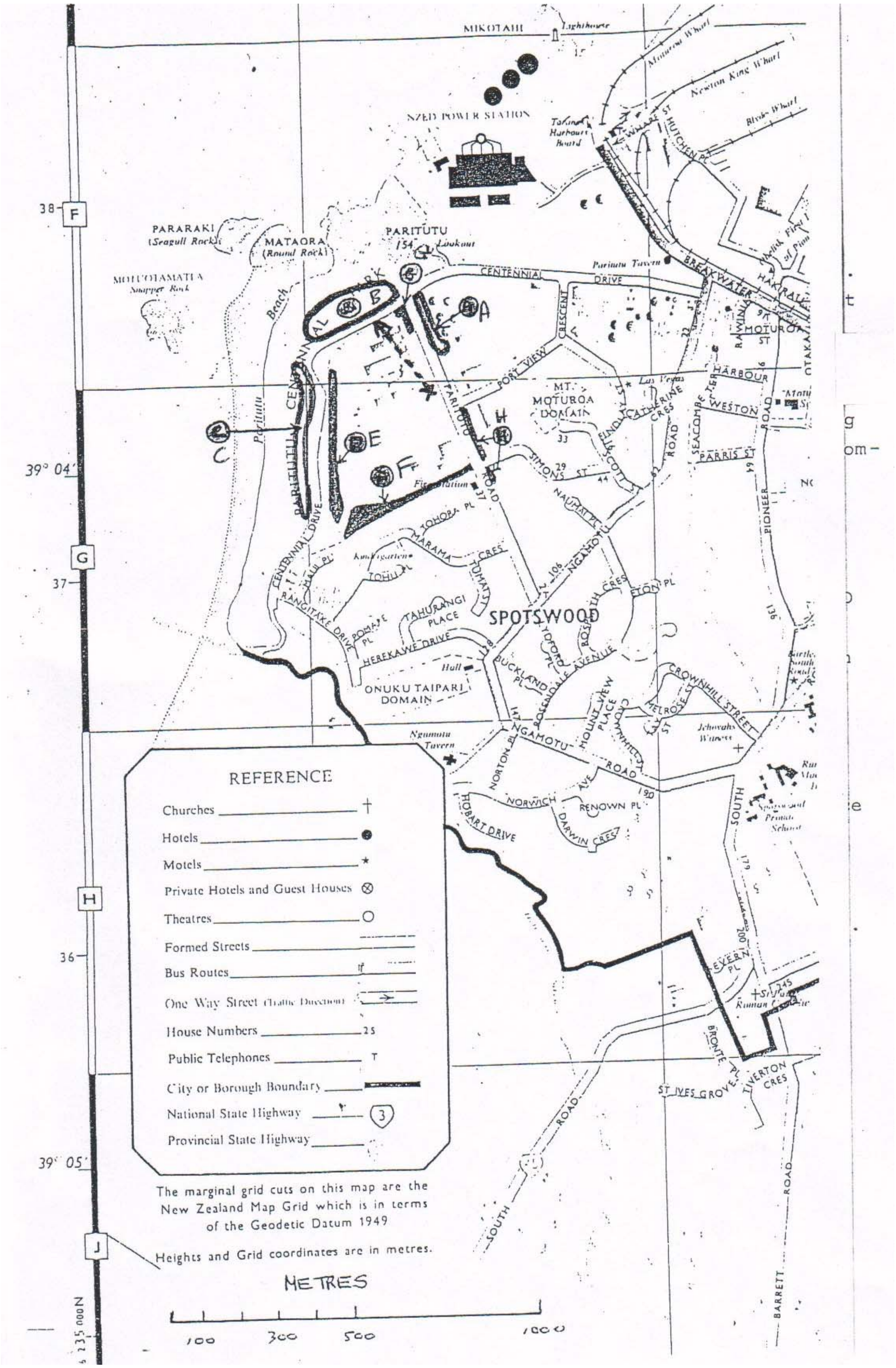


Figure B-3: Sampling locations for Department of Health investigations, 16/04/86. Source: Pilgrim, 1986 [Appendix A]

Table B-4: Ministry for the Environment soil survey of provincial centres[1]

Sample location	2,3,7,8-TCDD (ng/kg dry wt)	PCDD and PCDF (ng I-TEQ/kg dry wt)
Mt Moturoa Domain	31.2	33.0
Churchil Heights, Marsland Hill and Brooklands Park	0.53	2.23
National average[2]	nr [3]	1.50

1. Source: Buckland *et al.*, 1998
2. These data represent the national average for all eight provincial towns, excluding the Mt Moturoa Domain site
3. The national average for 2,3,7,8-TCDD was not reported (nr) because 2,3,7,8-TCDD was not detected in any other provincial centre.

The predominant congener quantified in the sample from Mt Moturoa Domain was 2,3,7,8-TCDD (contributing 95% of the I-TEQ level), characteristic of the PCDD and PCDF micro-contaminant profile of the herbicide 2,4,5-T.

The full results from the national soil survey, together with the sampling strategy, analytical method and quality assurance programme are reported in *Organochlorines in New Zealand: Ambient Concentrations of Selected Organochlorines in Soil* (Buckland *et al.*, 1998).

B.4 Taranaki Regional Council Environmental Investigations, 2001

The Taranaki Regional Council has undertaken investigations into possible dump sites in New Plymouth and surrounds, arising from the alleged inappropriate disposal of agrichemical waste from operations at IWD (TRC, 2001). These investigations involved the collection of soil (plus other media) from a variety of sites, including residential properties and parklands within the vicinity of the Dow AgroSciences plant. Five soil samples were collected from the following four sites (Table B-5):

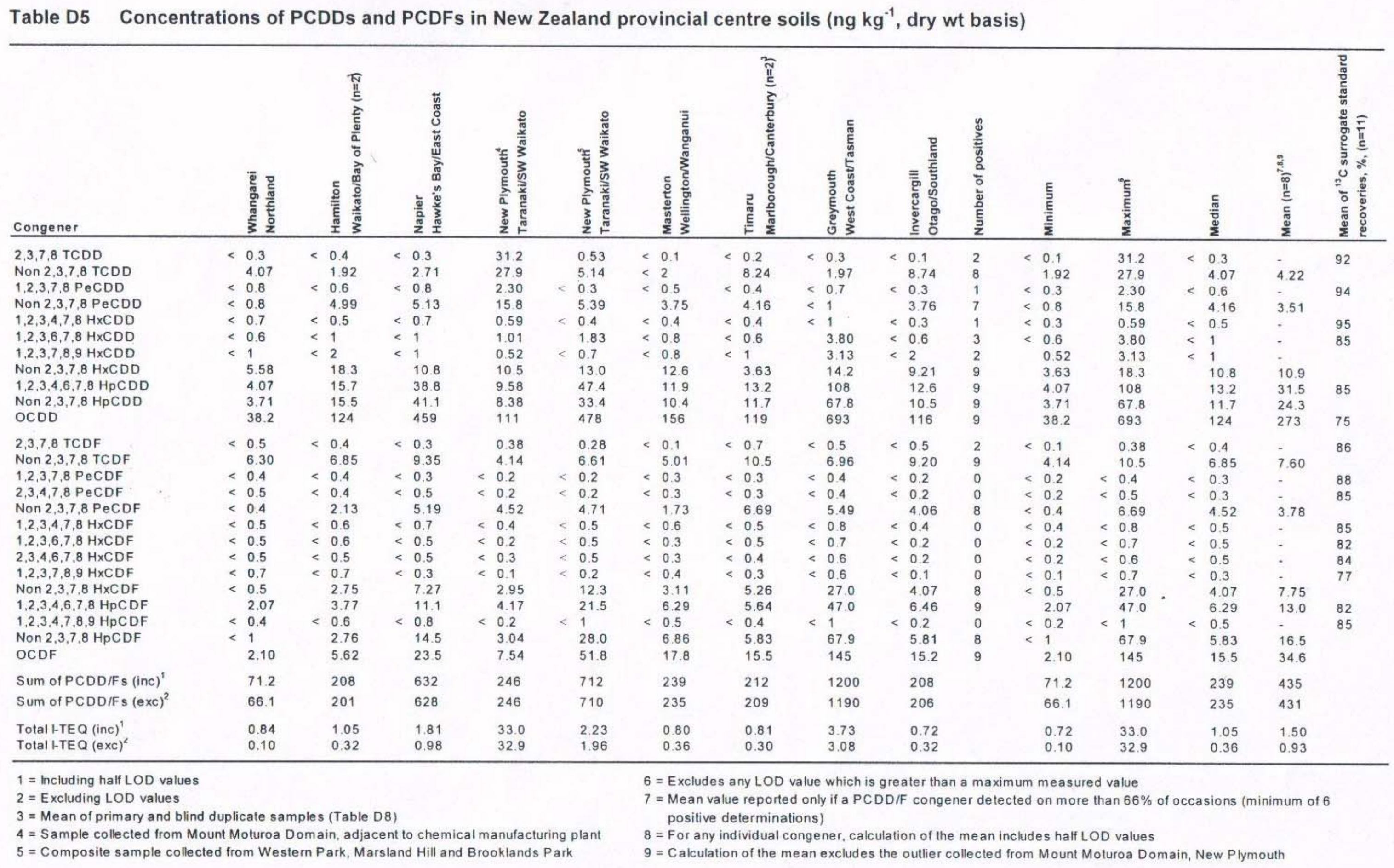


Table D5 Concentrations of PCDDs and PCDFs in New Zealand provincial centre soils (ng kg^{-1}, dry wt basis)

Congener	Whangarei Northland	Hamilton Waikato/Bay of Plenty (n=2)	Napier Hawke's Bay/East Coast	New Plymouth[4] Taranaki/SW Waikato	New Plymouth[5] Taranaki/SW Waikato	Masterton Wellington/Wanganui	Timaru Marlborough/Canterbury (n=2)[3]	Greymouth West Coast/Tasman	Invercargill Otago/Southland	Number of positives	Minimum	Maximum[6]	Median	Mean (n=8)[7,8,9]	Mean of ^{13}C surrogate standard recoveries, %, (n=11)
2,3,7,8 TCDD	< 0.3	< 0.4	< 0.3	31.2	0.53	< 0.1	< 0.2	< 0.3	< 0.1	2	< 0.1	31.2	< 0.3	-	92
Non 2,3,7,8 TCDD	4.07	1.92	2.71	27.9	5.14	< 2	8.24	1.97	8.74	8	1.92	27.9	4.07	4.22	
1,2,3,7,8 PeCDD	< 0.8	< 0.6	< 0.8	2.30	< 0.3	< 0.5	< 0.4	< 0.7	< 0.3	1	< 0.3	2.30	< 0.6	-	94
Non 2,3,7,8 PeCDD	< 0.8	4.99	5.13	15.8	5.39	3.75	4.16	< 1	3.76	7	< 0.8	15.8	4.16	3.51	
1,2,3,4,7,8 HxCDD	< 0.7	< 0.5	< 0.7	0.59	< 0.4	< 0.4	< 0.4	< 1	< 0.3	1	< 0.3	0.59	< 0.5	-	95
1,2,3,6,7,8 HxCDD	< 0.6	< 1	< 1	1.01	1.83	< 0.8	< 0.6	3.80	< 0.6	3	< 0.6	3.80	< 1	-	85
1,2,3,7,8,9 HxCDD	< 1	< 2	< 1	0.52	< 0.7	< 0.8	< 1	3.13	< 2	2	0.52	3.13	< 1	-	
Non 2,3,7,8 HxCDD	5.58	18.3	10.8	10.5	13.0	12.6	3.63	14.2	9.21	9	3.63	18.3	10.8	10.9	
1,2,3,4,6,7,8 HpCDD	4.07	15.7	38.8	9.58	47.4	11.9	13.2	108	12.6	9	4.07	108	13.2	31.5	85
Non 2,3,7,8 HpCDD	3.71	15.5	41.1	8.38	33.4	10.4	11.7	67.8	10.5	9	3.71	67.8	11.7	24.3	
OCDD	38.2	124	459	111	478	156	119	693	116	9	38.2	693	124	273	75
2,3,7,8 TCDF	< 0.5	< 0.4	< 0.3	0.38	0.28	< 0.1	< 0.7	< 0.5	< 0.5	2	< 0.1	0.38	< 0.4	-	86
Non 2,3,7,8 TCDF	6.30	6.85	9.35	4.14	6.61	5.01	10.5	6.96	9.20	9	4.14	10.5	6.85	7.60	
1,2,3,7,8 PeCDF	< 0.4	< 0.4	< 0.3	< 0.2	< 0.2	< 0.3	< 0.3	< 0.4	< 0.2	0	< 0.2	< 0.4	< 0.3	-	88
2,3,4,7,8 PeCDF	< 0.5	< 0.4	< 0.5	< 0.2	< 0.2	< 0.3	< 0.3	< 0.4	< 0.2	0	< 0.2	< 0.5	< 0.3	-	85
Non 2,3,7,8 PeCDF	< 0.4	2.13	5.19	4.52	4.71	1.73	6.69	5.49	4.06	8	< 0.4	6.69	4.52	3.78	
1,2,3,4,7,8 HxCDF	< 0.5	< 0.6	< 0.7	< 0.4	< 0.5	< 0.6	< 0.5	< 0.8	< 0.4	0	< 0.4	< 0.8	< 0.5	-	85
1,2,3,6,7,8 HxCDF	< 0.5	< 0.6	< 0.5	< 0.2	< 0.5	< 0.3	< 0.5	< 0.7	< 0.2	0	< 0.2	< 0.7	< 0.5	-	82
2,3,4,6,7,8 HxCDF	< 0.5	< 0.5	< 0.5	< 0.3	< 0.5	< 0.3	< 0.4	< 0.6	< 0.2	0	< 0.2	< 0.6	< 0.5	-	84
1,2,3,7,8,9 HxCDF	< 0.7	< 0.7	< 0.3	< 0.1	< 0.2	< 0.4	< 0.3	< 0.6	< 0.1	0	< 0.1	< 0.7	< 0.3	-	77
Non 2,3,7,8 HxCDF	< 0.5	2.75	7.27	2.95	12.3	3.11	5.26	27.0	4.07	8	< 0.5	27.0	4.07	7.75	
1,2,3,4,6,7,8 HpCDF	2.07	3.77	11.1	4.17	21.5	6.29	5.64	47.0	6.46	9	2.07	47.0	6.29	13.0	82
1,2,3,4,7,8,9 HpCDF	< 0.4	< 0.6	< 0.8	< 0.2	< 1	< 0.5	< 0.4	< 1	< 0.2	0	< 0.2	< 1	< 0.5	-	85
Non 2,3,7,8 HpCDF	< 1	2.76	14.5	3.04	28.0	6.86	5.83	67.9	5.81	8	< 1	67.9	5.83	16.5	
OCDF	2.10	5.62	23.5	7.54	51.8	17.8	15.5	145	15.2	9	2.10	145	15.5	34.6	
Sum of PCDD/Fs (inc)[1]	71.2	208	632	246	712	239	212	1200	208		71.2	1200	239	435	
Sum of PCDD/Fs (exc)[2]	66.1	201	628	246	710	235	209	1190	206		66.1	1190	235	431	
Total I-TEQ (inc)[1]	0.84	1.05	1.81	33.0	2.23	0.80	0.81	3.73	0.72		0.72	33.0	1.05	1.50	
Total I-TEQ (exc)[2]	0.10	0.32	0.98	32.9	1.96	0.36	0.30	3.08	0.32		0.10	32.9	0.36	0.93	

1 = Including half LOD values
2 = Excluding LOD values
3 = Mean of primary and blind duplicate samples (Table D8)
4 = Sample collected from Mount Moturoa Domain, adjacent to chemical manufacturing plant
5 = Composite sample collected from Western Park, Marsland Hill and Brooklands Park
6 = Excludes any LOD value which is greater than a maximum measured value
7 = Mean value reported only if a PCDD/F congener detected on more than 66% of occasions (minimum of 6 positive determinations)
8 = For any individual congener, calculation of the mean includes half LOD values
9 = Calculation of the mean excludes the outlier collected from Mount Moturoa Domain, New Plymouth

Figure B-4: Dioxin concentrations measured in provincial centres from the Ministry for the Environment national soil survey. Source: Buckland et al., 1998 [Appendix D]. Source: Pilgrim, 1986 [Appendix 6]

Table B-5: Taranaki Regional Council soil samples details and descriptions

Sample location	Sample details and description
Pylon 3, Centennial Drive	GPS: 2598521E, 6237539N Date sampled: 28/06/01 This site comprises an area of land (part recreational area) between the Dow north-west boundary and Back Beach extending to Mt Moturoa, with a pylon outside the boundary corner of the Dow property and extending to the beech. A composite soil sample (six cores) was collected from beneath and adjacent to Pylon 3.
Pylon 4, Herekawe Cliff site	GPS: 2598475E, 6237228N Date sampled: 28/06/01 This site comprises an area below a pylon on the west boundary of the Dow property, extending to the beach. A composite soil sample (six cores) was collected from beneath and adjacent to Pylon 4.
44 Rangitake Drive	GPS: 2598570E, 6236617N Date sampled: 28/06/01 This site was at the southern end of Rangitake Drive, and includes the house site and an adjacent vacant section (42 Rangitake Drive). A composite sample of six soil cores was collected from 42 Rangitake Drive only, as 44 Rangitake Drive showed evidence of soil disturbance (Bedford, personal communication).
23C Tahurangi Place	GPS: 2598732E, 6236974N Date sampled: 26/06/01 A residential property. One sample (composite of six cores) was collected along the rear (up gradient) boundary of the site. A second sample (composite of six cores) was collected from below the house.

Each sample was taken from an area representing surface soils at the property that had remained undisturbed since initial establishment (i.e. the land had not been modified as a result of earthworks/landscaping/building construction).

All soil cores were 25 mm diameter by 75 mm deep; vegetation was removed together with the top 25 to 30 mm of soil prior to sampling. Samples were analysed by AgriQuality (formerly DSIR), Lower Hutt, for 2,3,7,8-TCDD using high-resolution mass spectrometry (isotope dilution). Concentrations measured are reported in Table B-6.

Table B-6: Taranaki Regional Council investigations

Sample location	**2,3,7,8-TCDD (ng/kg)**[1]
Pylon 3, Centennial Drive	29
Pylon 4, Herekawe Cliff site	8.1
44 Rangitake Drive	nd (< 5)[2]
23C Tahurangi Place	nd (< 4) nd (< 6)

1. The TRC report does not specify the basis for reporting of results, but subsequently confirmed as dry weight (Bedford, personal communication)
2. nd = not detected; limit of detection in parenthesis

The full details of these investigations are given in the report *Investigation of Alleged Agrichemical Waste Disposal Sites in New Plymouth* (TRC, 2001).

B.5 Community Residents Action Group Soil Sampling, 2001

In 2001, the environmental consulting firm Kingett Mitchell and Associates, Auckland, collected soil samples from residential properties in Paritutu on behalf of a community action group. Four of the samples collected were sent to the United States for dioxin analysis. Two results are publicly available following reports of this work in the local New Plymouth newspaper (The Daily News, 2001). Concentrations of 19 ng/kg and 0.7 ng/kg were quoted. It is understood that these data are TEQ values from a full PCDD and PCDF analysis.

At present, no other details or written report on this study is publicly available. Despite several attempts, the Ministry for the Environment has been unable to confirm important aspects of the work, specifically the:

- concentrations of PCDDs and PCDFs measured in other samples analysed
- concentrations of 2,3,7,8-TCDD measured
- locations of the properties sampled
- basis for reporting of results (i.e. dry weight or wet weight).

B.6 References

Bedford, G. 2001. G. Bedford, Taranaki Regional Council, personal communication to S Buckland, Ministry for the Environment.

Buckland, SJ, HK Ellis, RT Salter (1998). *Organochlorines in New Zealand: Ambient Concentrations of Selected Organochlorines in Soils*, Ministry for the Environment, Wellington, Wellington, December 1998

Pilgrim, RC (1986). *Submission to the Committee of Enquiry into Possible Health Effects of Manufacture of Agricultural Chemicals in New Plymouth*, Central Regional Air Pollution Group, Department of Health, Wellington, July 1986.

The Daily News (2001). *Scientist offers proof of high dioxin level,* New Plymouth, 20 August 2001

TRC (2001). *Investigation of Alleged Agrichemical Waste Disposal Sites in New Plymouth*, Taranaki Regional Council, August 2001

Appendix C Study Design

C.1 Introduction

The detail of the study design is set out in the Study Design and Sampling protocol document (PDP, 2002) and is based on the study brief appended to that document. The study brief required the basic target of the study to be 2,3,7,8-TCDD on the assumption that this is the principal dioxin contaminant of 2,4,5-T, and that its presence would therefore be an indication of escape from the manufacturing process, whether through fugitive emissions, the 1986 incident or breakthrough of TCDD from the incineration of TCDD contaminated waste. While it was recognised that PCDDs and PCDFs are generated by combustion processes (including back-yard burning), such processes generate a broad range of dioxin congeners, with 2,3,7,8-TCDD being a minor or absent component.

From the brief, the study was based on the assumptions that:

1. The former IWD plant was the principal source of dioxin soil contamination in the area;
2. Contamination occurred via discharges to air with subsequent deposition over the residential neighbourhood, and
3. Sampling was to be focused on residential properties, that is, properties to the east and south of the factory. The industrial or reserve land to the north or west of the factory, where previous studies of dioxin contamination have been carried out (TRC, 2001; Pilgrim, 1986), was not to be sampled unless residential properties were identified within the industrial areas, in which case sampling of those properties was to be considered.

The study design considered areas of likely maximum deposition through the review of meteorological data, topography, age and location of residential areas and results of the earlier studies. However, given the considerable community interest in Paritutu, it was important that the study considered not just the likely areas of maximum dioxin deposition, but also the broader residential areas surrounding the plant. The primary study area was therefore defined as the arc of residential properties running from Maui Place and Rangitake Drive to the south-west of the Dow plant, to the residential properties in Findlay and Catherine streets and Ngamotu Road, adjacent to the industrial land to the east. In addition, samples were to be taken from residential areas up to 2.5 km in the predominant downwind directions, and from within or close to any residential land that might be situated within the primarily industrial land to the north and north east of the plant.

Sampling was primarily to measure 2,3,7,8-TCDD in surface soil, which was defined as being between 0 and 75 mm deeper. In addition a small number of deeper samples (75 – 150 mm) were to be taken distributed around the study area to measure deeper effects.

Given that the intent of the study was to measure cumulative effects, it was an obvious requirement to target areas that had been minimally disturbed over the period of deposition or since. However, it was also decided to measure concentrations in gardens at a small number of locations distributed about the study area.

C.2 Study Design Considerations

In developing the study design, no attempt was made to calculate dioxin emission rates or to differentiate between the various sources over time, as this was not part of the study brief. It was considered that the current dioxin concentration in soil would represent the majority of the dioxin deposited into the soil over the period of manufacture, given its slow degradation in soil. In addition, the measured dioxin concentrations in the soil were expected to be representative of current exposure of site occupants to dioxin from soil. Further, these concentrations are assumed to be typical of concentrations that occupants may have been exposed to over at least the last 15 years, since 2,4,5-T manufacturing stopped at the plant.

This assumption ignores the deposition of dioxin emitted from the incinerator that the Dow plant still operates. However, resource consent compliance monitoring (reported to TRC by Dow) shows the incineration process is under good control, with very low emissions. These emissions are expected to be a negligible contribution to present-day soil concentrations compared with the plant emissions between 1960 and 1987.

The direction and strength of the wind is a significant factor in the pattern of deposition from air emissions. There are two predominant wind directions in the New Plymouth area. Data were obtained from the National Institute of Water and Atmospheric Research (NIWA) climate database for New Plymouth airport, several kilometres east, and from Omata (the Waireka research farm operated by Dow), a few kilometres south-east, and also from the TRC for a site they operate in Fitzroy. Examination of wind records for a number of periods in the 1970’s, 80’s and 90’ show the wind is predominantly either from the west or from the south-east. Winds from the north are rare and light. Data for the Omata climate station for the five-year period 1976 – 1980 are shown in Table C-1. The wind pattern for the Paritutu area is expected to be similar.

Table C-1: Wind direction, Omata, 1976 – 1980

Wind Direction	N	NE	E	SE	S	SW	W	NW	Calm	Total
% of time	6.3	6.2	11.7	23.6	5.8	10.0	21.3	6.8	8.2	100

The south-easterly wind will carry emissions from the factory towards the coast, away from the residential areas to the south, south-east and east of the plant. The westerly winds will tend to carry emissions over industrial properties and the port, but also towards residential areas around Mount Moturoa Domain. Comparatively elevated dioxin concentrations have previously been reported in these directions (see Pilgrim, 1986 and TRC, 2001). In general, emissions will not tend to be carried towards the residential properties to the south and south-east of the factory site, except during the time (about 13% of the time from the figures above) when the wind is blowing in that direction.

Despite there being a lower likelihood of deposition to the south and south-east of the site, there is considerable community interest in this area. It was therefore a requirement of the study that not only were residential properties in the predominant down-wind direction to be sampled, but also residential areas to the south and south-east of the Dow plant. A lower density of sampling was proposed for the area to the south and south-east than for the area to the east.

While the general expectation was that concentrations would show a trend of decreasing dioxin concentration further from the site, and higher concentrations to the east of the site than to the south, it was recognised that there could also be local concentration variations as a result of particular wind conditions or topographic variations. However, it was not the intention of the study to establish the fine detail of localised concentration “highs” or “lows”, as the density of sampling to obtain this sampling would have been well in excess of the resources available. In addition, high-concentration “hotspots” from aerial discharge and deposition over particular small areas were not expected and there was no information to suggest that particular locations should be targeted. Rather, the study was aimed at establishing concentration trends over the general area.

The study design was also not intended to address the potential for “hotspots” as a result of dumped material. This would also require a significantly higher density of sampling. Previous investigations into alleged waste dumps have failed to detect elevated dioxin concentrations in residential areas (TRC, 2001).

A grid-sampling scheme was chosen as an appropriate method to achieve the study objectives.

C.3 Grid design

The choice of grid spacing is inevitably a compromise between a large number of sampling points (to be certain that spatial variability is being measured) and the resources available. A curved grid was chosen, with the sampling points being defined by the intersection of radii and concentric arcs centred about the Dow facility. This arrangement gave a smaller lateral spacing, and therefore more detail, closer to the plant. The grid was positioned so that expected variability as a result of wind direction or topography would be adequately measured. An average grid spacing of around 200 m (equivalent to the length/width of about five to eight residential properties, depending on orientation) was chosen. The resultant grid gave a primary spacing of between about 140 m and 270 m in the transverse direction and radial spacing of 200 m. Intermediate grid points were located in the eastern zone of the sample area, giving a diagonal spacing of about 150 m. This gave more detail where, based on wind patterns and topography, greater deposition could be expected.

The grid was positioned to optimise the coverage of the residential area by rotation of the grid about the Dow plant and to take into account the topography, particularly around Mount Moturoa. The grid was also adjusted at the western end so that the points fell within the area of residential properties.

The outermost arc of grid points is 800 m from the centre of the Dow plant. Based on past sampling (TRC, 2001 and Buckland *et al*, 1998) this was considered to be a reasonable distance over which 2,3,7,8-TCDD might be detected above the New Plymouth background concentration. However, provision was made to collect further samples out to 2500 m to the east of the plant, including four at 1000 m and two each at 1500 m and 2500 m, with the decision whether to analyse these made later.

The resultant grid had 23 primary and intermediate grid points, plus the further eight, more distant, points to the east, up to 2500 m from the centre of the Dow plant.

Information from the community had indicated that a small number of isolated houses are located within the industrial area to the north and north east of the plant. An allowance for four such properties to be sampled was made, the choice to be guided by information received from community groups.

C.4 Sampling Sites

The primary grid samples were located within residential properties, or if no residential properties could be sampled, nearby public lands such as parks. However, for the more distant points, samples were to be taken from public land, but road verges or other land in the immediate vicinity of roads would be avoided. The actual sampling location was to be a property or public space at or near the grid point that:

- is long-established, preferably dating from the 1960's, to maximise the opportunity for deposition of dioxin
- has remained undisturbed, with no major changes to the ground surface – by excavation, filling or cultivation – over that period
- has a current occupier, or an easily-traced previous occupier, who has resided at the property for as long as possible. This gives the opportunity to link this study with the blood serum study (see Section 2) and provide a more reliable site history for each site.
- meets the on-site criteria as set out in Section 4.3

It was decided that that lawn areas would provide the most suitable sampling sites as these will generally have a lower likelihood of disturbance. Garden areas, or areas that were previously garden, are less suitable as turning of soil during gardening is likely to reduce any dioxin contamination by dilution with deeper soil. However, up to six vegetable gardens were to be sampled in addition to lawn areas at selected properties. This was to benchmark gardens that may have received dioxin from:

- direct deposition from the air

- spreading of lawn clippings, or compost containing lawn-clippings, noting that some airborne 2,3,7,8-TCDD may bind to the grass in the vapour phase, and subsequently be cut and removed, rather than falling/being washed into the soil.

The vegetable gardens sampled were distributed as evenly as possible over the study area, with an emphasis on the properties at 400 m and 600 m from the Dow plant.

Public records held by the New Plymouth District Council and the TRC were initially searched to establish a short list of sites within 50 m of each grid point that appear to fit the criteria given above. Inquiries of owner/occupiers were then made (assisted by TRC staff) to ascertain site history and determine whether specific sampling sites were available. Local topography was also taken into account to ensure a site was not unusually sheltered relative to other nearby sites. When a property that fell on a grid point did not meet site criteria, the next adjacent suitable site/property was identified and considered for sampling.

C.5 References

Buckland, SJ, HK Ellis, P Dyke (2000). *New Zealand Inventory if Dioxin Emissions to Air, Land and Water, and Reservoir Source,* Ministry for the Environment, Wellington, March 2000

Buckland, SJ, HK Ellis, RT Salter (1998). *Organochlorines in New Zealand: Ambient Concentrations of Selected Organochlorines in Soil*s, Ministry for the Environment, Wellington, Wellington, December 1998

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TRC (2001). *Investigation of Alleged Agrichemical Waste Disposal Sites in New Plymouth*, Taranaki Regional Council, August 2001.

Appendix D Summary of NZ and Overseas Soil Guidelines for Dioxin

D.1 Summary

A summary of dioxin soil criteria established for residential soil in New Zealand and overseas is provided in Table D-1. Further details for each country are provided following the summary table. References to dioxin in this summary are either to TCDD or to TEQ.

Table D-1: Summary of dioxin criteria

Country	Residential soil criteria	Comment [Reference]
New Zealand	1,500 ng I-TEQ/kg	Present criterion - set as an interim value in the timber treatment guidelines. Currently under review. (MfE/MoH, 1997).
Germany	1,000 ng I-TEQ/kg	Set as an "action value" by the Federal Soil Protection and Contaminated Sites Ordinance (BbodSchV) (BMU, 1999).
Japan	1,000 ng TEQ/kg	Environmental Quality Standard set under the Law Concerning Special Measures against Dioxin (Law No. 105 of 1999) (MoE, 2001)
Canada	4 ng TEQ/kg	Soil Quality Guideline. Derived using ambient background concentrations; i.e. is not effects based. (CCME, 2001)
United States Federal Environmental Protection Agency (USEPA)	1,000 ng TEQ/kg	Preliminary Remediation Goal. Based on criterion developed by Kimbrough *et al.* (1984).
USEPA Region 6	39 ng/kg (for TCDD)[1]	Screening Level for 2,3,7,8-TCDD [US EPA R6, 2001]
USEPA Region 9	39 ng/kg (for TCDD)[1]	Preliminary Remediation Goal for 2,3,7,8-TCDD (US EPA R9, 2000)
Michigan Department of Environmental Quality	90 ng TEQ/kg	Direct Contact Criterion. Derived based on a 1 in 100,000 cancer risk. (DEQ, 1998)
US Department of Health and Human Services – Agency for Toxic Substances and Disease Register	≤50 ng TEQ/kg >50 – <1,000 ng TEQ/kg ≥1,000 ng TEQ/kg	Screening level Evaluation level Action level. (ATSDR, 1998).

Notes:

1. Set at 3.9 ng/kg for a one in a million cancer risk. Figure of 39 ng/kg is adjusted value for 1 in 100,000 cancer risk, consistent with other NZ guideline values.

D.2 Country Specific Dioxin Criteria

D.2.1 New Zealand

The current New Zealand criterion of 1500 ng TEQ/kg dry weight is taken from the timber treatment guidelines published by the MfE and MoH (1997). This criterion was established as an interim guideline value.

The 1500 ng TEQ/kg value was derived using a risk methodology and was based on a tolerable daily intake (TDI) of 10 pg TEQ/kg bw/day. This TDI has since been superseded by an Interim Maximum Monthly Intake of 30 pg TEQ/kg bw/month (MoH, 2002), which, when expressed on a daily basis, is equivalent to one tenth the TDI used to derive the timber treatment guideline value.

The timber treatment guideline value is currently under review, which is expected to be completed by June 30 2003.

D.2.2 Germany

The Federal Soil Protection and Contaminated Sites Ordinance (BbodSchV) has set the following action values (ng I-TEQ/kg dry matter) for the protection of human health (BMU, 1999):

∴ Playgrounds	100
∴ Residential areas	1,000
∴ Parks and recreational facilities	1,000
∴ Land used for industrial and commercial purposes	10,000

The action values are for the direct intake of dioxins for the “soil-human health” pathway.

D.2.3 Japan

The Japanese Government have set an environmental quality standard for soil of 1,000 ng TEQ/kg, with an index of research of 250 ng TEQ/kg (MoE, 2001). If the soil concentration exceeds the index of research, then investigations need to be undertaken. The environmental quality standard is set under Article 7 of the Law Concerning Special Measures against Dioxin (Law No. 105 of 1999) (EA, 1999).

The environmental quality standard was established taking account of the direct intake of dioxin from soils, and is applied to residential (as well as agricultural and industrial) land (Takabatake, pers com).

The standard was set for the protection of human health and promotion of necessary policy measures. When an area’s dioxin contamination exceeds the environmental quality standard the responsible prefectural governor can specify it as a soil protection policy area based on the Law Concerning Special Measures against Dioxin. The local government must take necessary corrective action, including removal of contaminated soil (EA, 1999; MoE, 2001b).

D.2.4 Canada

The basis for the Canadian policy on dioxins is their classification of dioxin as ‘toxic’ under the Canadian Environmental Protection Act. As such, they are slated for virtual elimination under the federal Toxic Substances Management Policy and the CCME Policy for the Management of Toxic Substances.

In 2001, as part of their Environmental Quality Guidelines, the Canadian Council of Ministers of the Environment (CCME) set a soil quality guideline for residential/parkland of 4 ng TEQ/kg (CCME, 2001). The same value also applies to agricultural, commercial and industrial land. This soil quality guideline replaces the interim soil quality criteria set in 1991.

The 4 ng TEQ/kg was set because it was considered representative of the mean background concentration of dioxins in Canadian soils. For residential/parkland use, exposure analysis showed that the estimated daily intake (EDI) for the most sensitive receptor was greater than the tolerable daily intake (TDI), and therefore according to CCME protocol, it is desirable to prevent or disallow any additional soil contamination above background levels. Consequently the soil quality guidelines were set based on mean background ambient concentrations.

The supporting documentation notes that:

> *the soil quality guidelines for dioxins are considered to be management levels, rather than levels that are protective of human or environmental health, because they are not effects based. However, due to the conservative nature of the TDI and EDI values and of the guideline derivation protocol, risks associated with ambient levels are considered to be minimal.*

D.2.5 United States

Federal EPA

The EPA is the primary agency for setting regulations for air, water and soil in the United States. It can receive input from other agencies, such as the Centres for Disease Control (CDC) or the ATSDR, and has often relied on data developed by these agencies, but it is not under any mandate to accept their recommendations.

The current preliminary remediation goal (PRG) adopted by the federal EPA is 1,000 ng TEQ/kg. This dates back to Times Beach and several other early cases of soil contamination. Renate Kimbrough, then employed by CDC, worked in an official capacity in evaluating the health effects at those sites. She and her co-workers developed the criterion of 1,000 ng/kg for 2,3,7,8-TCDD, articulated in Kimbrough et al. (1984), which was subsequently adopted by CDC, ATSDR, and the EPA. Their paper states:

> *One ppb of 2,3,7,8-TCDD in soil is a reasonable level at which to begin consideration of action to limit human exposure to contaminated soil. This 1,000 ng/kg level was used as the clean-up standard for Times Beach.*

The policy directive for EPA's clean-up criteria is best articulated in a memo by Timothy Fields, Jr. Acting Administrator in the Office of Solid Waste and Emergency Response (OSWER), dated April 13 1998 (Fields, 1998). This is OSWER Directive 9200.4-26. It states:

> *One ppb (TEQs, or toxicity equivalents) is to be generally used as a starting point for setting cleanup levels for CERCLA removal sites and as a PRG for remedial sites for dioxin in the surface soil involving a residential exposure scenario.*

The EPA have urged the various EPA regions to follow this guidance and do not believe it is prudent to establish new, and possibly varying, precedents for dioxin levels in soil prior to the release of the EPA dioxin reassessment report (see actions taken by various EPA regions as outlined below). This is specifically addressed in the latter portion of the Fields memo:

> *In the interim, for sites that require the establishment of a final dioxin soil cleanup level prior to the release of the reassessment report and development of OSWER guidance, EPA should generally use 1 ppb (TEQs) as a starting point for residential soil cleanup levels for CERCLA non-time critical removal sites (time permitting, for emergency and time critical sites) and as a PRG for remedial sites.*

EPA Region 6 and Region 9

EPA Regions 6 and 9 have set their own risk-based criteria for 2,3,7,8-TCDD for residential land use. The derivations of these criteria are consistent with the USEPA Soil Screening Guidance (USEPA, 1996a, 1996b).

The Region 6 criterion, referred to as a Human Health Medium-Specific Screening Level, is 3.9 ng/kg for residential soil (USEPA R6, 2001). Similarly, the Region 9 criterion, referred to as a Preliminary Remediation Goal (PRG), is also 3.9 ng/kg for residential soil (USEPA R9, 2000).

These criteria are based on a one in 1,000,000 cancer risk, and take into consideration exposure via soil ingestion, inhalation of particles and dermal absorption. The method of their derivation allows for the criteria to be adjusted for different cancer risks. For a one in 100,000 cancer risk (the risk normally adopted for the setting of New Zealand standards and guidelines), the adjusted criteria for 2,3,7,8-TCDD become 39 ng/kg.

The Region 6 and Region 9 criteria are applied as a screening level, triggering further investigation, and are not regulatory values. Region 9 states that PRGs are considered to be protective of humans, including sensitive groups, over a lifetime. Chemical concentrations above these levels would not automatically designate a site as “dirty” or trigger a response action. However, exceeding a PRG suggests that further evaluation of the potential risks that may be posed by site contaminants is appropriate. Further evaluation may include additional sampling, consideration of ambient levels in the environment, or a reassessment of the assumptions contained in these screening-level estimates.

Michigan Department of Environmental Quality

The Department of Environmental Quality has established generic criteria for a range of contaminants in soil, including dioxin (DEQ, 1998). These direct contact criteria are risk based concentrations that are considered to be protective against adverse health effects due to long-term ingestion of and dermal contact with contaminated soil.

For residential land, and using a one in 100,000 cancer risk, the direct contact criterion for 2,3,7,8-TCDD is 90 ng/kg. This is also applied as 90 ng TEQ/kg for all PCDDs and PCDFs, which are considered as one hazardous substance. The residential land use setting includes single family dwellings, condominiums and apartment buildings.

Agency for Toxic Substances and Disease Registry

The ATSDR has adopted a policy guideline to assess the public health implications of dioxin and dioxin-like compounds in residential soils (ATSDR, 1998). The policy applies to human exposure for the direct ingestion of soils contaminated with dioxin.

The guideline specifies a screening level of ≤50 ng TEQ/kg, an evaluation level of >50 but <1,000 ng TEQ/kg and an action level of ≥1,000 ng TEQ/kg.

The screening level is based on a minimal risk level (MRL) of 1 picogram/kilogram body weight/day (1 pg/kg bw/day) for 2,3,7,8-TCDD.[16] When concentrations exceed 50 ng TEQ/kg, site specific evaluations are needed. Evaluation levels consider site specific factors such as bioavailability, ingestion rates, pathway analysis, soil cover, community concerns, background exposures. When exposures to dioxin concentrations in residential soils exceed I,000 ng TEQ/kg, public health actions such as surveillance, research, health studies and exposure investigations are considered. The ATSDR action level of 1,000 ng TEQ/kg is based on the original work of Kimbrough et al. (1984).

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[16] An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration and route of exposure. The Ministry of Health has recently adopted an interim maximum monthly intake of 30 pg/kg bw/month (MoH, 2002), which is equivalent to the MRL of 1 pg/kg bw/day recommended by the ATSDR and used by them to develop their dioxin screening level.

ATSDR conclude that:

> *the action level of 1 ng/kg (TEQ) for dioxin and dioxin-like compounds, when coupled to a site-specific context of evaluation for the range >50 ng/kg to <1,000 ng/kg TEQs in residential soil, is protective of public health and continues to represent a level at which consideration of health action to indirect exposure, including clean-up, should occur.*

D.2.6 Other Known Guideline Values

The following information is taken from AEA Technology (1999). This report provided a summary of European Union member-state legislation. However, the details given for soil criteria were not comprehensive, some questions remain about application of the dioxin values reported and their current standing is unknown.

D.2.7 Finland

The Ministry of the Environment, Department for Environmental Protection have proposed a guideline of 2 ng I-TEQ/kg and a limit value of 500 ng I-TEQ/kg for contaminated soils. The report (AEA Technology, 1999) indicates that the 500 ng I-TEQ/kg value is applicable to residential soils. When this guideline and limit value were set, and the basis for their derivation is not stated.

D.2.8 The Netherlands

No legislative standards have been set for dioxins in soil. In 1987 guidance levels were proposed for soil pollution that included values of 1000 ng I-TEQ/kg dry matter for residential areas and 10 ng I-TEQ/kg dry matter for dairy farming (AEA Technology, 1999; Zorge and Liem, 1994). The basis for these values is unclear; they are also somewhat old.

D.2.9 Sweden

There are generic guidance values for risk assessment involving dioxin concentrations in soil. They are not binding and are applicable when it is intended that the use of a contaminated area be changed to residential, agricultural and other such uses. If the current levels exceed the guidance values, decisions on site remediation must be taken on a case-by-case basis. The guidelines are:

Land with sensitive use	10 ng I-TEQ/kg dry matter
Land with less sensitive use	250 ng I-TEQ/kg dry matter.

AEA Technology (1999) indicates that residential soil is categorised as “land with sensitive use”, whereas industrial areas are “land with less sensitive use”. The basis for the derivation of these values is not stated.

D.3 References

AEA Technology (1999). *Compilation of EU Dioxin Exposure and Health Data: Task 1 – Member State Legislation and Programmes*. Report for the European Commission DG Environment and the UK Department of the Environment, Transport and Regions. http://europa.eu.int/comm/environment/dioxin/download.htm#Compilation%20of%20EU%20Dioxin%20exposure%20and%20health%20data

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USEPA (1996b). *Soil Screening Guidance: User's Guide.* EPA/540/R-96/018. Office of Emergency and Remedial Response, Washington DC. PB96-963505.

USEPA R6 (2001). USEPA Region 6, *Human Health Medium-Specific Screening Levels*, US Environmental Protection Agency, Region 6, Dallas, Texas, November 2001 revisions. http://www.epa.gov/earth1r6/6pd/rcra_c/pd-n/screen.htm

USEPA R9 (2000). USEPA Region 9 *Preliminary Remediation Goals.* US Environmental Protection Agency, region 9, San Francisco California. 200 Updates. http://www.epa.gov/region09/waste/sfund/prg/index.htm

Zorge JA, AKD Liem (1994). Dioxins and related compounds – regulatory aspects in the Netherlands. *Organohalogen Compounds*, 20, 577-580.

Address	36 Marama Crescent	Site no.: 01
Date Sampled	31 May 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, windy	
Comments / Interviews/ Sampling Observations	This was the closest suitable site to the grid point, with the least likelihood of site alterations. The sampling location was chosen to be clear of some vehicle maintenance works and to be exposed to any wind borne deposition from the Dow plant. The garden was thought to be for vegetables, but may have been a sandpit.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	5.9	Not sampled	Sampled: not analysed	Not sampled	Not sampled

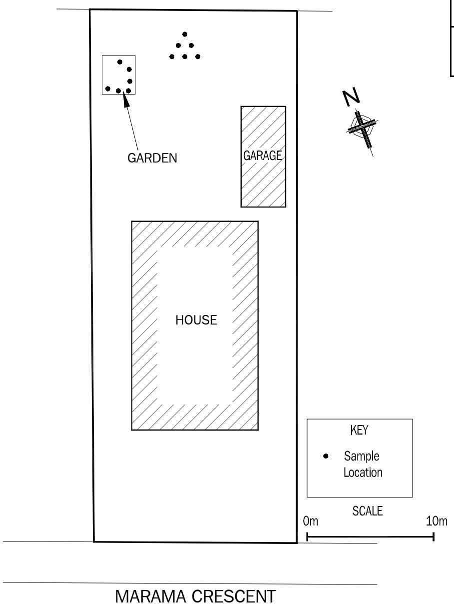
Soil Description

Grassed area: Silt loam, brown

Garden: Sand, grey, with minor brown silt

Site Plan

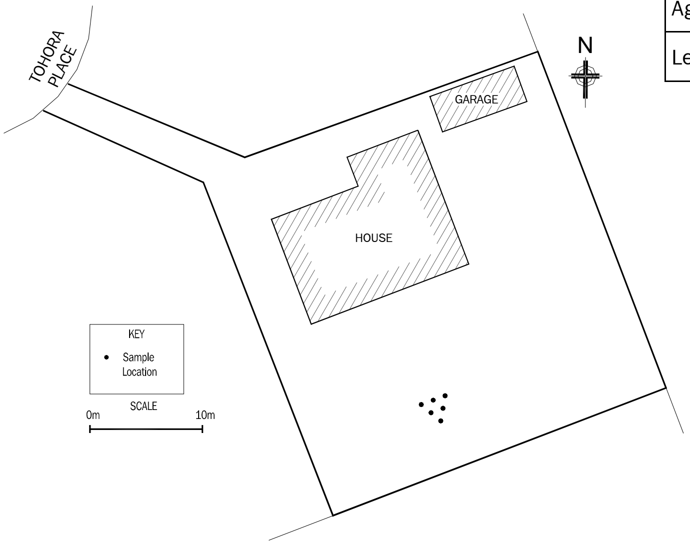
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	~30
Length of time at house: (Yr)	2



Address	12A Tahora Place				Site no.: 02
Date Sampled	28 May 2002				
Observer(s)	DIN representative				
Field Conditions	Blustery with occasional squalls				
Comments / Interviews/ Sampling Observations	The lawn behind the house was selected as being the closest likely undisturbed location to the grid point. The sampling location was on the northern face of a small rise.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	4.8	3.2	Not sampled	Not sampled	Not sampled
Soil Description	Grassed area: Silt loam, brown				

Site Plan

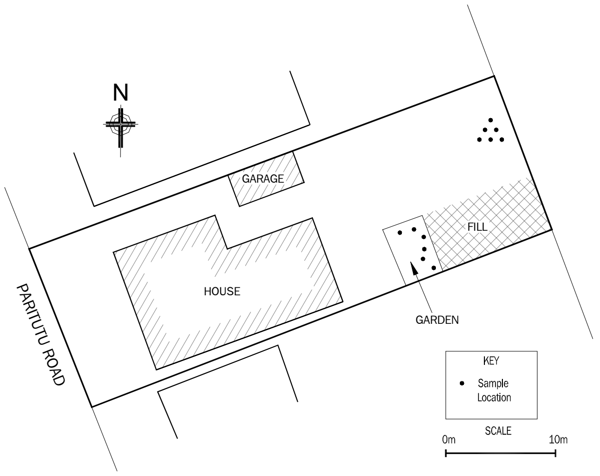
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	35-40
Length of time at house: (Yr)	2



<table>
<tr><td>ADDRESS</td><td colspan="4">42 Paritutu Road</td><td>Site no.: 03</td></tr>
<tr><td>DATE SAMPLED</td><td colspan="5">4 June 2002</td></tr>
<tr><td>OBSERVER(S)</td><td colspan="5">DIN representative</td></tr>
<tr><td>FIELD CONDITIONS</td><td colspan="5">Clear skies with mild wind.</td></tr>
<tr><td>COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS</td><td colspan="5">This was the closest suitable open and undisturbed site to the grid point. Most of the other sites were either too closed in, or were likely to have recently disturbed ground.
The sampling location was chosen to be clear of a vehicle entrance, from some filled area and from the shelter of the house.
The garden was for vegetables.</td></tr>
<tr><td rowspan="2">2,3,7,8-TCDD RESULTS
ng/kg
dry weight</td><td>Grassed area
0 mm – 75 mm</td><td>Grassed area
75 mm – 150 mm</td><td>Garden</td><td>Rinsate Blank</td><td>Trip Blank</td></tr>
<tr><td>5.8</td><td>Not sampled</td><td>4.5</td><td>Sampled: not analysed</td><td>Not sampled</td></tr>
<tr><td>SOIL DESCRIPTION</td><td colspan="5">Grassed area: Silt loam, brown
Garden: Silt loam, brown</td></tr>
</table>

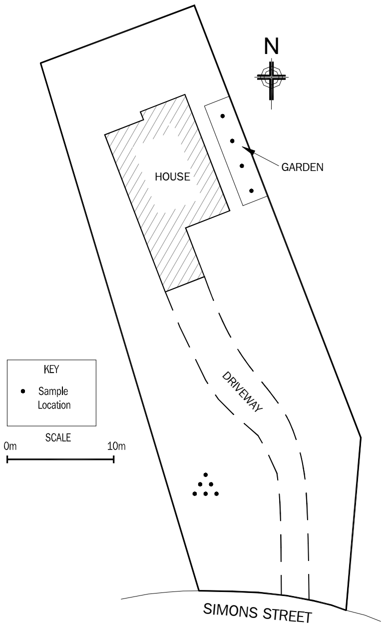
SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	35-40
Length of time at house: (Yr)	2



Address	11 Simons Street				Site no.: 04
Date Sampled	30 May 2002				
Observer(s)	DIN representative				
Field Conditions	Windy with some rain showers.				
Comments / Interviews/ Sampling Observations	This site was the nearest open space to the grid point. The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant, and to be clear of adjacent earthworks. The owner's father, who built the house, identified the sampling location as being a relatively untouched area. The garden was raised and ornamental.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	7.4	2.2	4.9	Not sampled	Not sampled
Soil Description	Grassed area: Sandy with some silt, brown Garden: Silt loam, brown				

Site Plan



Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	50
Length of time at house: (Yr)	2

Address	Mt Moturoa Domain	Site no.: 05
Date Sampled	30 May 2002	
Observer(s)	DIN representative	
Field Conditions	Windy.	
Comments / Interviews/ Sampling Observations	The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant, and was as close as possible to the grid point. The ground slopes down towards the Dow site.	

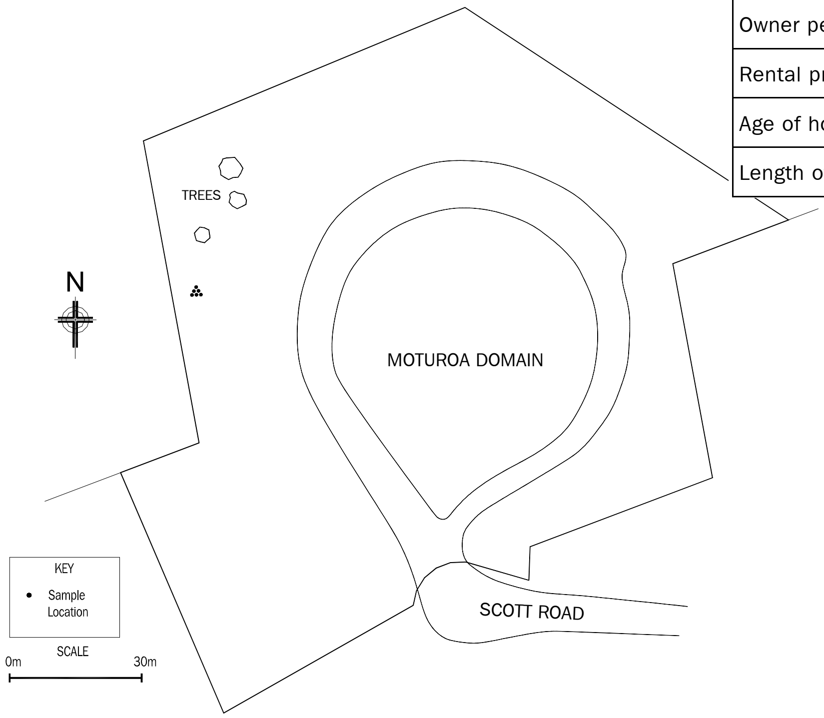
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	92	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description

Grassed area: Silt loam, brown

Site Plan

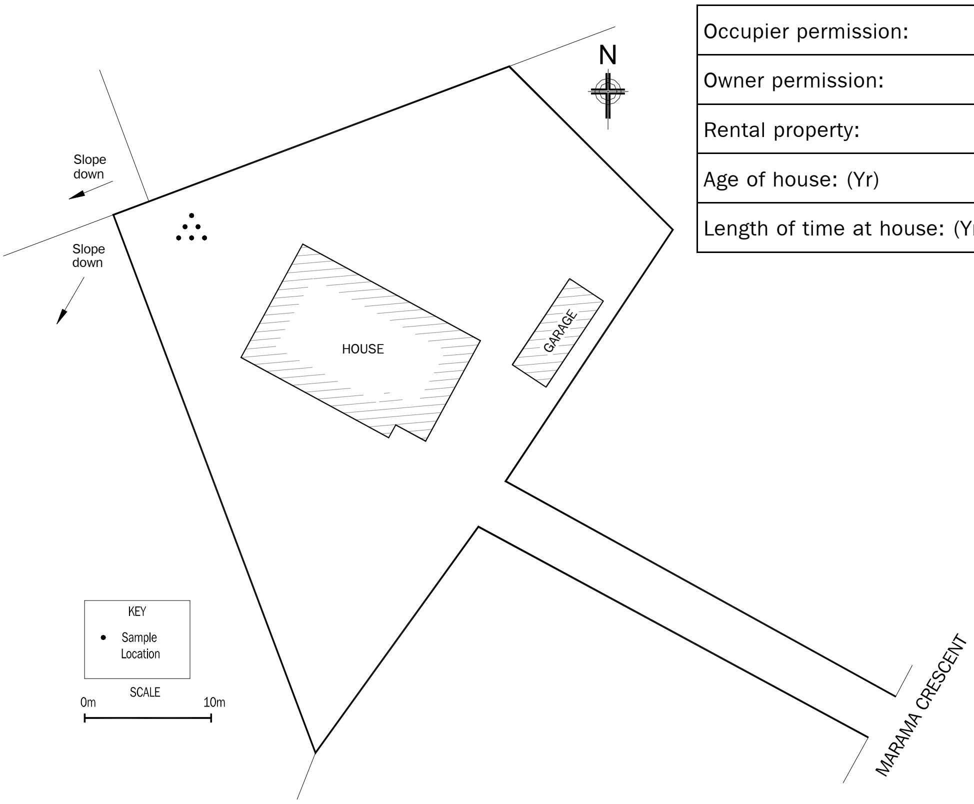
Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



ADDRESS	52A Marama Crescent				Site no.: 06
DATE SAMPLED	31 May 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Windy, fine				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	This was the closest site to the grid point. The site was at the top of a ridge, avoiding being on a slope facing away from the Dow plant, and thus less likely to accumulate wind carried particulate material. The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant. The sampling location was about 3 m from a wire mesh fence.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	15	Not sampled	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	~35
Length of time at house: (Yr)	1.5



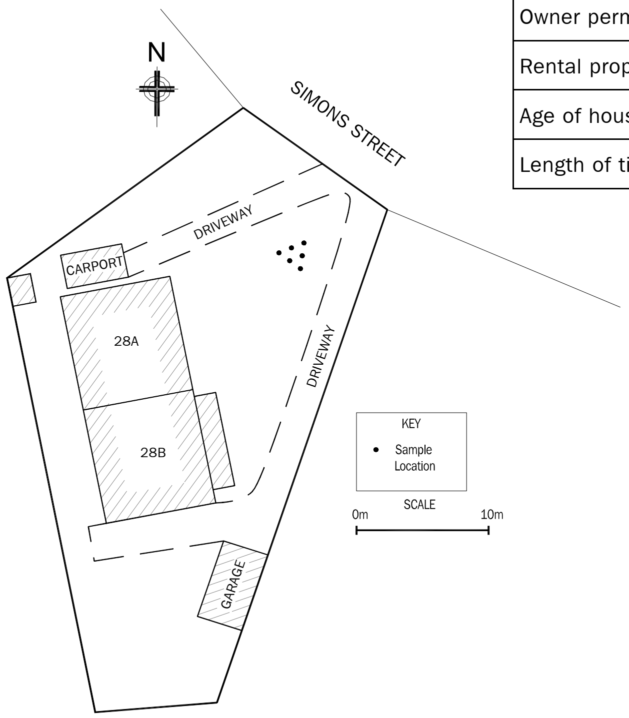
Address	28A Simons Street	Site no.: 07
Date Sampled	29 May 2002	
Observer(s)	DIN representative	
Field Conditions	Squally rain	
Comments / Interviews/ Sampling Observations	The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant, and to avoid possible ground disturbances. The sampling location was in a grassed patch between two driveways. It was later identified by the owner as probably being the oldest patch of ground on the site.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	3.4	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown

Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	20-30
Length of time at house: (Yr)	1.5



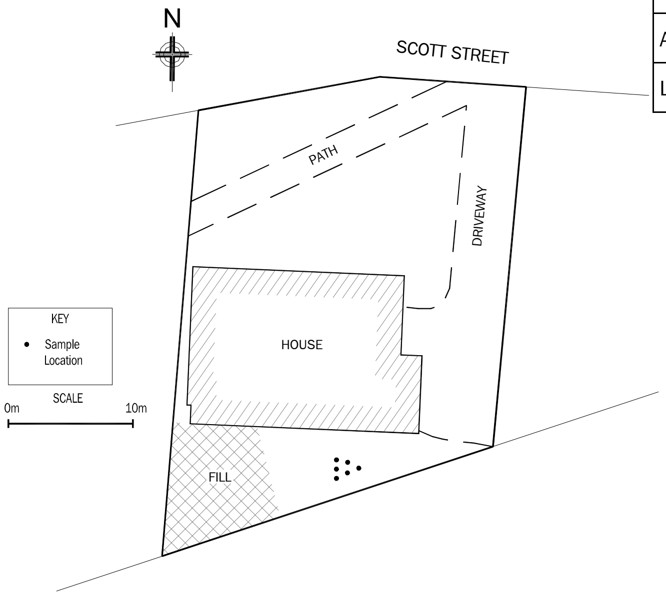
Address	29 Scott Street	Site no.: 08
Date Sampled	28 May 2002	
Observer(s)	DIN representative	
Field Conditions	Squally, driving rain and wind.	
Comments / Interviews/ Sampling Observations	This site was chosen as the closest open area to the grid point with undisturbed ground. The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant, to avoid a filled area, and to avoid adjacent site works. The sampling location was within 1.6 m of a 1.2 m high fence, but there was >5 m of clear space in the direction of the Dow plant.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	6.1	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown

Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	30
Length of time at house: (Yr)	22



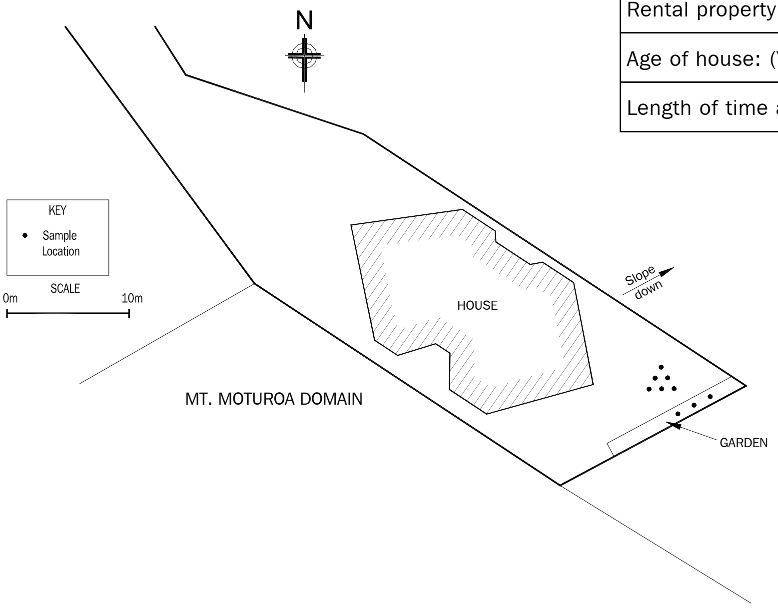
Address	19 Port View Road	Site no.: 09
Date Sampled	29 May 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, sunny. Little wind due to shelter from house	
Comments / Interviews/ Sampling Observations	This site was the closest flat area to the grid point. The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant, and to avoid a concrete drain across the lawn. The sample location was >5 m from the house. The garden was raised and ornamental.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	17	14	2.8	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown Garden: Silt loam, brown

Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	33
Length of time at house: (Yr)	13



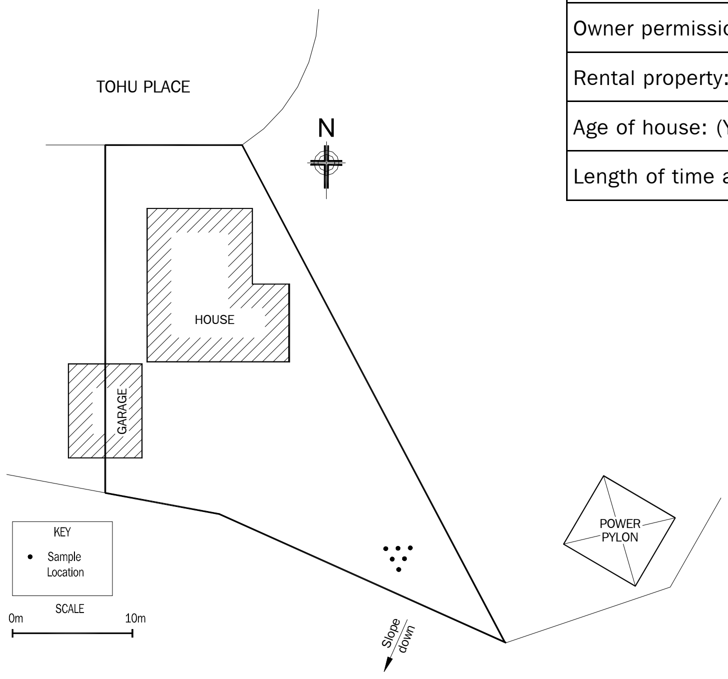
Address	12 Tohu Place	Site no.: 10
Date Sampled	30 May 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, blustery	
Comments / Interviews/ Sampling Observations	The grid point was at the base of a slope facing away from the Dow plant, and thus less likely to accumulate wind borne deposition from the Dow plant. Therefore, the site at the top of the slope was selected for sampling. The sampling location was chosen to be exposed to any wind borne deposition from the Dow plant, and to avoid any possible ground disturbances. The sampling location was within 3 m of the boundary fences, but both fences were wire mesh.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	3.6	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown

Site Plan

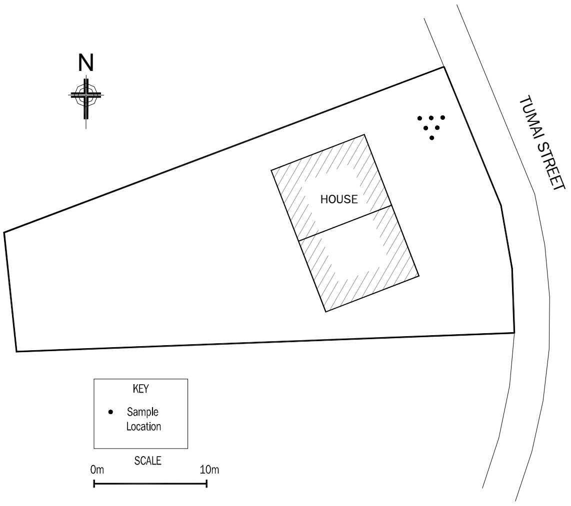
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	~30
Length of time at house: (Yr)	3



ADDRESS	8 Tumai Place				Site no.: 11
DATE SAMPLED	31 May 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Calm, no wind or rain.				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The front lawn was chosen as a sampling location, due to its exposure to any wind borne deposition from the Dow plant. No trees or high objects exist for 20 m in the direction of Dow plant.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	2	1.6	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	~30
Length of time at house: (Yr)	3



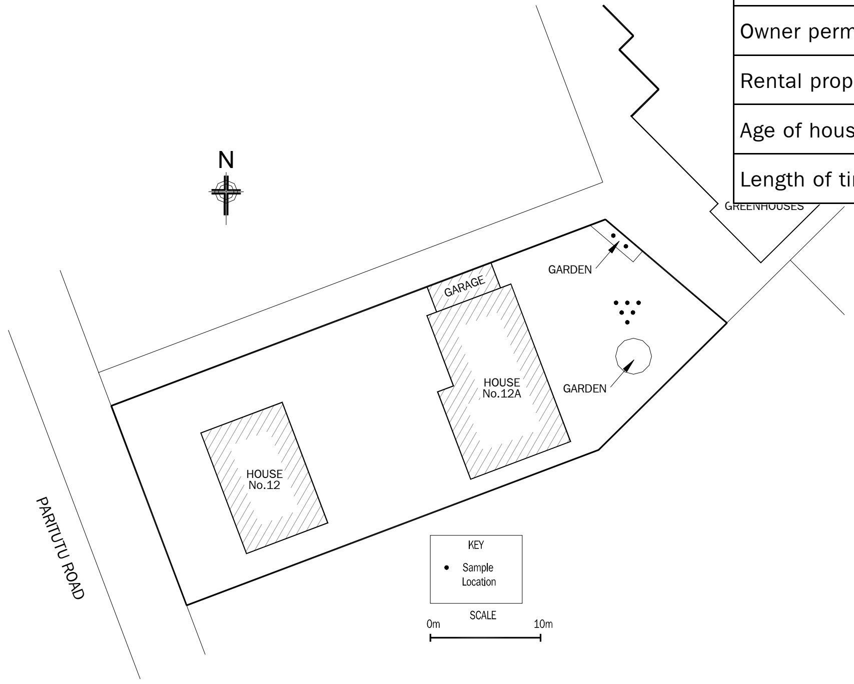
Address	12A Paritutu Road	Site no.: 12
Date Sampled	28 May 2002	
Observer(s)	DIN representative	
Field Conditions	Windy, with occasional rain	
Comments / Interviews/ Sampling Observations	This site was the closest suitable open area to the grid point. The sampling location was chosen to be as far from the shelter of the house, and to avoid some filled areas.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	2.9	Not sampled	2	Not sampled	Not sampled

Soil Description	Grassed area:	Silt loam, brown
	Garden:	Silt loam, brown

Site Plan

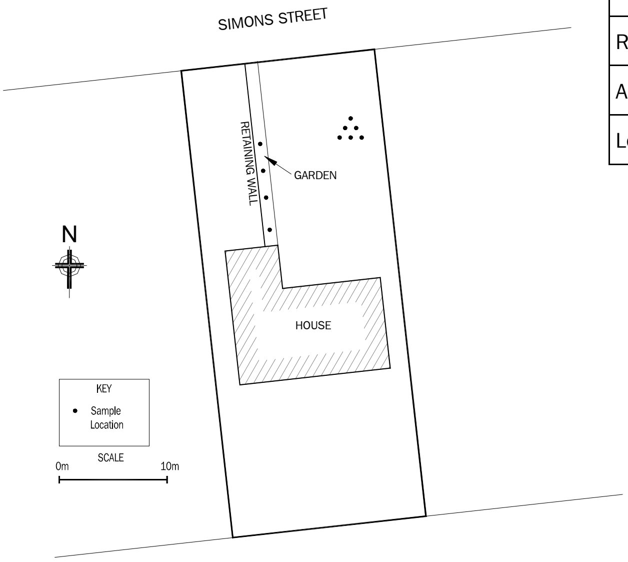
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	28
Length of time at house: (Yr)	25



Address	36 Simons Street				Site no.: 13
Date Sampled	30 May 2002				
Observer(s)	DIN representative				
Field Conditions	Fine, mild wind				
Comments / Interviews/ Sampling Observations	This was the closest available site to the grid point. The sampling position was chosen to avoid some timber that was stacked on the lawn. The sampling location was 3 m from the lee fence, but was exposed to any wind borne deposition from the Dow plant. The garden was ornamental, along the top of a retaining wall adjoining the lawn.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	6.2	Not sampled	Sampled: not analysed	Not sampled	Not sampled
Soil Description	Grassed area: Silt loam, brown Garden: Silt loam, brown				

Site Plan

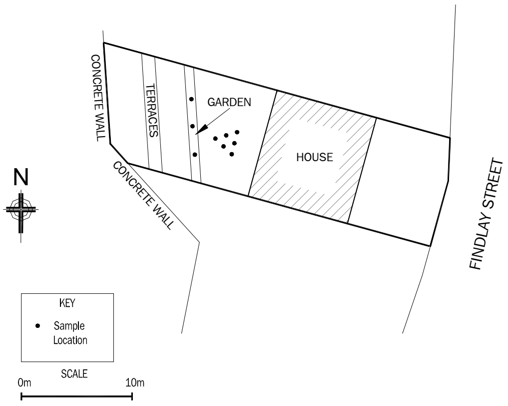
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	~30
Length of time at house: (Yr)	13



Address	7 Findlay Place				Site no.: 14
Date Sampled	31 May 2002				
Observer(s)	None				
Field Conditions	Fine, but with occasional showers				
Comments / Interviews/ Sampling Observations	The lawn has been terraced – an estimated 20 to 28 years ago. The original slope is visible on adjoining properties. The sample location was chosen to be as far from surrounding walls as possible, and to be from near-to-original ground level, based on observations of the adjacent properties. The garden was ornamental, at the base of the terracing walls.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	8.0	Not sampled	7.3	Not sampled	Not sampled
Soil Description	Grassed area: Silt loam, brown Garden: Silt loam, brown				

Site Plan

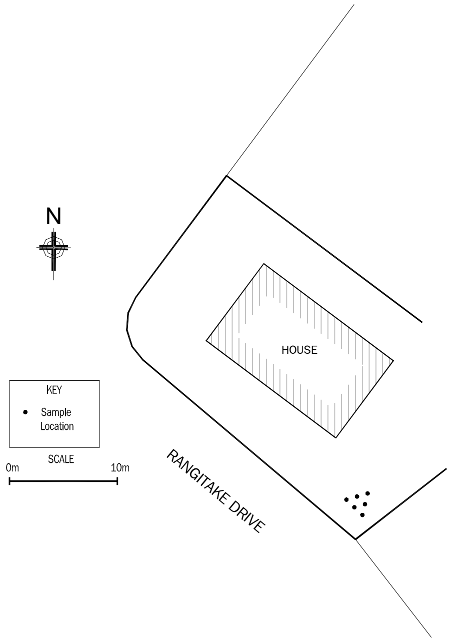
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	28
Length of time at house: (Yr)	28



ADDRESS	19 Rangitake Place				Site no.: 15
DATE SAMPLED	31 May 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Sunny, not much wind				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	This was the closest suitable site to the grid point. Closer sites were not considered suitable due to the short length of occupancy or because no permission was obtained for sampling. The sampling location was chosen to be as far as possible from the shelter of the house and upwind trees. A 2 m high fence was located 2.5 m to the side of the location, but was not considered to reduce any wind borne deposition from the Dow plant.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	1.9	Not sampled	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	~25
Length of time at house: (Yr)	8



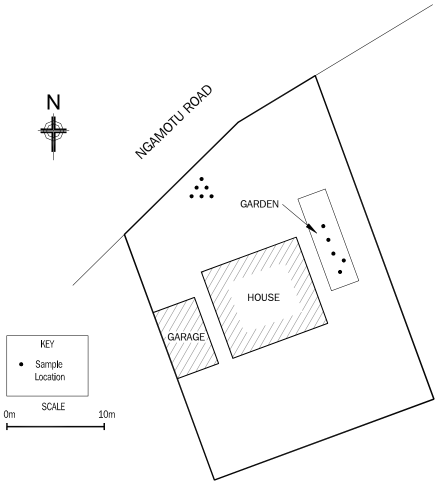
Address	79 Ngamotu Road	Site no.: 16
Date Sampled	29 May 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, windy	
Comments / Interviews/ Sampling Observations	This property was the closest suitable site to the grid point. The sampling location was chosen to be 2 m from a low concrete wall, to get the best exposure to any wind borne deposition from the Dow plant, to avoid a vehicle parking area, and to avoid some indentations that indicated former plants were nearer the fence. The garden was for vegetables, but was in the lee of some large trees and the house.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	1.8	1.2	Sampled: not analysed	Not sampled	Not sampled

Soil Description	Grassed area: Sandy silt loam, brown Garden: Sandy sill loam, brown

Site Plan

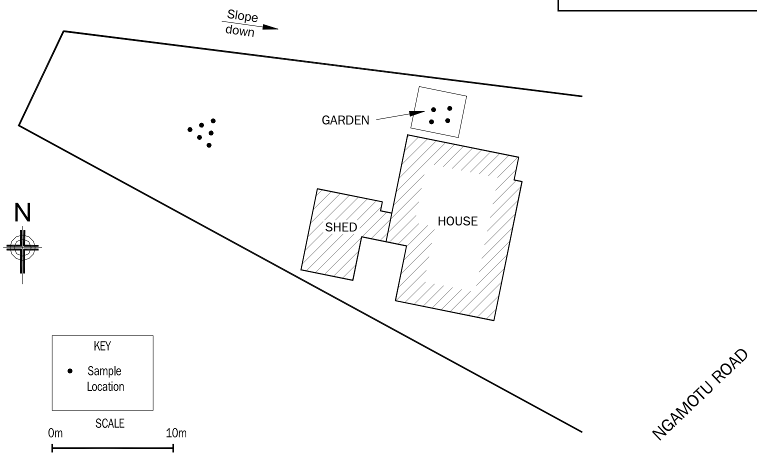
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	~25
Length of time at house: (Yr)	7



ADDRESS	58 Ngamotu Road				Site no.: 17
DATE SAMPLED	30 May 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Little wind, some showers				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	This site was the closest open area to the grid point. The sampling location is on a slope facing away from the Dow plant, and thus has less exposure to any wind borne deposition from the Dow plant, but was chosen to be clear of the shelter of surrounding objects, including trees. The lawn is reported to have been sprayed by non-dioxin containing herbicides. The garden was for vegetables, but was in the shelter of some trees and the house.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	0.93	Not sampled	Sampled: not analysed	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown Garden: Silt loam, brown				

SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	57
Length of time at house: (Yr)	2



Address	9 Catherine Crescent	Site no.: 18
Date Sampled	31 May 2002	
Observer(s)	DIN representative	
Field Conditions	Little wind, some showers	
Comments / Interviews/ Sampling Observations	The site is the closest suitable residential site to the grid point. Other sites were considered unsuitable due to recent construction, returfing, and/or insufficient open area. The sampling location was a small front lawn, with no obstructions above a 30º angle in the direction of the Dow plant. The distance to the obstructions on either side was 2 m. The garden was ornamental.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	4.5	Not sampled	Sampled: not analysed	<0.01	Sampled: not analysed

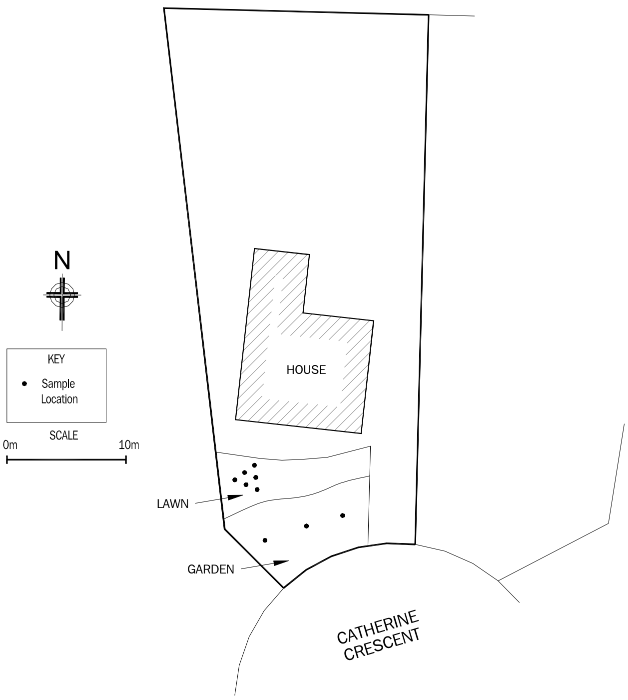
Soil Description

Grassed area: Silt loam, brown

Garden: Silt loam, brown

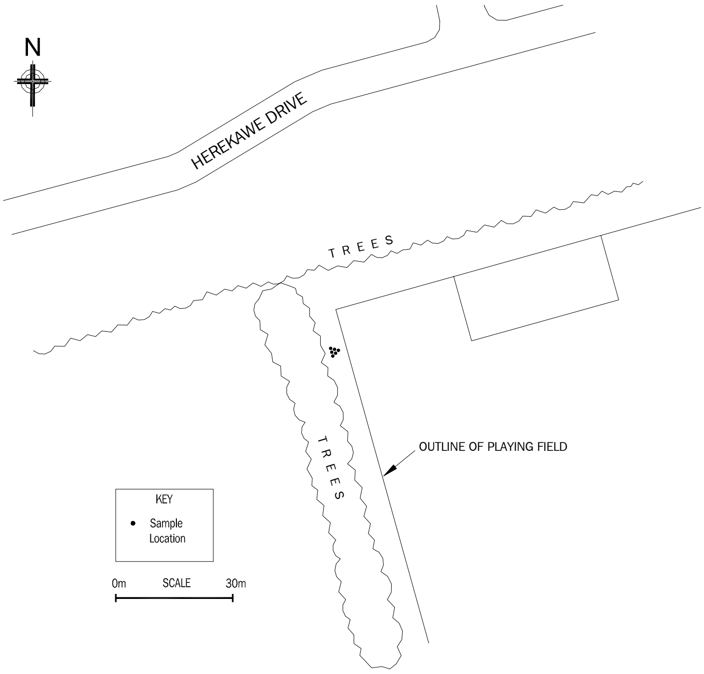
Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	31
Length of time at house: (Yr)	6



Address	Onuku Taipari Domain				Site no.: 19
Date Sampled	29 May 2002				
Observer(s)	DIN representative				
Field Conditions	Windy, occasional showers				
Comments / Interviews/ Sampling Observations	The sampling location was chosen to be away from the sports playing surface, and from some underground lighting cables. A line of trees was located 3 m to the side, but there was 20 m clearance in the direction of the Dow plant.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	1.0	Not sampled	Not sampled	Not sampled	Not sampled
Soil Description	Grassed area: Silt loam, brown				

Site Plan



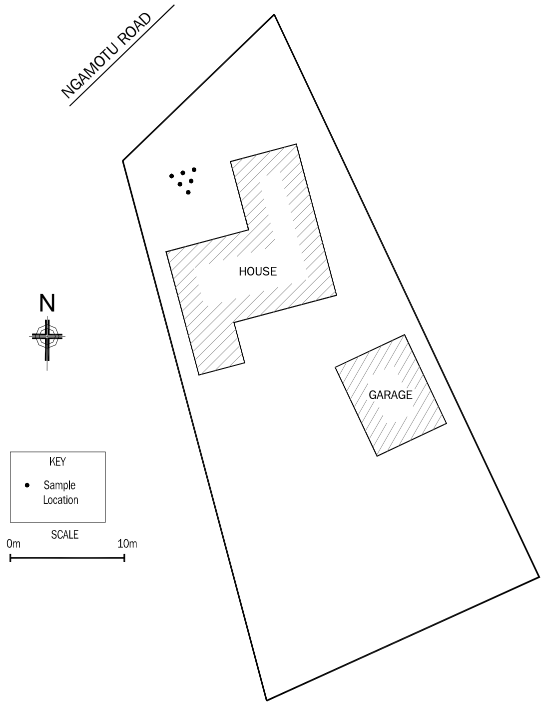
Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA

Address	133 Ngamotu Road	Site no.: 20
Date Sampled	4 June 2002	
Observer(s)	DIN representative	
Field Conditions	Showers, windy	
Comments / Interviews/ Sampling Observations	The sampling location was chosen to be on the front lawn rather than the back, to avoid being in the shelter of the house.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	4.8	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown

Site Plan

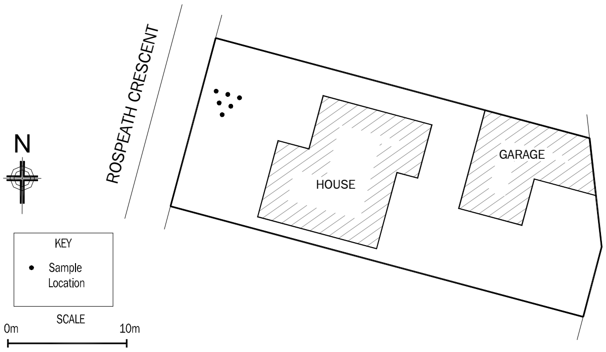


Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	40
Length of time at house: (Yr)	6

ADDRESS	20 Rospeath Crescent				Site no.: 21
DATE SAMPLED	29 May 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Fine, windy				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The site is adjacent to that with the grid point. The sampled lawn is retained above the road level by a 1 m high concrete wall, but appears to have been largely untouched since the construction of the house.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	0.75	Not sampled	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	39
Length of time at house: (Yr)	10



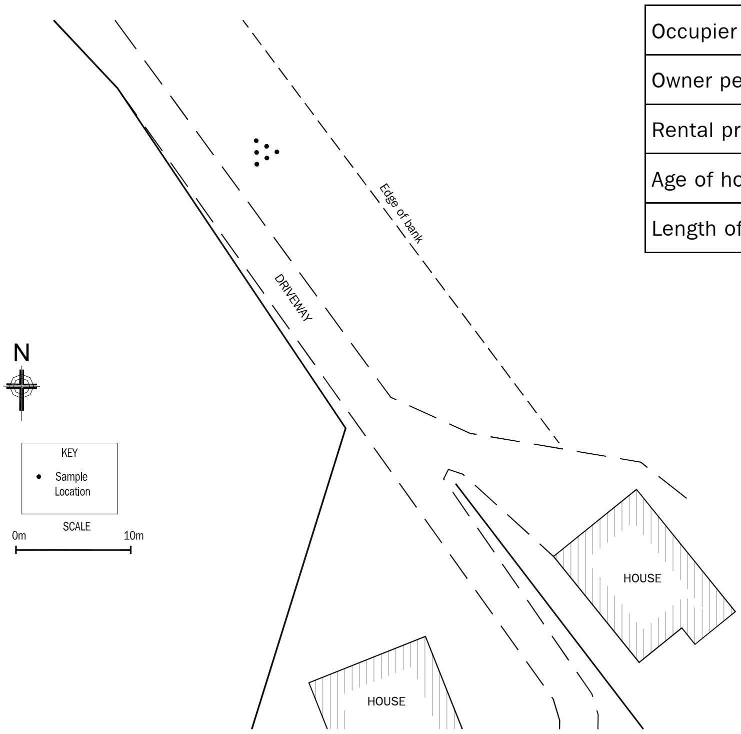
ADDRESS	55A Ngamotu Road	Site no.: 22
DATE SAMPLED	30 May 2002	
OBSERVER(S)	DIN representative	
FIELD CONDITIONS	Sunny, windy	
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The site is the closest suitable open area to the grid point. The sampling location was a grazed area beside the driveway, with a steep drop-off on the other side. It was chosen to be as far as possible from a sheltering upwind wall, and to be in a largely undisturbed area.	

2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	0.76	Not sampled	Not sampled	Not sampled	Not sampled

SOIL DESCRIPTION	Grassed area: Silt loam, brown

SITE PLAN

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	30
Length of time at house: (Yr)	20



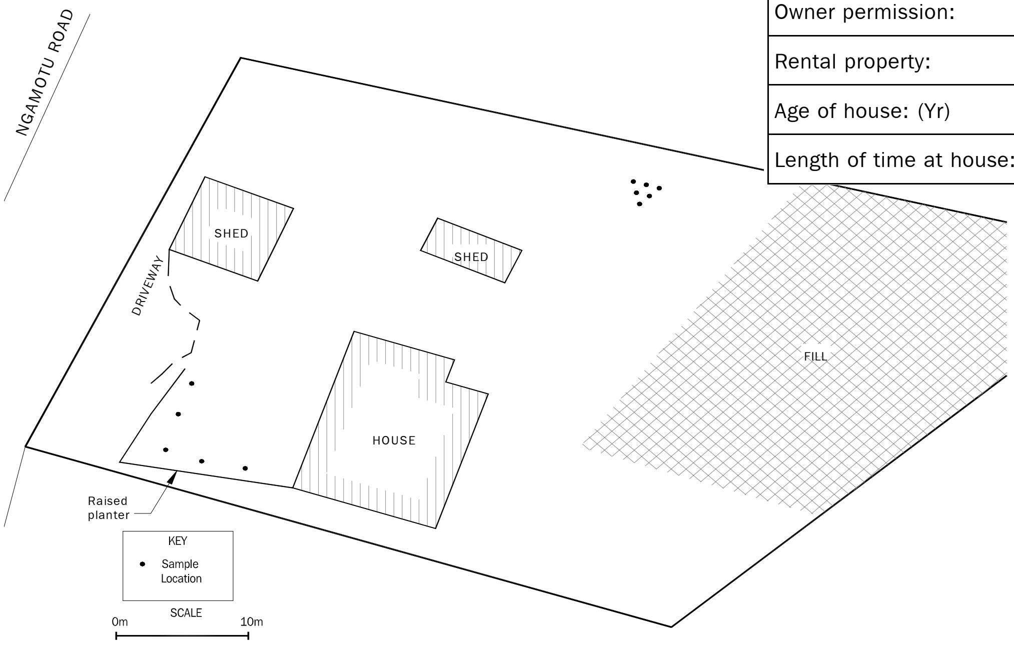
Address	37 Ngamotu Road	Site no.: 23
Date Sampled	30 May 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, light wind	
Comments / Interviews/ Sampling Observations	The grid point location is thought to be in an area of fill. The sampling location was chosen to be as far from sheltering objects as possible, while avoiding an area of fill by at least 10 m. The garden was ornamental.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	0.71	0.61	1.3	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown Garden: Silty sand with friable matter, brown

Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	30
Length of time at house: (Yr)	11



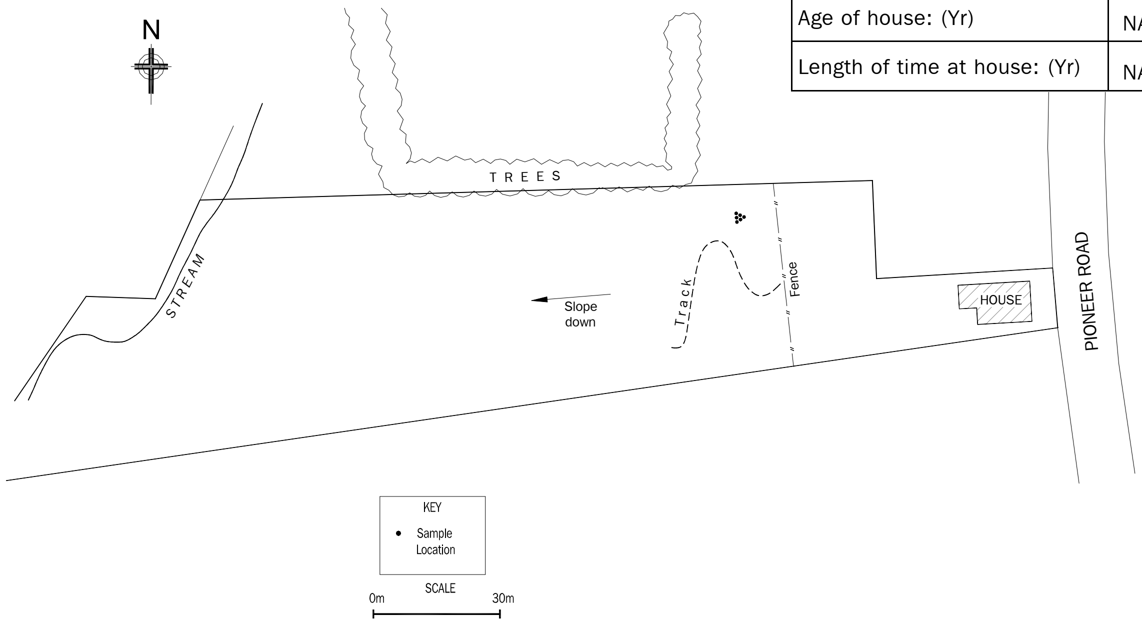
Address	108 Pioneer Road	Site no.: 24
Date Sampled	5 June 2002	
Observer(s)	DIN representative	
Field Conditions	Overcast, windy	
Comments / Interviews/ Sampling Observations	The sampling location was chosen to avoid a track on the property, and is on a slope that faces the Dow plant. A stand of radiata and Cyprus is 4 m to the side of the sampling location, but the trees were estimated by the DIN representatives to be about 10 years old, and thus would not have blocked any wind borne deposition from the Dow plant.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	2.7	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description	Grassed area: Silt loam, brown

Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



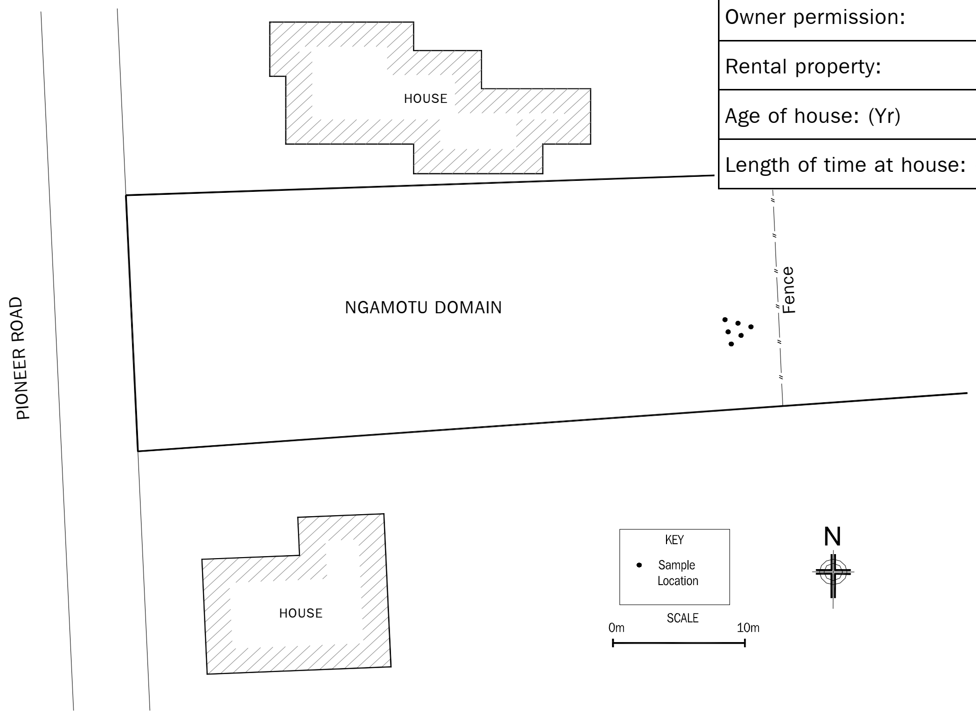
ADDRESS	81 Pioneer Road (Ngamotu Domain)	Site no.: 25
DATE SAMPLED	4 June 2002	
OBSERVER(S)	DIN representative	
FIELD CONDITIONS	Windy, few showers	
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The site was selected as being the nearest public land to the grid point. The sampling location, on a slope facing the Dow plant, was chosen to be away from the road and any tracks (the site is grazed by horses).	

2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	2.2	Not sampled	Not sampled	Not sampled	Not sampled

SOIL DESCRIPTION	Grassed area: Silt loam, brown

SITE PLAN

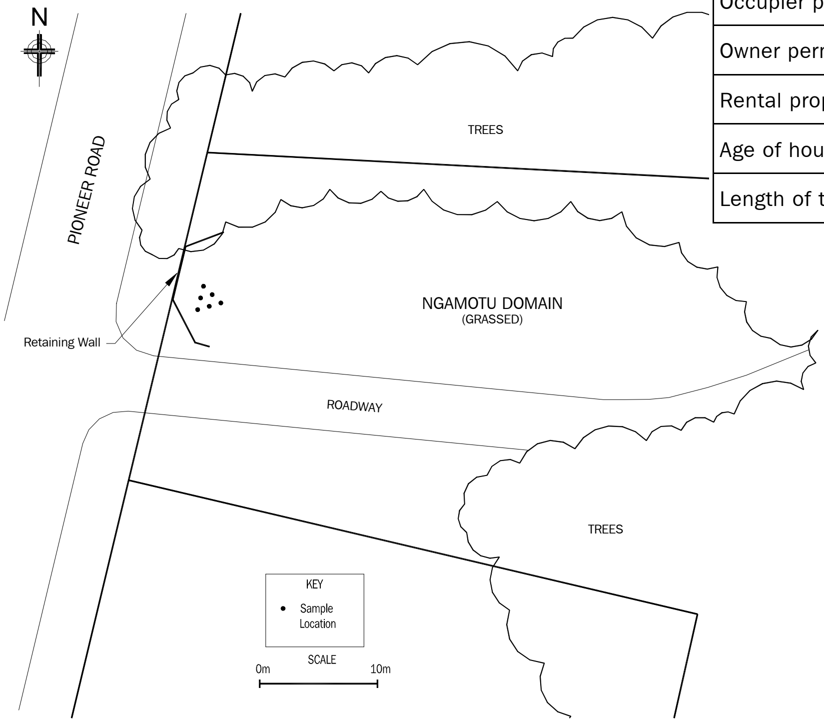
Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



Address	53 Pioneer Road (Ngamotu Domain)				Site no.: 26
Date Sampled	4 June 2002				
Observer(s)	DIN representative				
Field Conditions	Windy, few showers				
Comments / Interviews/ Sampling Observations	The site had vehicle tracks across it, so the sampling location was chosen to be within 2 m of the front retaining wall to avoid vehicular wastes and to avoid the shelter of the surrounding trees. The soil is likely to be original, as it appears that the road was cut rather than the site being filled.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	3.0	Not sampled	Not sampled	Not sampled	Not sampled
Soil Description	Grassed area: Silt loam, brown				

Site Plan

Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



ADDRESS	Permission to publish site address withheld				Site no.: 27
DATE SAMPLED	5 June 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Windy, overcast.				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The selected sampling location was exposed in the direction of the Dow plant.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	27	Not sampled	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

Permission to publish site address withheld

Occupier permission:	Yes
Owner permission:	No
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA

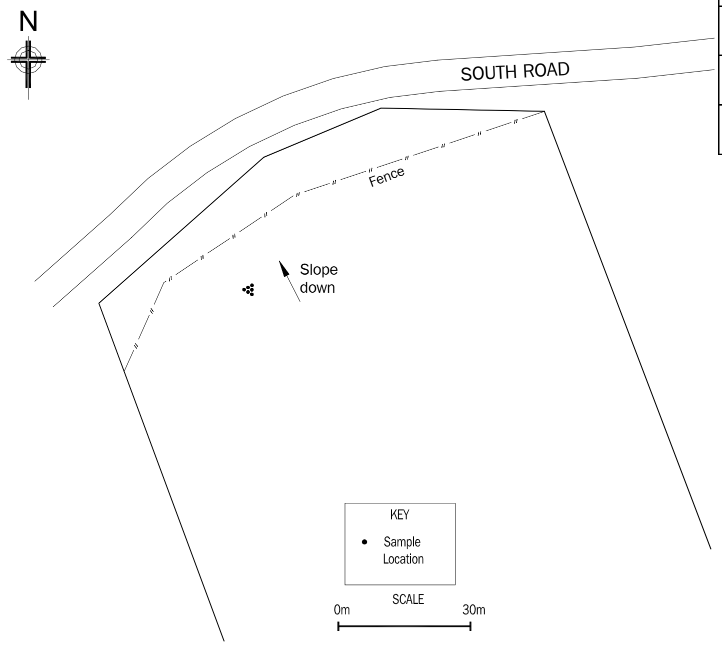
ADDRESS	81 South Road	Site no.: 28
DATE SAMPLED	4 June 2002	
OBSERVER(S)	DIN representative	
FIELD CONDITIONS	Windy, overcast.	
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The site was selected as the nearest suitable public land to the grid point. The sampling location, sited on a slope facing the Dow plant, was chosen for its exposure to any wind borne deposition from the Dow plant. The site is used for grazing.	

2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	0.88	Not sampled	Not sampled	Not sampled	Not sampled

SOIL DESCRIPTION	Grassed area: Silt loam, brown

SITE PLAN

Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



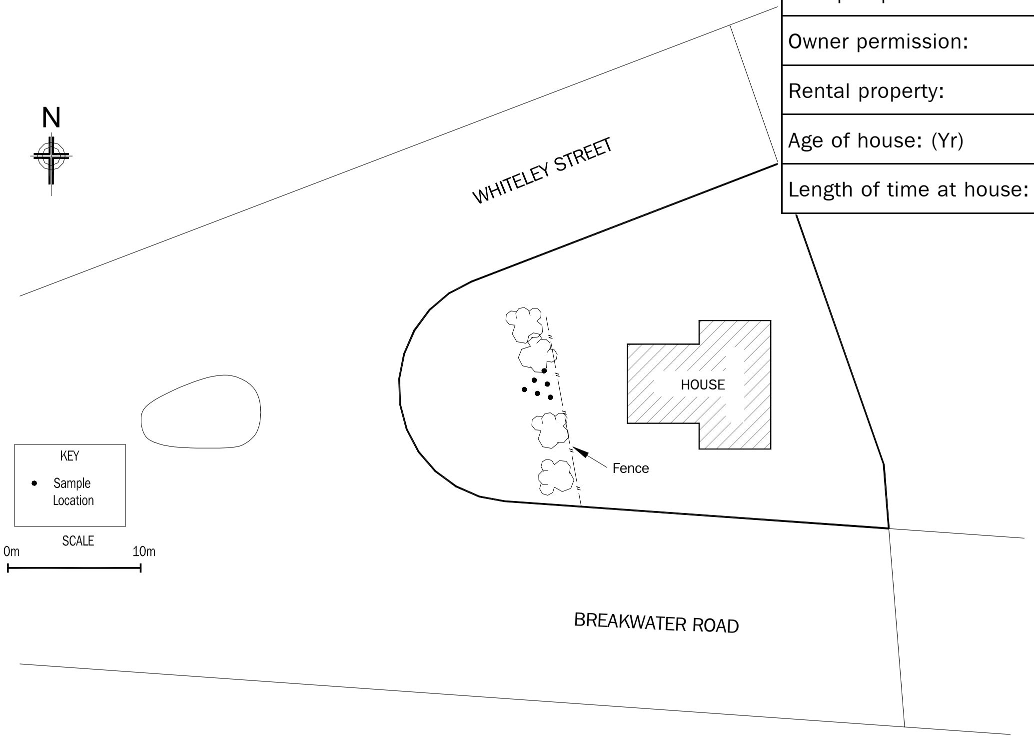
ADDRESS	cnr Whiteley & Breakwater	Site no.: 29
DATE SAMPLED	4 June 2002	
OBSERVER(S)	DIN representative	
FIELD CONDITIONS	Windy, overcast.	
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The site was selected as the nearest suitable public land to the grid point. All closer suitable land is privately owned. The sampling location was on road reserve. It was beneath some young trees (less than 10 years old), but was chosen because of its exposure to any wind borne deposition from the Dow plant.	

2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	3.3	Not sampled	Not sampled	Not sampled	Not sampled

SOIL DESCRIPTION	Grassed area: Silt loam, brown

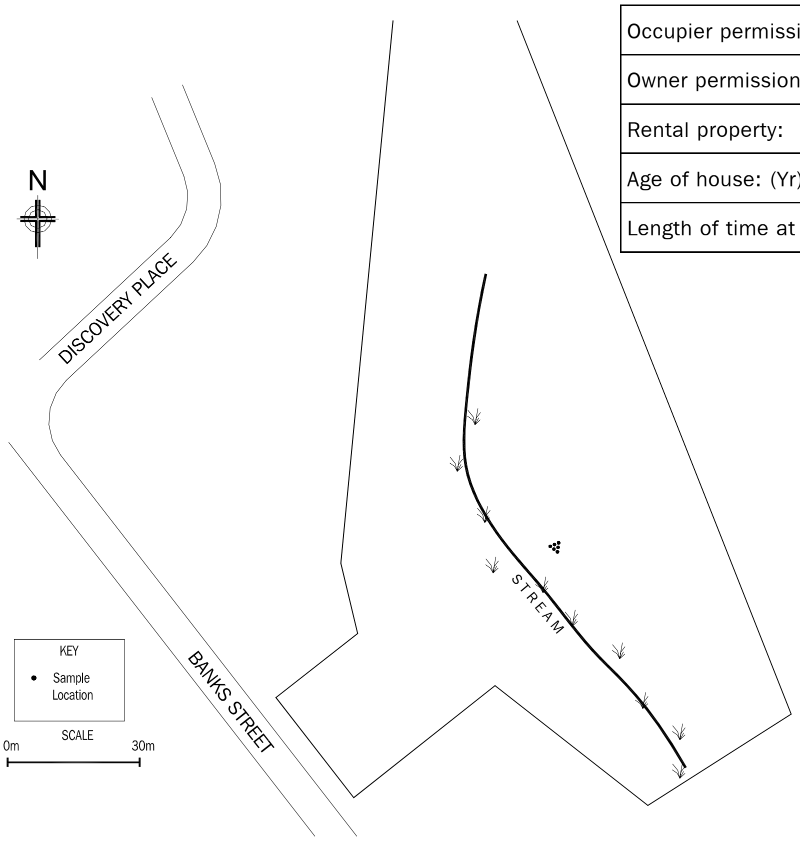
SITE PLAN

Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



ADDRESS	70 Banks Street				Site no.: 30
DATE SAMPLED	4 June 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Overcast, no rain				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	The site is grazed by stock, and has a stream flowing through the centre of it. The sampling location was chosen to be in an open area, and to be on a slope that faces the Dow plant.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	2.4	Not sampled	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

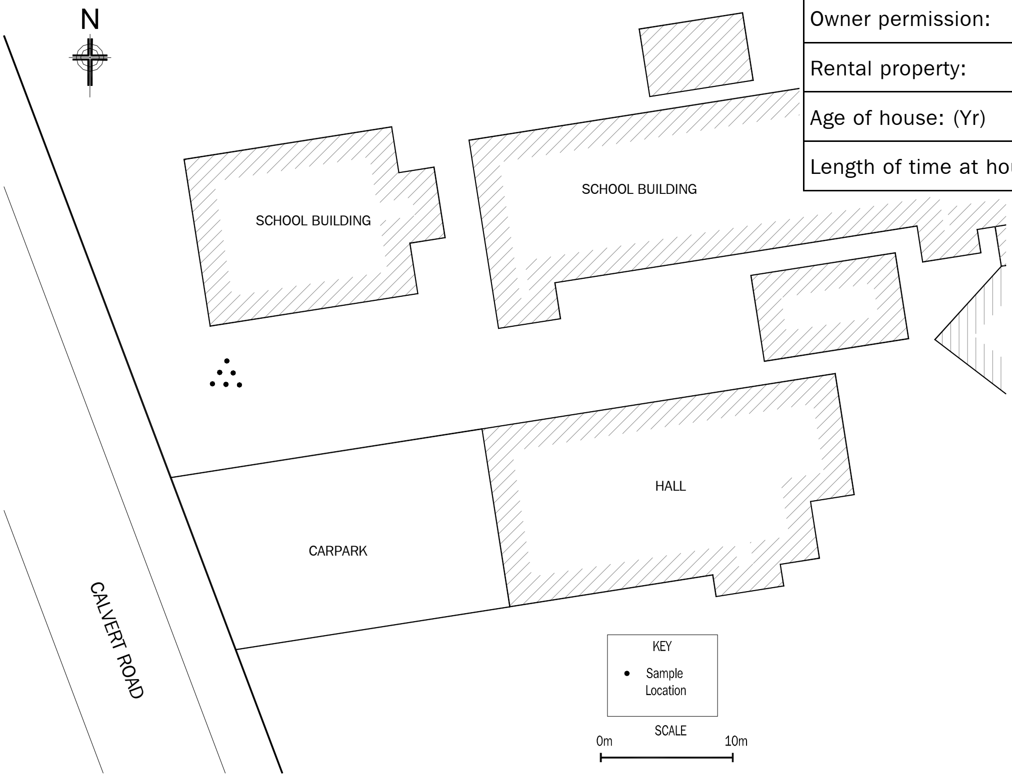


Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA

Address	St Josephs School				Site no.: 31
Date Sampled	4 June 2002				
Observer(s)	DIN representative				
Field Conditions	Fine, little wind				
Comments / Interviews/ Sampling Observations	The site was the nearest site to the grid point. A possible public site in the area was not considered suitable, as it appeared to have been disturbed within the past few years. The sampling location was chosen to be on a slope that is likely to have remained undisturbed for most of the time since the school was established in 1926, and that was exposed to any wind borne deposition from the Dow plant.				
2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	0.81	Not sampled	Not sampled	Not sampled	Not sampled
Soil Description	Grassed area: Silt loam, brown				

Site Plan

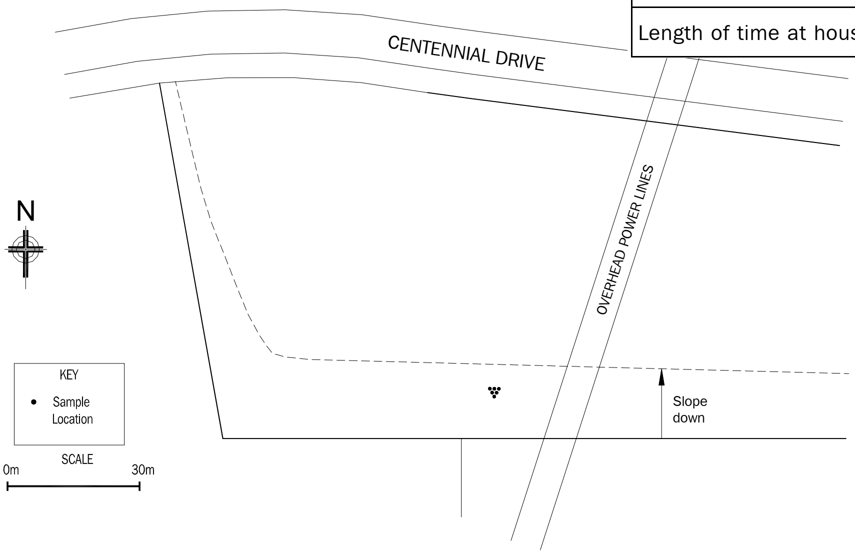
Occupier permission:	Yes
Owner permission:	Yes
Rental property:	No
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



ADDRESS	105 Centennial Drive				Site no.: 32
DATE SAMPLED	5 June 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Fine, little wind				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	This site was selected in conjunction with DIN as being as close as possible to the former camp for the power station workers. The sampling location, on an embankment, was chosen to avoid most of the asphalt paved site, but, as a result, had less exposure to any wind borne deposition from the Dow plant.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	6.1	Not sampled	Not sampled	Not sampled	Not sampled
SOIL DESCRIPTION	Grassed area: Silt loam, brown. Heavy grass cover.				

SITE PLAN

Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



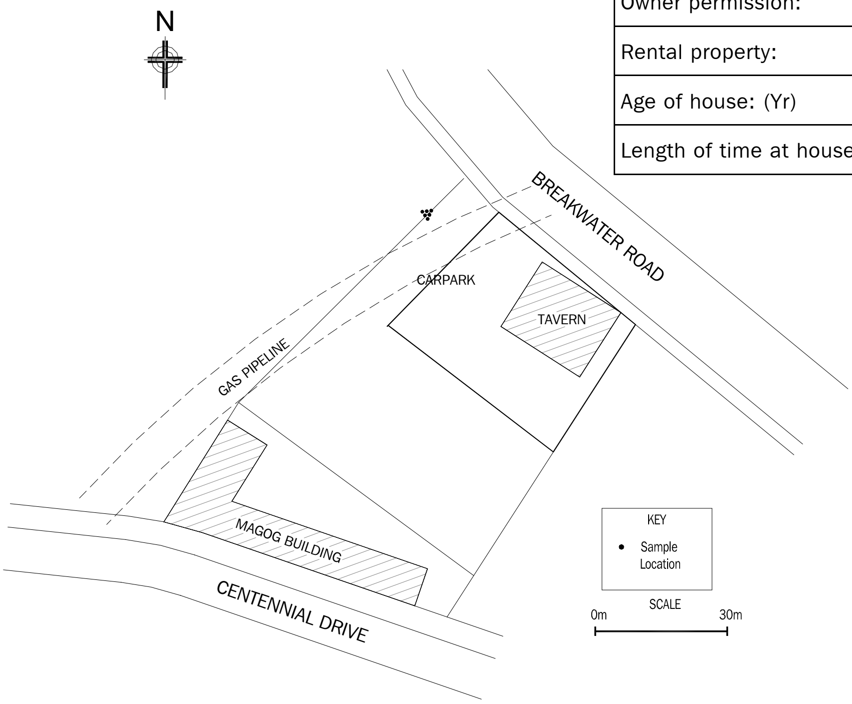
Address	151 Breakwater Road	Site no.: 33
Date Sampled	5 June 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, little wind	
Comments / Interviews/ Sampling Observations	This site was selected in conjunction with DIN as being as close as possible to a residential address north of the Dow plant. The sampling location, the face of a bank at the edge of the property, was chosen as the only on-site location that avoided areas disturbed by a gas main, new fill, and onsite activities. However, it was sheltered from any wind borne deposition from the Dow plant.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	10	Not sampled	Not sampled	Not sampled	Not sampled

Soil Description	Grassed area: Sand with little silt, brown

Site Plan

Occupier permission:	Yes
Owner permission:	Yes
Rental property:	Yes
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



ADDRESS	Permission to publish site address withheld				Site no.: 34
DATE SAMPLED	5 June 2002				
OBSERVER(S)	DIN representative				
FIELD CONDITIONS	Fine, little wind				
COMMENTS / INTERVIEWS/ SAMPLING OBSERVATIONS	This site was selected in conjunction with DIN as being indicative of impacts on residential properties near the port. The selected sampling location was exposed in the direction of the Dow plant.				
2,3,7,8-TCDD RESULTS ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	7.3	Not sampled	Not sampled	Sampled: not analysed	Sampled: not analysed
SOIL DESCRIPTION	Grassed area: Silt loam, brown				

SITE PLAN

Permission to publish site address withheld

Occupier permission:	Yes
Owner permission:	No
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA

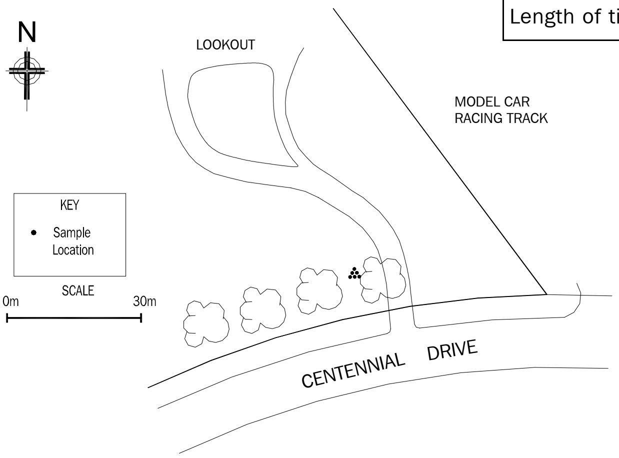
Address	100 Centennial Drive (NPDC Domain)	Site no.: 35
Date Sampled	5 June 2002	
Observer(s)	DIN representative	
Field Conditions	Fine, little wind	
Comments / Interviews/ Sampling Observations	This site was selected in conjunction with DIN as being as close as possible to the residential area of an adjacent marae. The selected area was beneath the canopy of some trees, but was considered to be the best location undisturbed by vehicular or human activities and was exposed to any wind borne deposition from the Dow plant.	

2,3,7,8-TCDD Results ng/kg dry weight	Grassed area 0 mm – 75 mm	Grassed area 75 mm – 150 mm	Garden	Rinsate Blank	Trip Blank
	2.3	Not sampled	Not sampled	Sampled: not analysed	Not sampled

Soil Description	Grassed area: Silt loam, brown

Site Plan

Occupier permission:	NA
Owner permission:	Yes
Rental property:	NA
Age of house: (Yr)	NA
Length of time at house: (Yr)	NA



REPORT FOR PATTLE DELAMORE PARTNERS LTD

SAMPLE PREPARATION AND ANALYSIS PROCEDURES FOR TCDD AND FULL CONGENER DIOXIN ANALYSIS

PREPARED BY

P C BRIDGEN

INTRODUCTION

This report describes the method of analysis of soil samples for the determination of 2,3,7,8 tetrachlorinated dibenzo-*p*-dioxin (TCDD), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The analytical methodology was based on USEPA Method 1613B.

SAMPLE PREPARATION

Following receipt at the laboratory, samples were stored at <-10 ºC pending analysis. Each soil sample was emptied onto an aluminium dish and dried in a 30 ºC oven overnight. The semi-dried sample was thoroughly homogenised by riffling. A sub-sample for analysis was then taken.

A separate sub-sample was taken for the determination of moisture.

SAMPLE EXTRACTION

The analytical sample was loaded into a soxhlet extractor body and spiked with a range of isotopically labelled standards (Wellington Laboratories). Details of nominal amounts of each surrogate standards added are given in Table 1. The soil was extracted by soxhlet ethanol/toluene (68:32). The extract was reduced using rotary evaporation and solvent exchanged into hexane

Table 1. Nominal Weights of Isotopically Labelled Surrogate Standards added to Samples

PCDD Analysis

$^{13}C_{12}$ PCDD Congener	pg added	$^{13}C_{12}$ PCDF Congener	pg added
2,3,7,8 TCDD	400	2,3,7,8 TCDF	400
1,2,3,7,8 PeCDD	400	1,2,3,7,8 PeCDF	400
1,2,3,4,7,8 HxCDD	400	2,3,4,7,8 PeCDF	400
1,2,3,6,7,8 HxCDD	400	1,2,3,4,7,8 HxCDF	400
1,2,3,4,6,7,8 HpCDD	400	1,2,3,6,7,8 HxCDF	400
OCDD	800	2,3,4,6,7,8 HxCDF	400
		1,2,3,7,8,9 HxCDF	400
		1,2,3,4,6,7,8 HpCDF	400
		1,2,3,4,7,8,9 HpCDF	400

SAMPLE PURIFICATION

The extract was purified by column chromatography as follows:

- acid modified silica gel	(eluent: hexane)
- alumina (basic)	(eluent: hexane, 50:50 DCM/hexane)

The extract was reduced by rotary evaporation and transferred to a blow down vial. A volume of $^{13}C_{12}$ labelled recovery spike (1,2,3,4 TCDD and 1,2,3,7,8,9 HxCDD) and keeper was added then blown down gently under a stream of nitrogen and transferred to a GCMS vial for analysis by HRGC-HRMS.

ANALYSIS

Extracts were analysed by GCMS. All extracts were run on ZB5 capillary column. If a peak was detected at the correct retention times for 2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PCDF, 1,2,3,4,7,8-HxCDF or 1,2,3,7,8,9-HxCDD, the extract was re-analysed on an SP2331 capillary column for full isomer specific quantification. Chromatographic and mass spectrometer conditions are given below.

HP6890 Series/HP6890N GC coupled with Micromass-Ultima HRMS

Column	60 m ZB5	60 m SP2331
Flowrate	1.5 mL min^{-1}	N/A
Carrier Gas Head Pressure	N/A	200 kPa
Injector Temperature	260 ºC	260 ºC
Injection	1 µl splitless	1 µl splitless
Temperature Programme	initial temp 180 ºC (hold 2 min), 30 ºC min^{-1} to 210 ºC, 3 ºC min^{-1} to 300 ºC (5.75 min).	initial temp 170 ºC (hold 1 min), 10 ºC min^{-1} to 210 ºC (1 min), 3 ºC min^{-1} to 250 ºC (16.7 min), 50 ºC min^{-1} to 270 ºC (6.6 min).

Table 2. Ions Monitored for PCDDs and PCDFs

Congener Group	^{12}C Quantification Ion (m/z)	^{12}C Confirmation Ion (m/z)	^{13}C Quantification Ion (m/z)	^{13}C Confirmation Ion (m/z)
TCDF	305.8987	303.9016	317.9389	315.9419
TCDD	321.8936	319.8965	333.9339	331.9368
PeCDF	339.8597	337.8626	351.9000	349.9029
PeCDD	355.8546	353.8575	367.8949	365.8978
HxCDF	373.8207	375.8178	385.8610	387.8580
HxCDD	389.8156	391.8127	401.8559	403.8530
HpCDF	407.7818	409.7788	419.8220	421.8191
HpCDD	423.7767	425.7737	435.8169	437.8140
OCDF	443.7398	441.7428		
OCDD	459.7347	457.7377	471.7750	469.7780

ANALYTE IDENTIFICATION CRITERIA

For positive identification the following criteria must be met:

- The retention time of the analyte must be within one second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard
- The ion ratio obtained for the analyte must be plus or minus 10 % of the theoretical ion ratio
- The signal to noise must be greater than 3:1

QUANTIFICATION

Quantification was by the isotope dilution technique using the surrogate standards listed in Table 1. Relative response factors (RRFs) were calculated for each targeted analyte from a series of calibration standards analysed under the same conditions as the samples. Non 2,3,7,8 substituted PCDD and PCDF congeners were quantified using the RRF of the first eluting surrogate standard in each GCMS group. Targeting of all analytes was performed by the MS software (MassLynx). Text files created by the software were electronically transferred to a customised spreadsheet for further data reduction and preparation of final analytical report.

LIMITS OF DETECTION

If no peak was distinguishable above the background noise at the retention time for a targeted analyte or if a peak was present at the correct retention time for the targeted analyte but failed to meet all analyte identification criteria, the result was reported as a limit of detection.

ISOTOPICALLY LABELLED SURROGATE STANDARD RECOVERY CALCULATIONS

The recovery of the isotopically labelled surrogate standards was calculated using relative response factors, relative to the calibration standards.

QUALITY CONTROL

- The batch size was typically 8-10 samples
- A laboratory blank was analysed with each batch of samples
- An ongoing performance and recovery sample (OPR) was analysed with each batch of samples as a replicate to assess method precision
- The GCMS resolution, performance and sensitivity were established for each MS run
- The recoveries of all isotopically labelled surrogate standards were calculated and reported. The quality control acceptance criteria for surrogate standard recovery is given in USEPA method 1613B.

DATA REPORTING

All samples were reported as picograms per gram (pg/g) on a dry weight basis. The total toxic equivalents (I-TEQ) were calculated using international toxic equivalency factors (I-TEFs).

Laboratory blanks were calculated using the average dry weight of all samples analysed in batch.

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Lower Hutt, New Zealand

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Facsimile: +64 4 569 4500

I-TEFs: USEPA Method 1613B

Analyte	I-TEFs
2378 TCDF	0.1
Total TCDF	0
2378 TCDD	1
Total TCDD	0
12378 PeCDF	0.05
23478 PeCDF	0.5
Total PeCDF	0
12378 PeCDD	0.5
Total PeCDD	0
123478 HxCDF	0.1
123678 HxCDF	0.1
234678 HxCDF	0.1
123789 HxCDF	0.1
Total HxCDF	0
123478 HxCDD	0.1
123678 HxCDD	0.1
123789 HxCDD	0.1
Total HxCDD	0
1234678 HpCDF	0.01
1234789 HpCDF	0.01
Total HpCDF	0
1234678 HpCDD	0.01
Total HpCDD	0
OCDF	0.001
OCDD	0.001

I-TEFs = International toxic equivalency factors
I-TEQ = Total toxic equivalence

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Facsimile: +64 4 569 4500

23 July 2002

Certificate of Analysis

Client:	Pattle Delamore Partners Ltd PO Box 6136 Wellington
Attention:	Richard Lucy
Laboratory Reference:	188
Sample Type:	Soil
Analysis:	**2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

L J Porter
AgriQuality UltraTrace™
AgriQuality New Zealand

P C Bridgen
AgriQuality UltraTrace™
AgriQuality New Zealand

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/1**

Sample Identification: **SS#1**

Date Received: 4 June 2002
Date Extracted: 11 June 2002
Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	5.9			82	25 - 164	
37Cl-2378 TCDD				86		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB
Data Analyst: CR
Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/3**

Sample Identification: **SS#2**

Date Received: 4 June 2002
Date Extracted: 11 June 2002
Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	4.8			86	25 - 164	
37Cl-2378 TCDD				92		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB
Data Analyst: CR
Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/4**

Sample Identification: **SS#2-75mm**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	3.2			87	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/5**

Sample Identification: **SS#4**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	7.4			88	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/6**

Sample Identification: **SS#4G**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	4.9			85	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/7**

Sample Identification: **SS#4-75mm**

Date Received: 4 June 2002
Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.2			86	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB
Data Analyst: CR
Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/8**
Sample Identification: **SS#5**

Date Received: 4 June 2002
Date Extracted: 11 June 2002
Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	92			86	25 - 164	
37Cl-2378 TCDD				95		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB   Data Analyst: CR   Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/9**

Sample Identification: **SS#6**

Date Received: 4 June 2002
Date Extracted: 11 June 2002
Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	15			85	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB Data Analyst: CR Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank A**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	0.6		90	25 - 164	
37Cl-2378 TCDD				92		

† = Results are calculated using the average weight of samples in this batch

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

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AgriQuality New Zealand Limited
Huarangi Aotearoa

Gracefield Road
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Phone: +64 4 570 8800
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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

AgriQuality NEW ZEALAND

Attention: Richard Lucy

Laboratory Reference: 188

Sample Type: Soil

Analysis: **2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

L J Porter
AgriQuality UltraTrace™
AgriQuality New Zealand

P C Bridgen
AgriQuality UltraTrace™
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Results: USEPA Method 1613B

Laboratory Reference: **188/10**

Sample Identification: **SS#7**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	3.4			87	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB
Data Analyst: CR
Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/11**

Sample Identification: **SS#8**

Date Received: 4 June 2002
Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	6.1			74	25 - 164	
37Cl-2378 TCDD				95		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

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Results: USEPA Method 1613B

Laboratory Reference: **188/12**

Sample Identification: **SS#9**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	17			88	25 - 164	
37Cl-2378 TCDD				94		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/13**

Sample Identification: **SS#9-G**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.8			83	25 - 164	
37Cl-2378 TCDD				93		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/14**

Sample Identification: **SS#9-75mm**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	14			86	25 - 164	
37Cl-2378 TCDD				95		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/15**

Sample Identification: **SS#10**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	3.6			88	25 - 164	
37Cl-2378 TCDD				94		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: CR

Authorised: Lawrence J Porter

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/16**

Sample Identification: **SS#11**

Date Received: 4 June 2002
Date Extracted: 11 June 2002
Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.0			89	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB   Data Analyst: CR   Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/17**

Sample Identification: **SS#11-75mm**

Date Received: 4 June 2002
Date Extracted: 11 June 2002
Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	1.6			86	25 - 164	
37Cl-2378 TCDD				88		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB Data Analyst: CR Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/18**

Sample Identification: **SS#12**

Date Received: 4 June 2002
Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.9			87	25 - 164	
37Cl-2378 TCDD				94		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB
Data Analyst: CR
Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/19**

Sample Identification: **SS#12G**

Date Received: 4 June 2002

Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2			92	25 - 164	
37Cl-2378 TCDD				97		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB Data Analyst: CR Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank B**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Extracted: 11 June 2002

Date Analysed U2: 13 June 2002
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	0.2		86	25 - 164	
37Cl-2378 TCDD				95		

† = Results are calculated using the average weight of samples in this batch
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB   Data Analyst: CR   Authorised: Lawrence J Porter

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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

Attention: Richard Lucy

Laboratory Reference: 188

Sample Type: Soil

Analysis: **2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

L J Porter
AgriQuality UltraTrace™
AgriQuality New Zealand

P C Bridgen
AgriQuality UltraTrace™
AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **188/20**

Sample Identification: **SS#13**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	6.2			85	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR Data Analyst: BC Authorised: Lawrence J Porter

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/22**

Sample Identification: **SS#14**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	8.0			98	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/23**

Sample Identification: **SS#14-G**

Date Received: 4 June 2002
Date Extracted: 12 June 2002
Date Analysed U2: 17 June 2002
Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	7.3			89	25 - 164	
37Cl-2378 TCDD				87		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR   Data Analyst: BC   Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/24**

Sample Identification: **SS#15**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	1.9			87	25 - 164	
37Cl-2378 TCDD				88		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/25**

Sample Identification: **SS#16**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	1.8			94	25 - 164	
37Cl-2378 TCDD				100		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/27**

Sample Identification: **SS#16-75mm**

Date Received: 4 June 2002
Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002
Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	1.2			87	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

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Results: USEPA Method 1613B

Laboratory Reference: **188/28**

Sample Identification: **SS#17**

Date Received: 4 June 2002
Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002
Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.93			84	25 - 164	
37Cl-2378 TCDD				86		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/30**

Sample Identification: **SS#18**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	4.5			84	25 - 164	
37Cl-2378 TCDD				87		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/34**

Sample Identification: **SS#19**

Date Received: 4 June 2002
Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002
Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	1.0			90	25 - 164	
37Cl-2378 TCDD				90		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR
Data Analyst: BC
Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/35**

Sample Identification: **SS#21**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 18 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.75			75	25 - 164	
37Cl-2378 TCDD				74		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

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Results: USEPA Method 1613B

Laboratory Reference: **188/Blank C**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Extracted: 12 June 2002
Date Analysed U2: 17 June 2002
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	0.09		87	25 - 164	
37Cl-2378 TCDD				91		

† = Results are calculated using the average weight of samples in this batch
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR
Data Analyst: BC
Authorised: Lawrence J Porter

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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

Attention: Richard Lucy

Laboratory Reference: 188

Sample Type: Soil

Analysis: **2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

L J Porter
AgriQuality UltraTrace™
AgriQuality New Zealand

P C Bridgen
AgriQuality UltraTrace™
AgriQuality New Zealand

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/36**

Sample Identification: **SS#22**

Date Received: 4 June 2002

Date Extracted: 13 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.76			94	25 - 164	
37Cl-2378 TCDD				94		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR

Data Analyst: BC

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/37**

Sample Identification: **SS#23**

Date Received: 4 June 2002
Date Extracted: 13 June 2002
Date Analysed U2: 17 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.71			90	25 - 164	
37Cl-2378 TCDD				94		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR   Data Analyst: BC   Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/38**

Sample Identification: **SS#23-G**

Date Received: 4 June 2002
Date Extracted: 13 June 2002

Date Analysed U2: 17 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	1.3			97	25 - 164	
37Cl-2378 TCDD				100		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR   Data Analyst: BC   Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/39**

Sample Identification: **SS#23-75mm**

Date Received: 4 June 2002

Date Extracted: 13 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.61			89	25 - 164	
37Cl-2378 TCDD				88		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR   Data Analyst: BC   Authorised: Lawrence J Porter

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Results: USEPA Method 1613B

Laboratory Reference: **188/Blank D**
Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Extracted: 13 June 2002
Date Analysed U2: 17 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	0.07		87	25 - 164	
37Cl-2378 TCDD				91		

† = Results are calculated using the average weight of samples in this batch
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: RR
Data Analyst: BC
Authorised: Lawrence J Porter

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23 July 2002

Certificate of Analysis

Client:	Pattle Delamore Partners Ltd PO Box 6136 Wellington
Attention:	Richard Lucy
Laboratory Reference:	188
Sample Type:	Aqueous
Analysis:	**2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per litre (pg/L), equivalent to ppq, on an as received basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

L J Porter
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AgriQuality New Zealand

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AgriQuality UltraTrace™
AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **188/33**

Sample Identification: **SS#18-B**

Date Received: 4 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/L)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	10		84	25 - 164	
37Cl-2378 TCDD				89		

† = Results are reported on an as received basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: TG

Data Analyst: CR

Authorised: Lawrence J Porter

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank E**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Extracted: 18 June 2002
Date Analysed U2: 21 June 2002
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	2		83	25 - 164	
37Cl-2378 TCDD				83		

† = Results are calculated using the average weight of samples in this batch
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: TG
Data Analyst: CR
Authorised: Lawrence J Porter

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23 July 2002

Certificate of Analysis

Client:	Pattle Delamore Partners Ltd PO Box 6136 Wellington
Attention:	Richard Lucy
Laboratory Reference:	188
Sample Type:	Soil
Analysis:	**Polychlorinated dibenzo-*p*-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on an as dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures both including and excluding DL values.

The total toxic equivalence (I-TEQ) was calculated for the samples using international toxic equivalency factors (I-TEFs). The total I-TEQ level is reported both including and excluding the DL values.

Unless requested, samples will be disposed of three months from the date of this report.

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All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

S V Leathem
AgriQuality UltraTrace™
AgriQuality New Zealand

S R Dutt
AgriQuality UltraTrace™
AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **188/5**
Sample Identification: **SS#4**

Date Received: 4 June 2002
Date Extracted: 2 July 2002
Date Analysed U2: 4 July 2002
Date Analysed SP2331: 8 July 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	0.28			96	24 - 169	
Total TCDF	5.0					
2378 TCDD	9.7			83	25 - 164	
Total TCDD	40					
$^{37}Cl_4$ TCDD				91	35 - 197	
12378 PeCDF	0.23			96	24 - 185	
23478 PeCDF	ND	0.7		93	21 - 178	
Total PeCDF	6.3					
12378 PeCDD	1.2			95	25 - 181	
Total PeCDD	8.5					
123478 HxCDF	ND	0.6		93	26 - 152	
123678 HxCDF	ND	0.8		96	26 - 123	
234678 HxCDF	0.39			87	28 - 136	
123789 HxCDF	ND	0.3		82	29 - 147	
Total HxCDF	9.7					
123478 HxCDD	0.64			87	32 - 141	
123678 HxCDD	1.3			86	28 - 130	
123789 HxCDD	0.86					
Total HxCDD	11					
1234678 HpCDF	7.4			95	28 - 143	
1234789 HpCDF	ND	0.8		82	26 - 138	
Total HpCDF	19					
1234678 HpCDD	30			85	23 - 140	
Total HpCDD	51					
OCDF	24					
OCDD	300			80	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	475	475	pg/g
Total I-TEQ:	11.4	11.9	pg/g

† = Results are reported on an as dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: RR Data Analyst: SD Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **188/8**
Sample Identification: **SS#5**

Date Received: 4 June 2002
Date Extracted: 2 July 2002
Date Analysed U2: 4 July 2002
Date Analysed SP2331: 8 July 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	1.0			82	24 - 169	
Total TCDF	7.6					
2378 TCDD	74			93	25 - 164	
Total TCDD	110					
$^{37}Cl_4$ TCDD				103	35 - 197	
12378 PeCDF	0.35			103	24 - 185	
23478 PeCDF	ND	0.8		101	21 - 178	
Total PeCDF	6.3					
12378 PeCDD	4.1			100	25 - 181	
Total PeCDD	17					
123478 HxCDF	0.45			87	26 - 152	
123678 HxCDF	ND	1		85	26 - 123	
234678 HxCDF	0.56			85	28 - 136	
123789 HxCDF	ND	0.3		80	29 - 147	
Total HxCDF	6.3					
123478 HxCDD	1.4			89	32 - 141	
123678 HxCDD	2.1			78	28 - 130	
123789 HxCDD	1.3					
Total HxCDD	19					
1234678 HpCDF	5.4			90	28 - 143	
1234789 HpCDF	ND	0.6		82	26 - 138	
Total HpCDF	9.5					
1234678 HpCDD	20			61	23 - 140	
Total HpCDD	42					
OCDF	14					
OCDD	160			66	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	392	392	pg/g
Total I-TEQ:	77.2	77.7	pg/g

† = Results are reported on an as dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit **-** upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: RR   Data Analyst: SD   Authorised: Scott V Leathem

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/9**

Sample Identification: **SS#6**

Date Received:	4 June 2002	Date Analysed U2:	4 July 2002
Date Extracted:	2 July 2002	Date Analysed SP2331:	8 July 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	0.23			110	24 - 169	
Total TCDF	5.3					
2378 TCDD	13			82	25 - 164	
Total TCDD	28					
$^{37}Cl_4$ TCDD				94	35 - 197	
12378 PeCDF	0.16			126	24 - 185	
23478 PeCDF	ND	0.4		117	21 - 178	
Total PeCDF	3.5					
12378 PeCDD	0.53			111	25 - 181	
Total PeCDD	5.6					
123478 HxCDF	ND	0.6		89	26 - 152	
123678 HxCDF	ND	0.4		93	26 - 123	
234678 HxCDF	0.34			86	28 - 136	
123789 HxCDF	ND	0.2		81	29 - 147	
Total HxCDF	5.0					
123478 HxCDD	ND	0.2		85	32 - 141	
123678 HxCDD	0.55			82	28 - 130	
123789 HxCDD	0.54					
Total HxCDD	6.3					
1234678 HpCDF	2.8			83	28 - 143	
1234789 HpCDF	ND	0.3		77	26 - 138	
Total HpCDF	5.1					
1234678 HpCDD	10			65	23 - 140	
Total HpCDD	19					
OCDF	6.5					
OCDD	80			61	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	164	164	pg/g
Total I-TEQ:	13.7	14	pg/g

† = Results are reported on an as dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: RR   Data Analyst: SD   Authorised: Scott V Leathem

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank F**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable

Date Extracted: 2 July 2002

Date Analysed U2: 4 July 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.09		87	24 - 169	
Total TCDF	ND	0.09				
2378 TCDD	ND	0.2		80	25 - 164	
Total TCDD	ND	0.2				
^{37}Cl$_4$ TCDD				91	35 - 197	
12378 PeCDF	ND	0.09		92	24 - 185	
23478 PeCDF	ND	0.3		92	21 - 178	
Total PeCDF	ND	0.3				
12378 PeCDD	ND	0.2		89	25 - 181	
Total PeCDD	ND	0.2				
123478 HxCDF	ND	0.3		99	26 - 152	
123678 HxCDF	ND	0.2		105	26 - 123	
234678 HxCDF	ND	0.2		89	28 - 136	
123789 HxCDF	ND	0.2		77	29 - 147	
Total HxCDF	ND	0.7				
123478 HxCDD	ND	0.2		91	32 - 141	
123678 HxCDD	ND	0.2		84	28 - 130	
123789 HxCDD	ND	0.2				
Total HxCDD	ND	0.2				
1234678 HpCDF	ND	0.1		95	28 - 143	
1234789 HpCDF	ND	0.2		83	26 - 138	
Total HpCDF	ND	0.2				
1234678 HpCDD	ND	0.6		91	23 - 140	
Total HpCDD	ND	0.6				
OCDF	ND	0.4				
OCDD	ND	5		76	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	0	11.2	pg/g
Total I-TEQ:	0	0.628	pg/g

† = Results are calculated using the average weight of samples in this batch

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

^{37}Cl$_4$ TCDD: Clean-up recovery spike

Lab Analyst: RR   Data Analyst: SD   Authorised: Scott V Leathem

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

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23 July 2002

Certificate of Analysis

Client:	Pattle Delamore Partners Ltd PO Box 6136 Wellington
Attention:	Richard Lucy
Laboratory Reference:	188
Sample Type:	Soil
Analysis:	**Polychlorinated dibenzo-*p*-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on an as dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures both including and excluding DL values.

The total toxic equivalence (I-TEQ) was calculated for the samples using international toxic equivalency factors (I-TEFs). The total I-TEQ level is reported both including and excluding the DL values.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

S V Leathem
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S R Dutt
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AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **188/20**

Sample Identification: **SS#13**

Date Received: 4 June 2002

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: 15 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	0.95			77	24 - 169	
Total TCDF	19					
2378 TCDD	6.1			85	25 - 164	
Total TCDD	23					
$^{37}Cl_4$ TCDD				92	35 - 197	
12378 PeCDF	0.64			86	24 - 185	
23478 PeCDF	1.0			83	21 - 178	
Total PeCDF	9.8					
12378 PeCDD	1.2			92	25 - 181	
Total PeCDD	6.3					
123478 HxCDF	0.87			62	26 - 152	
123678 HxCDF	0.64			75	26 - 123	
234678 HxCDF	0.89			68	28 - 136	
123789 HxCDF	ND	0.4		57	29 - 147	
Total HxCDF	8.4					
123478 HxCDD			0.67	75	32 - 141	
123678 HxCDD	1.3			77	28 - 130	
123789 HxCDD	1.6					
Total HxCDD	14					
1234678 HpCDF	5.0			70	28 - 143	
1234789 HpCDF	ND	0.4		68	26 - 138	
Total HpCDF	8.0					
1234678 HpCDD	15			86	23 - 140	
Total HpCDD	28					
OCDF	5.0					
OCDD	110			75	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	232	232	pg/g
Total I-TEQ:	8.17	8.28	pg/g

† = Results are reported on an as dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: PD

Data Analyst: SD

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank G**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable

Date Extracted: 12 June 2002

Date Analysed U2: 17 June 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.2		71	24 - 169	
Total TCDF	ND	0.2				
2378 TCDD	ND	0.1		87	25 - 164	
Total TCDD	ND	0.1				
^{37}Cl$_4$ TCDD				92	35 - 197	
12378 PeCDF	ND	0.1		96	24 - 185	
23478 PeCDF	ND	0.1		81	21 - 178	
Total PeCDF	ND	0.1				
12378 PeCDD	ND	0.2		92	25 - 181	
Total PeCDD	ND	0.2				
123478 HxCDF	ND	0.2		63	26 - 152	
123678 HxCDF	ND	0.1		91	26 - 123	
234678 HxCDF	ND	0.2		67	28 - 136	
123789 HxCDF	ND	0.3		48	29 - 147	
Total HxCDF	ND	0.3				
123478 HxCDD	ND	0.2		80	32 - 141	
123678 HxCDD	ND	0.2		87	28 - 130	
123789 HxCDD	ND	0.2				
Total HxCDD	ND	0.2				
1234678 HpCDF	ND	0.2		59	28 - 143	
1234789 HpCDF	ND	0.5		39	26 - 138	
Total HpCDF	ND	0.5				
1234678 HpCDD	ND	0.9		91	23 - 140	
Total HpCDD	ND	1				
OCDF	ND	0.3				
OCDD	ND	4		95	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	0	6.9	pg/g
Total I-TEQ:	0	0.435	pg/g

† = Results are calculated using the average weight of samples in this batch.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

^{37}Cl$_4$ TCDD: Clean-up recovery spike

Lab Analyst: PD

Data Analyst: SD

Authorised: Scott V Leathem

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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

Attention: Richard Lucy

Laboratory Reference: 188

Sample Type: Soil

Analysis: **Polychlorinated dibenzo-*p*-dioxins (PCDDs)**
Polychlorinated dibenzofurans (PCDFs)

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per grams (pg/g), equivalent to ppt, on an as dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures both including and excluding DL values.

The total toxic equivalence (I-TEQ) was calculated for the samples using international toxic equivalency factors (I-TEFs). The total I-TEQ level is reported both including and excluding the DL values.

Unless requested, samples will be disposed of three months from the date of this report.

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

S V Leathem
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AgriQuality New Zealand

S R Dutt
AgriQuality UltraTrace™
AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **188/36**

Sample Identification: **SS#22**

Date Received: 4 June 2002
Date Extracted: 13 June 2002
Date Analysed U2: 17 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	0.64			104	24 - 169	
Total TCDF	5.3					
2378 TCDD	0.80			95	25 - 164	
Total TCDD	3.0					
^{37}Cl$_4$ TCDD				93	35 - 197	
12378 PeCDF	0.54			118	24 - 185	
23478 PeCDF	0.80			107	21 - 178	
Total PeCDF	4.4					
12378 PeCDD	ND	0.7		115	25 - 181	
Total PeCDD	0.88					
123478 HxCDF	0.88			55	26 - 152	
123678 HxCDF	0.70			65	26 - 123	
234678 HxCDF	0.90			77	28 - 136	
123789 HxCDF	ND	0.5		72	29 - 147	
Total HxCDF	9.2					
123478 HxCDD	ND	1		76	32 - 141	
123678 HxCDD	1.1			83	28 - 130	
123789 HxCDD	1.3					
Total HxCDD	12					
1234678 HpCDF	8.5			57	28 - 143	
1234789 HpCDF	ND	0.7		65	26 - 138	
Total HpCDF	16					
1234678 HpCDD	25			90	23 - 140	
Total HpCDD	44					
OCDF	12					
OCDD	180			90	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	287	287	pg/g
Total I-TEQ:	2.31	2.81	pg/g

† = Results are reported on an as dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
^{37}Cl$_4$ TCDD: Clean-up recovery spike

Lab Analyst: RR   Data Analyst: SD   Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank H**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Extracted: 13 June 2002
Date Analysed U2: 17 June 2002
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.08		85	24 - 169	
Total TCDF	ND	0.08				
2378 TCDD	ND	0.08		98	25 - 164	
Total TCDD	ND	0.08				
$^{37}Cl_4$ TCDD				99	35 - 197	
12378 PeCDF	ND	0.1		88	24 - 185	
23478 PeCDF	ND	0.1		75	21 - 178	
Total PeCDF	ND	0.1				
12378 PeCDD	ND	0.2		91	25 - 181	
Total PeCDD	ND	0.2				
123478 HxCDF	ND	0.1		73	26 - 152	
123678 HxCDF	ND	0.1		91	26 - 123	
234678 HxCDF	ND	0.1		81	28 - 136	
123789 HxCDF	ND	0.2		66	29 - 147	
Total HxCDF	ND	0.2				
123478 HxCDD	ND	0.3		88	32 - 141	
123678 HxCDD	ND	0.3		100	28 - 130	
123789 HxCDD	ND	0.2				
Total HxCDD	ND	0.3				
1234678 HpCDF	ND	0.2		70	28 - 143	
1234789 HpCDF	ND	0.2		60	26 - 138	
Total HpCDF	ND	0.2				
1234678 HpCDD	ND	0.4		93	23 - 140	
Total HpCDD	ND	0.4				
OCDF	ND	0.4				
OCDD	ND	2		92	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	0	3.96	pg/g
Total I-TEQ:	0	0.383	pg/g

† = Results are calculated using the average weight of samples in this batch.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: RR
Data Analyst: SD
Authorised: Scott V Leathem

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

AgriQuality New Zealand Limited
Huarangi Aotearoa

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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

Attention: Richard Lucy

Laboratory Reference: 188

Sample Type: Soil

Analysis: **Polychlorinated dibenzo-*p*-dioxins (PCDDs)**
Polychlorinated dibenzofurans (PCDFs)

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on an as dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures both including and excluding DL values.

The total toxic equivalence (I-TEQ) was calculated for the samples using international toxic equivalency factors (I-TEFs). The total I-TEQ level is reported both including and excluding the DL values.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory
All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

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S R Dutt
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Results: USEPA Method 1613B

Laboratory Reference: **188/16**

Sample Identification: **SS#11**

Date Received: 4 June 2002
Date Extracted: 12 June 2002

Date Analysed U2: 13 June 2002
Date Analysed SP2331: 14 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.6		102	24 - 169	
Total TCDF	16					
2378 TCDD	2.0			88	25 - 164	
Total TCDD	13					
^{37}Cl$_4$ TCDD				95	35 - 197	
12378 PeCDF	0.64			117	24 - 185	
23478 PeCDF	ND	0.5		104	21 - 178	
Total PeCDF	9.1					
12378 PeCDD	1.2			102	25 - 181	
Total PeCDD	5.9					
123478 HxCDF	ND	0.6		84	26 - 152	
123678 HxCDF	ND	0.5		106	26 - 123	
234678 HxCDF	ND	0.7		91	28 - 136	
123789 HxCDF	ND	0.2		55	29 - 147	
Total HxCDF	8.0					
123478 HxCDD	0.51			89	32 - 141	
123678 HxCDD	1.3			97	28 - 130	
123789 HxCDD	0.91					
Total HxCDD	14					
1234678 HpCDF	4.3			68	28 - 143	
1234789 HpCDF	ND	0.6		30	26 - 138	
Total HpCDF	5.9					
1234678 HpCDD	16			80	23 - 140	
Total HpCDD	30					
OCDF	2.0					
OCDD	100			68	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	204	204	pg/g
Total I-TEQ:	3.21	3.73	pg/g

† = Results are reported on an as dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
^{37}Cl$_4$ TCDD: Clean-up recovery spike

Lab Analyst: CH
Data Analyst: SD
Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **188/Blank I**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable

Date Extracted: 12 June 2002

Date Analysed U2: 13 June 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.1		89	24 - 169	
Total TCDF	ND	0.1				
2378 TCDD	ND	0.2		86	25 - 164	
Total TCDD	ND	0.2				
$^{37}Cl_4$ TCDD				95	35 - 197	
12378 PeCDF	ND	0.1		98	24 - 185	
23478 PeCDF	ND	0.1		90	21 - 178	
Total PeCDF	ND	0.1				
12378 PeCDD	ND	0.2		87	25 - 181	
Total PeCDD	ND	0.2				
123478 HxCDF	ND	0.3		91	26 - 152	
123678 HxCDF	ND	0.3		109	26 - 123	
234678 HxCDF	ND	0.3		93	28 - 136	
123789 HxCDF	ND	0.3		69	29 - 147	
Total HxCDF	ND	0.7				
123478 HxCDD	ND	0.3		87	32 - 141	
123678 HxCDD	ND	0.2		109	28 - 130	
123789 HxCDD	ND	0.3				
Total HxCDD	ND	0.3				
1234678 HpCDF	ND	0.5		83	28 - 143	
1234789 HpCDF	ND	0.2		56	26 - 138	
Total HpCDF	ND	0.5				
1234678 HpCDD	ND	0.9		88	23 - 140	
Total HpCDD	ND	1				
OCDF	ND	0.5				
OCDD	ND	6		70	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	0	9.6	pg/g
Total I-TEQ:	0	0.588	pg/g

† = Results are calculated using the average weight of samples in this batch.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: CH

Data Analyst: SD

Authorised: Scott V Leathem

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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

Attention: Richard Lucy

Laboratory Reference: 265

Sample Type: Soil

Analysis: **2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

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P C Bridgen
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AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **265/1**

Sample Identification: **SS#3**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	5.8			89	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/2**

Sample Identification: **SS#3-G**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	4.5			91	25 - 164	
37Cl-2378 TCDD				99		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/3**

Sample Identification: **SS#20**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	4.8			93	25 - 164	
37Cl-2378 TCDD				98		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/4**

Sample Identification: **SS#24**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.7			91	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/5**

Sample Identification: **SS#25**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.2			93	25 - 164	
37Cl-2378 TCDD				98		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/6**

Sample Identification: **SS#26**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	3.0			98	25 - 164	
37Cl-2378 TCDD				104		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/7**

Sample Identification: **SS#28**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.88			96	25 - 164	
37Cl-2378 TCDD				96		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD

Data Analyst: BC

Authorised: Scott V Leathem

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Results: USEPA Method 1613B

Laboratory Reference: **265/8**

Sample Identification: **SS#29**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	3.3			92	25 - 164	
37Cl-2378 TCDD				95		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD   Data Analyst: BC   Authorised: Scott V Leathem

THIS REPORT MUST ONLY BE REPRODUCED IN ITS ENTIRETY

Results: USEPA Method 1613B

Laboratory Reference: **265/9**

Sample Identification: **SS#30**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.4			95	25 - 164	
37Cl-2378 TCDD				95		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD   Data Analyst: BC   Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/10**

Sample Identification: **SS#31**

Date Received: 10 June 2002

Date Extracted: 18 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	0.81			97	25 - 164	
37Cl-2378 TCDD				104		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD Data Analyst: BC Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/11**

Sample Identification: **SS#32**

Date Received: 18 June 2002
Date Extracted: 10 June 2002

Date Analysed U2: 27 June 2002
Date Analysed SP2331: 2 July 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	6.1			94	25 - 164	
37Cl-2378 TCDD				95		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: CH   Data Analyst: PB   Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/12**

Sample Identification: **SS#33**

Date Received: 10 June 2002
Date Extracted: 18 June 2002
Date Analysed U2: 21 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	10			85	25 - 164	
37Cl-2378 TCDD				97		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD
Data Analyst: BC
Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/13**

Sample Identification: **SS#34**

Date Received: 10 June 2002
Date Extracted: 18 June 2002
Date Analysed U2: 21 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.[†] (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	7.3			88	25 - 164	
37Cl-2378 TCDD				93		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD   Data Analyst: BC   Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/BLANK-A**

Sample Identification: **Laboratory Blank A**

Date Received: Not applicable
Date Analysed U2: 21 June 2002
Date Extracted: 18 June 2002
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	0.1		94	25 - 164	
37Cl-2378 TCDD				92		

† = Results are calculated using the average weight of samples in this batch
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: PD   Data Analyst: BC   Authorised: Scott V Leathem

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23 July 2002

Certificate of Analysis

Client: Pattle Delamore Partners Ltd
PO Box 6136
Wellington

Attention: Richard Lucy

Laboratory Reference: 265

Sample Type: Soil

Analysis: **2378 Tetrachlorinated dibenzo-*p*-dioxin (TCDD)**

Method: Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on a dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

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Results: USEPA Method 1613B

Laboratory Reference: **265/16**

Sample Identification: **SS#35**

Date Received: 10 June 2002

Date Extracted: 19 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	2.3			89	25 - 164	
37Cl-2378 TCDD				93		

† = Results are reported on a dry weight basis.

⚐ = Recovery outside method guidelines

NQ = Not quantitated

ND = Not detected

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB Data Analyst: BC Authorised: Scott V Leathem

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Results: USEPA Method 1613B

Laboratory Reference: **265/18**

Sample Identification: **SS#37**

Date Received: 10 June 2002
Date Extracted: 19 June 2002
Date Analysed U2: 21 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	27			89	25 - 164	
37Cl-2378 TCDD				91		

† = Results are reported on a dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated
ND = Not detected

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB Data Analyst: BC Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/Blank-B**

Sample Identification: **Laboratory Blank B**

Date Received: Not applicable

Date Extracted: 19 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDD	ND	0.2		94	25 - 164	
37Cl-2378 TCDD				96		

† = Results are calculated using the average weight of samples in this batch

⚐ = Recovery outside method guidelines

NQ = Not quantitated

DL: Sample specific estimated detection limit

EMPC: Estimated maximum possible concentration

^{13}C %RE: Labelled compound recovery

LCL-UCL: Lower control limit - upper control limit

Lab Analyst: EB

Data Analyst: BC

Authorised: Scott V Leathem

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23 July 2002

Certificate of Analysis

Client:	Pattle Delamore Partners Ltd PO Box 6136 Wellington
Attention:	Richard Lucy
Laboratory Reference:	265
Sample Type:	Soil
Analysis:	**Polychlorinated dibenzo-*p*-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on an as dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures both including and excluding DL values.

The total toxic equivalence (I-TEQ) was calculated for the samples using international toxic equivalency factors (I-TEFs). The total I-TEQ level is reported both including and excluding the DL values.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

S V Leathem
AgriQuality UltraTrace™
AgriQuality New Zealand

S R Dutt
AgriQuality UltraTrace™
AgriQuality New Zealand

Results: USEPA Method 1613B

Laboratory Reference: **265/4**

Sample Identification: **SS#24**

Date Received: 10 June 2002
Date Analysed U2: 21 June 2002
Date Extracted: 18 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	0.95			102	24 - 169	
Total TCDF	18					
2378 TCDD	2.5			92	25 - 164	
Total TCDD	32					
$^{37}Cl_4$ TCDD				98	35 - 197	
12378 PeCDF	0.85			105	24 - 185	
23478 PeCDF	0.59			95	21 - 178	
Total PeCDF	5.5					
12378 PeCDD	1.0			97	25 - 181	
Total PeCDD	6.7					
123478 HxCDF	0.77			90	26 - 152	
123678 HxCDF	0.6			97	26 - 123	
234678 HxCDF	1.0			87	28 - 136	
123789 HxCDF	ND	0.2		79	29 - 147	
Total HxCDF	13					
123478 HxCDD	0.64			93	32 - 141	
123678 HxCDD	1.6			81	28 - 130	
123789 HxCDD	1.2					
Total HxCDD	24					
1234678 HpCDF	9.7			83	28 - 143	
1234789 HpCDF	ND	0.4		69	26 - 138	
Total HpCDF	17					
1234678 HpCDD	25			87	23 - 140	
Total HpCDD	48					
OCDF	17					
OCDD	220			71	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	401	401	pg/g
Total I-TEQ:	4.60	4.62	pg/g

† = Results are reported on an as dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: PD
Data Analyst: SD
Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/Blank C**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable
Date Analysed U2: 21 June 2002
Date Extracted: 18 June 2002
Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.4		91	24 - 169	
Total TCDF	ND	0.4				
2378 TCDD	ND	0.1		95	25 - 164	
Total TCDD	ND	0.1				
$^{37}Cl_4$ TCDD				94	35 - 197	
12378 PeCDF	ND	0.1		92	24 - 185	
23478 PeCDF	ND	0.1		86	21 - 178	
Total PeCDF	ND	0.1				
12378 PeCDD	ND	0.2		90	25 - 181	
Total PeCDD	ND	0.2				
123478 HxCDF	ND	0.3		97	26 - 152	
123678 HxCDF	ND	0.3		104	26 - 123	
234678 HxCDF	ND	0.3		92	28 - 136	
123789 HxCDF	ND	0.5		79	29 - 147	
Total HxCDF	ND	0.5				
123478 HxCDD	ND	0.3		97	32 - 141	
123678 HxCDD	ND	0.3		100	28 - 130	
123789 HxCDD	ND	0.2				
Total HxCDD	ND	0.3				
1234678 HpCDF	ND	0.7		83	28 - 143	
1234789 HpCDF	ND	0.4		68	26 - 138	
Total HpCDF	ND	0.7				
1234678 HpCDD	ND	2		93	23 - 140	
Total HpCDD	ND	3				
OCDF	ND	0.4				
OCDD	ND	7		84	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	0	12.7	pg/g
Total I-TEQ:	0	0.553	pg/g

† = Results are calculated using the average weight of samples in this batch.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: PD
Data Analyst: SD
Authorised: Scott V Leathem

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AgriQuality New Zealand Limited
Huarangi Aotearoa

Gracefield Road
P.O. Box 31 242
Lower Hutt, New Zealand

Phone: +64 4 570 8800
Facsimile: +64 4 569 4500

23 July 2002

Certificate of Analysis

Client:	Pattle Delamore Partners Ltd PO Box 6136 Wellington
Attention:	Richard Lucy
Laboratory Reference:	265
Sample Type:	Soil
Analysis:	**Polychlorinated dibenzo-*p*-dioxins (PCDDs)** **Polychlorinated dibenzofurans (PCDFs)**
Method:	Based on USEPA Method 1613B (Isotope Dilution)

Results are reported in picograms per gram (pg/g), equivalent to ppt, on an as dry weight basis to two significant figures. The DL value is reported to one significant figure. Results have been corrected for recoveries. The sum of PCDDs and PCDFs is calculated and reported to three significant figures both including and excluding DL values.

The total toxic equivalence (I-TEQ) was calculated for the samples using international toxic equivalency factors (I-TEFs). The total I-TEQ level is reported both including and excluding the DL values.

Unless requested, samples will be disposed of three months from the date of this report.

new zealand accredited laboratory

All tests reported herein have been performed in accordance with the laboratory's scope of accreditation

S V Leathem
AgriQuality UltraTrace™
AgriQuality New Zealand

S R Dutt
AgriQuality UltraTrace™
AgriQuality New Zealand

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Results: USEPA Method 1613B

Laboratory Reference: **265/18**

Sample Identification: **SS#37**

Date Received: 10 June 2002
Date Extracted: 19 June 2002

Date Analysed U2: 21 June 2002
Date Analysed SP2331: 19 June 2002

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	3.1			99	24 - 169	
Total TCDF	49					
2378 TCDD	26			90	25 - 164	
Total TCDD	120					
$^{37}Cl_4$ TCDD				93	35 - 197	
12378 PeCDF	1.5			110	24 - 185	
23478 PeCDF	1.8			106	21 - 178	
Total PeCDF	36					
12378 PeCDD	3.8			108	25 - 181	
Total PeCDD	22					
123478 HxCDF	1.4			94	26 - 152	
123678 HxCDF	ND	1		103	26 - 123	
234678 HxCDF	1.6			89	28 - 136	
123789 HxCDF	ND	0.8		80	29 - 147	
Total HxCDF	24					
123478 HxCDD	1.6			93	32 - 141	
123678 HxCDD	2.6			76	28 - 130	
123789 HxCDD	1.7					
Total HxCDD	30					
1234678 HpCDF	13			91	28 - 143	
1234789 HpCDF	0.6			78	26 - 138	
Total HpCDF	23					
1234678 HpCDD	34			88	23 - 140	
Total HpCDD	64					
OCDF	16					
OCDD	230			77	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	614	614	pg/g
Total I-TEQ:	30.8	31.0	pg/g

† = Results are reported on an as dry weight basis.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: SS
Data Analyst: SD
Authorised: Scott V Leathem

Results: USEPA Method 1613B

Laboratory Reference: **265/Blank D**

Sample Identification: **Laboratory Blank**

Date Received: Not applicable

Date Extracted: 19 June 2002

Date Analysed U2: 21 June 2002

Date Analysed SP2331: Not applicable

Analyte	Conc.† (pg/g)	DL	EMPC	^{13}C %RE	LCL-UCL	Qualifiers
2378 TCDF	ND	0.1		99	24 - 169	
Total TCDF	ND	0.1				
2378 TCDD	ND	0.2		95	25 - 164	
Total TCDD	ND	0.2				
$^{37}Cl_4$ TCDD				98	35 - 197	
12378 PeCDF	ND	0.06		121	24 - 185	
23478 PeCDF	ND	0.06		107	21 - 178	
Total PeCDF	ND	0.06				
12378 PeCDD	ND	0.2		112	25 - 181	
Total PeCDD	ND	0.2				
123478 HxCDF	ND	0.1		84	26 - 152	
123678 HxCDF	ND	0.1		105	26 - 123	
234678 HxCDF	ND	0.1		81	28 - 136	
123789 HxCDF	ND	0.2		69	29 - 147	
Total HxCDF	ND	0.2				
123478 HxCDD	ND	0.2		89	32 - 141	
123678 HxCDD	ND	0.2		89	28 - 130	
123789 HxCDD	ND	0.2				
Total HxCDD	ND	0.2				
1234678 HpCDF	ND	0.2		72	28 - 143	
1234789 HpCDF	ND	0.5		52	26 - 138	
Total HpCDF	ND	0.5				
1234678 HpCDD	ND	0.7		87	23 - 140	
Total HpCDD	ND	1				
OCDF	ND	0.3				
OCDD	ND	4		80	17 - 157	

	Minimum	Maximum	Units
Sum of PCDD and PCDF congeners:	0	6.76	pg/g
Total I-TEQ:	0	0.471	pg/g

† = Results are calculated using the average weight of samples in this batch.
⚐ = Recovery outside method guidelines
NQ = Not quantitated

DL: Sample specific estimated detection limit
EMPC: Estimated maximum possible concentration
^{13}C %RE: Labelled compound recovery
LCL-UCL: Lower control limit - upper control limit
$^{37}Cl_4$ TCDD: Clean-up recovery spike

Lab Analyst: SS   Data Analyst: SD   Authorised: Scott V Leathem

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Pace Analytical™
www.pacelabs.com

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
Minneapolis, MN 55414
Phone: 612.607.1700
Fax: 612.607.6444

DETERMINATION OF 2,3,7,8-TCDD LEVELS

Prepared for:
Pattle Delamore Partners Ltd.
Attn: Richard Lucy
PO Box 6136
Wellington
New Zealand

This report contains 18 pages.

The results reported herein conform to the most current NELAC standards, where applicable, unless otherwise narrated in the body of the report.

Project: Chemical Analysis

Client Purchase Order Number: NA

REPORT OF LABORATORY ANALYSIS

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REPORT OF: CHEMICAL ANALYSES

PROJECT: **TCDD ANALYSES**

DATE: August 7, 2002

ISSUED TO:
Pattle Delamore Partners Ltd.
Attn: Mr. Richard Lucy
PO Box 6136
Wellington
New Zealand

REPORT NO: 02-1060110

INTRODUCTION

This report presents the results from the analysis performed on two samples which were submitted by a representative of Pattle Delamore Partners Ltd. The samples were analyzed for the presence or absence of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) using a modified version of USEPA Method 1613 as described below.

SAMPLE IDENTIFICATION

Client ID	Sample Type	Date Received	Pace ID
SS#2 188-3	Solid	07/05/02	103695656
SS#5 188-8	Solid	07/05/02	103695664

METHODOLOGY

Sample Extraction

A portion of each sample was spiked with 2.0 nanograms (ng) of $^{13}C_{12}$-labeled 2,3,7,8-TCDD internal standard and extracted with methylene chloride in a seperatory funnel. Each extract was quantitatively transferred to a Kuderna-Danish flask, concentrated, solvent exchanged to hexane, and processed through the analyte enrichment procedures described below.

Analyte Enrichment

The extraction procedure often removes a variety of compounds, in addition to 2,3,7,8-TCDD from the sample matrix. Some of these compounds, for example polychlorinated biphenyls, can directly interfere with the analyses. Other compounds can overload the capillary column, causing a degradation in chromatographic resolution or sensitivity. The analyte enrichment steps described below were used to remove interfering compounds from the extract.

Analyte Enrichment (Continued)

Each extract was diluted to 100 mL with hexane, spiked with $^{37}Cl_4$-2,3,7,8-TCDD and washed with concentrated sulfuric acid, 1 N sodium hydroxide, and aqueous sodium chloride (5% w/v) as needed. Each extract was then quantitatively transferred to a liquid chromatography column containing alternating layers of silica gel, 40% concentrated sulfuric acid on silica gel, and 33% 1 N sodium hydroxide on silica gel. The column was eluted with 90 mL of hexane and the entire eluate was collected and concentrated, under ambient conditions, to a volume of 1 mL.

Each extract was then fractionated on a liquid chromatography column containing 4 g of activated alumina. The column was eluted with 20 mL of hexane followed by 15 mL of 60% methylene chloride/hexane. The 60% methylene chloride/hexane fraction was concentrated to 1 mL under a stream of dry nitrogen and applied to the top of a chromatography column containing 1 g of 5% AX-21 activated carbon in silica gel. The column was eluted with two 2 mL portions of hexane, 2 mL of cyclohexane/methylene chloride (50:50 v/v) and cyclohexane/methanol/toluene (75:20:5 v/v) in the forward direction, and then with toluene in the reverse direction. The toluene fraction was collected, spiked with recovery standards (1,2,3,4-TCDD-$^{13}C_{12}$) and taken to a final volume of 20 uL.

HRGC/HRMS Analyses

Each sample extract was analyzed for the presence of 2,3,7,8-TCDD using combined capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS). The instrumentation consisted of a Hewlett Packard Model 6890 gas chromatograph interfaced to a Micromass Ultima high-resolution mass spectrometer. The capillary column was interfaced directly into the ion source of the mass spectrometer, thus providing the highest possible sensitivity while minimizing degradation of the chromatographic resolution.

The mass spectrometer was operated in the electron impact ionization mode at a mass resolution of 10,000-11,000 (M/ΔM, 10 percent valley definition). Operating parameters for the HRGC/HRMS analyses are summarized in Table 1. The data were acquired by selected-ion-recording (SIR), monitoring a group of ion masses as described in EPA Method 1613. Two ion masses were monitored for each native and $^{13}C_{12}$-labeled class so that the ratio between the low and high ion masses could be compared to the expected theoretical value (0.77). The actual ion masses monitored are listed below.

HRGC/HRMS Analyses (Continued)

	Native TCDD	$^{13}C_{12}$-labeled TCDD
Ion Masses	319.8965	331.9367
	321.8936	333.9338

A lock mass was used by the data system to automatically correct the mass focus of the instrument. Most modern mass spectrometers are stable on a short term basis (1 - 10 minutes); however, they can drift from the center of the mass peak during the course of a 30 - 60 minute analysis. The data system determined the centroid of the lock mass during each data acquisition cycle and corrected the mass focus of the analyte and internal standard ion masses to assure that the centers of the mass peaks were monitored.

The criteria used to judge positive responses for the 2,3,7,8-TCDD included:

- Simultaneous response at both ion masses
- Signal to noise ratio equal to or greater than 2.5:1.0 for both ion masses
- Chlorine isotope ratio within 15 percent of the theoretical value
- Chromatographic retention times within +/- 2 seconds of the expected retention time

Quantification and Calculations

The 2,3,7,8-TCDD was quantified by comparison of its responses to the responses of the labeled internal standard. Relative response factors were calculated from analyses of standard mixtures containing the natives at five concentration levels, and the internal standards at fixed concentration levels, as shown in Table 2. The response factors were calculated by comparing the sum of the responses from the two ion masses monitored for the native compound to the sum of the responses from the two ion masses of the isotopically labeled internal standard. The formula for the response factor calculation is:

$$Rf = \frac{An \times Qis}{Ais \times Qn}$$

where:

Rf = Response factor
An = Sum of integrated areas for analyte
Qis = Quantity of internal standard
Ais = Sum of integrated areas for internal standard
Qn = Quantity of analyte

The level of 2,3,7,8-TCDD in each sample was quantified using the following equation:

$$C = \frac{An \times Qis}{Ais \times W \times Rf}$$

where:

C = Concentration of 2,3,7,8-TCDD
An = Sum of integrated areas for 2,3,7,8-TCDD
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard
W = Sample amount
Rf = Response factor

Quantification and Calculations (Continued)

The Pace Reporting Limit (PRL), equivalent to the practical quantitation limit, was determined based on the sample aliquot weight that was extracted, the volume of the final extract, and the concentration of the lowest level in the standard curve. A PRL was calculated using the following equation:

$$PRL = \frac{(C \times V)}{W}$$

where:

PRL = Pace Reporting Limit
C = Concentration of Lowest Level Standard
V = Volume of Final Extract
W = Initial Sample Amount

The recoveries of the 2,3,7,8-TCDD-$^{13}C_{12}$, relative to 1,2,3,4-TCDD-$^{13}C_{12}$, were calculated using the following equation:

$$\%R = \frac{Ais \times Qrs \times 100\%}{Rfr \times Ars \times Qis}$$

where:

%R = Percent recovery of the labeled internal standard
Ais = Sum of integrated areas of labeled internal standard
Qrs = Quantity of recovery standard
Ars = Sum of integrated areas of recovery standard
Rfr = Response factor of the labeled internal standard relative to the recovery standard
Qis = Quantity of the labeled internal standard added to the sample

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1700 Elm Street, Suite 200
Minneapolis, MN 55414
Phone: 612.607.1700
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REPORT OF: CHEMICAL ANALYSES

PROJECT: **TCDD ANALYSES** **DATE:** August 7, 2002

REPORT NO: 02-1060110

Quality Control

The performance of the sample processing steps and the instrumentation are monitored on a routine basis. The procedures and criteria are summarized below.

One method blank and one laboratory spike sample are typically prepared with each ten samples of any given matrix. Recoveries of the native analytes in the laboratory spike samples generally range from 70 to 130%. Recoveries of selected analytes outside this range do not invalidate the data but provide information which is used by the laboratory to monitor recovery trends and to assure optimization of the method.

Internal standards are spiked into each sample prior to extraction in order to monitor the level of recovery which is achieved for each individual sample. Acceptable recoveries range from 25 to 150 percent unless a deviation is due to variation in instrument response as a result of analytical interferences.

The resolution of the mass spectrometer is verified prior to each analysis to be 10,000 or greater. Hardcopies of the reference peaks are printed at the beginning and end of each analysis day. The resolving power of the DB-5MS chromatographic column is checked daily by analyzing a standard solution containing 2,3,7,8-TCDD and the adjacent TCDD isomers. Acceptable performance is achieved when 2,3,7,8-TCDD is resolved from the adjacent isomers by a valley of 25% or less.

Initial calibrations are generated by analyzing standard solutions (see Table 2) containing target native and labeled compounds. Response factors are calculated and averaged for each compound. These averages are used for quantification and for comparison to the daily continuing calibration. The relative standard deviation for each native compound must be 20% or less ($\pm$ 30% or less for the labeled compounds) as specified in Method 8290. A continuing calibration standard is analyzed at the beginning of each 12-hour shift on days when initial calibrations are not performed. The initial calibration is considered to be valid when the values obtained from the continuing calibration analyses fall to within the ranges specified in Method 1613.

RESULTS

The results from the 2,3,7,8-TCDD analyses are summarized in the following:

Appendix A - Chain of Custody Documentation
Appendix B - 2,3,7,8-TCDD Analysis Results

DISCUSSION

The isotopically-labeled 2,3,7,8-TCDD internal standard in the extracts were recovered at 70%, indicating a level of efficiency through the extraction and enrichment steps that is considered typical for this matrix. All of the labeled internal standard recoveries obtained for this project were within the target range specified in Method 1613. Since the quantification of the native 2,3,7,8-TCDD is based on isotope dilution, the data are automatically corrected for recovery and accurate values are obtained.

A laboratory method blank was prepared and analyzed with the sample batch as part of our routine quality control procedures. The results, included at the beginning of Appendix B, show that 2,3,7,8-TCDD was not detected at the reported limit of detection. This indicates that the sample processing steps were free of background levels of this isomer.

A laboratory quality control spike sample was also prepared with the sample batch by extracting clean sand that had been fortified with native standard material. The results, included at the end of Appendix B, show that the spiked native 2,3,7,8-TCDD was recovered at 98%. This indicates a high degree of accuracy for these determinations.

REPORT OF: CHEMICAL ANALYSES

PROJECT: **TCDD ANALYSES** **DATE:** August 7, 2002

PAGE: 7 **REPORT NO:** 02-1060110

REMARKS

The sample extracts will be retained for a period of 30 days from the date of this report and then discarded unless other arrangements are made. The raw mass spectral data will be archived on magnetic tape for a period of not less than one year. Questions regarding the data contained in this report may be directed to the authors at the numbers provided below.

Pace Analytical Services, Inc.

Scott C. Unze
Project Manager, Dioxins
(612) 607-6383

TABLE 1. HRGC/HRMS Operating Parameters

Mass Resolution	10,000-11,000 ($M/\Delta M$, 10% valley)
Instrument	VG 70SE
Electron Energy	32 electron volts
Accelerating Voltage	8,000 volts
Source Temperature	275°C
Preamplifier Gain	10^{-6} amp/volt
Electron Multiplier Gain	$\tilde{}10^{5}$
Chromatographic Column	60M DB-5MS
Transfer Line Temperature	260°C
Injection Mode	Splitless
Carrier Gas	Helium
Carrier Flow Velocity	˜30 cm/sec

TABLE 2. High Resolution TCDD Calibration Solutions

		Concentration (pg/uL)		
Solution#	TCT#	2,3,7,8-TCDD	1,2,3,4-TCDD-$^{13}C_{12}$	2,3,7,8-TCDD-$^{13}C_{12}$
1	CS1	0.5	100	100
2	CS2	2.0	100	100
3	CS3	10	100	100
4	CS4	40	100	100
5	CS5	200	100	100

APPENDIX A

Attn: Richard Lacey

1060110

FAXED

REQUEST FOR ANALYSES / CHAIN OF CUSTODY

Project : WJ366
Laboratory : AgriQuality

SHEET 1 of 2

Pattle Delamore Partners Ltd
wellington

REQUEST FOR ANALYSES

Sample I.D.	Date	Lab ID	Container	Sample Type	Analyses Requested	
✓ SS#1	31-5-2002	188-1	280mL Glass	Soil	Hold Cold	2378-TCDD
✓ SS#1G	"	2				
✓ SS#2	30/May	3				103695656
X SS#2-GX	"	Not Received				
✓ SS#2-75mm	"	4				
✓ SS#4 * ~~SS#4-G~~	30/May	5				
✓ SS#4-75mm	"	7				
✓ SS#5	30/May	8				103695664
✓ SS#6	31/May	9				
✓ SS#7	29 May	10				
✓ SS#8	28 May	11				
✓ SS#9	29 May	12				
✓ SS#9-G	"	13				
✓ SS#9-75mm	"	14				
✓ SS#10	30 May	15				
✓ SS#11	31 May	16				
✓ SS#11-75mm	"	17				
✓ SS#12	28 May	18				
✓ SS#12G	"	19				
✓ SS#13	30 May	20				
✓ SS#13-G	"	21				
* SS#4-G	30 May	6				

CHAIN OF CUSTODY

	Signature	Affiliation	Date	Time	Quote Details:
Collected by :		Pattle Delamore Partners Ltd	31-5-2002	6pm	20 Samples will be reported today 19/6 remainer will be reported early next week
Transferred to :		AgriQuality	4-6-2002	8am	
Transferred to :	B	Ruce	7-5-02	10:30	

NOTE: Please acknowledge receipt of these samples by signing this form and faxing it to: Pattle Delamore Partners Ltd, Wellington. Fax number 04 - 472 1958

T=22°C

APPENDIX B

Method 1613B Blank Analysis Results

Client - PATTLE

Lab Sample ID	BLANK-1942	Matrix	SOLID
Filename	F20728A_04	Dilution	NA
Total Amount Extracted	10.2 g	Extracted	07/24/2002
ICAL Date	05/04/2002	Analyzed	07/28/2002 20:17
CCal Filename(s)	F20728A_01	Injected By	BAL

Native Isomers	Conc ng/Kg	EMPC ng/Kg	PRL ng/Kg	Internal Standards	ng's Added	Percent Recovery
2,3,7,8-TCDD	ND	-----	0.98	2,3,7,8-TCDD-13C	2.00	75
				Recovery Standard 1,2,3,4-TCDD-13C	2.00	NA
				Cleanup Standard 2,3,7,8-TCDD-37Cl4	0.20	83

Conc = Concentration
EMPC = Estimated Maximum Possible Concentration
PRL = Pace Analytical Reporting Limit.
I = Interference
P = Recovery outside of method 1613 control limits
ND = Not Detected
NA = Not Applicable
NC = Not Calculated
* = See Discussion

Report No.....02-1060110

REPORT OF LABORATORY ANALYSIS

Method 1613B Analysis Results

Client - PATTLE

Client's Sample ID	SS#2 188-3		
Lab Sample ID	103695656		
Filename	U20729B_08		
Injected By	CVS		
Total Amount Extracted	11.57 g	Matrix	SOLID
% Moisture	11.7	Dilution	NA
Dry Weight Extracted	10.2 g	Collected	05/30/2002
ICAL Date	07/28/2002	Received	07/05/2002
CCal Filename(s)	U20729A_17	Extracted	07/24/2002
Method Blank ID	BLANK-1942	Analyzed	07/30/2002 07:11

Native Isomers	**Conc** ng/Kg	**EMPC** ng/Kg	**LOD** ng/Kg	**Internal Standards**	**ng's Added**	**Percent Recovery**
2,3,7,8-TCDD	3.9	-----	0.14	2,3,7,8-TCDD-13C	2.00	70
				Recovery Standard 1,2,3,4-TCDD-13C	2.00	NA
				Cleanup Standard 2,3,7,8-TCDD-37Cl4	0.20	75

Results reported on a dry weight basis

Conc = Concentration (Totals include 2,3,7,8-substituted isomers).
EMPC = Estimated Maximum Possible Concentration
LOD = Limit of Detection. Totals are averages of individual isomer LODs.
D = Result obtained from analysis of diluted sample
B = Less than 10 times higher than method blank level
P = Recovery outside of method 1613 control limits
J = Concentration detected is below the calibration range
Nn = Value obtained from additional analysis

I = Interference
E = PCDE Interference
ND = Not Detected
NA = Not Applicable
NC = Not Calculated
* = See Discussion

Report No.....02-1060110

REPORT OF LABORATORY ANALYSIS

Method 1613B Analysis Results

Client - PATTLE

Client's Sample ID	SS#5 188-8		
Lab Sample ID	103695664		
Filename	U20729B_09		
Injected By	CVS		
Total Amount Extracted	13.59 g	Matrix	SOLID
% Moisture	26.1	Dilution	NA
Dry Weight Extracted	10.0 g	Collected	05/30/2002
ICAL Date	07/28/2002	Received	07/05/2002
CCal Filename(s)	U20729A_17	Extracted	07/24/2002
Method Blank ID	BLANK-1942	Analyzed	07/30/2002 08:00

Native Isomers	**Conc** ng/Kg	**EMPC** ng/Kg	**LOD** ng/Kg	**Internal Standards**	**ng's Added**	**Percent Recovery**
2,3,7,8-TCDD	94	-----	0.28	2,3,7,8-TCDD-13C	2.00	70
				Recovery Standard 1,2,3,4-TCDD-13C	2.00	NA
				Cleanup Standard 2,3,7,8-TCDD-37Cl4	0.20	87

Results reported on a dry weight basis

Conc = Concentration (Totals include 2,3,7,8-substituted isomers).
EMPC = Estimated Maximum Possible Concentration
LOD = Limit of Detection. Totals are averages of individual isomer LODs.
D = Result obtained from analysis of diluted sample
B = Less than 10 times higher than method blank level
P = Recovery outside of method 1613 control limits
J = Concentration detected is below the calibration range
Nn = Value obtained from additional analysis

I = Interference
E = PCDE Interference
ND = Not Detected
NA = Not Applicable
NC = Not Calculated
* = See Discussion

Report No.....02-1060110

REPORT OF LABORATORY ANALYSIS

Method 1613B Laboratory Control Spike Results

Client - PATTLE

Lab Sample ID	SPIKE-1943		
Filename	F20728A_02	Matrix	SOLID
Total Amount Extracted	10.42 g	Dilution	NA
ICAL Date	05/04/2002	Extracted	07/24/2002
CCal Filename	F20728A_01	Analyzed	07/28/2002 18:09
Method Blank ID	BLANK-1942	Injected By	BAL

Compound	Cs	Cr	Lower Limit	Upper Limit	% Rec.
2,3,7,8-TCDD	10	9.8	7.3	14.6	98
2,3,7,8-TCDD-37Cl4	10	8.5	3.7	15.8	85
2,3,7,8-TCDD-13C	100	65.6	25.0	141.0	66

Cs = Concentration Spiked (ng/mL)
Cr = Concentration Recovered (ng/mL)
Rec. = Recovery (Expressed as Percent)
Control Limit Reference: Method 1613, Table 6a, 10/94 Revision
X = Background subtracted value
P = Recovery outside of control limits
* = See Discussion

Appendix G Abbreviations and Terms

2,3,7,8- and similar	In organic chemistry, positions of atoms or functional groups substituted in place of hydrogen atoms around the base molecule. In the case of dioxin, chlorine atoms on up to eight possible positions around two joined benzene molecules.
2,4-D	2,4-dichlorophenoxyacetic acid – a selective herbicide.
1,2,3,7,8-PeCDD	1,2,3,7,8-pentachlorobdibenzo-p-dioxin
2,3,7,8-TCDD	2,3,7,8-tetrachlorobdibenzo-p-dioxin
2,4,5-T	2,4,5-trichloropheoxyacetic acid – a herbicide for woody plants
AgriQuality	AgriQuality New Zealand Limited
ATSDR	Agency for Toxic Substance and Disease Registry (USA)
DIAG	Dioxin Action Group
dibenzo	Molecule with two hexagonal benzene rings
dioxin	Generic term for PCDDs and PCDFs (see below) but also commonly used for 2,3,7,8-TCDD.
DIN	Dioxin Investigation Network
Dow	Dow AgroSciences (NZ) Limited
ESR	Institute of Environmental Research and Science limited
GC-MS	Gas chromatograph-mass spectrometer – equipment for chemical analysis
heptachloro	seven chlorine atoms
hexachloro	six chlorine atoms
I-TEQ	TEQ calculated using the “International” TEF scheme – see WHO-TEQ
LOD	limit of detection
MfE	Ministry for the Environment
MoH	Ministry of Health
MCPB	4-(4-chloro-2-methylphenoxy) butanoic acid – a selective herbicide
MRL	minimum risk level
ng	nanogram – a billionth of a gram
ng/kg	nanogram/kilogram = parts per trillion (by mass)
nk/L	nanogram/litre = parts per trillion in water

NOAEL	no observable adverse affects level
OCDD	octachlorodibenzo-p-dioxin
OCDF	octachlorodibenzofuran
cctachloro	eight chlorine atoms
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzo-furan
PCP	pentachlorophenol – a wood-treatment fungicide
pentachloro	five chlorine atoms
PDP	Pattle Delamore Partners Limited
PRG	preliminary remediation goal
TDI	Tolerable daily intake
TCDD	tetrachlorinated dibenzo-p-dioxin =2,3,7,8-TCDD
TCP	trichlorophenol – raw material for 2,4,5-T
TEF	toxic equivalency factor (relative to 2,3,7,8-TCDD)
TEQ	toxic equivalent concentration (of 2,3,7,8-TCDD)
tetrachloro	four chlorine atoms
TDHB	Taranaki District Health Board
TRC	Taranaki Regional Council
trichloro	three chlorine atoms
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
WHO-TEQ	TEQs calculated using the WHO TEF scheme