ENVI II

Assessment of the New Zealand Environment for Levels of PCDDs, PCDFs, PCBs and other Organochlorine Contaminants

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1 Introduction

In July 1995 the Ministry for the Environment initiated a major study to characterise and manage the issue of organochlorine substances in the New Zealand environment. The primary focus of this national Organochlorines Programme is on the polychlorinated dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs). These substances are found as global environmental contaminants and have been associated with a wide variety of adverse health effects [1]. However, the study is not restricted solely to the PCDDs and PCDFs. It will also investigate the polychlorinated biphenyls (PCBs); organochlorine pesticides including DDT, aldrin, dieldrin and chlordane; and pentachlorophenol (PCP).

Within the last decade a series of investigations have been carried out which have identified and assessed PCDD and PCDF emission sources and the distribution of these contaminants within New Zealand. Many of these studies have however investigated specific sources or industries [2-5] rather than providing an assessment of background environmental levels [6-9]. A fundamental component of the Organochlorines Programme is therefore a rigorous survey of the levels of PCDDs, PCDFs, and other organochlorines, in the environment. The objectives of this survey are to:

- Provide data on the level of organochlorine contaminants within New Zealand ecosystems.
- Enable the level of contamination of the New Zealand environment to be seen in an international context.
- Support the development and application of national environmental standards and guidelines for these substances in the media of air, soil and water.

In this paper, some of the initial results of this study are presented.

2 Materials and Methods

2.1 Study Design

A detailed study design was prepared that would allow for an assessment of background organochlorine contaminant levels within important ecosystems. This required a comprehensive sampling programme for the collection of air, soil, water, sediment and biota from selected sites around New Zealand. Potential sites were identified using a variety of criteria, including the nature of

the site (i.e. pristine vs. impacted), the type and extent of industrial and domestic activity within the vicinity of the site, and the compatibility of the site with other sampling sites in the study. Wherever possible, sites were chosen that were not only representative of major areas of New Zealand, but also provided for as wide a geographical coverage of the country as possible. In addition, the study design required that all procedures with respect to sampling, analysis and quality assurance were to be consistent with those applied in comparative international studies.

2.2 Sample Collection

River Water Samples

River water samples were collected from 13 rivers at 16 sites, representing 12.7 % of the total New Zealand catchment. The rivers were carefully selected as being representative of the range of uses to which the country's waterways are put. They therefore included pristine sites as well as rivers which are recipients of a range of domestic, industrial and agricultural wastes. Monthly samples (10 litres) were collected during the period January to March 1996. Typically, these were collected as four grab samples taken from four positions across the width of the river in the flowing reaches. Eel and trout samples were also collected from the same rivers.

Soil Samples

A total of 52 soil samples were collected during the period February through to May 1996. Here the country was divided into eight strata on the broad basis of climate and geology with 36 samples collected from four key land types, namely: (i) pristine land (both indigenous forest and indigenous grassland sampled), (ii) agricultural pasture on hill country land, (iii) agricultural pasture on flat land and (iv) urban residential land in provincial towns and cities. A further 16 samples were collected from the major metropolitan cities of Auckland and Christchurch.

Samples collected from pristine and agricultural lands were obtained from a number of 'sampling stations' within each strata. Soils collected from provincial and metropolitan areas were sampled from selected local authority parks or reserves. Each sample was obtained as a series of individual cores (ranging in number from 26 to 48 depending upon the land type), with each core taken to a depth of 10 cm. Litter and surficial material were removed prior to sample collection.

Other Media

As part of the Organochlorines Programme, other environmental media are also being assessed for levels of organochlorine contaminants. This involves the collection of ambient air samples over a 12 month period from 10 sites throughout the county, (20 day sampling period, approximately 4,000 m^3 sample volume) and the collection of sediment and shellfish (cockle and oyster) samples from 12 estuaries representative of New Zealand.

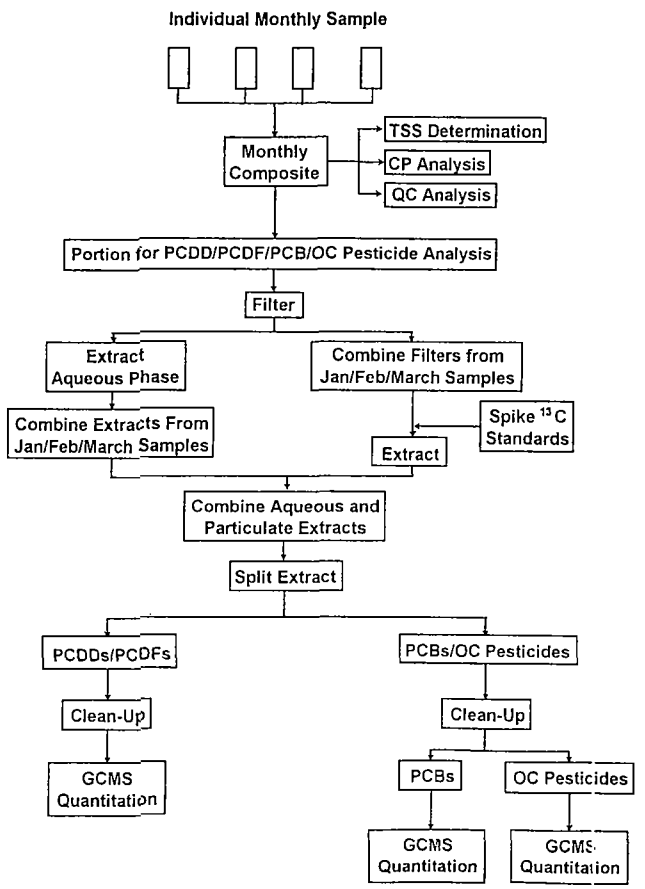
2.3 Analytical Procedures

Water Samples

Each river water sample analysed was a composite prepared from the individual January, February and March samples. A detailed sample preparation procedure was followed in order to provide a fully representative analytical sample, Figure 1. Using this procedure, a total volume of 4.8 litres of sample was taken for analysis. The aqueous phase from each monthly composite was extracted with *dichloromethane*. The filters were spiked with $^{13}C_{12}$ PCDD, PCDF, PCB and organochlorine pesticide surrogate standards (Cambridge Isotope Laboratories, Massachusetts, USA), and subject to

accelerated solvent extraction (ASE). The extracts were combined and split for PCDD/PCDF analysis (40%), PCB/organochlorine pesticide analysis (40%) and reserve (20%). The PCDD and PCDF extract was partitioned with conc H_2SO_4, and then chromatographed sequentially on columns of silica/H_2SO_4 silica, Al_2O_3, and Carbopack C (18 % dispersed on Celite). The PCB and organochlorine pesticide extract was chromatographed from florisil.

Figure 1. Analysis of River Water Samples



Quantitation was carried out by GCMS on a VG70S mass spectrometer operating in the SIM mode. Resolution for PCDDs and PCDFs was 10,000. Extracts were chromatographed on an Ultra 2 capillary column. Standard quality assurance criteria for $^{13}C_{12}$ surrogate recoveries, ion ratios (theoretical ± 10 %), signal to noise (S/N > 3:1), retention times and laboratory blanks were applied.

Soil Samples

Composite soil samples were prepared from individual soil cores using sieving in conjunction with a cone and quartering process. Only material < 2 mm was analysed. Typically a 20 g sample was spiked with $^{13}C_{12}$ standards and subject to ASE. The extract was split and for PCDD/PCDF analysis chromatographed sequentially on columns of Al_2O_3, silica/H_2SO_4 silica/silica/NaOH silica/silica, and Carbopack C. Quantitation was as described above with additional GCMS analysis on a SP2331 capillary column.

3 Results and Discussion

No PCDDs or PCDFs were quantified in any of the 16 composite water samples. Limits of detection (LODs) for the tetra-, penta- and hexa- congeners were typically 1 pg L^{-1} or less. Total toxic equivalents (I-TEQ), Table 1, were in the range 0.25 - 2.4 pg L^{-1}, with a mean value of 0.97 pg L^{-1}. The approximate 10 fold range of TEQ values determined for these samples is a result of the variation

in the LODs from the analyses rather than any inherent differences in the samples. In calculating TEQs, half the LODs were taken for non detectable congeners.

A total of 24 PCBs (tri- through to nona- chlorinated) covering the most environmentally persistent and toxicologically significant congeners were targeted for analysis. No PCBs were quantified in any of the 16 composite water samples. LODs were generally 0.01 ng L^{-1} (#77, #126, #169) and 0.1 ng L^{-1} (other PCB congeners). Toxic equivalents (WHO-ECEH/IPCS [10]) are reported in Table 1. No organochlorine pesticides (14 targeted compounds) were detected in any of the 16 composite water samples, with typical LODs in the range 0.1 - 1 ng L^{-1}.

There appears no discernible difference for those sites considered to be pristine (sites that are subject to no, or minimal, agricultural run-off and with no major point source discharges) compared to those sites which are recipients of a range of industrial and domestic wastes. However, association of contaminants with these river systems is evidenced by their bioaccumulation into resident biota populations. Initial data shows that there is significantly enhanced bioaccumulation occurring in biota collected from impacted rivers compared to biota from pristine rivers.

Table 1. TEQ [a] Values for PCDDs, PCDFs and PCBs in River Water Samples

River and Sampling Site	PCDDs/PCDFs (I-TEQ), pg L^{-1}	PCBs (TEQ)[10], pg L^{-1}
Waipa River at Whatawhata	0.90, 1.3 [b]	0.65, 0.65 [b]
Rangitaiki River at Te Teko	1.4	0.65
Waingongoro River at SH45	1.4	0.66
Wanganui River at Te Maire	2.4	0.66
Manawatu River at Opiki	1.4, 1.1 [c]	0.65, 0.66 [c]
Mohaka River at Raupunga	0.33	0.65
Tukituki River at Tamumu Bridge	1.3	0.66
Ruamahanga River at SH2	0.25	0.65
Ruamahanga River at Waihenga	0.51	0.65
Haast River at Roaring Billy	0.78	0.65
Waimakariri River at old H/W Bridge	0.70	0.66
Halswell River at McCartneys Bridge	0.97, 0.88 [c]	0.65, 0.65 [c]
Taieri River at Sutton Stream	0.32	0.65
Taieri River at Allanton	1.8, 0.86 [b]	0.66, 0.66 [b]
Mataura River at Parawa	0.47	0.66
Mataura River at Seaward Downs	0.27	0.65

a) Includes ½ limit of detection for non detectable congeners.
b) = Laboratory duplicate analysis
c) = Blind duplicate sample

The PCDD and PCDF data for the soil samples show low to background levels of these contaminants. I-TEQ values were generally in the range 0.2 to 2 pg g^{-1} dry weight, and were dominated by non detectable congeners (for which one half the LOD was taken). The most common congeners present were the HpCDDs and OCDD. These congeners were generally more abundant in samples taken from

urban centres compared to samples taken from pristine and agricultural environments. PCDD and PCDF levels determined are consistently lower than those reported in several European studies [11-13].

4. Conclusion

A major study is being undertaken aimed at determining background environmental levels of PCDDs, PCDFs and other organochlorine contaminants in the New Zealand environment. No PCDDs or PCDFs were detected at low pg L^{-1} limits of detection in composite samples collected from 13 river systems. No PCBs or organochlorine pesticides were similarly detected in these samples. Low to background levels of PCDDs, predominantly HpCDD and OCDD, and PCDFs, were detected in a series of soil samples. Highest concentrations were found in samples collected from urban areas in provincial and metropolitan centres. Generally, the I-TEQ values were lower than those reported in soils from comparable European studies.

5 References

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