

Measurement of wet deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans at Burlington, Ontario, Canada: An initial survey.

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Introduction

It has been known for several decades that the atmosphere serves as an important compartment for distributing persistent organic, and other anthropogenic pollutants on a global scale. In the atmosphere, persistent organic pollutants (POPs) partition between the gas phase and aerosol phase, a process which has been reviewed by Pankow¹ and Bidleman². The removal of POPs from the atmosphere can occur through wet and dry deposition, and chemical transformations. Wet (rain/snow) and dry (fine/coarse particles) deposition, and gaseous air-water exchange are major pathways for the loading of POPs to the Great Lakes.³ The binational (Canada/United States) Integrated Atmospheric Depositional Network (IADN) measures the basin wide (i.e., regional) atmospheric signal for many of these POPs in the Great Lakes Basin. Sites are typically located in background areas away from local sources. However, it is known that emissions in urban/industrial areas can cause elevated concentrations and increased atmospheric deposition in these areas that are not observed in the regional signal⁴. Many such centers exist in the Great Lakes Basin (e.g. Hamilton, On , Chicago, Il).

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^{5,6}. They may have relatively localized sources, but once emitted into the atmosphere, they become widely dispersed geographically. Lohmann and Jones⁷ have reviewed the levels, behavior and processes PCDD/Fs in air and deposition. Czuczwa and Hites⁸ have reported on their concentrations in urban air particulates and sediments in the Great Lakes. Eitzer and Hites have also reported on their concentrations in ambient air and rain in the Great Lakes⁹. In this paper, we report on the concentrations of PCDD/Fs in wet deposition from our site in Burlington, Ontario, Canada. This site is located in close proximity to the industries in Hamilton, and is adjacent to a major highway in southern Ontario. Specifically, we were interested in determining whether PCDD/Fs could be quantified in atmospheric precipitation at this location.

Material and Methods

Sampling: The collection of precipitation samples has been described in detail previously¹⁰. Briefly, the samples were collected using in 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 June 2003–November 2003 at a site in Burlington, Ontario, Canada.

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 then 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

Deposition of PCDD/Fs: Table 1 lists the PCDD/F fluxes measured in wet deposition. In general fluxes of the sum of $\Sigma P_{4,8}$ CDD/F in bulk monthly samples show little variability with a mean value of $5.3 \text{ pg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ ($0.62 \text{ pg TEQ} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$). These values are similar in magnitude to recent measurements reported in Venice, Italy¹¹. The relative contribution of OCDD to the Σ PCDD/F shows a slight decline from summer to winter. The total flux of $\Sigma P_{4,8}$ CDD/Fs also show little variation in seasonality over the period studied. This trend needs to be investigated with more samples during the winter months. Studies on seasonality must also be conducted and 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 ~42% of the Σ PCDD/F flux. 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 does not vary on a monthly basis and has a mean value of 2.83.

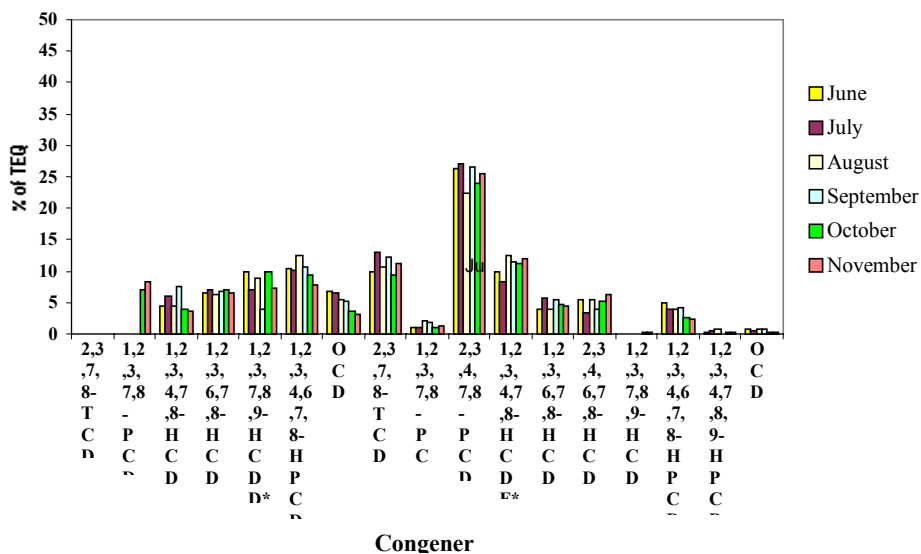
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Table 1. Atmospheric fluxes of 2,3,7,8-substituted dioxins and furans (P₄₋₈ CDD/F) at Burlington, Ontario (urban) from June 2003 to November 2003, together with information on other variables.

Sampling Month	ΣP_{4-8} CDD/F $\text{pg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$	OCDD (% of Σ)	PCDD/PCDF ratio	Σ TEQ $\text{pg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$
June	5.6	48	2.94	0.56
July	4.9	47	2.86	0.42
August	3.7	42	2.89	0.18
September	3.3	45	2.82	0.23
October	8.5	38	3.01	1.1
November	5.5	35	2.52	1.2

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 20% and 30% (**Figure 1**). PCDFs typically contribute >50% of the Σ TEQ.⁷ Σ TEQ deposition fluxes are at the low end of the ranges found at recently in Venice, Italy¹¹ and in remote-rural stations as reviewed by Lohmann and Jones⁷.

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



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-Davidson¹² saw no such trend in an urbanized area of the UK. The concentrations of the tetra-through octachloro-PCDD/F in the monthly samples are presented in Table 2. These values were

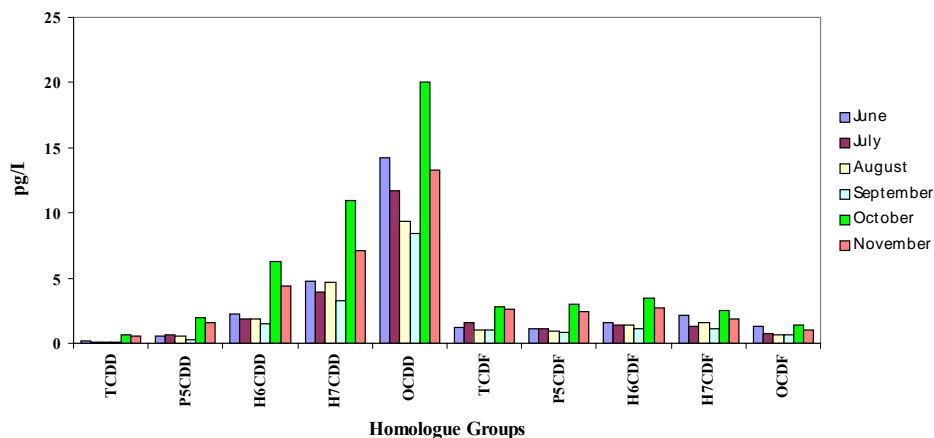
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blank corrected from an average of three blanks collected throughout the sampling period. Comparison of the PCDD/F patterns of the homologue groups for the monthly samples (Figure 2.) show high similarity for this one station. Again no seasonality effects were observed, however, this trend needs to be investigated with more samples during the winter months.

Table 2. Concentrations (pg/L) of PCDD/Fs in rain samples taken at Burlington, Ontario (urban) from June 2003 to November 2003.

Sampling Month	June	July	August	September	October	November
TCDD	0.2	<DL	0.1	0.1	0.6	0.6
P5CDD	0.5	0.6	0.5	0.2	1.9	1.6
H6CDD	2.3	1.9	1.9	1.5	6.2	4.4
H7CDD	4.8	3.9	4.7	3.3	11.0	7.1
OCDD	14.2	11.7	9.4	8.4	20.0	13.3
TCDF	1.2	1.6	1.1	1.0	2.9	2.7
P5CDF	1.2	1.2	0.9	0.8	3.0	2.5
H6CDF	1.6	1.4	1.4	1.1	3.4	2.7
H7CDF	2.1	1.3	1.6	1.1	2.5	1.8
OCDF	1.3	0.8	0.7	0.7	1.4	1.0
Total PCDD/F	29.6	24.7	22.5	18.6	53.2	37.9

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



Comparison with Guidelines: PCDDs/PCDFs are relatively persistent in the environment and a large amount of the total TEQ intake is not so much from inhalation as from foods such as fish and cattle. Therefore, the overall atmospheric behavior of emitted PCDDs/PCDFs is an important concern. By means of selected transfer models¹³, daily intake values have been translated into quality objectives for dioxin deposition of 3.4-13.6 pg TEQ m⁻²day⁻¹.¹⁴ The EU strategy on PCDD/Fs and PCBs has aimed at reducing human intake levels to 14 pg TEQ kg⁻¹·week⁻¹, corresponding to approximately 7 pg TEQ m⁻²·day⁻¹.¹⁵ The maximum ΣTEQ for PCDDs/PCDFs observed at this site was 1.2 pg·m⁻²·day⁻¹.

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