AIR & ENVIRONMENTAL SCIENCES LIMITED

# Multipathway Assessment of Exposures from Dioxin Releases in the Paritutu Area

**Prepared for**
**Institute of Environmental Science and Research Ltd**
**September 2002**

# Multipathway Assessment of Exposures from Dioxin Releases in the Paritutu Area

**Prepared by**
**Air and Environmental Sciences Ltd**
**September 2002**

**Air and Environmental Sciences Limited**
**114 Woodbay Road**
**Tiritangi**
**Auckland**
**New Zealand**
**Phone: +64 9 8172676**
**Fax: +64 9 8172675**

# EXECUTIVE SUMMARY

Exposures to dioxins for people living in the vicinity of the Dow Agrosciences chemical plant in New Plymouth have been assessed using multi-pathway modelling techniques. Dioxin emissions from the operation of the liquid waste incinerator over the 1975-79 period and those from the solid waste incinerator over the 1983-86 period have been modelled. The 2378-TCDD emissions over the 1975-79 period were the highest documented dioxin emissions from the plant, with subsequent incinerator emissions from both the more recent operation of the liquid waste incinerator (1985) and the solid waste incinerator totaling about 1.4% of the estimated emissions for 1975-79. However, it is generally accepted that non-incineration emissions from the plant earlier than 1975 are likely to have been substantially higher because of less stringent process emission control and higher levels 2378-TCDD contamination in the products and waste from 2,4,5-T manufacture.

Multi-pathway modelling combines dispersion modelling of emissions to determine concentrations in air and deposition rates for contaminants with calculations that estimate the rates of transfer of contaminants between environmental media, including air, soil, vegetation, animals and food, and the concentrations of contaminants in those media. Combination of this information with scenarios describing the quantities of the various media that are exposed to the source of contamination being studied that are inhaled or ingested by people allows estimation of the overall levels of exposure resulting from the source. Multi-pathway exposure assessment is particularly important for contaminants, such as dioxins, for which inhalation is commonly only a minor exposure pathway.

**Concentrations in environmental media**

Multi-pathway exposure modelling of the 1975-79 liquid waste incinerator emissions predicts maximum annual average concentrations of 2378-TCDD very much higher than found in air in New Zealand towns and cities by the MfE Organochlorines Programme in 1996-97. However, 2378-TCDD is only a small contributor to total toxic equivalent (TEQ) concentrations in typical urban air, which include contributions from all of the 17 toxic polychlorinated dioxin and furan congeners. Emissions data from the liquid waste incinerator in 1988 showed that 2378-TCDD made up about two-thirds of the total toxic equivalent (TEQ) emissions and the 1975-79 emissions are likely to contain higher proportions of 2378-TCDD than the 1988 emissions. Accordingly, TEQ concentrations calculated for 1975-79 emissions are unlikely to be more than 50% higher than the predicted 2378-TCDD concentrations. This means that the maximum annual average TEQ concentrations calculated for the 1975-79 emissions (about 120 fg TEQ/$m^3$) are slightly higher than the average TEQ concentrations found during the Organochlorines Programme in a number of towns and cities, which are in the range 28-100 fg TEQ/$m^3$. However, the maximum predicted concentration from the 1975-79 emissions is at the top of Mt Moturoa, which is not a residential location. The concentrations predicted for residential locations are in the range 5-50 fg TEQ/$m^3$, no higher than found in towns and cities not subject to any known unusual dioxins sources during the Organochlorines Programme.

This information indicates that unusually high exposures to dioxins compared with people living in typical New Zealand towns and cities are unlikely to have resulted from emissions from the Ivan Watkins Dow liquid waste incinerator over the 1975-1979 period. The multi-pathway modelling confirms this.

The range of predicted increases in 2378-TCDD concentrations in soils and as a result of the 1975-79 incinerator emissions (0.05-0.5 ng TEQ/kg expressed for a 10cm mixing depth) are 1/10 of those found for urban soils in the Organochlorines Programme (0.5-5 ng TEQ/kg).

The concentrations of 2378-TCDD predicted to result from the 1975-79 emissions in eggs from free-range poultry raised in residential areas in the vicinity of the IWD plant are between about 2 and 10 times higher than the TEQ concentration measured in supermarket eggs in the organochlorines programme dietary intake study. However, these higher predicted concentrations in the Paritutu area result from consideration of free-range poultry, compared with commercial egg production, rather than from unusually high levels of contamination from incinerator emissions. The major dioxin source for free-range poultry is ingestion of soil together with their food, and this contamination pathway is generally not present in commercial operations. Similar higher levels of dioxins in eggs compared with typical commercial eggs would be expected from free-range poultry in any urban area. A closely similar situation applies to poultry meat.

The concentrations of 2378-TCDD predicted to result from the 1975-79 emissions in fruit and vegetables are low. The Organochlorines Programme did not examine dioxin levels in these foods.

**Incremental exposures for residents near the IWD plant.**

Two exposure scenarios for residents have been assessed:

- Scenario 1 - 100% of inhalation and soil ingestion exposed to emissions and 10% of typical consumption of fruit and vegetables exposed to emissions;
- Scenario 2 - as for Scenario 1, plus 10% of typical consumption of eggs and poultry meat from free-range poultry exposed to emissions.

The estimated incremental exposures are compared with:

- ALDE - average lifetime daily exposure: the measure of exposure estimated from serum TCDD/F concentrations that reflect historic and current exposures from all routes.
- Dietary intakes - the daily intake of dioxins in food, estimated from quantities of food consumed and dioxin concentrations in the food.

The Ministry for the Environment has published studies that estimate a typical population ALDE of 1.4 pg TEQ/kg-bw/day and a typical population dietary intake of 0.18 pg TEQ/kg-bw/day.

Scenario 1 incremental 2378-TCDD exposures resulting from the 1975-79 incinerator emissions are 0.4% and 0.8% of the ALDE at the maximum residential locations south and west respectively of the IWD plant, and 2.7% and 6.2% of the typical general population dietary intakes. Scenario 2 incremental exposures are 0.7 and 1.4% of the ALDE, and 5.6% and 11% of the typical general population dietary intake at the same locations.

These estimates indicate that the 1975-79 incinerator emissions are likely to have made only minor contributions to dioxin exposures for residents in the area, with most exposure resulting from the same pathways and sources as those for the general population (e.g. dairy

foods and meat). Increasing the 2378-TCDD incremental exposure estimates by 50% to take account of the possible presence of other toxic polychlorinated dioxin and furan congeners in the incinerator emissions does not change this conclusion.

**Contributions via exposure pathways**

Inhalation is the pathway making the largest contribution (60-65%) to incremental exposures for Scenario 1 and Scenario 2 (29-37%). Consumption of exposed above-ground garden produce (eg leafy vegetables) contributed 28-29% for Scenario 1 and 15-16% for Scenario 2. Soil ingestion contributed about 8% for Scenario 1 and 4% for Scenario 2, with contributions from protected above-ground produce (e.g. sweetcorn) and below ground produce less than 0.2% for both scenarios. For Scenario 2, consumption of eggs and poultry meat each contributed 22-26% of the total incremental intake.

**Residual exposures after emissions stop.**

When the 1975-79 emissions stopped, the inhalation pathway would no longer apply, and the exposed above ground produce would become similar to the protected above ground produce pathway. The soil ingestion and egg and poultry meat consumption pathways would continue to apply, since these are determined predominantly by the concentrations that have accumulated and will persist in soils.

The overall result is that exposures for Scenario 1 would drop to about 7% of those estimated during the period of emissions and exposures for Scenario 2 would be about half of those while emissions continued.

**Modelling of 1983-86 emissions from the solid waste incinerator.**

Modelling of the 2378-TCDD emissions from the solid waste incinerator during its operation over the 1983-86 period predicted incremental exposures about 175 times smaller than those predicted from the 1975-79 emissions from the liquid waste incinerator. This is as expected on the basis of the much lower dioxin emissions from the solid waste incinerator.

**Measured concentrations of dioxins in soils.**

2378-TCDD concentrations have been determined in a number of soil samples from a range of locations mostly within the IWD plant site and nearby non-residential areas, collected since 1985. Most of these samples show considerably higher concentrations than predicted from the multi-pathway modelling of the 1975-79 emissions from the liquid waste incinerator. Of the two samples of soils from residential locations, one contained no 2378-TCDD above the analysis detection limit and the other was a composite sample that may not give a reliable indication of typical residential soil concentrations.

**Dioxin exposures resulting from the measured concentrations of dioxins in soil.**

At the higher soil concentrations measured (not in residential areas) very high levels of dioxin exposure could result from Scenario 2, ranging up to over 4 times the ALDE. Clearly, raising free-range poultry in these contaminated areas is undesirable.

At the residential locations, the estimated exposures are small percentages (0.1-2%) of the ALDE and small to moderate percentages (1-17%) of the typical dietary intake. For Scenario 2, the estimated daily intakes are considerably higher, corresponding to 3-50% of the ALDE and 22-389% of the typical dietary intake. Because the scenarios assessed here consider that only 10% of resident's total consumption of the food items considered is exposed to the measured soil dioxin concentrations, daily exposures could be much higher if people did obtain a high proportion of a normal intake of, for example eggs from free-range poultry raised at the locations considered. Even at only 10% of total typical consumption of eggs and poultry meat, soil concentrations as measured in the composite sample could result in as much as a 4-5 fold increase compared with typical in general population dioxin exposures. Clearly, it is undesirable to raise free-range poultry for consumption on dioxin-contaminated soils.

**Source contributions to dioxin concentrations in soils**

In addition to the estimates of the contribution to 2378-TCDD concentrations in the soil available from the multi-pathway modelling, the probable contribution to these concentrations of resulting from a release of trichlorophenol and 2378-TCDD from a bursting disc incident in 1986 has also been assessed by considering the likely evaporation rates of these compounds, combined with transfer from air to soil via an air-grass-soil pathway.

Neither the emissions that have been estimated to have occurred since 1975 from both incinerators, nor the bursting disc release in 1986 can account for the concentrations of 2378-TCDD measured in soils in the vicinity of the IWD plant. The 2378-TCDD emissions that the air-grass-soil pathway modelling suggests would be needed to account for the approximately 30 ng/kg concentration measured in soil at the top of Mt Moturoa are about 150 times the maximum estimates of emissions from both incinerators since 1975 and the bursting disc release in 1986.

Accordingly, it appears necessary to invoke very high 2378-TCDD emissions during the earlier operations of the plant. It is widely accepted that the processes were not well controlled from an emissions perspective and the levels of 2378-TCDD contamination in 2,4,5-T produced at the plant are generally considered to have been very much higher during the early period of production. Accordingly, it appears credible that the very large 2378-TCDD emissions that are evidently required to account for soil concentrations measured may in fact have occurred.

**CONTENTS**

## INDEX OF TABLES

INDEX OF FIGURES

# 1. INTRODUCTION

The potential exposure of residents to polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) released from industrial sources at the Ivon Waktins Dow (IWD) chemical plant (currently owned by Dow AgroSciences (N.Z.) Ltd), at Paritutu, New Plymouth during the 1970's to 1980's is an ongoing source of concern for the local community. This document outlines the methodology and preliminary results used to assess the potential total dioxin (and furan) exposures and intakes of residents living near the chemical plant.

The assessment primarily focuses upon the potential dioxin intakes related to contaminants emitted from the company's operation of a liquid waste incinerator between 1975 and 1988; and a solid waste incinerator, that has operated on a non-continuous basis from 1983 until present. The only other documented release of dioxins at the site occurred from a bursting disc failure at the TCP Plant on the 15$^{th}$ April 1985. This incident has also been considered with regard to potential residential intakes of contaminated environmental media. Although other dioxin emission may have occurred at the site at other times, the current evaluation is limited by availability of data from which estimates of dioxin emission rates can be made.

The assessment uses a combination of atmospheric dispersion modelling and multi-pathway exposure techniques to estimate the likely intakes from the known emission sources. These estimations are then compared against dioxin concentrations that have been measured in various environmental media (predominantly soils) sampled in the area.

## 1.1 OVERVIEW

Dioxins are highly toxic and stable pollutants. As they do not rapidly break down they can persist in the environment for many years and gradually accumulate in different media including soils, plants and animals. In New Zealand, typically 90% of the populations dioxin intakes is estimated to occur through diet, particularly the consumption of food stuffs that contain animal fats (e.g. poultry, dairy, and meats) (MfE, 2002). When assessing the potential dioxin exposures of residents who live near the Ivan Waktins Dow chemical plant it is necessary to consider the possible intakes routes of dioxin from different environmental media that may have become contaminated by emissions from the plant. The approach taken in this evaluation is consistent with the United States Environmental Protection Agency (US EPA) "Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities" (referred to as the HHRAP) (USEPA, 1998).

The methodology initially uses an atmospheric air pollutant dispersion model to estimate the average annual ambient air dioxin concentrations and wet and dry deposition rates for dioxins associated with historical and incidental emission sources located at the Paritutu plant. In the assessment the USEPA air pollutant model ISC3-Prime has been utilised to calculate concentrations in air and rates of wet (rain) and dry deposition. Emission rates and source parameters incorporated into the model have been derived from historic records and source monitoring data.

From the predicted ambient air concentrations and deposition rates the multi-pathway risk assessment protocol calculates the concentrations of dioxins in different environmental media.

In this instance air, soil, and homegrown produce are likely to be the predominant media of concern.

However, because it is also feasible that a small number of households in the affected area may have also kept poultry for eggs or even meat these pathways have also been considered in the analysis. The HHRAP uses a number of parameters, (which are provided in the US EPA protocol), that are specific to each dioxin congener, and which describe the behavior and transfer of the congener from air concentration and deposition rates to the land, and directly or indirectly, into each of the various other media.

Once the concentrations in the various media have been estimated, information about people's typical intakes (exposures) for each of the media (or food types) is used to calculate the exposures or intakes for each of the contaminants. Overall dioxin intake rates are calculated by the summation of estimated dioxin intakes for each potential exposure pathway. An overview of the methodology is presented in the Figure 1.

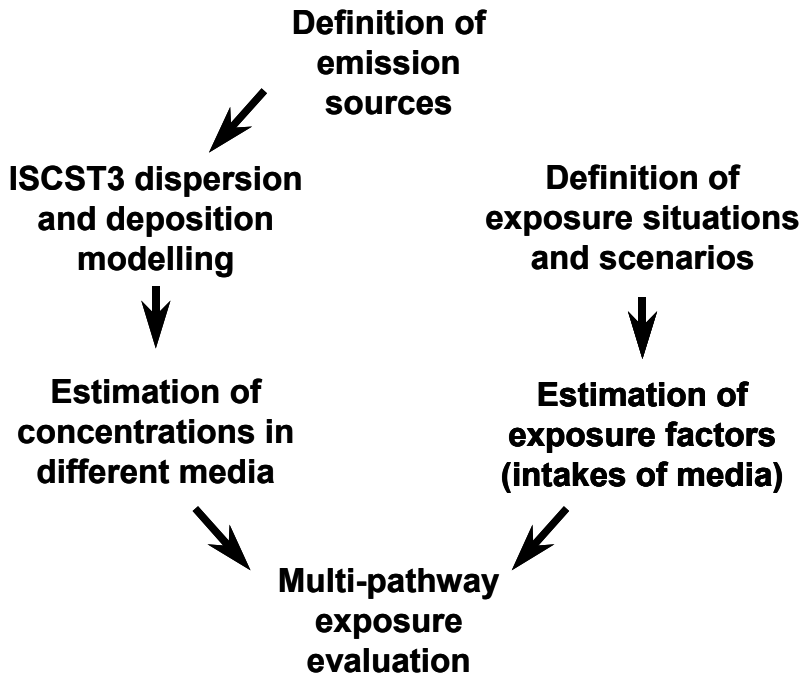


**Figure 1. Overview of the multi-pathway assessment methodology**

A similar approach has been used by Air and Environmental Sciences Ltd working with the Ministry for the Environment when investigating options for establishing National Environmental Standards for dioxin industrial point sources.

Potential dioxin intake rates have also been evaluated using measured soil concentrations of the dioxin congener 2378-TCDD in samples taken at and around the plant between 1985 and 1998 and then using the HHRAP methodology to estimate other environmental media concentrations, and subsequently average daily intake rates. Most soil samples were taken immediately, and one year after the April 1986 TCP plant bursting disc failure incident. A summary of the sampling regimes and predicted spatial distribution of soil concentrations are presented in Section 4.

## 1.2 DIOXIN TOXICITY

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively known as dioxins, are aromatic compounds that have up to eight chlorine atoms attached to their aromatic rings. Of the possible 75 PCDD and 135 PCDF congeners, only 17 congeners, having 4 to 8 chlorine atoms, are thought to pose a significant human health and environmental risk. The toxicities of the 17 congeners vary widely and since dioxins generally occur in complex mixtures, a weighting system of toxic equivalents (TEQs) is used to assess the relative toxicity of such mixtures. The total TEQ of a mixture is calculated from the summation of the mass of each congener in a sample multiplied by a toxicity equivalent factor (TEF). A separate TEF is assigned to each of the 17 congeners based upon its relative toxicity in comparison to the congener 2378-TCDD, which is assigned a TEF of 1 (Buckland, Ellis and Salter, 1998).

The most recent and now widely used toxicity equivalent factors are those determined by the World Health Organisation (WHO, 1998), as set out in Table 1.

**Table 1. WHO (1998) Toxic Equivalent Factors (TEFs)**

| Congener | I-TEF |
|---|---|
| 2378 TCDD | 1 |
| 12378 PeCDD | 1 |
| 123478 HxCDD | 0.1 |
| 123678 HxCDD | 0.1 |
| 123789 HxCDD | 0.1 |
| 1234678 HpCDD | 0.01 |
| OCDD | 0.0001 |
| 2378 TCDF | 0.1 |
| 12378 PeCDF | 0.05 |
| 23478 PeCDF | 0.5 |
| 123478 HxCDF | 0.1 |
| 123678 HxCDF | 0.1 |
| 234678 HxCDF | 0.1 |
| 123789 HxCDF | 0.1 |
| 1234578 HpCDF | 0.01 |
| 1234789 HpCDF | 0.01 |
| OCDF | 0.0001 |

For the current assessment the focus of the analysis has been upon 2378-TCDD congener. The reason for this approach is primarily because 2378-TCDD was a known contaminant produced during the TCP process at the Ivon Waktins-Dow plant. This congener was therefore continuously monitored in the waste incinerators flue gas emissions and during soil sampling and wipe tests conducted at the site. There appears to be very little historical documentation of the distribution of other congeners emitted from the plant.

However, since 2378-TCDD has the highest TEF and is the dioxin congener emitted in the greatest quantity from operations at the site, the focus upon this contaminant in the analysis provides a good estimate of the overall potential health risks associated with all emitted dioxins from the plant.

# 2. METHODOLOGY

## 2.1 SOURCES CONSIDERED

The two most documented emission sources of dioxins at the Ivon Watkins-Dow plant are the solid and liquid waste incinerators and these have been considered in depth and modelled in the work covered by this report. Emission rates and characteristics of dioxin from these incinerators used in the models are based upon the analysis of the emission testing conducted throughout their operation.

Dioxin releases from the TCP Plant bursting disc failure in April 1986 have also been reviewed.

The primary source of information has been the Pilgrim (1986) evidence to the committee of enquiry into possible health effects of manufacture of agricultural chemicals in New Plymouth, and the DSIR investigation of the 1986 TCP plant bursting disc failure (Nicol and Smith, 1986). In addition, during the preparation of this report, Dow AgroSciences (N.Z.) Ltd was also approached through ESR, but could provide little additional information.

### *2.1.1 Liquid waste incinerator*

The IWD liquid waste incinerator began the routine destruction of TCDD-containing liquid wastes on 26 November 1975. The incinerator was used to destroy TCDD-containing liquids and solids dissolved in xylene produced during the production of sodium tricholorphenate. The initial period of operation lasted until 20 April 1979. During this period 566,080 litres (approximately 538,342 kg) of TCDD-containing wastes with an estimated average TCDD concentration of 10.6ppm (ranging between 0.57 to 27.2ppm) were incinerated. The incinerator operated for approximately 17200 hours, and flue gas emissions were monitored for 17119 hours by the company. Occasional auditing checks were also made by the Department of Health (Pilgrim, 1986).

Pilgrim (1986) estimated that approximately 1.57g of TCDD were emitted into the atmosphere during the initial period of operation, based upon the average TCDD concentration in the flue gas measured by the company (20.5ng/$m^3$), multiplied by the design volumetric flue gas emission rate (9153 $m^3$/hr) and the hours of operation. The incinerator was estimated to have an overall TCDD destruction efficiency of 99.97%.

However, it should be noted that during this period the TCDD detection limit was approximately 10ng/$m^3$ (at ambient temperature). Approximately 73% of the hours sampled recorded concentrations were below this detection limit. When evaluating the possible emission of TCDD to air Pilgrim (1986) conservatively assumed that during these periods the incinerator was emitting at the detection limit. It is common practice, however, to assume that "non-detect" samples are equal to half the detection limit, which in this instance would have been 5ng/$m^3$.

Similarly the design flue emission rate used in analysis is probably higher than what would normally be expected. Pilgrim (1986) estimates normal operation between 4000 to 6800 $m^3$/hr for approximately 43% to 74% of flue gas emission rates used in the calculations.
Consequently actual emissions could have been considerably lower than those estimated. For instance, if it is assumed that 'non detects' were equal to 5ng/$m^3$ the estimated average TCDD

concentration in the flue gas during the operating period would be approximately 16.8ng/$m^3$. If it was also assumed that the typical volumetric flue gas emission rate was 6800 $m^3$/hr then an estimated 0.96g of TCDD would be emitted during this three and a half year period, about 60% of Pilgrim's conservative maximum estimate.

Pilgrim (1986) also notes that the use of gas chromatography with electron capture to measure TCDD concentrations at IWD during this period is not TCDD-specific and may give higher levels than those actually present, as a result of contamination present in solvents.

The liquid incinerator was later refitted and operated from 25 April to 26 August 1985. During this period approximately 57,500 litres of liquid was destroyed. The incinerator was operated for 2035 hours and continuously monitored by either the company or the Department of Health. From the monitoring data Pilgrim (1986) estimates an average TCDD destruction efficiency of 99.976% and an average flue gas concentration of 4.3ng/$m^3$. Assuming a typical volumetric flow rate 4500 $m^3$/hr (at 388°C), approximately 17mg of TCDD was emitted during this period.

Sample analyses were done by both the company using gas chromatography with electron capture (GCEC) and the DSIR on behalf of the Department of Health using gas chromatography mass spectrometry (GCMS). Pilgrim (1996) states a detection limit as 1ng/$m^3$ but it is difficult to determine from the text if this assumption was for both the GCEC and GCMS methods. Either way the results indicate that total TCDD emissions during this period were considerably less than what was released 1975-79.

A third period of operation started on the 11$^{th}$ May 1988 but not on a continuous basis. From the available documentation it is difficult to determine how long the incinerator operated during this period. Pilgrim *et al*. (undated) states that Department of Health monitored the flue gas emissions for 132 hours between May and June 1988 and for 50 hours in September 1988. The 2378-TCDD concentrations in the emissions averaged 0.43ng/$m^3$ during the May to June testing period and 1.42ng/$m^3$ in the September tests (concentrations at ambient temperature).

The Pilgrim *et al.* summary indicates that during the 1988 sampling periods, all PCDD/PCDF congeners were measured. Average total dioxin/furan emission concentrations were estimated to be 0.75ng TEQ/$m^3$ and 2.15ng TEQ/$m^3$ in the first and second sampling periods respectively. Accordingly, 2378-TCDD evidently made up about two thirds of the total TEQ emissions.

Since the actual period of operation during 1988 is unknown it is difficult to estimate the total quantity of 2378-TCDD that was likely to have been released during this phase of the incinerator's operation. However, a comparison of 2378-TCDD flue gas concentrations during this period (0.73-1.42 ng/$m^3$) with average concentrations estimated for the 1986 and 1975-79 periods (4.3ng/$m^3$ and 20.5ng/$m^3$ respectively) indicates that total 2378-TCDD emissions are likely to have been considerably less than in past emissions, even if it is assumed the incinerator was in constant use between May and September. Therefore, residential exposure from emissions during 1988 is likely to be comparatively minor compared to those during 1975-79 phase of operation.

### *2.1.2 Solid waste Incinerator*

The Sunbeam-Comtro Model A35 solid waste incinerator installed at the IWD was specifically designed for the incineration of chemical wastes. The incinerator was initially operated between 13th July 1983 and 14th March 1986. During this period of operation, flue emissions were regularly monitored by either the company or the Department of Health. The mean TCDD flue concentration was estimated to be 2.51 ng/m3 (at ambient temperature) with a range between <1ng/$m^3$ to 8ng/$m^3$. The incinerator was operated for 1887 hours with an estimated volumetric flue gas flux of 7800$m^3$/hr at 1000°C releasing approximately 8.24mg of TCDD into the environment during the total period of use (Pilgrim, 1986).

The incinerator has also been in periodic use since March 1986 however, the historical documentation detailing the usage and performance of the incinerator during this period appears to be relatively sparse. Pilgrim *et al* (undated) identified two trials in December 1988 when dioxin concentrations in the flue gas were monitored by the Department of Health. In the first trial 63.6kg of 245-T butyl ester with a chorine content of about 34%, but containing negligible amounts of 2378-TCDD was incinerated. Flue gas concentrations of 0.056ng/$m^3$ of 2378-TCDD and 0.55 ng TEQ/$m^3$ of total PCDD/PCDF were recorded. In the second trial 39.75kg of T-Butyl ester containing a 2378-TCDD content of 3 mg/kg was incinerated. Flue gas concentration of 0.013ng/$m^3$ of 2378-TCDD and 0.21 ng-TEQ/$m^3$ of total PCDD/PCDF were recorded. Although the results were preliminary the author suggested that the quantities of 2378-TCDD present in the waste feed stock (when concentrations are relative small) make little difference to the actual quantities of 2378-TCDD emitted when incinerating highly chlorinated organics. In other words most of the PCDD/PCDF emitted from the stack are likely to have formed during the incineration process rather than have initially been present in the waste but have not been destroyed during combustion.

In 1994 the solid waste incinerator was upgraded to including the expansion of the secondary combustion chamber, which increased the residence time from one to three seconds. In 1999 the waste streams to the incinerator also changed following the closure of the Phenoxy plant in 1998 and the associated reduction in chlorinated herbicide waste (pers. com., Dow AgroSciences Ltd, 2002).

In 2001, Watercare Services Ltd measured total and individual PCDD/PCDF congener concentrations in the flue gas when the waste feedstock was composed of either crushed drums, liquid waste, or 'general waste' (Mills, 2001). With the exception of a single 'Non 2378 TCDF' sample take during the incineration of liquid wastes all congener concentrations were below detection limits. If, following usual dioxin reporting protocols, 'non-detects' congener concentrations are assumed to be equal to half the analytical detection limits, total PCDD/PCDF flue gas concentrations would be approximately 0.0052ng-TEQ/$m^3$ (corrected to 11% $O_2$). These results indicate the very small quantity of dioxins that are currently emitted from the incinerator, relative to previous measurements, likely the result of both the 1994 refit and the reduction in highly chlorinated waste feedstock.

### *2.1.3 TCP Plant Bursting Disc Failure*

At approximately 3:10am on the 15th April 1986 a bursting disc on a reactor ruptured such that an uncontrolled amount of material was released into the environment. The reactor was being used for the manufacture of sodium 2,4,5 trichlorophyenate (Na TCP) from tetrachlorobenzene (TCB). The vapour released potentially contained significant quantities of

2378-TCDD, which is a by-product of the TCP process. The incident report indicates that the vapour released exited through an open door and dispersing in a northwesterly direction (Nicol and Smith, 1986).

Nicol and Smith (1986) estimated that approximately 1415 kg of material was released during the incident. Although the proportion of the material, released either as flashed vapour or entrained liquid, was unknown. Due to the physical properties of 2378-TCDD the quantity of entrained liquid released during the incident is assumed to be proportional to the quantity of 2378-TCDD emitted. Nicol and Smith's estimate of the total 2378-TCDD released range between a minium of 70mg and a maximum of 735mg.

Since the vapour released from the incident dispersed in a northwesterly direction it is unlikely that nearby residents will have been exposed to significant concentrations of TCDD during the initial phase of the release. A potential risk to the community would occur if the pollutants deposited to the ground were re-volatilised. The expected emission rates and consequent soil concentrations has been estimated in the results section.

### *2.1.4 Other emission sources*

Although it is acknowledged that dioxins may have been released by other sources located at the Ivon Watkins Dow plant, including fugitive or accidental releases and particularly during the earlier stages of operation, it is currently difficult, to characterise these emissions with the available documentation of plant activities. However, an appreciation of the contribution of other sources to levels of contamination, including non-airborne sources, can be obtained by considering the 2378-TCDD concentrations measured in the soils surrounding the plant, compared with maximum concentrations calculated by the multi-pathway health risk assessment process.

### *2.1.5 Overview of emission sources*

A summary of the estimated (apparent 2378 or measured 2378) TCDD emission rates are presented in Table 2. The results clearly indicate the relatively high quantity of TCDD emitted from the liquid incinerator between 1975 and 1979. Other sources (and other time periods of the liquid incinerators operation) for which information is available appear to make only a small contribution to the total quantity of TCDD estimated to be released.

Only the maximum emissions from the TCP Plant bursting disc incident approach the magnitude of TCDD emissions from the liquid waste incinerator. However, because the wind direction of the time of the bursting disc incident was south-easterly, the plume was carried in a north-westerly direction away from residential areas and this is likely to have minimised residential exposures.

**Table 2. Estimated quantities of 2378-TCDD emitted from sources at the Ivon Watkins-Dow Plant**

| Liquid Waste Incinerator | | Solid Waste Incinerator | | TCP Plant Bursting Disc | |
|---|---|---|---|---|---|
| 1975-79: | 1,570mg | 1983-86: | 8.24mg | 1986: | 70-735mg |
| 1985: | 17mg | 1986+: | unknown | | |
| 1988: | unknown | | | | |

Therefore, the focus of the multi-pathway exposure assessment has been upon modelling the dispersion and intakes of contaminants released from the liquid waste incinerator during the 1975-79 period of operation. Although the other emission sources will increase the total level of contamination in the area, they will not significantly increase the predicted overall dioxin intake level. A brief comparison of the magnitude of intakes associated with different sources and operating periods is presented in the results.

## 2.2 DISPERSION MODELLING DETAILS

Air dispersion models are mathematical constructs designed to simulate the physical processes occurring in the atmosphere that directly influence the dispersion (and deposition) of gaseous and particulate pollutants emitted from industrial stacks. The models require data inputs that define the characteristics of the emission source (such as gas discharge temperature, stack height, emission rate), meteorological data that represent the atmospheric dispersive conditions, and relevant terrain and building parameters.

In this instance the Gaussian atmospheric dispersion model ISC3-Prime was used to estimate average annual dioxin ambient air concentrations and wet and dry deposition fluxes. ISC3-Prime is a United States Environmental Protection Agency (USEPA) dispersion model that uses the same dispersion modelling parameters as the USEPA regulatory Industrial Source Complex Short-Term model (ISCST3) but incorporates algorithms that provide a more accurate assessment of pollutant ground level concentrations near emission sources that are affected by building structures. The model is generally considered to be conservative, tending to over-predict pollutant concentrations rather than underestimate them.

In this assessment only emissions from the liquid and solid waste incinerators have been modelled using ISC3-Prime, and then used in calculating possible intakes using the HHRAP.

### *2.2.1 Emission characteristics used in the dispersion model*

Source characteristics associated with the liquid and solid waste incinerators were derived from the historical documentation of incinerator operational parameters including recent source emission tests conducted for the solid waste incinerator. Compiled source characteristics representative of typical operating conditions were submitted to Dow AgroSciences (N.Z.) (current operators of the Paritutu plant) for comment and confirmation. A summary of the source parameters used in the dispersion model are presented in Table 3.

**Table 3. Emission Source parameters**

| Source Parameters | Liquid waste incinerator | Solid waste incinerator |
|---|---|---|
| Stack Height (m) | 15.1 | 9.5 |
| Stack Diameter (m) | 0.39 | 0.607 |
| Exit gas velocity (m/s) | 8.4 | 6.8 |
| Exit gas temperature ($^{o}$C) | 350* | 1000** |
| Heat release (kW) | ≈303 | ≈1111 |

* The combustion chamber operates at > 1000 °C, with quench air cooling the discharge, the flue gas drops to approximately 350°C.
**The solid waste incinerator was upgraded in 1994. The Upgrade expanded the secondary combustion chamber to increase the residence time to 3 seconds. The stack flue exit temperature post 1994 is expected to be greater than 1100°C.

For both the liquid and waste incinerator particle size distributions have been assumed to be comparable to an uncontrolled incinerator. In the ISC3-Prime model particulate size distributions influence the wet and dry deposition rates and use of a particle size distribution for an uncontrolled incinerator (i.e. with no particulate control device such as an electrostatic precipitator or bag filters) results in higher predicted deposition rates and higher concentrations in environmental media.

### *2.2.2 Meteorological data*

Accurate atmospheric pollutant dispersion modelling requires good meteorological information that is representative of dispersion conditions near an emission source and is processed into a format that can be used by the dispersion model. Since no onsite meteorological data was available, a synthetic meteorological data input file was developed using The Air Pollution Model (TAPM v2.0) developed by CSIRO. TAPM is a sophisticated model that predicts the three dimensional meteorology and air pollutant concentrations by solving the fundamental fluid dynamic and scalar transport equations. It consists of coupled diagnostic meteorological and air pollution components that predict the air flows important to local scale air pollution, such as sea breezes, against a background of larger scale synoptic meteorological patterns (Hurley, 1999).

One of the primary functions of the TAPM model's design is the provision of high quality meteorological data for dispersion models where suitable onsite information is not available. Validation studies show that TAPM can accurately predict localised meteorological conditions. In this instance TAPM was used to generate a one-year meteorological data set suitable for use with ISC3-Prime for the Parituru situation. TAPM incorporates a prognostic meteorological component that solves the fundamental fluid dynamic and scalar transport equations. Using historical synoptic scale meteorological analyses in conjunction with local land use and terrain information, TAPM can produce realistic and high quality meteorological inputs for a number of air pollutant dispersion modelling systems, including ISC3-Prime, that are virtually site specific.

In this analysis TAPM was configured using a 30x30x25 km grid with nested grid spacing of 10, 3 and 1 km spacings. Surface vegetation effects, non-hydrostatic pressure, and prognostic eddy dissipation options were selected in the simulation. A meteorological data file for 1999 was generated from the 1km spaced nested grid corresponding to the approximate locations of the Paritutu plant. The monthly deep soil moisture content parameters used by for the model were estimated from local precipitation and evaporation rates measured at New Plymouth Airport.

### *2.2.3 Terrain data*

Topography can have a significant influence on the dispersion and deposition rates of pollutants. Generally higher pollutant concentrations occur on elevated terrain features relative to flat areas, as source emissions tend to impinge on raised areas before the plume has time to more fully disperse in the environment. Because a number of significant terrain features are located in the immediate vicinity of the Ivon Watkins Dow incinerators these features have been incorporated into the ISC3-Prime models. A Cartesian grid network with receptor points spaced every 50m for areas within 1100m of the emission sources and every 100m intervals for areas betweens 1100 and 3000m from sources has been used. The Institute

of Environmental Science and Research Ltd provided terrain heights for each receptor point, from their GIS topological database.

A representation of the topography in the immediate area is presented in Figure 2. The most significant terrain features include Mt Motoroa, which rises to an estimated 81m above sea level, and is located approximately 350m to the east of the liquid waste incinerator and a small hill 450m to the north-west of the incinerator with a summit approximately 154m above sea level.

**Figure 2. Topological map of the immediate area surrounding the Ivon Waktins Dow plant (ESR, 2002)**


### *2.2.4 Building wake effects*

Buildings near emission sources can influence the rate at which air pollutants are dispersed into the environment. Depending on the dimensions and location of buildings relative to the release height of the emissions, the net effect of nearby obstacles can be to either increase (in most instances) or decrease ground level concentrations. Because both incinerators have relatively low stack heights, building effects could likely have influence dispersion rates of dioxin emitted from the two sources. However, over the years a number of buildings have been removed, added or modified and Dow AgroSciences (N.Z.) Ltd were unable to provide historical information from which these effects could be accurately incorporated into the model.

However, although ground level concentration deposition rates are expect to be much higher if building wakes were incorporated into the model assumptions, these effects would be localised in the immediate vicinity of the emission sources. It is not expected that estimates of community exposure would be greatly affected. Future refinement to the modelling may incorporate these influences.

## 2.3 MULTI-PATHWAY CALCULATIONS

Dioxin properties and environmental media concentration calculation procedures used in the multi-pathway assessment have followed the USEPA Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities (1998). The only exception has been to use a soil half-life of 25-years as recommended by USEPA (2000).

In the assessment the possible intake routes considered to be feasible through which local resident may have come exposed to dioxins released from the IWD plant include:

- Inhalation of particulate and gas phase PCDD/PCDF
- Ingestion of contaminated soil
- Ingestion of below-ground vegetables (e.g. potatoes, carrots)
- Ingestion of 'protected' above-ground vegetables and fruits (e.g. sweet corn, oranges, nuts)
- Ingestion of 'exposed' above ground vegetables and fruits (e.g. lettuce, apples)

Produce is defined as either 'protected' or 'exposed' depending upon whether the edible proportion of the fruit or vegetable is likely to have been exposed directly to dioxin congeners emitted from the emission sources either through direct deposition or vapour uptake by the plant's foliage. For instance fruits such as oranges whose skins are not generally consumed are classified as 'protected'. The major route of contamination for 'protected' and below ground produce is via root uptake of contaminants present in the soil.

As it possible that some residents could have kept poultry for eggs or (less likely) meat, the additional intakes of dioxins associated with these pathways have also been considered in the assessment.

As recommended by the HHRAP, when calculating soil concentrations, a soil mixing depth of 1 cm was used, except for cultivated garden soils for which the mixing depth was set to 20 cm.

Since dioxins can persist in the environment for many years, even when contaminants are not being emitted from sources located at the IWD plant, there will still be intakes of dioxins associated with the media contaminated by past emissions. However, during these periods, intakes from the inhalation exposure pathway will be zero, and the contamination of 'exposed' produce via direct particulate deposition and gaseous uptake mechanisms will also be zero (although there will be still some contamination via root uptake from the soil as with 'protected' produce).

## 2.4 DIETARY INTAKE SCENARIOS

Average daily dioxin intakes have been estimated for each receptor point included in the dispersion model. Intakes are presented in terms of the quantity (picograms) of toxic equivalents (TEQ) of 2378-TCDD per day per kg body weight (i.e. pg TEQ/kg bw/day kg). Based upon assessment of dietary intakes and blood serum levels, the Ministry for the Environment has estimated the average lifetime daily exposures (ALDE) to dioxins and dioxin-like PCBs, for the general New Zealand male population at between 0.37 and 1.4 pg TEQ/kg bw/day (Ministry for the Environment, 2001).

Total dioxin intakes are dependent upon the typical dietary consumption and inhalation rates of the resident (represented by the model receptor point), the concentration of the contaminants in the media calculated at the receptor point, and the mean body weight of the resident. Consequently, different dietary consumption rates will influence total exposure of the residents to dioxin contamination. In the multi-pathway exposure calculations the average dietary intakes and body weights have been based upon a typical 80kg adult New Zealand male.

The MfE Organochlorines Programme assessment of dietary intakes for dioxins and dioxin-like PCBs (Buckland et al., 1998) was also based on diets selected to be representative of the adult New Zealand male population. Adult males generally have higher levels of exposure, due to higher average food and energy intake than females. Therefore, the multi-pathway exposure analysis presented in this report indicates higher levels of community exposure than the population average.

Although other demographic groups, such as adolescent males, may have higher average dietary intakes it is important to note that the health effects associated with dioxin intakes are based upon long-term exposure. The intake scenario used in the calculation is based upon longer-term dietary trends rather than looking at the shorter period, over which adolescent males might maintain a high-energy intake.

Intakes have been calculated assuming that the average resident would be potentially exposed to contaminated soil, produce and air for 350 days in a typical year. The resident is assumed to have been away from the immediate vicinity of the site for the other 15 days and therefore not exposed to media contaminated by the plant. This assumption is consistent with the HHRAP.

Two exposure scenarios have been used in the analysis:

- Scenario 1: assumes that residents are exposed to dioxins emitted from the plant via the consumption of contaminated homegrown produce, the inhalation of contaminated air and the ingestion of contaminated soil.

- Scenario 2: assumes that residents are exposed to dioxins emitted from the plant via the consumption of contaminated home grown produce, the inhalation of contaminated air, the ingestion of contaminated soil and the consumption of eggs and meat from free range poultry grown at the household.

Both intake scenarios assume that a typical resident obtains 10% of their daily fruit and vegetables, and chicken and egg intakes from their place of residence. In other words, 10% of

typical dietary produce and poultry intakes are assumed to be contaminated by emissions from the IWD plant. The calculations also assume that 100% of the air that residents breathe and soil that they ingest is contaminated, approximating exposures for a person who spends most of their day at home. A summary of intake rates used in the analysis is presented in Table 4.

**Table 4. Summary of Scenario Intake Rates**

| Exposure Pathway | Units | Typical Daily Intakes per kg/BW | Percentage contaminated | Average resident intake per kg/BW* |
|---|---|---|---|---|
| Air | $m^3$/kg-day | 0.83 | 100% | 0.24 |
| Soil | kg/kg-day | 0.000025 | 100% | 0.00000030 |
| Produce exposed above-ground | kg DW/kg-day | 0.00030 | 10% | 0.000029 |
| Produce protected above-ground | kg DW/kg-day | 0.00057 | 10% | 0.000055 |
| Produce below-ground | kg DW/kg-day | 0.00023 | 10% | 0.000022 |
| Chicken | kg FW/kg-day | 0.00057 | 10% | 0.000055 |
| Eggs | kg FW/kg-day | 0.00042 | 10% | 0.000041 |

*Adjusted for exposure 350 days of year
**kg DW denotes kg on a dry weight basis; kg FW denotes kg on a fresh weight basis

The typical air inhalation rate of 20$m^3$/day is the value recommended by the US EPA (1998) for an adult male. The intake of soil (25 mg/day for an adult), is the same at that used by the MfE in *"Health and Environmental Guidelines for Selected Timber Treatment Chemicals"* (MoH, MfE, 1997). Total dietary intakes of eggs and poultry are based upon the estimates used in the Organochlorines programme, for which the fat intakes are the same as those from the National Nutrition Survey and similar to the US EPA's estimates. In the calculations it is assumed that the typical fat content of eggs is 11.2% and 8.4% for chicken meat.

Exposed and protected above ground produce consumption rates are also based upon the USEPA (1998) HHRAP recommendations. The HHRAP is based on data from the Exposure Factors Handbook (US EPA, 1997). The below-ground produce intake is taken from *"Health and Environmental Guidelines for Selected Timber Treatment Chemicals"* (MoH, MfE, 1997).

The same assumptions have been previously used by AES when modelling exposures as part of the MfE National Emission Standard programme for Dioxins, and are discussed in more detail in Stevenson and Noonan (2001).

# 3. RESULTS OF MULTIPATHWAY EXPOSURE MODELLING

## 3.1 LIQUID WASTE INCINERATOR 1975-79

The multi-pathway calculations assume the quantity of "apparent" TCDD estimated to be released from the liquid incinerator is equivalent to the actual quantity of the 2378-TCDD congener released. The average 2378-TCDD emission rate of 14.2ng/s used in the model calculations assumes the 1570mg of 2378-TCDD was emitted at a constant rate over the entire 3.5 years of operation (i.e. 365 days per year, 24 hours per day).

### *3.1.1 Concentrations in environmental media*

Predicted concentrations of 2378-TCDD in the local ambient air, soil, poultry and produce associated with 2378-TCDD emissions from the liquid waste incinerator between November 1975 and April 1979 are presented in Figure 3 to Figure 9. Within the exception of soil concentrations, the media concentrations shown in the figures are calculated as the average concentration over the 3.5 years of the incinerator's initial period of operation. The presented soil concentrations are calculated at the end of the operational period when 2378-TCDD concentrations are at their maximum as dioxins accumulate in the ground. The origin of the plots is the estimated location of the liquid waste incinerator.

All maximum media concentrations are predicted to occur approximately 300m to the west of the liquid waste incinerator on Mt Moturoa. The higher concentration estimated to occur at this point is primarily associated with the emission plume impinging upon elevated terrain (approximately 78m above sea-level). The peak predicted ambient air, soil, egg, chicken, exposed above-ground produce, protected above-ground produce and below-ground produce 2738 TCDD concentrations are 77fg/$m^3$, 5.6ng/kg, 0.24ng/kg-FW, 0.18ng/kg-FW, 0.24ng/kg-DW, 0.00080ng/kg-DW, 0.0016ng/kg-DW respectively.


**Figure 3. Predicted incremental annual average 2378-TCDD ambient air concentrations (fg-TEQ/m$^3$) from emissions from the IWD liquid waste incinerator between 1975 and 1979**

The predicted concentrations of 2378-TCDD in air can be put in context by consideration of the toxic equivalent concentrations of dioxins found in the Organochlorines Programme, summarised in Table 5.

**Table 5. Dioxin concentrations in ambient air from the Organochlorines Programme.**

| | Sample results | Site annual averages |
|---|---|---|
| | fg I-TEQ/m$^3$ | |
| Remote sites | 0.8 - 7.5 | 1.4 - 3.4 |
| Rural site | 0.9 - 10 | 3.8 |
| Town & urban sites | 6.1 - 255 | 28.0 - 100 |
| Industrial site | 39 - 1107 | 232 |

The concentrations of 2378-TCDD are very much higher than the 2378-TCDD concentrations found in the Organochlorines Programme, but are in the same range as the total toxic equivalent (TEQ) concentrations from the Organochlorines Programme. However, whereas 2378-TCDD was generally only a small contributor to total toxic equivalent concentrations found in the Organochlorines Programme, the emissions data from 1988 (when all congeners were measured) indicates that 2378-TCDD is likely to have been at least two-thirds of the total toxic equivalent concentration in the emissions, and therefore the total toxic equivalent concentration resulting from the incinerator

emissions would be not more than about 50% higher than the 2378-TCDD concentrations indicated in Figure 3. If anything, it is likely that the 1975-1979 emissions would have had a still higher proportion of 2378-TCDD contribution to total TEQ levels than in 1988, because of the higher concentrations of dioxins in the wastes being incinerated, and the probable lower efficiency of destruction by incineration. The total toxic equivalent (TEQ) concentrations are therefore likely to be less than 50% higher than the 2378-TCDD concentrations.

Accordingly, the annual average 2278-TCDD and total toxic equivalent (TEQ) concentrations predicted by the modelling of the incinerator emissions approximate the annual average TEQ concentrations estimated for New Zealand town and urban sites not subject to unusual dioxin emission sources. This information indicates that unusually high exposures to dioxins compared with people living in typical New Zealand towns and cities are unlikely to have resulted from emissions from the Ivan Watkins Dow liquid waste incinerator over the 1975-1979 period. The multi-pathway modelling presented in this report confirms this.

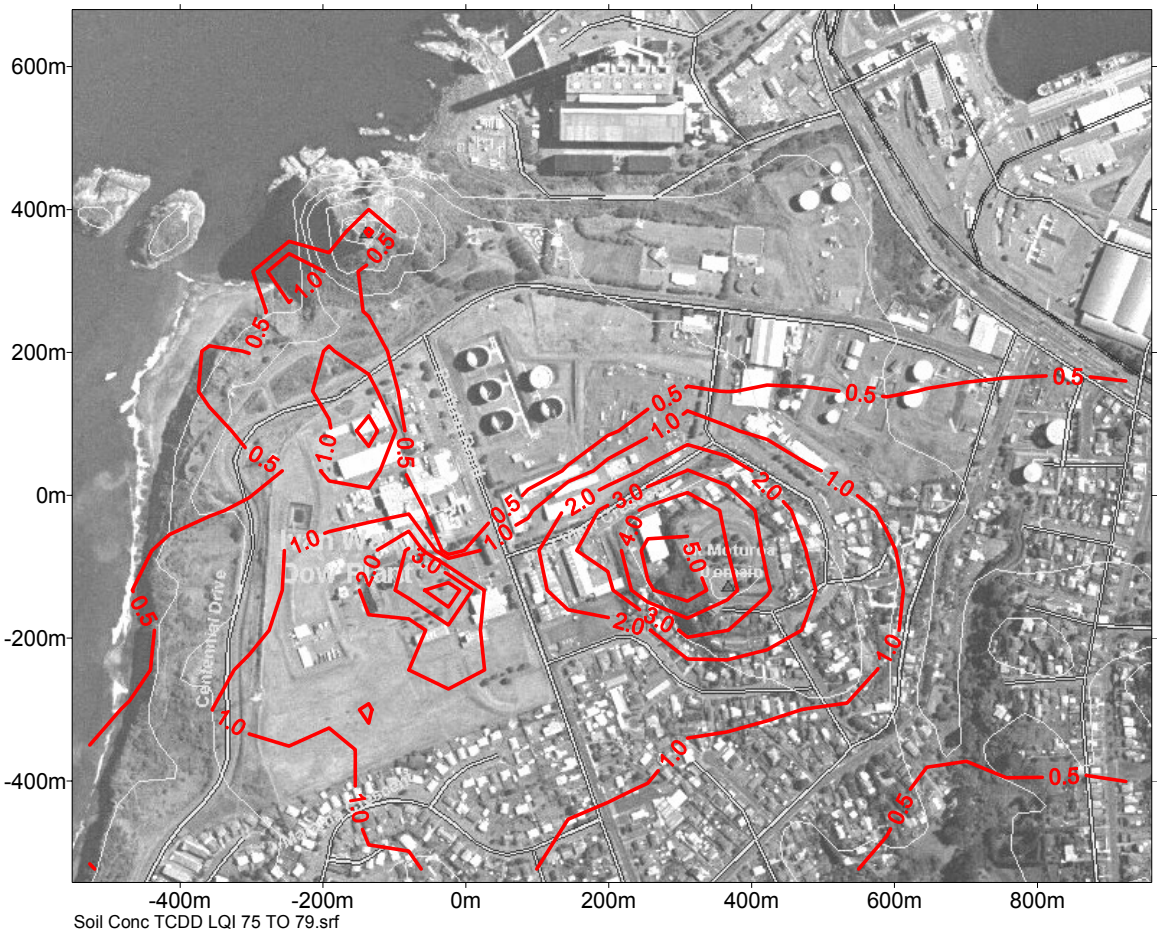


**Figure 4. Predicted incremental 2378-TCDD soil concentrations (ng-TEQ/kg for 1cm mixing depth) from emissions from the IWD liquid waste incinerator between 1975 and 1979**

The increases in dioxin concentration in soils indicated in Figure 4 as a result of incinerator emissions over the 1975-1979 period are similar to those found in urban soils in the Organochlorines Programme, which are in the range 0.5-5 ng I-TEQ/kg. However, the Organochlorines Programme samples were composite samples of the top 10 cm of soil, whereas the mixing depth for modelling of soil concentration increments in Figure 4 is 1 cm, so that the predicted increments in soil concentrations in Figure 4 should be divided by 10 for

comparison with the Organochlorines Programme samples. Accordingly, multi-pathway modelling of the 1975-79 emissions from the liquid waste incinerator indicates 2378-TCDD increments that are only minor contributions to total toxic equivalent (TEQ) concentrations in soils compared with the total dioxin and furan toxic equivalent (TEQ) concentrations in typical urban soils.

A mixing depth of 1 cm is appropriate for consideration of exposure pathways where surface soil ingestion is a possible concern.


**Figure 5. Predicted incremental 2378-TCDD egg concentrations (ng-TEQ/kg-FW) from emissions from the IWD liquid waste incinerator between 1975 and 1979**

The 2378-TCDD concentrations predicted in eggs from free-range poultry raised in the vicinity of the IWD plant are higher than the I-TEQ concentration of dioxins and furans measured in supermarket eggs in the Organochlorines Programme dietary survey of dioxin intakes, which was 0.012 ng I-TEQ/kg-FW when concentrations of congeners below the detection limit are set to half of the detection limit and 0.0017 ng I-TEQ/kg-FW when concentrations of congeners below the detection limit are set to zero. The maximum concentration predicted on Mount Moturoa (0.22 ng I-TEQ/kg-FW) is almost 20 times higher than the higher Organochlorines Programme concentration. The concentrations predicted for much of the residential area surrounding the plant are also higher than the Organochlorines Programme concentration, ranging between about 0.02 and 0.1 ng I-TEQ/kg-FW.

In part, the predictions from the modelling would be expected to give higher concentrations than in typical supermarket eggs because the modelling considers free-range poultry, rather than commercial poultry operations. In most commercial poultry operations, birds have no access to soil, which is the predominant pathway by which free-range poultry accumulates dioxins, via soil ingestion during feeding from the soil surface.


**Figure 6. Predicted incremental 2378-TCDD chicken meat concentrations (ng-TEQ/kg-FW) from emissions from the IWD liquid waste incinerator between 1975 and 1979**

The 2378-TCDD concentrations in chicken meat indicated in Figure 6 are also higher than the concentrations measured in supermarket chickens in the Organochlorines Programme. These higher concentrations predicted by the modelling are also associated with the expected differences between commercially raised chickens and free-range birds.


**Figure 7. Predicted incremental 2378-TCDD exposed above-ground produce concentrations (ng-TEQ/kg-DW) from emissions from the IWD liquid waste incinerator between 1975 and 1979**

Fresh fruit and vegetables were not included in the Organochlorines Programme dietary intake study, presumably in part because it was recognised that dioxin concentrations would be likely to be below detection limits in all samples. The maximum concentrations predicted in Figure 7 would probably be above the detection limit, but those for protected and below-ground produce in Figure 8 and Figure 9 would certainly be below detection limits.

It is interesting to note that the predicted exposed produce 2378-TCDD concentrations are approximately 300 times higher than those of the protected produce (Maximum 0.0008ng/kg-DW vs 0.24ng/kg-DW). The comparisons between the protected and exposed produce concentration highlight the significance of the direct dioxin exposure pathway of above ground produce contamination in the calculations. After the period of incinerator operation stops in April 1979, concentrations in exposed produce predicted by the multi-pathway model would be similar to those currently predicted for the protected above-ground produce.


**Figure 8. Predicted incremental 2378-TCDD protected above-ground produce concentrations (ng-TEQ/kg-DW) from emissions from the IWD liquid waste incinerator between 1975 and 1979**


**Figure 9. Predicted incremental 2378-TCDD below ground produce concentrations (ng-TEQ/kg-DW) from emissions from the IWD liquid waste incinerator between 1975 and 1979**

### *3.1.2 Estimated 2378-TCDD exposures*

Estimated dioxin intakes during this period for a typical New Zealand 80kg male adult are presented in Figure 10 and Figure 11. Figure 10 presents the estimated incremental intake of 2378-TCDD via inhalation, and the consumption of soil and home-grown produce contaminated by emissions from the liquid waste incinerator. Figure 11 shows the incremental intake of 2378-TCDD associated with all modelled residential exposure pathways (i.e. air, soil, produce, eggs and chicken). Intakes are recorded in terms of pg-TEQ/kg-BW/day.

Two exposure scenarios for residents have been assessed:

- Scenario 1 - 100% of inhalation and soil ingestion exposed to emissions and 10% of typical consumption of fruit and vegetables exposed to emissions;
- Scenario 2 - as for Scenario 1, plus 10% of typical consumption of eggs and poultry meat from free-range poultry exposed to emissions.

On each figure the point where maximum 2378-TCDD intakes are predicted to occur have been labelled ("Max"). In this instance the maximum intake for both exposure scenarios occur on top of Mt Moturoa. Two other sample points have also been identified (P1 and P2) corresponding to the location where nearby residents are potentially most exposed to the released contaminants towards the west and south.

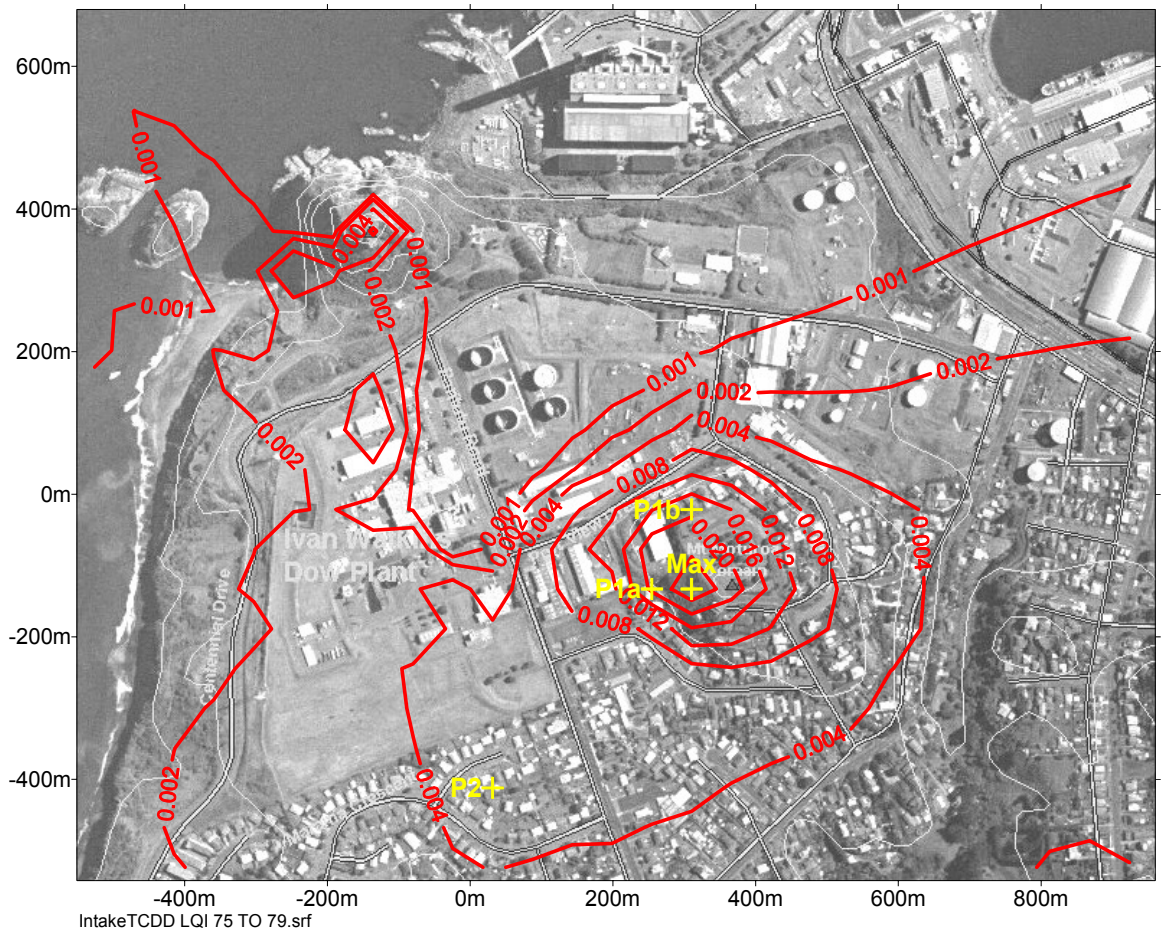


**Figure 10. Predicted incremental increase in the 2378-TCDD exposures (pg TEQ/kg-BW/day) of residents from contaminated air, soil, and garden produce (Scenario 1) from emissions from the IWD liquid waste incinerator between 1975 and 1979.**

The estimated incremental exposures are compared with:

- ALDE - average lifetime daily exposure: the measure of exposure estimated from serum TCDD/F concentrations that reflect historic and current exposures from all routes.
- Dietary intakes - the daily intake of dioxins in food, estimated from quantities of food consumed and dioxin concentrations in the food.

The Ministry for the Environment has published studies that estimate a typical population ALDE of 1.4 pg TEQ/kg-bw/day (Smith and Lopipero, 2001) and typical population dietary intakes (Buckland et al., 1998). The estimated adult male dietary intake of dioxins detected at levels above detection limits in the Organochlorines Programme dietary study is 0.05 pg TEQ/kg-bw/day (the <LOD=0 estimate), and that including half limit of detection values for congeners at concentrations below their detection limits is 0.18 pg TEQ/kg-bw/day (the

<LOD=1/2LOD estimate). The true typical adult male dietary intake is likely to be between these two estimates, but by convention the <LOD=1/2LOD estimate is the one usually quoted.

For a steady exposure to dioxins, the ALDE and dietary intake would be expected to be similar, because dietary intakes are generally thought to be the largest exposure for the general population. The larger ALDE compared with the dietary intake is thought to result from decreasing exposures to dioxins and furans over the last decade or more as the sources of dioxin exposure have become better understood and controlled.

The predicted incremental dioxin exposures resulting from incinerator emissions over the 1975-1979 period are small compared with the typical population ALDE. The predicted exposures for incinerator emissions are at most about 3.4% of this ALDE for exposure via inhalation, soil ingestion and consumption of 10% typical consumption of garden produce, poultry meat and eggs from the hypothetical maximum exposure site on Mt Moturoa.

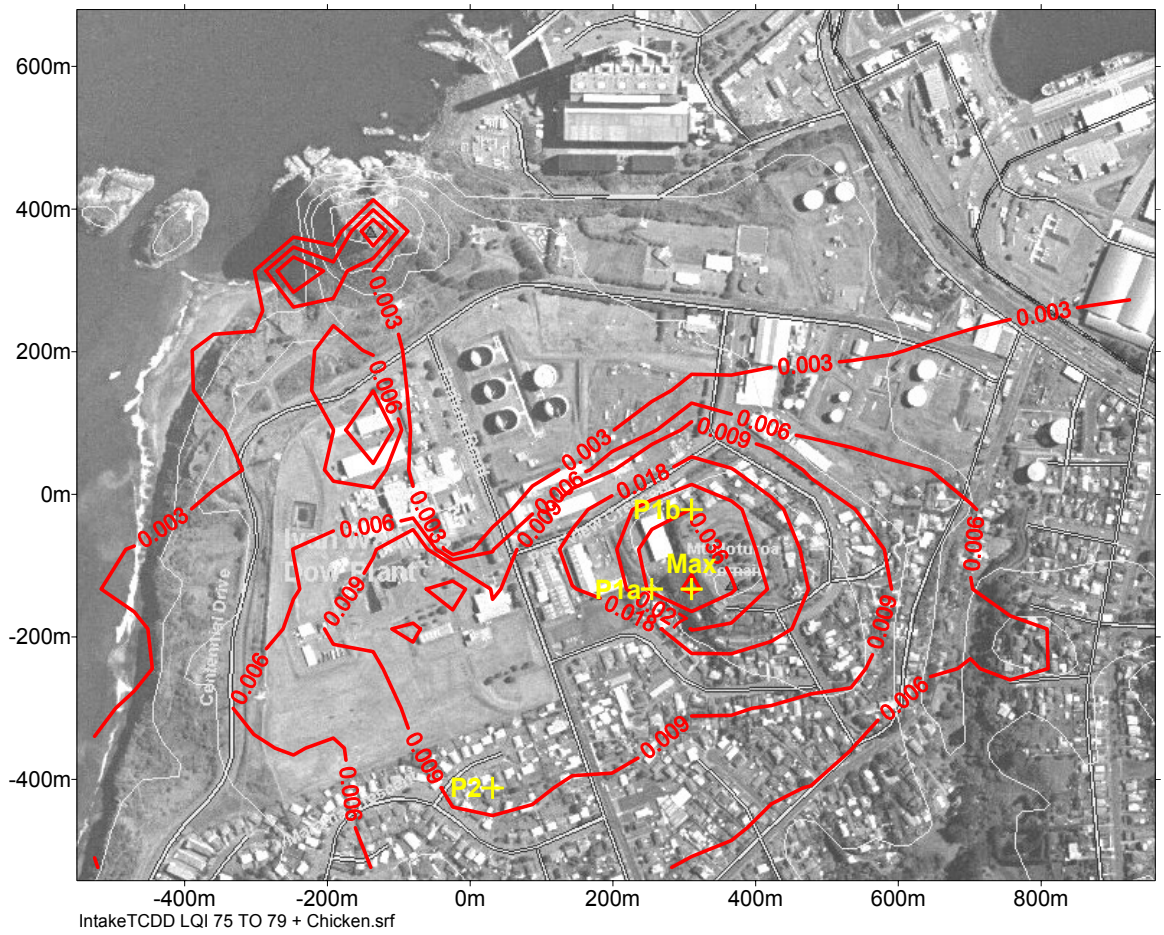


**Figure 11. Predicted incremental increase in the 2378-TCDD intakes (pg TEQ/kg-BW/day) of residents from contaminated air, soil, garden produce and poultry (Scenario 2) from emissions from the IWD liquid waste incinerator between 1975 and 1979.**

The predicted maximum exposure (0.047 pg TEQ/kg-bw/day at the top of Mt Moturoa) is approximately the same as the <LOD=0 dietary intake estimate and about a third of the <LOD=1/2LOD estimate.

Levels of incremental exposure resulting from incinerator emissions are smaller in the residential areas potentially most affected. The maximum residential intake estimated by the model (point P1a) is approximately is 1.5% and 2.7% of the typical population ALDE for consumption scenarios excluding and including consumption of eggs and poultry meat, respectively.

The predicted maximum residential intake for Scenario 1 at point P1a is 0.021 pg TEQ/kg-bw/day, approximately 40% of the estimated adult male the <LOD=0 dietary intake estimate, and 12% of the <LOD=1/2LOD estimate. For Scenario 2 (including 10% of eggs and poultry meat consumption from the exposure location), the intake is 0.038 pg TEQ/kg-bw/day, approximately 75% of the estimated adult male the <LOD=0 dietary intake estimate, and 21% of the <LOD=1/2LOD estimate.

The predicted typical residential intake for Scenario 1 at point P2 is 0.005 pg TEQ/kg-bw/day, approximately 10% of the estimated adult male the <LOD=0 dietary intake estimate, and 2.6% of the <LOD=1/2LOD estimate. For Scenario 2 (including 10% of eggs and poultry meat consumption from the exposure location), the intake is 0.01 pg TEQ/kg-bw/day, approximately 20% of the estimated adult male the <LOD=0 dietary intake estimate, and 5% of the <LOD=1/2LOD estimate.

Accordingly, the maximum predicted intake for residential locations is a small percentage of the blood serum-based ALDE and could result in a 5-75% increase in exposure for people consuming a typical diet, except for the 10% fruit and vegetables, eggs and poultry meat used here as the proportions of consumption exposed to incinerator emissions. The latter is a modest increase compared with the variability in dietary intakes likely between different individuals unaffected by local emissions, resulting from different dietary choices.

### *3.1.3 Breakdown of 2378-TCDD exposures by exposure route*

A breakdown of predicted intake rates via the different exposure pathways for each of the locations identified in Figure 10 and Figure 11 is presented in Table 6. Intake Scenario 1 in the Table corresponds to air, soil and produce intake pathway. Intake Scenario 2 incorporates all potential residential exposure routes, including poultry.

Table 6 shows relatively high proportions of the total predicted intakes for Scenario 1 associated with inhalation (62%-67%) and the consumption of exposed above ground produce (26%-29%). These high percentage contributions from inhalation may seem surprising in light of typical breakdowns of overall dioxin exposure via the various exposure of routes for the general population, which typically show contributions from inhalation of about 2% or less. The high percentage contributions for Scenario 1 arises from omission of the major exposure routes for total dioxin exposures for the general population, which are consumption of meat, dairy products, chicken and eggs, and fish. When these major contributors are omitted from consideration, because they are not relevant exposure routes affected by incinerator emissions (apart from chicken and eggs for people who raise their own), inhalation becomes the major contributor to exposure to the particular emission source under consideration. The small proportion (10%) of total consumption of fruit and vegetables that is considered to be contaminated by incinerator emissions also increases the percentage contribution that inhalation makes to the resulting small overall exposure to the particular emission source.

**Table 6. Predicted 2378-TCDD intake rates (pg TEQ/kg BW/day) for four sample locations associated with emissions from the liquid waste incinerator between 1975 and 1979**

| | Air | Soil | Exposed above-ground produce | Protected above-ground produce | Below ground produce | Total Intake Scenario 1 | Egg | Chicken | Total Intake Scenario 2 |
|---|---|---|---|---|---|---|---|---|---|
| **Maximum possible intake (Mt Moturoa)** | | | | | | | | | |
| Intake rate | 0.018 | 0.0017 | 0.0071 | 0.000044 | 0.000035 | **0.027** | 0.01 | 0.01 | **0.047** |
| Percentages of total intake for: | | | | | | | | | |
| Scenario1 | 67% | 6% | 26% | 0.2% | 0.1% | **100%** | - | - | **-** |
| Scenario 2 | 38% | 4% | 15% | 0.1% | 0.1% | **-** | 21% | 21% | **100%** |
| **Maximum Residential Exposure (P1a)** | | | | | | | | | |
| Intake rate | 0.013 | 0.0015 | 0.006 | 0.00004 | 0.00003 | **0.021** | 0.0086 | 0.0086 | **0.038** |
| Percentages of total intake for: | | | | | | | | | |
| Scenario1 | 64% | 7% | 29% | 0.2% | 0.1% | **100%** | - | - | **-** |
| Scenario 2 | 35% | 4% | 16% | 0.1% | 0.1% | **-** | 23% | 23% | **100%** |
| **Typical Residential Exposure (P2)** | | | | | | | | | |
| Intake rate | 0.0030 | 0.00040 | 0.0014 | 0.00001 | 0.00001 | **0.005** | 0.0024 | 0.0024 | **0.010** |
| Percentages of total intake for: | | | | | | | | | |
| Scenario1 | 62% | 8% | 29% | 0.2% | 0.2% | **100%** | - | - | **-** |
| Scenario 2 | 31% | 4% | 14% | 0.1% | 0.1% | **-** | 25% | 25% | **100%** |

When the incinerator is no longer in use (in this instance after April 1979), although the emitted dioxins still persist in the environment (i.e. soil), inhalation exposures become zero and intake rates from exposed produce would fall to about those shown in the Table 6 for protected produce. Therefore, during non-operational periods total exposures for Scenario 1 would be about 7% of those presented and the exposures for Scenario 2 would be about 50% of those shown.

The predicted concentrations also assume that the average 2378-TCDD emission rate is the same as the "apparent TCDD" emission rate estimated by Pilgrim (1986). As previously discussed, if volumetric flue gas emission rates and TCDD concentrations are re-evaluated using more typical values then average TCDD emission rates, and hence exposure intakes, could reasonably be 61% of those shown in Table 6.

### *3.1.4 Estimated total toxic equivalent (TEQ) exposures*

The dioxin intakes above are only those estimated to result from 2378-TCDD emissions from the liquid waste incinerator, not total daily TEQ intakes including all of the dioxin congeners emitted. Only 2378-TCDD was measured during the initial operating period of the incinerator (1975-79). Therefore, it is not possible to directly calculated emission rates of other 16 toxic PCDD and PCDF congeners.

The emissions data from 1988 (when all congeners were measured) indicates that 2378-TCDD is likely to have been at least two-thirds of the total toxic equivalent concentration in the emissions, and therefore the total toxic equivalent exposure increments resulting from the incinerator emissions would be not more than about 50% higher than the 2378-TCDD-only exposures. If anything, it is likely that the 1975-1979 emissions would have had a still higher proportion of 2378-TCDD contribution to total TEQ levels than in 1988, because of the higher concentrations of dioxins in the wastes being incinerated, and the probable lower

efficiency of destruction by incineration. The total toxic equivalent (TEQ) incremental exposures are therefore likely to be less than 50% higher than the 2378-TCDD concentrations.

The 1998 soil samples taken on Mt Moturoa as part of the MfE Organochlorines Programme, which measured the concentrations of all congeners (Buckland, Ellis and Salter, 1998) also indicate the likelihood of the predominance of 2378-TCDD in emissions. 94% of the total toxic equivalent (TEQ) concentration in this sample was 2,3,7,8-TCDD.

However, as shown subsequently, it is most likely that most of the measured concentrations of dioxins in soils in the vicinity of the IWD plant originated from emissions other than from the incinerators. Emissions from sources other than the incinerators are likely to contain predominantly 2378-TCDD. The incineration process is likely to substantially increase the proportions of other dioxin and furan congeners both through destruction of much of the 2378-TCDD and the combustion reactions producing a wide range of dioxin and furan congeners from the combusted organochlorine materials. Accordingly, while the congener distribution in the Mt Moturoa soil sample is suggestive, the most definite indication of the high proportion of 2378-TCDD in the total toxic equivalent (TEQ) emissions from the incinerators is from the 1998 emissions test results.

Adjustment of exposures to take account of possible contributions from dioxins and furans other than 2378-TCDD does not change the overall conclusion that the maximum predicted intake for residential locations is a small percentage of the blood serum-based average population exposure estimate and could result in moderate increases in current exposure for people consuming a typical diet, except for the 10% fruit and vegetables, eggs and poultry meat used here as the proportions of consumption exposed to incinerator emissions. The maximum predicted increase is similar to the variability in dietary intakes likely between different individuals unaffected by local emissions, resulting from different dietary choices.

## 3.2 SOLID WASTE INCINERATOR 1983-86

In comparison with predicted 2378-TCDD exposures associated with emissions from the liquid waste incineration between 1975 and 79, the incremental increase in residential dioxin intakes from the consumption of environmental media contaminated by emissions from the solid waste incinerator is likely to be negligible. The maximum potential exposure associated with emissions from the solid waste incinerator can be quantified by considering intake rates between 1983 and 1986 associated with emissions from the source. The solid waste incinerator emission rates were at their highest during this period.

If it is assumed that the total 8.24mg of 2378-TCDD is released evenly between 1983-1986 the average emission rate is 0.098ng TEQ/s for the 2.7 years of initial operation. The estimated emission rate for this period is approximately 145 times less than that calculated for liquid waste incinerator between 1975 and 1979.

The spatial distribution of concentrations in the various media and of incremental exposures predicted for the emissions from the solid waste incinerator are similar to those for the liquid waste incinerator, although all are at very much lower levels. The maximum residential intakes for exposure Scenario 1 and Scenario 2 are predicted to be 0.00013 pg TEQ/kg-BW/day and 0.00022 pg TEQ/kg-BW/day respectively. Maximum average daily intake

increments are 162-175 times less than maximum intakes predicted for the liquid waste incinerator for 1975 to 1979.

These incremental contributions are clearly negligible compared with those resulting from emissions from the liquid waste incinerator over the 1975-79 period and accordingly contour plots for the various concentrations and intakes are not shown.

# 4. MEASURED SOIL CONCENTRATIONS

Between 1985 and 1998 a number of soil samples were taken either from within the boundaries of the IWD plant, or nearby locations. Results from these sampling programmes provide a means of assessing the soil concentrations predicted by the multi-pathway model, and also identifying the possible contribution from other sources of dioxins to the overall levels of environmental contamination.

From the review of the available literature there appears to have been four periods between April 1985 and 1998 when soil samples were taken in the vicinity of the Ivon Waktins Dow Plant. A summary of each programme derived is presented below (Buckland, Ellis and Salter, 1998; Pilgrim, 1986):

- In April 1985 ten composite soil samples were taken inside and outside the IWD boundary by the Department of Health and IWD personnel. Each soil sample comprised of seven to nine separate core samples 25mm in diameter and 50mm in depth. As of the 31/7/1986 analysis results for 2378-TCDD were obtained for only 9 of the samples.

- On the 15th April 1986, immediately after the TCP Process bursting disc failure release three soil samples and seven area wipe samples were taken from locations in the general direction of the likely plume. Although, the documentation reports values as TCDD, the results are probably for the specific congener 2378-TCDD, as the samples were analysed by DSIR.

- Four composite soil samples (together with six composite grass samples) were taken for 2378-TCDD analysis on 16th April 1986 by the Ministry of Health. Each composite sample comprised of 10 to 15 random samples taken over an area

- One soil sample taken was taken in 1998 on Mt Moturoa as part of the Ministry for the Environment Organochlorines soil sampling programme.

The measured soil concentrations are shown in Table 7. The approximate locations where the soil samples were taken is presented in Figure 12 for the 1985 and 15th April 1986 tests and in Figure 13 for 16th April 1986 and 1998 tests. In the figures, composites are represented by a number of individual sample points corresponding to the general area where the testing was done. These sample points have also been used to represent area concentrations in the predicted soil concentration contour plots.

**Table 7. Soil sample summary**

| Location ID | Date | Total TCDD (ng/kg) | 2378-TCDD (ng/kg) | Notes |
|---|---|---|---|---|
| Pt 1 | Apr-85 | - | 50 | |
| Pt 2 | Apr-85 | - | 140 | |
| Pt 3 | Apr-85 | - | - | No result as of 31/7/86 |
| Pt 4 | Apr-85 | - | 100 | |
| Pt 5 | Apr-85 | - | 90 | |
| Pt 6 | Apr-85 | - | 20 | |
| Pt 7 | Apr-85 | - | 60 | |
| Pt 8 | Apr-85 | - | 5* | Half the detection limit (10 ng/kg) has been used |
| Pt 9 | Apr-85 | - | 170 | |
| Pt 10 | Apilr-85 | - | 110 | |
| S9** | 15-Apr-86 | 40 | - | |
| S10** | 15-Apr-86 | 15* | - | Concentration represents half the detection limit (30ng/kg) |
| S8** | 15-Apr-86 | 15* | - | Concentration represents half the detection limit (30ng/kg) |
| Sector A | 16-Apr-86 | - | 100 | |
| Sector B | 16-Apr-86 | - | 10* | A value of less than 20 ng/kg recorded so 10ng/kg assumed |
| Sector C | 16-Apr-86 | - | 60 | |
| Sector E | 16-Apr-86 | - | 310 | |
| MfE | 1998 | 59.1 | 31 | |

** Although recorded as TCDD concentration it is probable that they are in fact 2378-TCDD specific

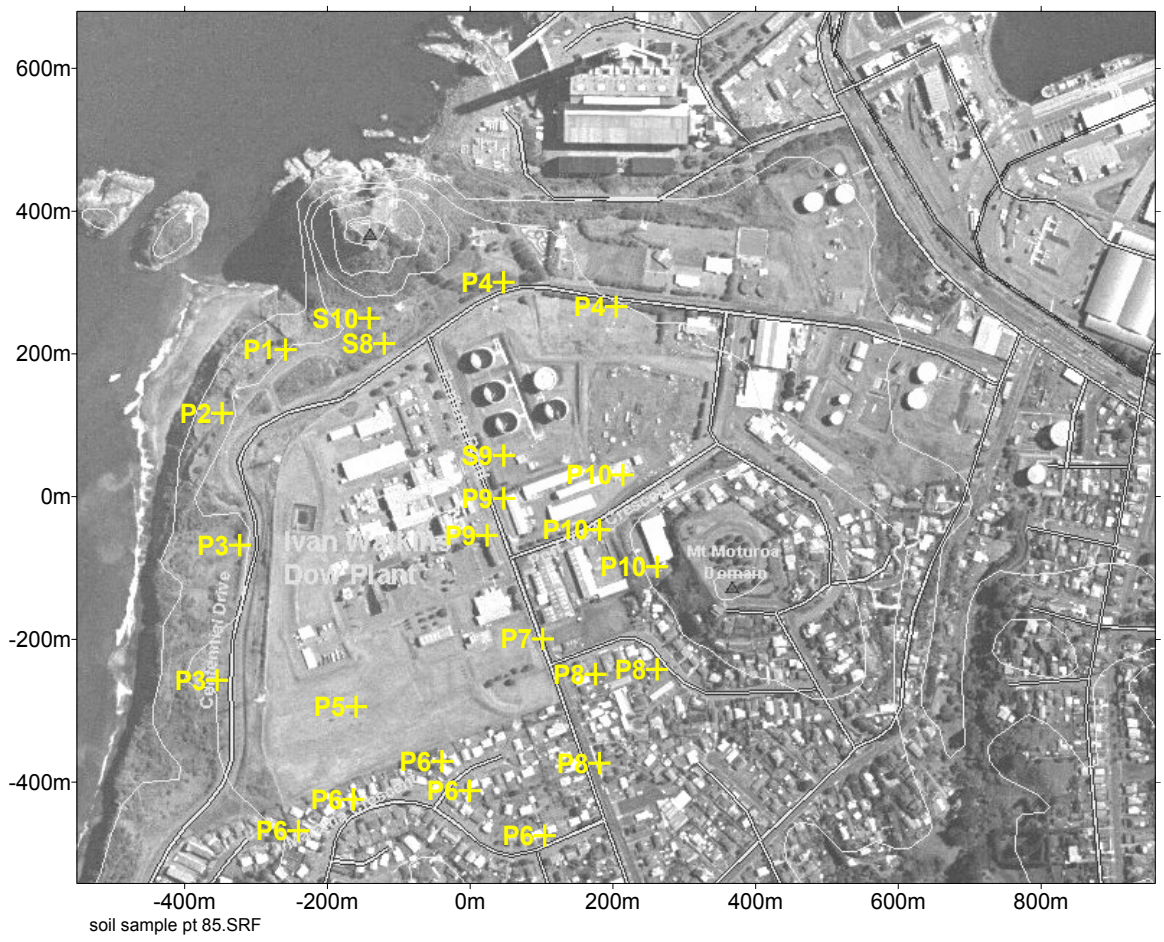


**Figure 12. Location of soil samples taken in April 1985 and 15th April 1986**

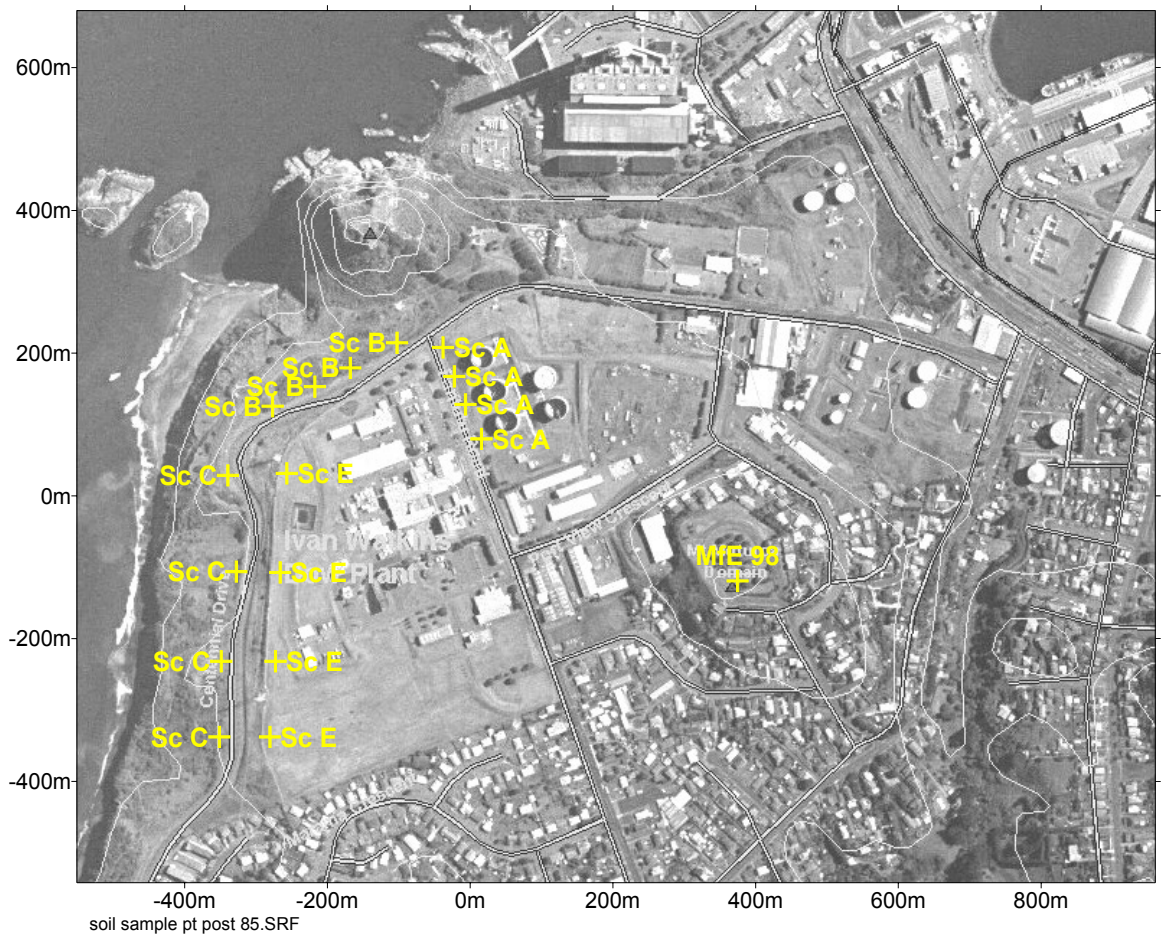


**Figure 13. Location of soil samples taken in 16th April 1985 and 1998**

Contours of 2378-TCDD soil concentrations are presented in Figure 14 and Figure 15. Figure 14 includes all measured soil concentrations between 1985 and 1998. Figure 15 only includes soil concentration between 1985 and 1986. The recorded TCDD concentrations from the 15th April 1986 test programmes are assumed to be 2378-TCDD concentrations. Soil concentration contours have been estimated using the Surfer-6 (Golden Software, 1996) kriging function.

The predicted concentration distributions are intended to be indicative of general trends rather than absolutes values. The concentration profiles are based upon the clustered distributions of soil samples and do not account for terrain effects or other environmental and source influences. Figure 15 provides an indication of soil concentration profiles if the influence of the Mt Moturoa sample, which may not be representative of larger spatial trends, is removed from the analysis.

It should also be noted that the Mt Moturoa sample was taken approximately 12 years after the other soil samples. As the half-life of dioxins in surface soils is estimated to be between 9 to 25 years it could be expected that if the site was sampled in 1985-86 higher dioxin level would be more likely to have been recorded (assuming that only minimal quantities of dioxins have been deposited between 1986 and 1998).

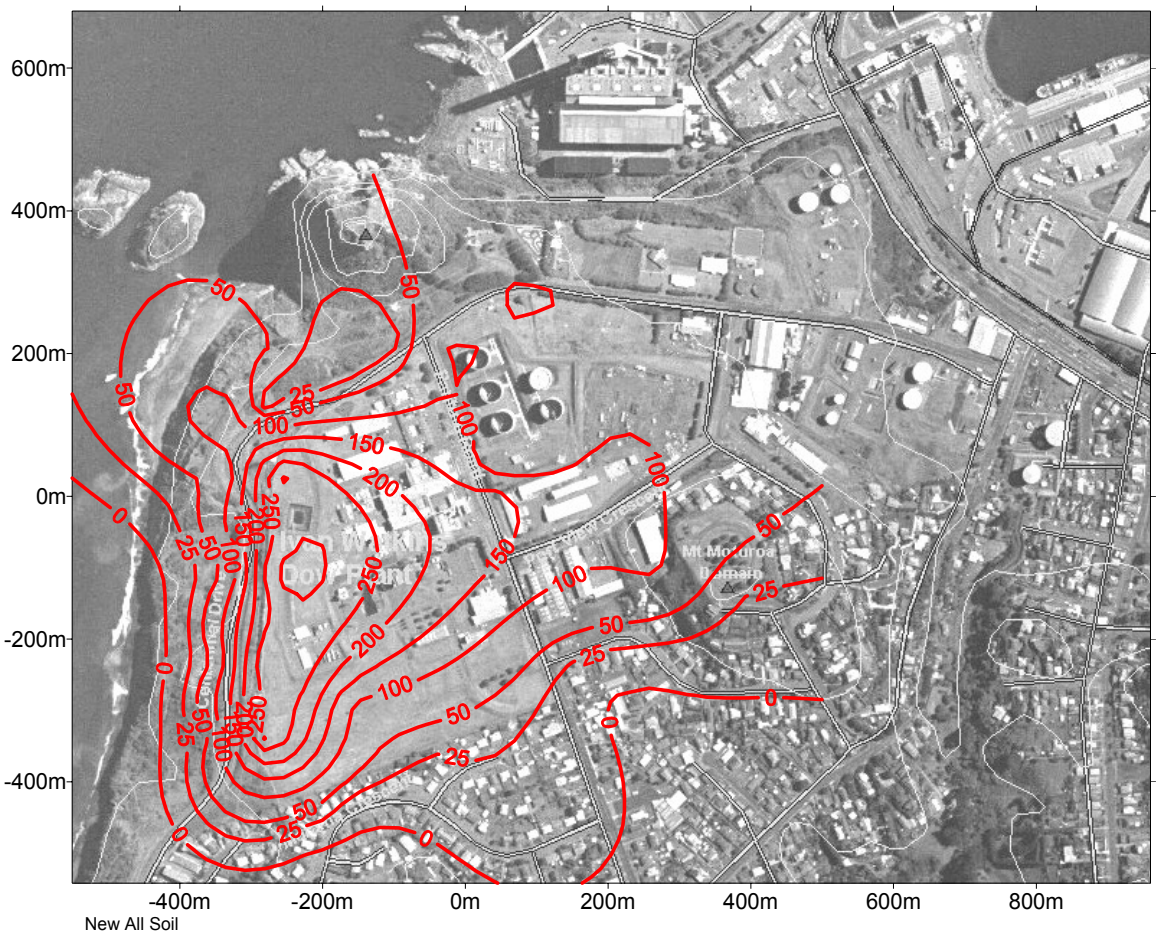


**Figure 14. 2378-TCDD soil concentration (ng/kg) contours from soil samples taken between 1985 to 1998**

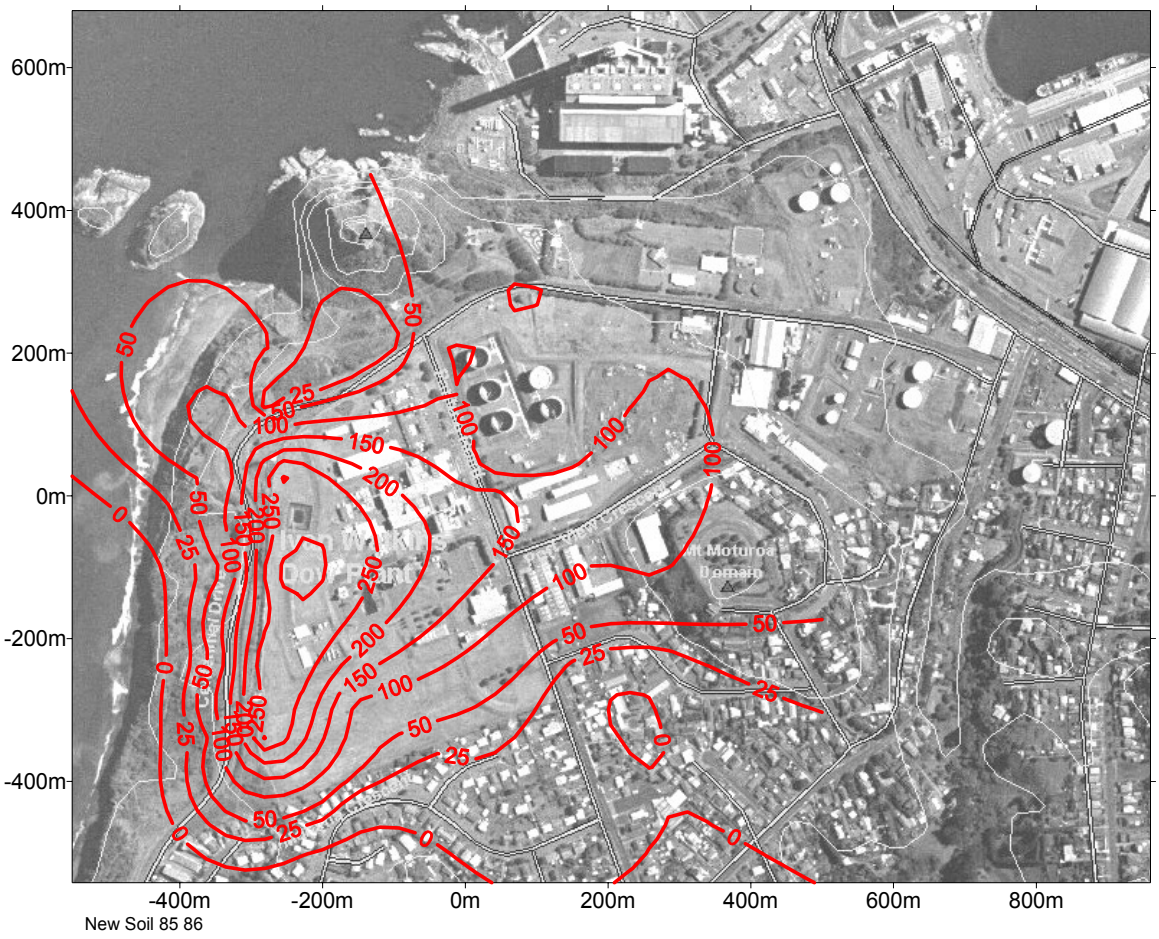


**Figure 15. 2378-TCDD soil concentration (ng/kg) contours from soil samples taken between 1985 to 1996**

Comparisons of soil concentration contours developed from the measured soil concentrations with those predicted by the multi-pathway model, based upon the operation of the Liquid Waste Incineration between 1975 and 1979 (Figure 4) indicate that observed soil concentrations and their spatial distribution cannot be explained by emissions from incineration. Also, as shown above, the solid waste incinerator would have made only a relatively small contribution to total 2378-TCDD concentrations in the soil. Both multi-pathway models also indicate that if these were the largest contributors to surrounding 2378-TCDD soil levels, the peak concentration would be expected to occur on top of Mt Moturoa. The soil sampling programmes indicate that maximum in-soil concentrations occur on the western boundary of the plant and that higher concentrations occur on land at about the same elevation as the plant between the plant and Mt Moturoa than found at the top of Mt Moturoa. The dispersion modelling predicts that the highest concentrations anywhere as a result of the incinerator emissions would be at the top of Mt Moturoa.

The soil samples taken at the various locations around the plant were cores 4-5cm deep. The measured dioxin concentrations were calculated assuming even distribution over this depth. In the multi-pathway calculations the methodology assumes the 2378-TCDD deposited to the ground were evenly distributed over the first 1cm depth of soil. Therefore, if the modelled soil concentrations adjusted to the same mixing depth, the predicted concentrations in Figure 4 would be 4 to 5 times lower than those shown.

These results indicate that other emission sources are likely to have been greater contributors to the 2378-TCDD concentrations observed in the soils that the emissions from the incinerators. Pilgrim (1986) suggests that the major contribution may have been from the manufacture of 2,4,5-T between 1964 and 1969, when TCP was imported and, in comparison with post 1969, process control was rudimentary.

## 4.1 2378-TCDD MULTI-PATHWAY INTAKES ESTIMATED FROM MEASURED SOIL CONCENTRATIONS

An estimate of residential dioxin intakes can be made based upon the measured soil concentration presented in Table 7. Predicted average 2378-TCDD intakes (pg-TEQ/kg-bw/day) are shown in Table 8. Daily intakes presented have assumed the observed 2378-TCDD concentration are present evenly throughout a 5cm, 2cm and 1cm mixing depth. Varying untilled mixing depth assumptions change the TCDD intakes associated with soil, and poultry consumption. The 1cm mixing depth assumption, although consistent with the previous multi-pathway predictions for the solid and liquid waste incinerators, may overestimate actual soil concentrations. The USEPA (2000) is currently considering recommending of a mixing depth 2cm for untilled soil. Therefore a 2cm soil mixing depth is also included in Table 8 to provide a comparative range of potential intakes. Tilled (garden) soils are still assumed to be 20cm in depth

The results of multi-pathway calculations presented in the table do not take into account the effects of direct inhalation or the contamination of exposed above ground produce through direct particulate deposition or foliage vapour uptake. As both of these exposure routes apply only when an air emission source is operating (see Table 6), predicted intakes could have been considerably higher than those shown in Table 8 during emission periods - assuming that the soil contamination occurred as a consequence of deposition of 2378-TCDD from air emissions and not through any other mechanism such as the spillage.

The majority of the soil samples were taken either within the boundaries or the IWD plant or in non-residential areas. Therefore predicted intakes associated with these soil samples are not representative of typical daily exposures and are included only for comparative purposes. As shown in Table 8, soil ingestion makes the largest contribution to incremental exposures for Scenario 1 and consumption of eggs and chicken makes the predominant contribution for Scenario 2. At the higher soil concentrations measured, very high levels of dioxin exposure could result from Scenario 2, ranging up to over 4 times the ALDE of 1.4 pg TEQ/kg-bw/day. Clearly, raising free-range poultry in these areas is undesirable.

Only soil samples ‘P6’ and ‘P8’ are likely to indicate potential residential exposures. The marked difference between the concentration found for "P6" (20 ng/kg) and "P8" (below detection limit) suggests that concentrations in soils may change rapidly between the edge of the residential area and locations further into the residential area. "P6" was a composite sample and it is therefore possible that very high concentrations might have been present at one or more of the locations from which sub-samples were collected and very low at other locations. Accordingly, the indicated "P6" sampling locations do not necessarily give an accurate indication of the dioxin concentrations in soils there.

**Table 8. Estimated average daily intakes associated with soil sample taken between 1985 and 1998**

| Soil Sample | 2378-TCDD (ng/kg) | Estimated average daily intakes (pg TEQ/kg-BW/day) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 5 cm mixing depth | | | | | | | 1cm mixing depth | | 2cm mixing depth | |
| | | Soil | Exposed above ground produce | Protected above ground produce | Below ground produce | Egg | Chicken | Total Intake Scenario 1 | Total Intake Scenario 2 | Total Intake Scenario 1 | Total Intake Scenario 2 | Total Intake Scenario 1 | Total Intake Scenario 2 |
| Pt 1 | 50 | 0.015 | 0.002 | 0.004 | 0.003 | 0.174 | 0.173 | **0.024** | **0.37** | **0.08** | **1.8** | **0.05** | **0.9** |
| Pt 2 | 140 | 0.042 | 0.006 | 0.011 | 0.009 | 0.487 | 0.484 | **0.067** | **1.04** | **0.23** | **5.1** | **0.13** | **2.6** |
| Pt 3 | - | - | - | - | - | - | - | **-** | **-** | **-** | **-** | **-** | **-** |
| Pt 4 | 100 | 0.030 | 0.004 | 0.008 | 0.006 | 0.348 | 0.346 | **0.048** | **0.74** | **0.17** | **3.6** | **0.09** | **1.8** |
| Pt 5 | 90 | 0.027 | 0.004 | 0.007 | 0.006 | 0.313 | 0.311 | **0.043** | **0.67** | **0.15** | **3.3** | **0.08** | **1.6** |
| Pt 6 | 20 | 0.006 | 0.001 | 0.002 | 0.001 | 0.070 | 0.069 | **0.010** | **0.15** | **0.03** | **0.7** | **0.02** | **0.4** |
| Pt 7 | 60 | 0.018 | 0.002 | 0.005 | 0.004 | 0.209 | 0.208 | **0.029** | **0.45** | **0.10** | **2.2** | **0.06** | **1.1** |
| Pt 8 | 5* | 0.001 | 0.000 | 0.000 | 0.000 | 0.017 | 0.017 | **0.002** | **0.04** | **0.01** | **0.2** | **0.005** | **0.1** |
| Pt 9 | 170 | 0.051 | 0.007 | 0.013 | 0.010 | 0.592 | 0.588 | **0.081** | **1.26** | **0.29** | **6.2** | **0.16** | **3.1** |
| Pt 10 | 110 | 0.033 | 0.004 | 0.008 | 0.007 | 0.383 | 0.380 | **0.053** | **0.82** | **0.18** | **4.0** | **0.10** | **2.0** |
| S9 | 40 | 0.012 | 0.002 | 0.003 | 0.002 | 0.139 | 0.138 | **0.019** | **0.30** | **0.07** | **1.5** | **0.04** | **0.7** |
| S10 | 15* | 0.004 | 0.001 | 0.001 | 0.001 | 0.052 | 0.052 | **0.007** | **0.11** | **0.03** | **0.5** | **0.01** | **0.3** |
| S8 | 15* | 0.004 | 0.001 | 0.001 | 0.001 | 0.052 | 0.052 | **0.007** | **0.11** | **0.03** | **0.5** | **0.01** | **0.3** |
| Sector A | 100 | 0.030 | 0.004 | 0.008 | 0.006 | 0.348 | 0.346 | **0.048** | **0.74** | **0.17** | **3.6** | **0.09** | **1.8** |
| Sector B | 10* | 0.003 | 0.000 | 0.001 | 0.001 | 0.035 | 0.035 | **0.005** | **0.07** | **0.02** | **0.4** | **0.01** | **0.2** |
| Sector C | 60 | 0.018 | 0.002 | 0.005 | 0.004 | 0.209 | 0.208 | **0.029** | **0.45** | **0.10** | **2.2** | **0.06** | **1.1** |
| Sector E | 310 | 0.093 | 0.013 | 0.024 | 0.019 | 1.079 | 1.072 | **0.149** | **2.30** | **0.52** | **11.3** | **0.29** | **5.7** |
| MfE 1998 | 31 | 0.009 | 0.001 | 0.002 | 0.002 | 0.108 | 0.107 | **0.015** | **0.23** | **0.05** | **1.1** | **0.03** | **0.6** |

Grey shading indicates soil samples likely to be more representative of residential areas.

It is also possible that "P10" might indicate an extreme level for a residential location, although this is unlikely. The sampled area for the composite extends towards some residential properties off Simons Street, but it appears more likely that relatively high concentration found in the composite sample results mostly from high concentrations further north in the area sampled.

The estimated daily dioxin exposures for the concentrations measured on the "P6" and "P8" composite samples are summarised for the various scenarios and soil mixing depths in Table 9.

**Table 9. Summary of intakes resulting from residual dioxins in soils**

| Sampled area | | Scenario 1 | | | Scenario 2 | | |
|---|---|---|---|---|---|---|---|
| | | 1cm | 2cm | 5 cm | 1cm | 2cm | 5 cm |
| **P6** | | Estimated daily intakes pg TEQ/kg-bw/day | | | | | |
| | | 0.03 | 0.02 | 0.01 | 0.7 | 0.4 | 0.15 |
| | % of MfE ALDE | 2% | 1.4% | 0.7% | 50% | 29% | 11% |
| | % of average dietary intake | 17% | 11% | 6% | 389% | 222% | 83% |
| **P8** | | Estimated daily intakes pg TEQ/kg-bw/day | | | | | |
| | | 0.01 | 0.005 | 0.002 | 0.2 | 0.1 | 0.04 |
| | % of MfE ALDE | 0.7% | 0.4% | 0.1% | 14% | 7% | 3% |
| | % of average dietary intake | 6% | 3% | 1.1% | 111% | 56% | 22% |

For Scenario 1, the estimated exposures are small percentages (0.1-2%) of the ALDE of 1.4 pg TEQ/kg-bw/day and small to moderate percentages (1-17%) of the estimated typical adult male dietary intake of 0.18 pg TEQ/kg-bw/day from the Organochlorines Programme dietary study. For Scenario 2, the estimated daily intakes are considerably higher, corresponding to 3-50% of the ALDE and 22-389% of the typical dietary intake. Because the scenarios assessed here consider that only 10% of resident's total consumption of the food items considered is exposed to the measured soil dioxin concentrations, daily exposures could be much higher if people did obtain a high proportion of a normal intake of, for example eggs from free-range poultry raised at the locations considered. Even at only 10% of total typical consumption of eggs and poultry meat, soil concentrations as measured in sample "P6" could result in as much as a 4-5 fold increase compared with typical in general population dioxin exposures. Clearly, it is undesirable to raise free-range poultry for consumption on dioxin-contaminated soils.

However, the estimated exposures in Table 11 should only be considered as preliminary indications of possible dioxin exposures for residents resulting from dioxins in soils in the vicinity of the IWD plant. Because the dioxin concentration measured in the "P6" composite sample may have resulted from very high concentrations at one or more of the sub-sample locations and very low concentrations at others, it may not be representative of dioxin

concentrations in residential soils in the area. Also, the concentrations in sample "P8" were below the detection limit, and might have been significantly lower than the half detection limit concentration taken for this sample.

Substantially higher concentrations than found in composite sample "P6" were found in samples from other non-residential locations and the potential for dioxin exposures if these areas were used to raise free-range poultry is correspondingly higher. Very high levels of dioxin exposure could occur in this situation.

# 5. SOURCE CONTRIBUTIONS TO DIOXIN CONCENTRATIONS IN SOILS.

## 5.1 INCINERATOR EMISSIONS

The likely contribution to measured concentrations of dioxins in soils from incinerator emissions can be assessed by comparing the concentrations predicted in soils by the multi-pathway modelling with the measured soil concentrations. Figure 4 shows contours of predicted soil concentrations resulting from operation of the liquid waste incinerator between 1975 and 1979. This is the source and operating period for which the highest emissions of dioxins are documented for the IWD plant. The contours in Figure 4 are for a soil mixing depth of 1 cm, whereas the measured concentrations inTable 7, Figure 14 and Figure 15 are averaged over a 5 cm depth of sampled soil. Accordingly, the concentrations predicted by multi-pathway modelling for a 5 cm depth of soil are 1/5 of those in Figure 4.

The predicted soil concentrations (5 cm depth) from the liquid waste incinerator emissions over the 1975-79 period in the area where the highest dioxin concentrations have been measured are in the range 0.2-0.6 ng TEQ/kg. The contours from the measured concentrations are in the range 100-300 ng TEQ/kg over the same area. The measured concentrations are between about 150 and 1500 times higher than those predicted by the multi-pathway modelling.

While the possibility of some under-prediction by the multi-pathway modelling exists, there are conservative assumptions in the modelling that make it more likely to over-predict than under-predict. The emission rates used are higher than is likely to have occurred and the particle size distribution used is likely to result in higher rates of wet and dry deposition than may have occurred. It is difficult to see how under-prediction by a factor of as much as 150 could occur.

In relation to the accuracy of the multi-pathway modelling, it is relevant to note a study on a farm near Auckland (reported in Stevenson and Noonan (2001)), undertaken to validate a model for transfer of dioxins and furans from air, through grass and into milk. While the uncertainty in the predictions from the model, resulting from uncertainty in transfer coefficients for many of the congeners, is up to a factor of 4, the measured concentrations for all individual congeners in milk were within the range of concentrations predicted by the model from the measured air concentrations. Where congener concentrations in milk were below the analytical detection limit, the predicted concentrations were consistent with the detection limits. Unfortunately, the concentrations of 2378-TCDD were below the detection limit, so that the level of validation of the model is not as strong for this congener as for the congeners above the detection limit. Nevertheless the overall excellent performance of the model does give good grounds for reasonable confidence in the multi-pathway modelling methodology.

Calculation of the soil concentrations does not use the same calculations as in the air-grass-milk pathway, although it would be possible to calculate rates of deposition to soil using the air-grass pathway and taking the dioxin uptake on grass to be the rate of deposition to soil as will occur when the grass dies and degrades to become part of soil organic matter. However, the calculations for deposition rates to soil that are in the model give higher rates of

deposition than would be given by the air-grass-soil pathway. Accordingly, there are good indications that, if anything, the multi-pathway modelling of soil concentrations will over-estimate rather than under-estimate the actual soil concentration increments resulting from emissions modelled.

Apart from the measured soil concentrations being very much higher than those predicted by multi-pathway modelling, the pattern of predicted soil concentrations differs markedly from those measured. Modelling of the incinerator emissions predicts a maximum soil concentration at the top of Mt Moturoa, with substantially lower concentrations between Mt Moturoa and the plant and also towards the western boundary of the plant. The measured soil concentrations are highest near the western boundary of the plant, decreasing in the easterly direction towards Mt Moturoa, and with a concentration measured at the top of Mt Moturoa about one third of measurements close to its base. Accordingly, the distribution of modelled concentrations is almost the inverse of the measured concentrations.

These considerations suggest that it is most probable that emissions from the liquid waste incinerator over the 1975-79 period of operation have made, at most, only a minor contribution to measured soil concentrations in the vicinity of the IWD plant. The estimated emissions of dioxins from the liquid waste and solid waste incinerators in Table 2 indicate that emissions from the liquid waste incinerator over the 1975-79 period may have been about 50 times greater than the emissions from both incinerators over other operating periods. Accordingly, the overall contributions from incinerator emissions to soil dioxin levels in the vicinity of the IWD plant are probably, at most, minor.

## 5.2 THE TCP PLANT BURSTING DISC RELEASE

On 15$^{th}$ April 1986 as a consequence of a bursting disc failure at the TCP (trichlorophenol) plant, an estimated 70 to 735mg of 2378-TCDD was released (along with TCP). The estimated release is between 4% and 50% of the estimated emissions from the liquid waste incinerator over the 1975-79 period and it is possible because of the different conditions of release that this might have made a larger contribution to soil concentrations than emissions from the incinerators.

Some of the release was contained in the building, but the remainder is thought to have dispersed in a north-westerly direction. Because of the direction of dispersion, surrounding residents are unlikely to have been directly affected during the initial phase of dispersion. It is however possible that both the TCP and 2378-TCDD deposited on various surfaces including walls, grass and soil volatilised and may have contributed to dioxin concentrations in soil. Both compounds are sufficiently volatile for this to be a credible emission mechanism.

An initial estimate of the likely TCP and TCDD volatilisation rates can be obtained by considering diffusion rates and vapour pressure of the respective compounds.

Concentrations of 2378-TCDD and TCP in air very close to a surface on which TCP containing 2378-TCDD has been deposited can be assumed to be at equilibrium with the deposited material. Further from the surface, transport away from the surface by diffusion and then turbulence and wind decreases the concentrations below their equilibrium levels

faster than they can be replaced by evaporation. The rates of diffusion through the thin, quiescent air layer immediately adjacent to the surface, before convection and wind transport take over are likely to be the limiting factor on the rate of release of the volatile compounds from the surface. If it is assumed that over some small distance the concentration gradient varies between the concentration calculated from the relative vapour pressures and zero, then the rate of diffusion of the 2378-TCDD and TCP can also be calculated from diffusion constants. The equilibrium concentration can be estimated from the respective compounds' vapour pressures. Calculation of the rate of diffusion uses Fick's Law, as follows:

$$\text{Diffusion Rate } (fg/m^2/s) = \frac{\text{Da } (cm^2/s) * \text{Air Concentration } (fg/m^3)}{\text{Diffusion Distance } (cm) * 100}$$

Where Da is the diffusion constant in air for the compound.

The vapour pressure of 2378-TCCD can be taken to be approximately proportional to its mole fraction in the TCP. The concentration of 2378-TCDD as TCP was estimated by Nicol and Smith (1986) as 0.00032% (w/w) corresponding to a mole fraction of 0.00020%. Chemical properties and predicted 2378-TCDD and TCP diffusion rates for a number of different diffusion path lengths is shown Table 10. The 10cm diffusion path length shown in the table is highly improbable and is included only for comparative purposes.

**Table 10. Predicted TCP and 2378-TCDD diffusion rates**

| | **TCP** | **2378-TCDD*** |
|---|---|---|
| **$D_a$ ($cm^2/s$)** | 2.91E-02 | 1.27E-02 |
| **MW (g/mole)** | 198 | 321.98 |
| **Vp (atm) (revised, 1999)** | 2.15E-04 | 9.74E-13 |
| **Mass Conc ($fg/m^3$)** | 1.9E+09 | 1.40E+07 |
| **Diffusion distance (cm)** | **Diffusion rate ($fg/m^2/s$)** | **Diffusion rate ($fg/m^2/s$)** |
| 0.01 | 5.52E+07 | 3.53E-01 |
| 0.1 | 5.52E+06 | 3.53E-02 |
| 1 | 5.52E+05 | 3.53E-03 |
| 10 | 5.52E+04 | 3.53E-04 |

* Assumes 0.00032% (w/w) concentration of 2378-TCDD in TCP

Area wipe tests conducted just after the incident recorded TCP concentrations between 280 and 3870 $ng/m^2$. Assuming a 0.00032% (w/w) concentration of 2378-TCDD in the TCP, the quantities of deposited 2378-TCDD are estimated to be in the range of 0.00056 to 0.008 $ng/m^2$. An estimation of the time needed for all of the deposited 2378-TCDD to evaporate can be made based upon the calculated diffusion rates. Release times for different diffusion distances are presented in Table 11.

**Table 11. Estimated 2378-TCDD re-emission times**

| **Diffusion distance (cm)** | **Release Time (days)** | |
|---|---|---|
| | **0.00056 $ng/m^2$ TCDD** | **0.008 $ng/m^2$ TCDD** |
| 0.01 | 0.02 | 0.25 |
| 0.1 | 0.2 | 2.5 |
| 1 | 2 | 25 |
| 10 | 18 | 252 |

Based upon the calculations most of the deposited 2378-TCDD would be expected to have been released back into the atmosphere within a few days after the incident. It is reasonable to consider that all of the deposited material evaporates, and based on this an initial estimation of the increment in soil concentrations associated with the vapour uptake of the released material can be made. The most likely mechanism for transfer of such vapour phase 2378-TCDD to soils is via uptake on grass, followed by incorporation of the decaying grass material into the soil.

McLachlan (1997) describes a simple model for calculation of dioxin concentrations in grass, based on dioxin concentrations in ambient air. His calculation of dioxin concentrations in grass relies on the comparison of measurements of dioxin concentrations in air in the rural areas around Bayreuth with hay harvested from the same area in the same year. These comparisons indicated that grass fields take up dioxins from air at a rate equivalent to scavenging the dioxins from about 9 $m^3$ of air per gram dry matter of grass produced.

If all of the 2378-TCDD emitted during the accident is released back into the atmosphere over the next few days after the incident then 70 to 735mg of 2378-TCDD can be expected to be emitted during this period. An estimate can made of the typical ambient 2378-TCDD concentration by considering the total volume of air that is likely to have mixed with the TCDD released over the period. An approximate air flow volume can be calculated to be 4,000,000,000$m^3$ if it is assumed that the contaminant is deposited over a 100m cross sectional area, that the contaminant is mixed to a height of 15m in the air, that the release period is approximately 10 days and the average wind speed is 3m/s. Consequently the average ambient concentrations in this air mass would be 18,000 to 190,000 fg/$m^3$.

Due to variation in wind direction over the period no single location will be exposed to the released dioxin for all of the time. Periods of exposure will occur when the point is downwind of the 2378-TCDD/TCP deposits at the plant. Therefore, in order to account for wind variation at any down wind location, the predicted concentration has been divided by an arbitrary factor of 10.

The approximate annual yield of pasture is taken as 1000g/$m^2$/yr. Therefore over the release/exposure period of the 10 days considered here, an average yield of 27g/$m^2$ would be expected. Assuming that 9$m^3$ of air is scavenged per gram dry matter, 247$m^3$/$m^2$ of ambient air would be scavenged corresponding to average deposition flux of 0.4 to 4.7ng/$m^2$ of 2378-TCDD. For a typical soil sampling depth of 5cm, the estimated concentration increment would be approximately 0.006 to 0.06 ng/kg (using a bulk soil density of 1.5g/$cm^3$).

For soil concentration increments of the order of 30ng/$m^3$ to be observed (as at the top of Mt Moturoa) an estimated 355g of 2378-TCDD would need to be released during an incident or over a prolonged period. This is about 150 times larger than the maximum estimated quantity of 2378-TCDD in the reported estimates from both incinerators and the bursting disc incident since 1975. Although this analysis is intended to only provide an initial assessment, it does strongly suggest that soil concentrations observed in the vicinity the plant are unlikely to be attributable to the 1985 bursting disc incident at the TCP plant.

It should be noted that all of the soil concentration calculations are independent of the release time, and in this instance 10 days is a convenient arbitrary period.

## 5.3 OVERVIEW SUMMARY.

Neither the emissions that have been estimated to have occurred since 1975 from both incinerators, nor the bursting disc release in 1986 can account for the concentrations of 2378-TCDD measured in soils in the vicinity of the IWD plant. The 2378-TCDD emissions that the air-grass-soil pathway modelling suggests would be needed to account for the approximately 30 ng/kg concentration measured in soil at the top of Mt Moturoa are about 150 times the maximum estimates of emissions from both incinerators since 1975 and the bursting disc release in 1986.

Accordingly, it appears necessary to invoke very high 2378-TCDD emissions during the earlier operations of the plant. It is widely accepted that the processes were not well controlled from an emissions perspective and the levels of 2378-TCDD contamination in 2,4,5-T produced at the plant are generally considered to have been very much higher during the early period of production. Accordingly, it appears credible that the very large 2378-TCDD emissions that are evidently required to account for soil concentrations measured may in fact have occurred.

# 6. REFERENCES


Buckland, S. J, Ellis, H. K., and Salter, R. T. (1998). *Ambient concentration of selected organochlorines in soils*. Ministry for the Environment: Wellington. ISBN 0-478-09034-X.

Buckland, S. J., Scobie, S., Heslop, V. (1998). *Organochlorines in New Zealand: Concentrations of PCDDs, PCDFs and PCD in retail foods and an assessment of dietary intake for New Zealanders*. Ministry for the Environment: Wellington. ISBN 0-478-09037-4.

McLachlan, M. S. (1997). A Simple Model to Predict Accumulation of PCDD/Fs in an Agricultural Food Chain. *Chemosphere* 34 (5-7): 1263-1276.

Mills, B. (2001). *Report to Dow AgroSciences (NZ) Ltd, PCDD and PCDF Incinerator Emissions, December 2000*. Watercare Services Ltd; Auckland.

Nicol, R. S., and Smith, D. K. W. (1986). *Investigation of the Bursting Disc Failure: Ivon Watkins Dow TCP process*. DSIR Report No. IPD/RI/1658; Petone.

Pilgrim, R. C. (1996). *Submission to the committee of enquiry into possible health effects of manufacture of agricultural chemical*. Evidence submitted by Central Region Air Pollution Control Group, Department of Health; Wellington.

Pilgrim, R. C., Bulley, M. M., Millichamp, P., and Bird, M. (undated). *Incineration of hazardous wastes in New Zealand*.

Smith, A. H. and Lopipero, P. (2001). *Evaluation of the Toxicity of Dioxins and Dioxin-like PCBs: A Health Risk Appraisal for the New Zealand Population*. ME No.351. Ministry for the Environment, Wellington, New Zealand.

Stevenson,C.D., Noonan, M.G., (2001). *Multi-pathway estimates of exposures to dioxins from emissions to air: Supplementary Report on Methodology and Detailed Results.* Ministry for the Environment: Wellington.

US EPA. (1997). *Exposure Factors Handbook*. EPA/600/P-95/002Fa, August 1997

US EPA, (1998). *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities*. Available from http://www.epa.gov/earth1r6/6pd/rcra_c/pd-o/midlo.htm.

US EPA. (1998a). *Methodology for Assessing Health Risks Associated with Multiple Pathways of Exposure to Combustor Emissions*. EPA 600/R-98/137.

US EPA. (2000). *Draft Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds. Part III: Integrated Summary and Risk Characterization for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds*. Available from http://www.epa.gov/ncea/pdfs/dioxin/part3.htm.

WHO (1998). *Assessment of the health risk of dioxins: re-evaluation of the Tolerable Daily Intake (TDI)*. WHO Consultation, May 25-29 1998, Geneva, Switzerland