ASSESSMENT OF DIOXIN CONTAMINATION AT SAWMILL SITES

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1. INTRODUCTION

1.1 Background

A number of organochlorine pesticides (including herbicides and insecticides e.g. DDT, dieldrin, 2,4,5-trichlorophenoxyacetic acid [2,4,5-T] and pentachlorophenol [PCP] were used in New Zealand over the period from the late 1940s to the late 1980s. Many of these materials (at a technical or commercial grade specification) contained trace levels of impurities. For 2,4,5-T and PCP, this included the family of compounds known as "dioxins". As a consequence, at locations where 2,4,5-T or PCP were manufactured/formulated, stored or used, there is potential for the ground to be contaminated with the pesticides (including any degradation products) and concomitantly with the dioxin impurities. To assist with the management of contaminated timber treatment sites, health and environmental guidelines were published in 1997 (MfE/MoH, 1997). Dioxins are also widespread in the environment as a result of a number of other activities (Buckland *et al*., 2000).

There is worldwide concern about organochlorine contaminants in the environment as even low concentrations can contribute in the long term to significant risks to the health of animals (especially top of the food chain receptors such as predatory birds and marine mammals) and humans. In view of the international concern the Ministry for the Environment commenced a national Organochlorines Programme[1] to carry out research, assess exposure and health risks and to consider issues such as clean up targets and emission control standards. This report on "Dioxins at Sawmill Sites" is a part of this broad programme of work on dioxin and organochlorine issues.

Until its voluntary withdrawal by the timber industry in 1998, PCP (or its sodium salt NaPCP) was used by the industry in a variety of treatment processes.

PCP as a preservative

PCP in diesel oil was used as a permanent timber preservative (telegraph poles, railway sleepers etc) either through a pressure treatment process (known as the Rueping process) or through hot and cold dipping in a bath. The Rueping process was used at one site only, Waipa. Three sites are known to have used the hot and cold bath method. The concentration of PCP in both of these processes was 5% (w/v).

A preservative formulation of NaPCP in water (Immutan B and Tanalith FMP) was also used, again in a pressure treatment process in the late 1960s to mid 1970s. The concentration of pentachlorophenate in the treatment solution was relatively low at 0.06-0.14% w/v PCP.

NaPCP as an antisapstain fungicide

Pine species are susceptible to attack by fungi that feed on wood sap and their excretion may cause discolouration of the timber. NaPCP in water was used to prevent fungal attack on the timber while being dried before further processing. Freshly sawn (green) timber had antisapstain fungicide applied either in a dip bath or spray tunnel as it travelled

[1] http://www.mfe.govt.nz/issues/waste/organo.htm

from the saws to a sorting table. Logs, posts and poles were also often treated in dip baths, spray tunnels or hand or mechanical spraying. The concentration of NaPCP for sapstain control was generally 0.5% w/v although in some hand spraying operation the concentration was up to 1% w/v.

In the boron diffusion process, NaPCP was also added to the boron treatment chemicals (applied in a dip bath or spray tunnel). As the majority of this timber had already been treated in the "green chain" antisapstain process, the concentration of PCP in the boric treatment solution was 0.2 w/v. If the timber had not been treated at the "green chain" stage the concentration may have been raised to 0.5% w/v.

The use of PCP and NaPCP on a site varies from a single instance up to approximately 35 years duration. On many of the sites the locations where the chemicals were used, or the treated timber was stored, were unpaved. Consequently, spills of chemicals or drippage from freshly treated timber have resulted in contamination of the ground by PCP and dioxins.

1.2 Purposes of the Study

In 2000 the Ministry for the Environment published an inventory of dioxin sources covering a wide range of processes and activities (Buckland *et al*., 2000). This inventory included an estimate of the dioxin reservoir present in soil at sawmill sites. To estimate the reservoir, the soil burdens where calculated for each area at the sites, where contaminant concentration data were available. These burdens were then summed to give a total dioxin burden per site, and this burden multiplied by the estimated number of sawmill sites in the country. In this way, the dioxin reservoir at sawmill sites was estimated to be 310 g, measured as toxic equivalents (TEQ). It was noted that this estimate was based on limited data with inherent uncertainty over the national figure

The current study was initiated to provide more definitive data over the level of dioxin contamination at sawmill sites, and to better assess the risks that such sites may pose. There are four key tasks to the study, which are to:

1. Collect more reliable and nationally representative data on the concentration of dioxins at sawmill sites;

2. Revise the existing estimate of the dioxin reservoir at sawmill sites;

3. Detail the types of environmental and risk management conditions that may be found at sawmill sites, and develop a risk profile of these sites; and

4. Identify options for risk reduction measures in New Zealand.

This paper presents the preliminary findings from the collection of more nationally representative data (Task 1). Further consultation and data collection is underway to determine volumes of contaminated soil at sites to revise the national estimate (Task 2). A full report on this study will be published by the Ministry for the Environment in late 2002.

2. THE STUDY CONTEXT

2.1 Dioxin concentrations

The interpretation of the results of this study requires an understanding of the measurement of dioxins and the expression of dioxin concentrations in terms of toxic equivalents.

Structure

Dioxin is the generic name for two groups of aromatic compounds with very similar molecular structure. These are the polychlorinated dibenzo-p-dioxins (PCDDs or dioxins) and the polychlorinated dibenzofurans (PCDFs or furans). Both groups of compounds can have up to eight chlorine atoms attached at different carbon atoms and each individual compound, of which 210 are theoretically possible, is referred to as a congener. Each specific congener is identified by the number and position of chlorine atoms around the aromatic nucleus.

Toxic Equivalents

In environmental media, the PCDDs and PCDFs occur as complex mixtures of congeners. To enable a complex, set of analytical results to be reduced to a single number, a system of toxic equivalents (TEQs) has been developed. The toxic equivalents method is based in the available toxicological and in-vitro biological data, and knowledge of structural similarities to express the toxicity of a particular PCDD or PCDF congener in terms of an equivalent amount of 2,3,7,8-tetrachlorodibeno-p-dioxin (2,3,7,8-TCDD). Multiplication of the concentration of a PCDD or PCDF congener by this toxic equivalents factor (TEF) gives a corresponding 2,3,7,8-TCDD TEQ concentration. The toxicity of any mixture of PCDDs and PCDFs, expressed as 2,3,7,8-TCDD, is derived by summation of the individual TEQ concentrations. This is reported as the 'Total TEQ' for a mixture.

Although a number of toxic equivalents schemes have been developed, the most widely adopted system to date has been the International Toxic Equivalents Factor (I-TEF) scheme (Kutz *et al*., 1990).

The I-TEF scheme has recently been revised and expanded through the auspices of the World Health Organization (WHO) (Van den Berg *et al*., 1998). Results of the site investigations in this study are reported using both TEF schemes to allow comparison with results from previous investigations using the I-TEF scheme and for future studies where the Ministry for the Environment has indicated they favour the use of the WHO-TEF scheme.

2.2 Data collection and compilation

Information on timber treatment sites, where it was believed that PCP or NaPCP had been used, has been provided by the Ministry for the Environment, Department of Labour (Occupational Safety and Health), regional councils and territorial local authorities. The information varied from simple lists of sites to comprehensive reports detailing site investigations. For some regions the information appeared to be incomplete. Only a few councils provided an estimate of quantities of PCP used on the sites. The information was

supplemented by responses to a questionnaire circulated by the New Zealand Timber Industry Federation to its members and reviewing information held by the former Timber Preservation Authority.

The number and geographical distribution of the sites is as follows.

North Island		South Island	
Northland	19	Nelson	7
Auckland	16	Tasman	11
Waikato	25	Marlborough	5
Bay of Plenty	15	West Coast	10
Hawkes Bay	9	Canterbury	56
Gisborne	5	Otago	19
Taranaki	14	Southland	7
Manawatu/Wanganui	16		
Wellington	21		

Although no complete records were ever kept it is estimated that commencing around 1950 and over the next 40 years, about 5,500 tonnes of PCP was imported into New Zealand for use in the timber industry. At the height of its use (1970s) approximately 200 tonnes/year was used for antisapstain treatment and 100 tonnes/year for preservative treatment. The available information received from all sources has been used to classify the sites based on the quantity of PCP estimated to have been used: This gave:

Very large	(approximately 1000 tonnes)	=	1
Large	(100-500 tonnes)	=	6
Medium	(20-100 tonnes)	=	28
Small	(less than 20 tonnes.)	=	220
Total			255

Whilst this estimate is roughly similar to an earlier estimate of site number (Buckland *et al*., 2000) the following points need to be emphasised:

i. the classification into small, medium, large and very large users is based on the best information available and in most instances definitive quantities of PCP use are not available;
ii. there is a significant degree of uncertainty associated with classifying some sites as small or medium users;
iii. it is possible that there are some small and medium sites included that should not be there and there are some sites missing that should be included;
iv. the very large and large users are probably well identified and none have been overlooked;
v. the distribution of sites within the various use categories is consistent with survey returns from the timber industry
vi. information was not available for approximately 40% of the estimated 255 sites. The lack of information is considered to indicate that the majority of these sites would have been small PCP users and / or of brief operating period. These sites have been allocated to the medium and small categories in the same ratio as sites where information is available.

3. SITE INVESTIGATIONS FOR THIS STUDY

3.1 Contamination Investigation Design

Two of the tasks of this study were to obtain more definitive and representative information on site contamination and to extrapolate the results to a national figure of the dioxin reservoir at sawmill and timber treatment sites. The previous estimated reservoir from antisapstain treatment reported in the dioxin inventory (80 g I-TEQ, Buckland *et al*., 2000) was based on data from one very large user and preliminary data from three small users. Therefore, a primary objective of the study was to obtain information on medium and large-scale users and to supplement that already available on small users. In designing the data collection programme, it was recognised that the majority of the sites in the country were small users.

The timber industry was approached to provide sites for investigation. A general approach to the industry was made through the NZ Timber Industry Federation with follow up communication on a one-on-one basis. A key consideration in companies offering sites for investigation was an assurance of anonymity. A total of seventeen sites were offered with the following geographical spread:

Northland, Auckland, Waikato, Bay of Plenty, Taranaki, Manawatu / Wanganui, Wellington, Tasman, Canterbury and Otago.

Of these sites, seven were classified as small users, seven medium and three large[2]. Although this did not match the ideal distribution it was decided that all should be investigated. In practice, on one small site the relevant areas had been extensively modified (and concreted) so that sampling was not possible, and on a second only limited sampling was possible. The one PCP result for this particular site was low, and consequently no dioxin analyses were undertaken.

For each site it was considered that the minimum number of samples to provide a realistic measure of the dioxin contamination was 10 (two depths at five separate locations). The study allowed for 10% of the samples to be subject to a full dioxin congener analysis and the remaining 90% an OCDD screen analysis[3]. Soon after the start of site investigations it was decided to also analyse the samples for PCP content to determine if a PCP/dioxin relationship can be established to guide future investigation / remediation work.

3.2 Contamination Investigation Results

Typical results (the full data set is too extensive to reproduce here) from the investigation are shown in Tables I (small users), II (medium users) and III (large users).

[2] No investigation of the very large PCP user was required, since extensive data was already held for this site from previous investigations.

[3] The OCDD analysis is a screening method that quantifies only the heptachlorodibenzo-p-dioxin (HpCDD) and octachlorodibenzo-p-dioxin (OCDD) congeners. These congeners were the most prevalent in PCP formulations and collectively accounted for more than 50% of the total TEQ for a sample.

Table I: PCP and Dioxin Concentrations in Soil for Small PCP Users

T&T Sample No[1]	Sample Location[2]	PCP (mg/kg)	OCDD screen[3]		Full congener	
			I-TEQ (ng/g)	WHO-TEQ (ng/g)	I-TEQ (ng/g)	WHO-TEQ (ng/g)
14A 0.1	BD	5.76	0.042	0.029		
14A 0.3	BD	7.76	0.004	0.003		
14B 0.1	ST	7.34	0.13	0.078	0.30	0.24
14B 0.3	ST	4.73	0.027	0.014		
14C 0.1	Spray	4.02	0.18	0.14		
14C 0.3	Spray	12.0	5.4	4.3		
16A 0.1	ST	2.45	0.019	0.060	0.013	0.053
16A 0.3	ST	1.45	0.19	0.13		
16 B 0.1	ST	3.72	0.020	0.016		
16B 0.3	ST	1.14	0.014	0.010		
16C 0.1	BD	0.17	0.007	0.005		
16C 0.3	BD	0.39	0.003	0.002		
16 D 0.1	BD	0.64	0.035	0.026		
16D 0.3	BD	0.54	0.013	0.010		

1. Sampling site identifier with site number, sample location and depth (in metres). For example, "14A0.1" is Site 14, sample location A, sampling depth 0.1m (core from 0.05 – 0.15m). Sampling depth 0.3m is similarly a core from 0.25-0.35m.
2. Sampling area identifier: ASD = antisapstain dip; Spray = spray tunnel; BD = boric dip; ST = sorting table.
3. TEQ levels (using the I-TEF and WHO-TEF schemes) calculated solely from the concentrations of 1,2,3,4,6,7,8-HpCDD and OCDD as determined by the OCDD screen method. Where a full congener analysis was conducted, the TEQ level recorded under OCCD screen is for 1,2,3,4,6,7,8-HpCDD and OCDD from the full congener results.

Table II: PCP and Dioxin Concentrations in Soil for Medium PCP Users

T&T Sample No	Sample location	PCP (mg/kg)	OCDD screen		Full congener	
			I-TEQ (ng/g)	WHO-TEQ (ng/g)	I-TEQ (ng/g)	WHO-TEQ (ng/g)
1A 0.1	BD	0.57	0.37	0.35		
1A 0.3	BD	0.69	0.47	0.45		
1B 0.1	BD	0.61	0.40	0.27		
1B 0.3	BD	1.1	3.6	2.2		
1C 0.1	ST	4.17	17	12		
1C 0.3	ST	16.5	28	20		
1D 0.1	ST	17.4	8.1	5.6		
1D 0.3	ST	37.2	2.8	1.6		
1E 0.1	ST	3.52	3.4	2.0		
1E 0.3	ST	13.1	13	8.0		
1F 0.15	ASD	590	54	32		
1F 0.15	ASD		47	31	94	73
1F 0.3	ASD	904	33	23		
1G 0.3	ASD	374	12	7.5		
13A 0.1	BD	49	9.3	6.2		
13A 0.1	BD		12	7.1	20	15
13A 0.3	BD	16	5.4	4.1		
13B 0.1	BD	65	21	12		
13B 0.3	BD	12	16	9.5		
13C 0.1	BD	17	19	12		
13C 0.3	BD	9.35	6.8	4.9		

See Table I for an explanation of the T&T Sample No, Sample location and OCDD screen

Table III: PCP and Dioxin Concentrations in Soil for Large PCP Users

T&T Sample No	Sample location	PCP (mg/kg)	OCDD screen		Full congener	
			I-TEQ (ng/g)	WHO-TEQ (ng/g)	I-TEQ (ng/g)	WHO-TEQ (ng/g)
7A 0.0	ST	599	4.0	3.3		
7A 0.5	ST	131	0.53	0.43		
7B 0.1	ST	8.9	0.026	0.016		
7B 0.3	ST	12.6	0.082	0.056		
7C 0.0	ST	1300	7.7	5.8		
7C 0.5	ST	2920	26	216		
7D 0.0	ST	80	0.18	0.17		
7D 0.0	ST		0.30	0.17	0.51	0.36
7D 0.5	ST	5430	21	18		
7E 0.0	ASD	51.6	6.9	4.9		
7E 0.5	ASD	372	320	275		
7E 0.5	ASD		25	16.9	90	80.6
8A 0.0	ST	3.52	0.37	0.29		
8A 0.5	ST	4.31	1.7	1.3		
8B 0.0	ST	2.44	0.36	0.25		
8B 0.5	ST	1.62	0.47	0.39		
8C 0.0	ASD	51.4	13	9.6		
8C 0.5	ASD	13.6	2.5	1.9		

See Table I for an explanation of the T&T Sample No, Sample location and OCDD screen

An evaluation of the results from the full data set shows the following:

1. In general, the lower the use category the lower the level of PCP contamination.
2. Dioxin contamination is much lower for small use sites compared with medium and large use sites. For medium and large use sites, the average dioxin concentration across all sites and depths is roughly comparable. However the range of contamination concentrations is much greater at large use sites.
3. In general both PCP and dioxin concentrations decrease with depth below the ground surface. It is well documented that dioxins, and particularly the more highly chlorinated heptachloro- and octachloro congeners are significantly less mobile in soils than PCP. The results are generally consistent with this, with a more rapid decrease (particularly for the small PCP users) in dioxin concentrations with depth compared with PCP concentrations. Whilst there is often a correlation between PCP and dioxin contamination levels, at a particular depth (see discussion below), this is not always the case.
4. Where a full congener analysis has been undertaken, the hepta and octa congeners make up approximately 95% by weight, approximately 56% of the I-TEQ values and 46% of the WHO-TEQ values. This means that the OCDD screen provides a useful method for site assessment, as 2 x the OCDD WHO TEQ level will approximate to the TEQ that would be obtained from a full profile analysis.

3.5 PCP – Dioxin Relationship

The concentrations of PCP and dioxin TEQ (derived from the OCDD screen) have been compared (Figures 3.1 and 3.2) and these show some correlation between the concentrations of the two contaminants at the two different depths. The correlation is better for results from samples at the 0.1m depth and at higher contamination levels. This suggests that in some instances PCP may be used as an indicator of likely dioxin contamination.

Figure 3.1: Logarithmic Plot of Soil PCP vs I-TEQ and WHO-TEQ
0.1m Depth

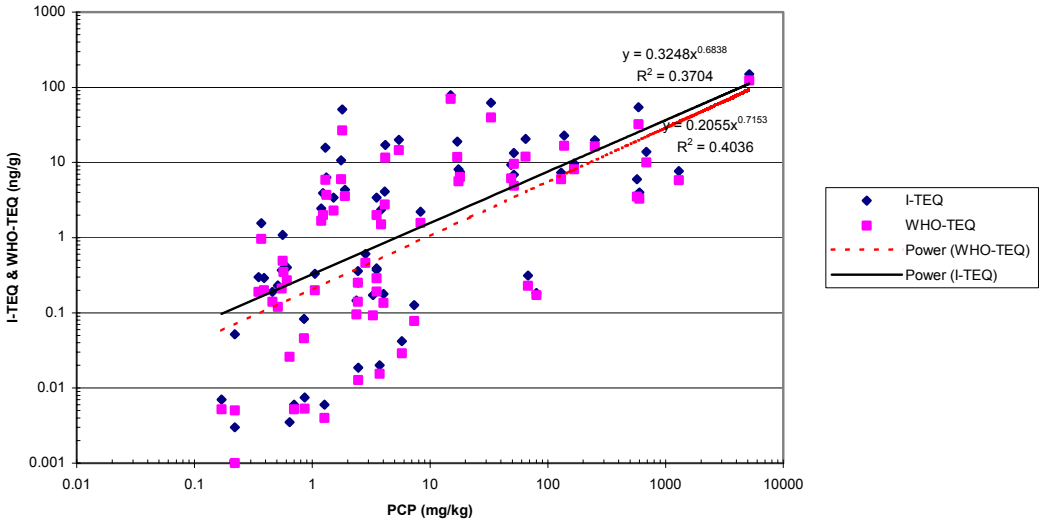
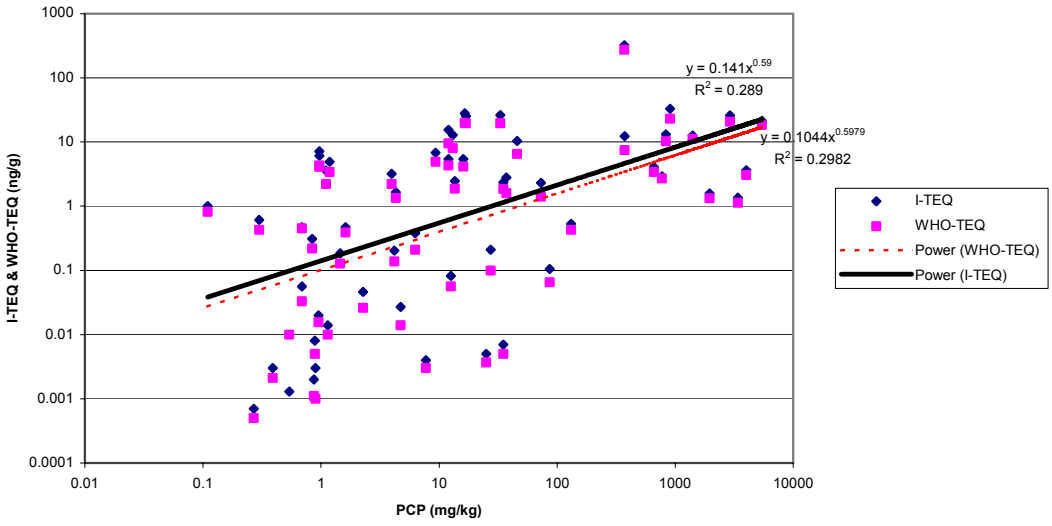


Figure 3.2: Logarithmic Plot of Soil PCP vs I-TEQ and WHO-TEQ
0.3m Depth



However, there are a number of results with poor correlation between PCP and dioxin levels (and a significant change in the relationship with depth of contamination, due to the different mobility of PCP and dioxins in soil). Therefore, it would not be appropriate to apply a generalised relationship between PCP and dioxin across different sites, due to the variability in site characteristics that may be encountered. Consequently, if PCP is to be used as an ”indicator” of dioxin contamination, it will be critical to undertake some dioxin analysis and demonstrate that this relationship holds true at each site under investigation. When comparing results against guideline values, such as in the case of validation of remedial work, the importance of sufficient dioxin testing, rather than using PCP as a surrogate, cannot be overemphasised.

4 CONCLUSIONS

A more comprehensive and reliable database of sites that used PCP in New Zealand has been developed, which will be of assistance to local government in the management of these sites, particularly at times and in situations involving a change in land use.

Considerably more data is now available on PCP and dioxin contamination on timber treatment sites. However, due to the changes that have occurred in the industry and on particular sites in the time since PCP was last used, the information that has been collected for specific processes or locations is still limited from a statistical analysis perspective.

The data generated from this study can be used to revise the existing estimate of the dioxin reservoir at timber treatment sites. However, whilst the quantity of data is substantially more than was available previously, it still does not provide the definitive picture of contamination across timber treatment sites throughout New Zealand. Therefore there will still be some inherent uncertainty in any reservoir estimate.

The study confirms the use of the OCDD screen as an excellent technique to assess dioxin contamination at a site. The data suggests a relationship between PCP and dioxin concentrations, which may allow PCP to be used as a useful surrogate for dioxin contamination. However, it will be important for the relationship to be validated on a site-by-site basis.

This paper presents only some of the initial results of this study. The Ministry for the Environment will publish a full report in late 2002, which will cover the development of a risk profile for timber treatment sites and options for risk reduction measures.

5 ACKNOWLEDGEMENTS

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