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Extended 20 Day Sampling of Ambient Air for PCDDs, PCDFs, PCBs, OC Pesticides and Chlorophenols.

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Abstract

Ambient air samples were collected from ten locations throughout New Zealand as part of a major environmental survey. Each sample was collected, nominally for 20 days and analysed for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), persistent organochlorine (OC) pesticides and chlorophenols (CPs). The volume of gas sampled was typically 4000m³. The recoveries of the isotopically labelled surrogate standards spiked prior to sampling were calculated for each individual sample, and ranged from 37-136% for the PCDDs and PCDFs, 29-143% for the PCBs, 25-141% for the OC pesticides and 7-110% for the chlorophenols.

Introduction

In 1995 a major survey, The Organochlorines Programme, was initiated by the New Zealand Ministry for the Environment to measure and characterise the levels of a range of persistent organochlorine contaminants^{1,2}. As part of this study, ambient air samples were collected from a range of locations over the period March 1996 to March 1997. This paper will discuss the ambient air sampling programme and the analytical procedures used. Sampling and laboratory recovery data and the limits of detection achieved is presented for samples collected in the first six months for PCDDs, PCDFs, PCBs, OCs and CPs. Further information will be presented after the completion of the sampling and analysis programmes.

For this environmental survey, careful consideration was given to the choice of sampling locations¹ that were representative of environmental ecosystems or geographical areas of the country. For the ambient air sampling, ten locations were chosen that covered baseline (pristine) sites, agricultural environments, provincial towns and cities, and major metropolitan and industrial environments (Figure 1). Six samples were collected over alternate months at six of the sites, with four samples being collected from each of the four remaining locations. Co-located samples were also collected as part of the quality assurance programme. Samples were collected, nominally for 20 days and typically realised sample volumes of 4000m³. This extended time

period was designed to provide for a greater time integrated sampling duration so as to minimise the impact of unexpected pollution events.

Sample Collection

Each sample was collected using a General Metal Works PS-1 high volume air sampler (Graseby GMW, Ohio). Each sampler was typically operated at a sampling rate of 150L min⁻¹. The sample collection medium used, was a glass fibre filter followed by a glass cartridge containing a polyurethane foam (PUF) enclosing a bed of XAD-2 resin³⁾. The PUF and XAD-2 resin

combination was chosen as it has been demonstrated to have a greater affinity for some of the more volatile contaminants³⁾. All sample collection media were appropriately prepared prior to sampling. The PS-1 samplers were calibrated either prior to or immediately following sampling.

Traditionally, ambient air sample volumes collected have been in the range of 1000m³.

This sampling programme will give a sample collection volume of approximately 4000m³. This follows an increasing trend to collect larger sample volumes⁴⁾ over extended periods of time⁵⁾.

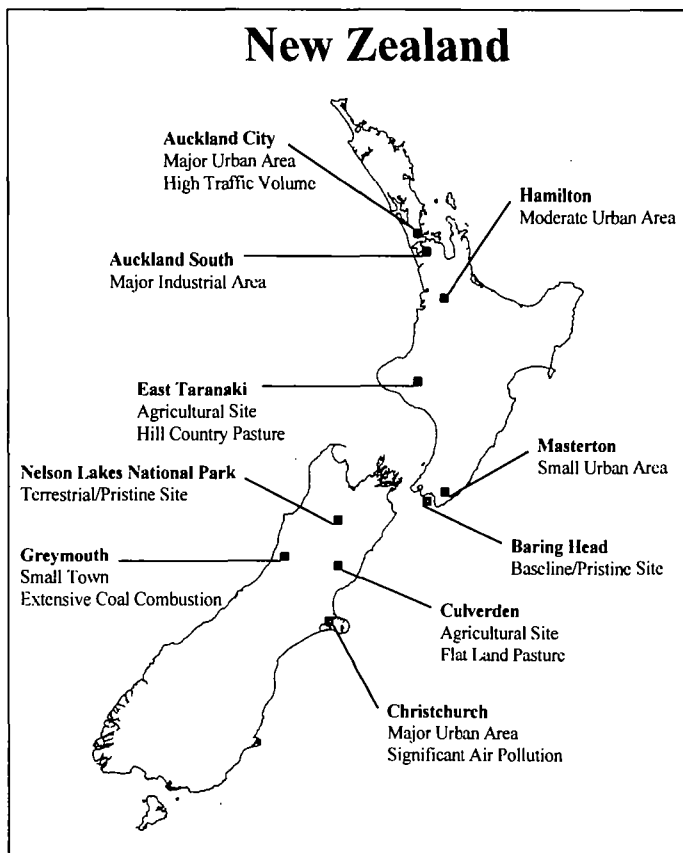


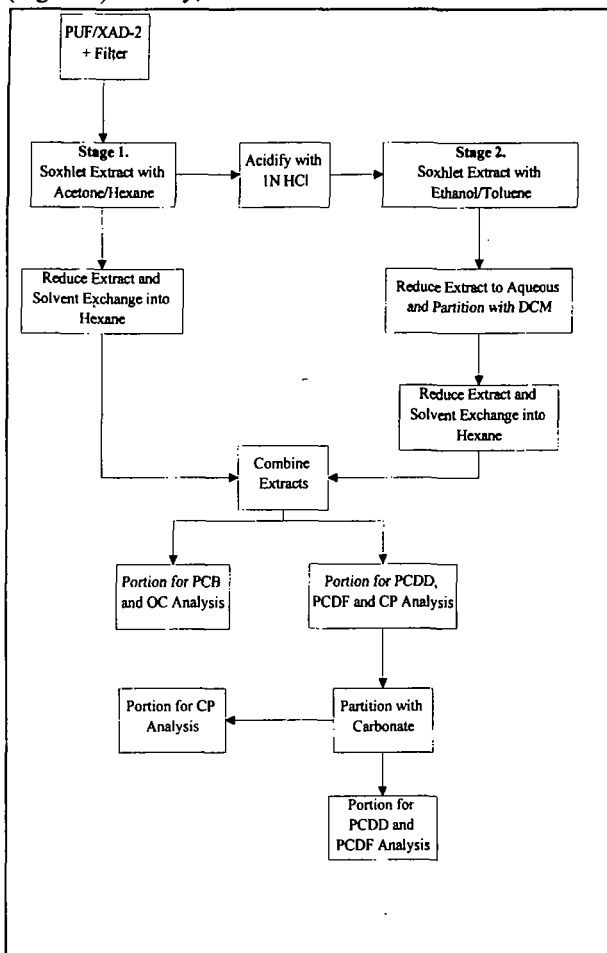
Figure 1. Sampling Sites and Characteristics.

Extraction and Analysis

For all contaminant groups analysed the PUF cartridge was spiked prior to sampling with a range of isotopically labelled surrogate standards. Once the sample was collected the PUF cartridge and associated filters were returned to the laboratory where a laboratory recovery spike was added for the PCDDs, PCDFs and PCBs (Table 2). The complexity of collecting and analysing a

Dioxin '97, Indianapolis, Indiana, USA

single 4000m³ sample for a range of analytes with differing physicochemical properties predisposes that some parts of the analysis will be compromised to achieve the overall result. The methodology used for the analysis of the PCDDs, PCDFs, PCBs and OC pesticide contaminants has been reported elsewhere⁶⁾. Briefly, the extraction was performed in two stages (Figure 2). Firstly, soxhlet extraction with 1:1 acetone/hexane (16 hours), followed by



acidification of the PUF/XAD-2 resin and filter with 1N HCl and soxhlet extraction with 68%/32% ethanol/toluene (16 hours). Without acidification between extractions the recovery of the CPs, particularly the tetrachlorophenols and PCP is markedly reduced. Initial acidification is not possible due to the acid sensitivity of some of the OC pesticides and the use of acetone as an extraction solvent. The combined extracts were split for PCDDs/PCDFs/CPs 40%, PCB/OC pesticides 40%, reserve 20%.

The PCDD, PCDF and CP fraction was partitioned with aqueous carbonate to extract the CPs. The CPs were then converted to their acetates by *in situ* acetylation with acetic anhydride. The PCDD and PCDF fraction was then partitioned with concentrated acid and distilled water. Purification was effected by solid phase clean up on a column of acid and base modified silica gels, followed by column chromatography using alumina and carbon dispersed on Celite.

Figure 2. Schematic of Extraction Methodologies.

The PCB and OC fraction was purified using gel permeation chromatography. Separation of the coplanar PCBs from the non-coplanar PCBs was effected using a FlorisilTM column.

Following the analysis of the PCBs by mass spectrometry, the co-planar and non co-planar fractions were combined for analysis of OC pesticides.

The analysis of all analytes was performed by high resolution gas chromatography high resolution mass spectrometry (HRGC/HRMS) using a VG70.

ANALYSIS

Target analytes and routine limits of detection for the various organochlorine contaminants is given in Table 1.

Table 1. Typical Limits of Detection for Contaminant Groups.

Contaminant Group	Typical Limit of Detection (units)
TCDDs and TCDFs	0.1 - 1 (fg m ³)
Co-planar PCBs (PCB#77 [†] , PCB#126, PCB#169)	0.002 - 0.02 (pg m ³)
Non Co-planar PCBs [‡]	0.01 - 0.1 (pg m ³)
OC Pesticides [‡]	0.02 - 0.2 (pg m ³)
PCP	0.05 (pg m ³)

† PCB#28+PCB#31, PCB#52, PCB#101, PCB#99, PCB#123, PCB#118, PCB#114, PCB#105, PCB#153, PCB#138, PCB#167, PCB#156, PCB#157, PCB#187, PCB#183, PCB#180, PCB#170, PCB#170, PCB#189, PCB#202, PCB#194, PCB#206.

‡ alpha-HCH, beta-HCH, gamma-HCH, HCB, Aldrin, Dieldrin, Heptachlor, Heptachlor epoxide, alpha-chlordane, gamma-chlordane, pp-DDE, pp-TDE, op-DDT, pp-DDT.

Results

Average recovery data for both the surrogate standards spiked prior to sampling and the laboratory recovery standards are given in Table 2. For the OC pesticides and CPs where no laboratory recovery spike was used, the recoveries, the laboratory matrix spikes are given.

The average recovery of the PCDD and PCDF congeners show that the collection of a sample volume of 4000m³ of ambient does not appear to effect the capture and retention of these contaminants. The average recovery of ³⁷Cl, TCDD, the laboratory recovery spike, is consistent with the recoveries calculated for the surrogate standards.

Similarly, the average recovery of the PCB congeners also shows that the collection of a sample volume of 4000m³ of ambient air does not appear to effect the capture and retention of these contaminants. However, the average recovery of PCB#28 is consistently lower than the average recoveries of the other surrogate standards. This may be due to either breakthrough of this during sampling or loss in the laboratory due to its volatility.

Regarding recoveries of the OC pesticide and CP surrogate standards, there is little difference in the average recoveries found when compared to the laboratory matrix spike data.

Dioxin '97, Indianapolis, Indiana, USA

Conclusion

The collection of 4000m³ of ambient air over a 20 day time frame, coupled with modern analytical techniques has proven to be successful for the collection of time integrated samples for a broad range of contaminants with different physiochemical properties. Lower than normal limits of detection are also achieved due to the 4000m³ volumes collected.

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References

1. Ministry for the Environment; Study Design for the Assessment of Organochlorine Contaminant Levels in the New Zealand Environment; **1995**.
2. Buckland, S.J.; Ellis, H.K.; Salter, R. T.; Assessment of the New Zealand Environment for Levels of PCDDs, PCDFs, PCBs and other Organochlorine Contaminants; *Organohalogen Compounds*; **1996**, 28, 140-145.
3. Wagel, D.J.; Tieman, T.O.; Taylor, M.L.; Garrett, J.H.; VanNess, G.F.; Solch, J.G.; Harden, L.A.; Assessments of Ambient Air Sampling Techniques for Collecting Airbourne Polyhalogenated Dibenzo-*p*-dioxins (PCDD), Dibenzofurans (PCDF) and Biphenyls (PCB); *Chemosphere*; **1989**, 18, 177-184.
4. Broman, D.; Näf, C.; Zebühr, Y.; Long-term High- and Low Volume Air Sampling of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans and Polycyclic Aromatic Hydrocarbons along a Transect from Urban to Remote Areas on the Swedish Baltic Coast; *Environ. Sci. Technol*; **1991**, 25, 11, 1841-1850.
5. Hiester, E.; Bruckmann, P.; Böhm, R.; Eynck, P.; Gerlach, A.; Müller, W.; Ristow, H.; Pronounced Decrease of PCDD/PCDF Burden in Ambient Air; *Organohalogen Compounds*; **1995**, 24, 147-152.
6. Hannah, D.J.; Banks, L.; Buckland, S.J.; Cloughly, M.; Czochanska, Z.; Duthie, J.; Fry, J.M.; Green, N.J.L.; Gray, D.; Jones, P.D.; Leathem, S.; Lister, A.R.; Porter, L.J.; Taucher, J.A.; van Maanen, T.; Multi-Analyte Determination of Organic Contaminants in Incinerator Emissions and Ambient Air; *Organohalogen Compounds*; **1993**, 11, 159-162.
7. Ballschimter, K.; Zell, M.; Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography. Composition of Technical Aroclor- and Clophen-PCB Mixtures; *Fresenius Z. Anal. Chem.*; **1980**, 302, 20-31.

Table 2. Recovery of Isotopically Labelled Surrogate Standards.

PCDDs and PCDFs			PCBs			OC Pesticides (Samples)			Chlorophenols (Samples)		
Congener n=21	Recovery (%)	Range (%)	Congener n=21	Recovery (%)	Range (%)	n=21	Recovery (%)	Range (%)	n=21	Recovery (%)	Range (%)
2378 TCDF	84	(37-116)	PCB#77	89	(50-114)	Gamma-HCH	54	(25-117)	246 TCP	38	(7-86)
2378 TCDD	102	(61-136)	PCB#28	52	(29-85)	HCB	56	(27-83)	245 TCP	52	(7-107)
12378 PeCDF	95	(53-128)	PCB#101	104	(68-143)	Dieldrin	61	(30-141)	2345 TeCP	70	(34-110)
23478 PeCDF	93	(39-133)	PCB#153	82	(53-109)	pp-DDE	94	(46-113)	PCP	55	(16-107)
12378 PeCDD	90	(59-120)	PCB#180	102	(61-139)	pp-DDT	52	(32-80)			
123478 HxCDF	80	(41-105)									
123678 HxCDF	80	(42-117)	PCB#52 ^B	72	(37-110)						
234678 HxCDF	91	(61-115)	PCB#126 ^B	76	(31-108)						
123789 HxCDF	82	(49-100)	PCB#169 ^B	89	(55-122)						
123478 HxCDD	98	(64-118)	PCB#202 ^B	111	(77-147)						
123678 HxCDD	91	(64-124)									
1234678 HpCDF	78	(37-112)									
1234789 HpCDF	85	(52-117)									
1234678 HpCDD	85	(66-116)									
OCDD	83	(56-120)									
³⁷ Cl ₄ 1234 TCDD ^A	77	(50-105)									

OC Pesticides (Matrix Spikes)			Chlorophenols (Matrix Spikes)		
n=4	Recovery (%)	Range (%)	n=4	Recovery (%)	Range (%)
Gamma-HCH	67	(60-76)	246 TCP	47	(19-56)
HCB	73	(66-79)	245 TCP	71	(35-109)
Dieldrin	68	(58-75)	2345 TeCP	55	(28-78)
pp-DDE	96	(92-101)	PCP	60	(26-119)
pp-DDT	64	(50-68)			

A PCDD and PCDF Laboratory Recovery Spike.
B PCB Laboratory Recovery Spikes.