

Measurement of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in wet deposition at two Integrated Atmospheric Deposition Network (IADN) master stations in the Great Lakes.

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Introduction

It has been known for several decades that persistent organic pollutants (POPs) and other anthropogenic pollutants are distributed globally by the atmosphere. In particular, numerous studies of toxic substances in the Great Lakes Basin have identified the atmosphere as the pathway for transporting contaminants originating from major sources outside the Basin to the lakes^{1,2}. The binational (Canada/United States) Integrated Atmospheric Deposition Network (IADN) is one program which measures the concentrations and deposition of atmospheric contaminants on a Basin wide (i.e., regional) scale. The IADN network consists of a master monitoring station located on each of the five Great Lakes and several satellite stations. Specifically, the goals of the program are to determine the temporal trends and spatial distributions of atmospheric pollutants in both air and precipitation in the Basin. Knowledge of these is important both scientifically and politically.

Polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) are two groups of persistent, semivolatile and toxicologically significant trace organic contaminants. They enter the environment in ultra-trace amounts from various combustion sources and as chemical impurities in a range of manufactured organochlorine products^{3,4}. They may have relatively localized sources, but once emitted into the atmosphere, they become widely dispersed geographically. Lohmann and Jones⁵ have reviewed the levels, behavior and processes PCDD/Fs in air and deposition. Eitzer and Hites have also reported on their concentrations in ambient air and rain in the Great Lakes⁶. The removal of POPs from the atmosphere can occur through wet and dry deposition, and chemical transformations. The current study was initiated to investigate the temporal trends and spatial distributions of polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) in wet-only precipitation at two IADN master stations (Lakes Huron and Ontario).

Material and Methods

Sampling: The collection of precipitation samples has been described in detail previously⁷. Briefly, the samples were collected using a modified MIC Sangamo wet-only precipitation collector. The sampler is equipped with a stainless steel square funnel (45 cm x 45 cm x 28 cm). An insulated cabin under the funnel houses the 4-L amber glass sampling bottles and its temperature maintained during the winter. Each sampling bottle is pre-filled with 250 ml of high purity grade methylene chloride and attached to an overflow bottle. At the end of a 2-week period, or whenever the sampling bottle was full, the funnel was rinsed with fresh methylene chloride, and the sample bottle was changed. If no precipitation occurred during the 2-week period, the bottle was changed in the usual manner and submitted as a field blank. The aqueous phase was separated from the solvent in a separatory funnel and its volume measured. It was then extracted twice with fresh methylene chloride. The combined extracts were sent to the Analysis and Air Quality Division, at the Environmental Technology Center, of Environment Canada. Sampling was carried out monthly during the period May 2004–December 2004.

Analysis: The dichloromethane extract is initially spiked with ¹³C₁₂-labelled 2,3,7,8 PCDD/F substituted isomers as surrogate standards. The extract is then dried through sodium sulphate, concentrated by rotary evaporation and exchanged to hexane. The concentrated extract is then passed through a multilayer silica column containing layers of silver nitrate fixed onto silica (1.5g), activated silica (1g), sodium hydroxide/silica (2g), activated silica (1g), sulphuric acid/silica (4g), and activated silica (2g). The column is capped with a layer of sodium sulphate. 50 mL of 2 % dichloromethane in hexane is used to elute the column. The extract is then exchanged to hexane and passed through an activated basic alumina column (2.5g) and eluted with 30 ml of hexane followed by 20 mL of 2 % dichloromethane in hexane. The PCDD/PCDF are eluted with 30 mL of 50% dichloromethane in hexane. The PCDD/PCDF fraction is then brought down to dryness and a known amount of recovery standard is added just prior to HRGC/HRMS

analysis. Reference method EPS 1/RM/19 was followed for concentration, cleanup and GC/MS analysis.

Results and Discussion

Temporal Trends and Spatial Distributions:

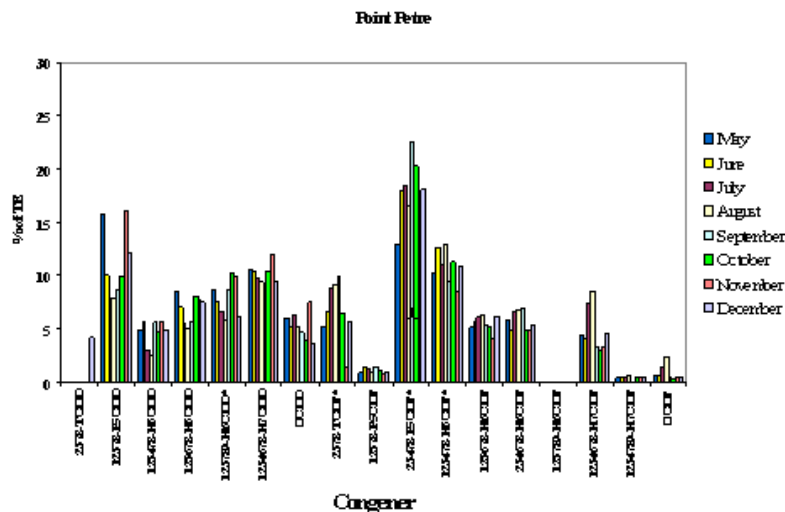
Fluxes: In general, fluxes of the sum of ΣP_{4-8} CDD/F in composited monthly samples show an increasing trend towards the winter season, with a mean value of 55 and 94 $\text{pg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (0.62 and 0.82 $\text{pg TEQ} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) for the Burnt Island and Point Petre sites respectively. (Table 1) These values are similar in magnitude to measurements reported in Venice, Italy⁸. Fluxes show an increase of approximate double from west (Burnt Island) to east (Point Petre). The relative contribution of OCDD to the Σ PCDD/F shows little variability between season and sites. Studies on seasonality must be interpreted with care, given the complex nature of this interpretation (temperature inversions, loss processes, and sources). Deposition is in general dominated by the higher chlorinated congeners and on average OCDD accounts for 40% and 44 % of the Σ PCDD/F flux for the Burnt Island and Point Petre sites respectively. Possible enhancement of the relative abundances of high-chlorinated dioxin/furans may be due to the dominance of this fraction in the particle phase. The PCDD:PCDF ratio in the deposition varies very little on a monthly basis and has a mean value of 2.93 for each of the two sites.

Table 1. Atmospheric fluxes of 2,3,7,8-substituted dioxins and furans (P_{4-8} CDD/F) at Burnt Island and Point Petre from May 2004 to December 2004, together with information on other variables.

Sampling Month	ΣP_{4-8} CDD/F		OCDD		PCDD/PCDF		Σ TEQ	
	$\text{pg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$		(% of Σ)		ratio		$\text{pg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$	
Station	Burnt	Petre	Burnt	Petre	Burnt	Petre	Burnt	Petre
May	-	110	-	49	-	3.1	-	0.91
June	-	30	-	45	-	2.8	-	0.26
July	24	86	47	44	3.3	1.9	0.20	0.61
August	25	41	42	36	2.6	1.3	0.27	0.28
September	8	21	37	47	2.1	2.9	0.12	0.21
October	76	56	38	41	2.7	3.3	0.87	0.58
November	120	190	39	55	3.5	5.5	1.3	1.4
December	80	220	36	37	3.4	2.6	0.95	2.3
Mean	55.5	94.3	39.8	44.3	2.93	2.93	0.62	0.82

TEQs: In all the data reported, 2,3,4,7,8-PeCDF makes the single most important contribution to the Σ TEQ, accounting for between 16% and 33% between the two sites. The distribution for the Point Petre site is shown in **Figure 1**. PCDFs typically contribute >50% of the Σ TEQ. Σ TEQ deposition fluxes (Table 1) are at the low end of the ranges found in remote-rural stations as reviewed by Lohmann and Jones⁵.

Figure 1. Relative individual contribution to overall TEQs in wet deposition at Point Petre.

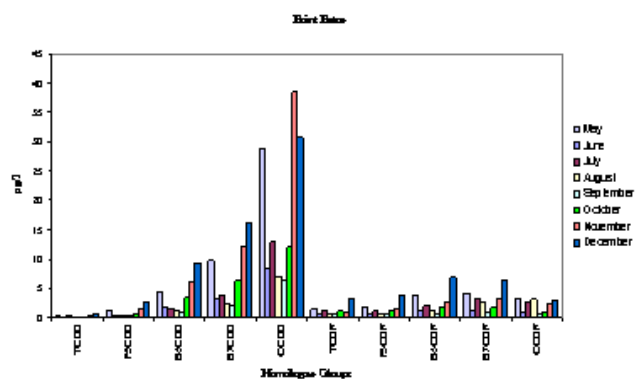


Fingerprinting: There is considerable interest in whether PCDD/Fs exhibit seasonality in air concentrations, as this provides clues as to the link with sources (domestic heating for example) and certain atmospheric loss processes which may also vary seasonally. Jones and Duarte-Davidson⁹ saw no such trend in an urbanized area of the UK. The concentrations of the tetra- through octachloro-PCDD/F in the monthly samples were blank corrected from an average of six blanks collected throughout the sampling period. Comparison of the PCDD/F patterns of the homologue groups for the monthly samples collected at Point Petre (Figure 2.) shows that while the concentration shows a seasonal difference the distribution of the homologues is consistent through the period and favors a sedimentary profile that shows higher concentrations of more chlorinated PCDD/Fs. This is valid for both sites, with little difference between the spatial distributions.

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Figure 2. Comparison of PCDD/F patterns in wet deposition at Point Petre.



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