

2.0 Background

2.1 Structure and Properties of PCDDs and PCDFs

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

2.1.1 Structure and Toxicity

PCDDs and PCDFs are two groups of chlorinated aromatic³ compounds. Both groups of chemicals may have up to eight chlorine atoms attached. Each individual compound is referred to as a congener, with each specific congener identified by the number and position of chlorine atoms around the aromatic nucleus. There are 75 possible PCDD congeners and 135 possible PCDF congeners. Groups of congeners with the same number of chlorine atoms are known as homologues.

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

2.1.2 Toxic Equivalents

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

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

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

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

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

2.1.3 Sources

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

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

2.1.4 Physical and Chemical Properties and Environmental Fate

In general, PCDDs and PCDFs have low water solubility, high octanol-water partition coefficients⁴ and low vapour pressure, and are resistant to chemical degradation under normal environmental conditions. These properties mean that they are extremely persistent in the environment, and their highly lipophilic⁵ nature results in bio-concentration into biota and biomagnification through the food chain.

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

The only environmentally significant transformation process in soil is photodegradation⁶ at the soil-air interface (ground surface). Although some volatilisation of PCDDs and PCDFs on soil does occur, the predominant fate of these chemicals adsorbed to soil is to remain in place near the surface of undisturbed soil, or to move to water bodies with soil erosion.

⁴ Measure of affinity to be absorbed to organic material

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

⁶ Destruction by the effects of sunlight

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

2.2 The Dow Plant

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

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

A key intermediate in the manufacture of 2,4,5-T was trichlorophenol (TCP). Formation of 2,3,7,8-TCDD occurred during the TCP manufacturing process and remained as a contaminant in 2,4,5-T. No additional TCDD⁷ is produced in the 2,4,5-T manufacturing process in the phenoxy plant. Until 1969 IWD used imported TCP, but from 1969 sodium trichlorophenate (Na-TCP) was manufactured on the Paritutu site (Pilgrim, 1986). During the first eight years of manufacturing Na-TCP, a xylene and trichloroanisole waste stream was significantly contaminated with 2,3,7,8-TCDD. This waste was initially stored, but was subsequently incinerated on site between late 1975 and April 1979.



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

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



Figure 1: Location of study area

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

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

A solid waste incinerator was established in 1981 for destroying an accumulated backlog of chemical wastes and chemically contaminated packaging. This incinerator is still in use⁸. Monitoring of dioxin emissions from the solid waste incinerator suggest negligible amounts are being emitted (Pilgrim *et al.*, 1990; G Bedford, TRC, 2002, pers comm.).

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

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

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

2.3 Previous Soil Studies

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

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

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

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

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

These studies are of variable quality. It is not clear from the reports of some of the early studies whether the results given are total TCDD or 2,3,7,8-TCDD, and it is also not clear whether reporting is wet or dry weight. It would be normal to report dry weights. Also, some of the 1985 and 1986 sample locations are rather vague, being shown as large crosses or areas over which composites were taken on sampling diagrams accompanying the results. This makes it difficult to compare these results with the specific locations of this study. Finally, detection limits for the early results were rather high, typically 20 – 30 ng/kg⁹, which considerably reduces their usefulness in comparing with the current study.

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

⁹ ng/kg = nanogram per kilogram, or one part per trillion. A nanogram is one billionth of a gram. To give a sense of scale, a part per trillion is equivalent to a teaspoonful distributed through 5,000,000 m³ of soil, which is the same as a teaspoon within the top 1 metre of soil over a thousand rugby fields, each 100 m x 50 m.