PCDDs, PCDFs and PCBs in Ambient Air in New Zealand

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Introduction

Since 1995, the New Zealand Ministry for the Environment has undertaken a major environmental investigation to measure ambient concentrations of organochlorines (PCDDs, PCDFs, PCBs, persistent organochlorine pesticides and chlorophenols) in a range of ecosystems. The information from this study will assist in the development of risk based acceptance criteria for organochlorines in air, soil, sediment and water. Details on the background to this environmental survey[1], and initial contaminant concentration data for soil[2] and aquatic environments[3] have previously been reported. This paper reports data on the levels of PCDDs, PCDFs and PCBs in ambient air. A detailed research report on this component of the study[4], and reports on organochlorines in soil, rivers and estuaries are available from the Ministry's web site[5].

Materials and Methods

A total of 52 air samples were collected from reference, rural, urban and industrial sites. Reference sites were located at Baring Head and Nelson Lakes National Park, and rural sites at Te Wera, Taranaki, and Culverden, Canterbury. Urban sites at Hamilton, Masterton, Greymouth and Christchurch were located within, or adjacent to, residential areas, whilst a site at Auckland City was at the intersection of a major arterial road. The industrial site was located at Auckland South.

Air samples were collected from March 1996 to May 1997 using General Metal Works PS-1 high volume air samplers. The sampling method was consistent with the approach given in US EPA Methods T04 and T09[6]. The samplers were loaded with a GF/C filter for collection of the particulate phase and a sampling cartridge holding PUF/XAD-2 adsorbent for collection of the gaseous phase. The filter, PUF and XAD-2 were all precleaned, and the PUF/XAD-2 cartridge was spiked with a range of ^{13}C surrogate standards prior to sample collection. Samplers were fully calibrated before each sampling period and checked upon completion. At all sites except Baring Head, extended sampling was undertaken by operating the samplers continuously over a period of typically 20 days at a flow rate of approximately 150 litres per minute[7]. Air sample volumes of approximately 4,000 m^3 of air were collected. At the Baring Head reference site, the sampler was operated intermittently for the periods when the wind was coming only from a southerly direction. This will reflect southern ocean maritime conditions. Over a 20 day sampling period and at a flow rate of 270 litres per minute, up to approximately 2,000 m^3 of air was collected at Baring Head. Quality control samples consisted of collocated samples, field blanks and equipment rinsate blanks.

All samples were analysed by GC high resolution MS as previously reported[1]. Full details on the sampling and analytical procedures are reported by Buckland *et al*.[4]

Results and Discussion

PCDDs and PCDFs

Concentrations of PCDDs and PCDFs measured are given in Table 1. The data reported includes half limit of detection values for non-detected congeners.

Table 1 PCDD and PCDF I-TEQ concentrations in New Zealand air (fg I-TEQ m^{-3})

	Min.	Max.	Median	Mean
Reference sites				
Baring Head (6)[1,2]	1.21	7.48	2.52	3.43
Nelson Lakes (4)	0.77	1.75	1.52	1.39
Rural sites				
Te Wera (5)	1.66	31.7	18.0	16.0
Culverden (6)	0.94	9.88	2.80	3.77
Urban sites				
Hamilton (6 + 2 CS)	6.99	234	17.1	53.6
Masterton (5)	6.73	158	42.5	57.5
Greymouth (5)	13.0	262	45.6	83.9
Christchurch (6)	6.15	232	31.7	77.3
Auckland City (4)	16.5	40.8	27.5	28.0
Industrial site				
Auckland South (5 + 3 CS)	40.3	1170	149	317

1 Number in parenthesis is the number of valid samples collected from each site.
2 Only 4 of the 6 samples from Baring Head were successfully analysed for PCDDs and PCDFs.
CS = Collocated sample.

Very few PCDD and PCDF congeners were measured at the reference sites, these being primarily HpCDDs and OCDD, and non 2,3,7,8-TCDFs. For both reference sites, particularly for Baring Head where smaller sample volumes were collected, the inclusion of half LOD values contributed markedly to the I-TEQ levels determined. At the rural Culverden site and the urban sites in Hamilton, Masterton, Christchurch and Greymouth, an order of magnitude variation was observed in PCDD and PCDF levels over the year. At these sites, the highest concentrations were measured in the colder winter months, with the lowest concentrations in the warmer summer months. This is shown for Christchurch in Figure 1.

PCDD and PCDF concentrations had a significant negative correlation (95% confidence interval) to mean night time temperatures at Culverden ($p = 0.007$), Hamilton ($p = 0.04$), Masterton ($p = 0.03$) and Christchurch ($p = 0.006$), and were positively correlated to the aromatic hydrocarbon retene at Masterton ($p = 0.07$) and Christchurch ($p = 0.002$).

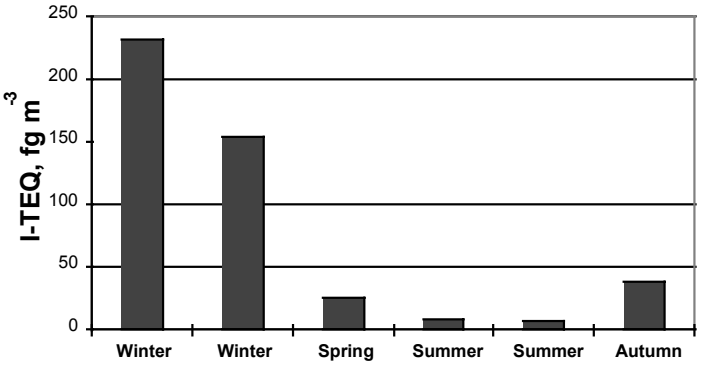

Figure 1 I-TEQ levels in Christchurch air

Retene has been identified as a molecular marker of wood combustion in ambient air[8]. PCDD and PCDF concentrations were also significantly correlated with total particulate concentrations ($p = 0.03$) and PM_{10} concentrations ($p = 0.0002$) at Christchurch. These data would suggest that domestic emissions, particularly from wood burning for home heating, are an important source of PCDDs and PCDFs in New Zealand.

In contrast, the Auckland City site, which was selected to assess impacts from motor vehicle emissions, had remarkably stable PCDD and PCDF air concentrations compared to other urban areas. These comparatively uniform concentrations are consistent with the continuous and relatively constant emission that would be expected from motor vehicles. Industrial impacts were observed at Auckland South, with all samples from this site recording elevated PCDD and PCDF concentrations compared to other sites at a similar time of year.

PCBs

PCB air concentrations, measured as the sum of 25 congeners, were fairly constant throughout the monitoring programme (Table 2). For any site, the minimum and maximum concentrations for the sum of PCB congeners were typically within ±50% of the mean of all samples collected at that site.

Whilst the intra-site variability was generally small, marked inter-site variability in PCB concentrations was observed (Figure 2). This was particularly evident when samples from the reference and rural sites were compared with samples collected from urban and industrial sites. Thus, median concentrations at the reference and rural sites were similar and were significantly lower than the median concentrations at the urban and industrial sites. Similarly, median PCB concentrations at the urban sites were generally similar, and were significantly lower than the median concentration at the industrial Auckland South site.

Table 2 Sum of PCB congener concentrations in New Zealand air (pg m^{-3})

	Min.	Max.	Median	Mean
Reference sites				
Baring Head	6.98	18.2	11.2	11.6
Nelson Lakes	5.72	13.9	11.6	10.7
Rural sites				
Te Wera	5.09	30.0	12.4	14.8
Culverden	4.99	14.5	9.60	10.3
Urban sites				
Hamilton	41.6	102	68.3	69.7
Masterton	34.9	67.1	50.4	50.7
Greymouth	30.7	66.9	39.5	47.8
Christchurch	29.9	48.6	42.6	41.8
Auckland City	102	129	109	112
Industrial site				
Auckland South	210	471	300	304

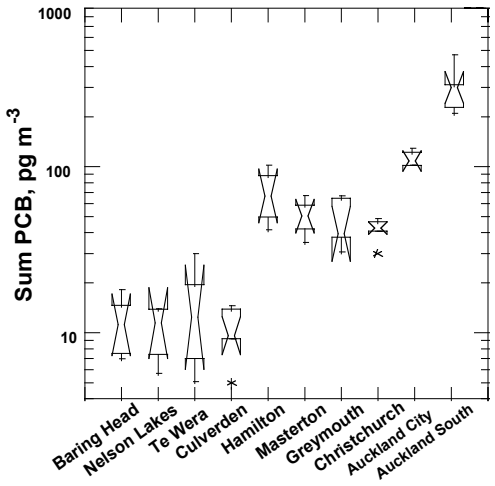

Figure 2 Sum of PCBs in New Zealand air

Seasonal variations in PCB concentrations were also observed during the study, broadly corresponding to seasonal changes. Thus, the minimum concentrations were generally found in the winter months and the maximum concentrations in the summer months. PCB air levels were significantly correlated to mean day time temperatures at the urban sites ($p = 0.00006$), although they were less well correlated at the rural sites (Figure 3). At all sites, the congener profiles for all samples were dominated by the less highly chlorinated, more volatile, PCBs.

This observation, that air levels with day time temperatures, supports the view

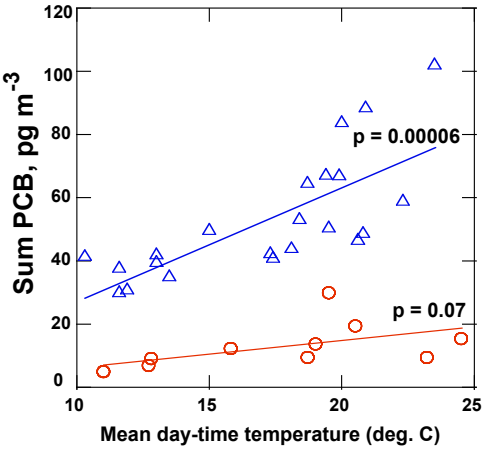

Figure 3 PCB air concentrations with mean day-time temperature
[Δ = urban sites, o = rural sites].

and the relationship of

volatilisation/environmental recycling from reservoir sources has a dominant influence on PCB air levels measured in New Zealand.

References

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