

ATMOSPHERIC CONCENTRATIONS OF PCDD/Fs AND PCBs IN AIR FROM BRISBANE, AUSTRALIA

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Introduction

The atmosphere is a key pathway for the distribution of dioxins and dioxin-like chemicals and ultimately the majority of the human body-burden of these chemicals has involved atmospheric transport and deposition of these chemicals. As a result, monitoring programs for these chemicals have been carried out in many countries. However, for the Southern Hemisphere and particularly for Australia to date little data are available and only in September 2002 an Australian wide monitoring program has been initiated in which dioxin-like chemicals are investigated at 9 Sites covering various geographical regions and different exposure scenarios (remote, agriculture, urban and industrial). In preparation for this wider investigation we carried out initial investigations in the winter of 2002 to evaluate the concentrations of dioxin-like chemicals at an urban and a rural site near Brisbane, the capital of Queensland, in the north-eastern state of Australia.

Methods

Sampling Sites

Two sampling sites were selected for this study, with both sites being monitoring sites of the Queensland EPA's basic air monitoring program. The sites were selected to represent an urban/industrial and rural exposures proximate however to the urban center, respectively. In detail, sampling site 1 was located in a north-eastern suburb of Brisbane that is bordered largely by Brisbane's international and domestic airports as well as the Brisbane River and is categorised by the Queensland EPA as a light-industrial area. Sampling site 2 located about 55 km SW of Brisbane, in rural SE Queensland is characterised by agricultural/grazing activities. The site location is approximately 150 m from a highway and 20 km from a power station. Samples were collected using a filter/adsorbent system (GFF/PUF/XAD-2) similar to the system that has been described and tested previously⁴. The sampler was run constantly at 4.5 m³ h⁻¹ collecting in excess of 2000 m³ per month (corrected for pressure drop in the system) at each site using a dry vane pump.

Analysis of PCDD/PCDF and dioxin-like PCB Analyses

Standards were all purchased from Wellington Laboratories (Ontario, Canada) and were used for calibration, quantification and determination of recovery of PCDD/PCDF and dioxin-like PCBs. Solvents were purchased as pesticide-quality standard and used as received. All chromatographic columns were purchased from Fluid Management Systems. (Waltham, MA, USA) and were used without any further treatment. They comprised multi-layer (basic/neutral/ acidic) silica, alumina and PX-21 carbon dispersed on celite.

For extraction the filter/PUF/XAD-2 resin combinations were transferred to a large soxhlet extractor, spiked with a known amount of the respective PCDDs/PCDFs and dioxin-like PCB isotopically labeled $^{13}\text{C}_{12}$ surrogate spiking solutions and then exhaustively extracted with ethanol:toluene (68:32). The dried extracts were then cleaned-up on the Power-Prep™ system. Samples were analysed on GCMS (Agilent 6890 GC coupled with a MAT95XL HRMS). A DB-5 (J & W Scientific, Folsom, CA, USA) capillary column (60m x 0.25mm i.d., film thickness 0.25 μm) was used as the primary analytical column with a DB-Dioxin (J & W Scientific, Folsom, CA, USA) capillary column (60m x 0.25mm i.d., film thickness 0.15 μm) used as the secondary analytical column for quantification of those 2,3,7,8- CDD & CDF congeners not completely resolved on the DB-5 column. Resolution was maintained at 10,000 (10 % valley definition) throughout the sample sequence. Multiple ion detection (MID) experiments were performed in the electron impact mode with monitoring of the exact masses of either M^+ $[\text{M}+2]^+$ or $[\text{M}+4]^+$ ions for native and labeled compounds. Individual congeners are identified using the GC retention time and ion abundance ratios with reference to internal standards.

Results and Discussion

PCDD/Fs were detectable in all air samples that have been collected. The concentration of the sum of detectable tetra-octachlorinated PCDD/Fs ($\Sigma\text{PCDD/Fs}$) ranged from about 65 fg/m^3 in June 2002 at Site 2 to about 2500 fg/m^3 at Site 1 in the same month (Figure 1). For Site 1 the concentration during the first sampling period i.e., June 2002 was elevated compared to the other periods. On a toxicity equivalency basis (WHO-TEQ_{DF}) the monthly air-concentrations ranged from 0.3 $\text{fg TE}/\text{m}^3$ in July 2002 at Site 2 to about 29 $\text{fg TE}/\text{m}^3$ at Site 1 in June 2002 (Figure 2). Although the concentrations at both sites varied substantially the data clearly showed a trend of substantially higher concentrations of PCDD/Fs at Site 1 compared to Site 2. For example if concentrations are expressed on WHO-TEQ_{DF} using only detectable PCDD/Fs then during all sampling periods the levels were between a factor 12 and 35 lower at Site 2 compared to Site 1.

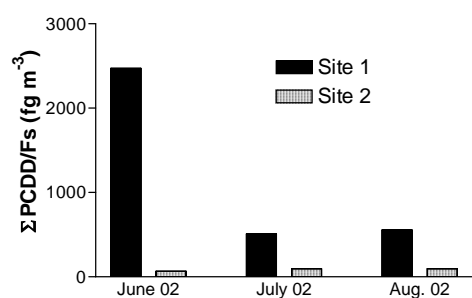


Figure 1: Concentrations of $\Sigma\text{PCDD/Fs}$ at Site 1 and Site 2 in monthly air samples collected from June to August 2002

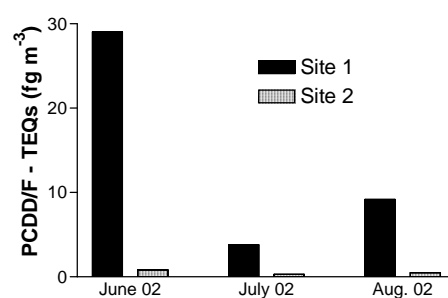


Figure 2: Concentrations of PCDD/Fs expressed as WHO-TEQ_{DF} at Site 1 and Site 2 in monthly air samples collected from June to August 2002

The difference between the two sampling sites is also observable in the PCDD/F congener and homologue profiles. The elevated concentrations observed in the sample collected in June 2002 at Site 1 showed substantial higher contribution of lower chlorinated PCDD/Fs to the Σ PCDD/Fs (Figure 2). For example the correlation between the concentration of the sum PCDD/Fs and lower chlorinated PCDFs (i.e. TCDFs and PeCDFs) is about 0.99 whereas OCDD does not correlate well with the concentrations expressed as Σ PCDD/F despite also being a key contributor to the sum PCDD/Fs.

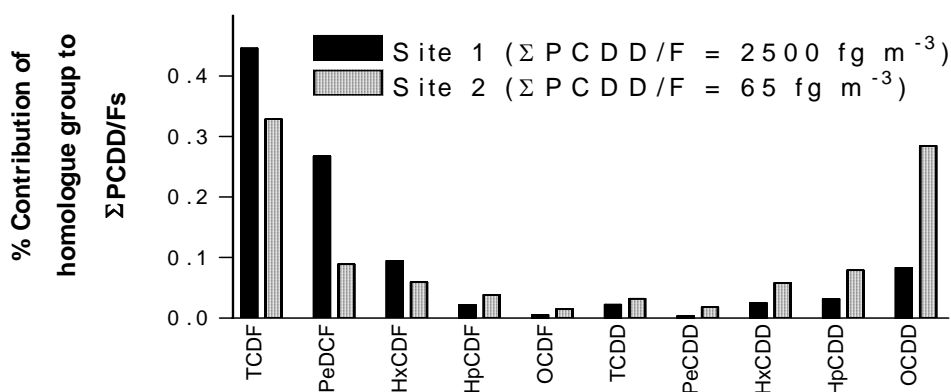


Figure 3: Homologue profile of PCDD/Fs in the June 2002 air samples from Sites 1 and 2.

Comparison of the data from this study with other studies shows that the PCDD/F concentrations observed at Site 2 are very low. Few data have been published on atmospheric levels of dioxins in non-urban regions. The concentrations found at Site 2 are similar or slightly higher compared with data from a control site used in a study by the NSW-EPA located in rural New South Wales⁶, data reported for the relatively remote agricultural sites and the remote reference site during New Zealand's Organochlorine Program¹ and lower than most results presented from the National Dioxin Network in the US which included 6 sites in National Parks². In contrast to the PCDD/F concentrations at Site 2 the concentrations observed at Site 1 are similar to those observed previously in the Brisbane area⁵ as well as to concentrations found in urban area in Sydney^{6,7}, industrial areas in Wollongong⁶, Auckland (New Zealand)¹ as well as rural area in the US² or 'semi-rural' areas in the UK³.

Dioxin-like PCBs were only analyzed during the last period of this study, in the air sample collected in August 2003. Similar to PCDD/Fs, the concentrations of PCBs congeners at Site 1 were substantially (i.e. an order of magnitude) higher than at Site 2. PCB 118 was with about 210 fg/m³ at Site 2 and 2 pg/m³ at Site 1 the dominant dioxin-like PCB. The concentration of PCB118 in the air from Site 2 is similar to concentrations observed at rural and remote reference sites in the

New Zealand study ¹. The most potent of the PCBs, PCB 126 with a TEF of 0.1 was also detectable in both air samples contributing with about 10 % to the TE value at Site 1 and more than 20 % to the TE value for detectable congeners at Site 2.

Table 1 Concentration of PCBs (pg/m³) in air samples from Sites 1 and 2 during sampling in August 2002

	Site 1	Site 2
PCB 77	244	22
PCB 81	15	1.9
PCB 105	800	78
PCB 114	56	<8
PCB 118	1960	212
PCB 123	98	8.4
PCB 126	16	1.4
PCB 156	145	17
PCB 157	31	<2
PCB 167	212	27
PCB 169	1	<0.1
PCB 189	7.6	<0.2

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