Concentrations and TEQs of PCDD/PCDF in Urban and Rural Precipitation

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1. Introduction

Since about 1987, the Ontario Ministry of the Environment has been monitoring the trace organic chemicals in precipitation at selected urban and rural sites in Ontario. Initial studies focused on the development of the sampling methodology, and the determination of the PCDD/PCDF congener groups. The results of these early studies have been reported previously[1-3]. Two of the limitations of this previous work were the absence of 2,3,7,8-congener-specific results, and the limited estimates of measurement precision based on analysis of replicates.

In the past few years the analytical methodology has been firmly established - including the determination of the 2,3,7,8-substituted PCDD/PCDF congeners. In addition, one rural site has been monitored by collocated samplers for a two-year period. The results of isomer-specific monitoring of an urban and rural site for this two-year period, and results of monitoring one of these locations by using collocated samplers, are presented here.

2. Experimental Procedures

Sample Collection. Precipitation samples were collected at a rural, background site near Dorset, Ontario (Lat. 45°13'26" N. Long. 78°55'50" W.) and at an urban site in Toronto, Ontario (Lat. 43°36'50' N., Long. 79°22'58"). Collocated samples were collected at Dorset to provide an estimate of sampling and analysis precision. Precipitation samples were collected every 28 days by using an automated, wet-only collector outfitted with a Teflon-coated 0.21 m^2 funnel. The collector's samping train, used to partition the precipitation's particulate-bound and dissolved phases, was connected to the underside of the funnel and was housed in an insulated, heated compartment. Particulate-bound PCDD/PCDF were captured on an in-line 47 mm glass-fibre filter, and the dissolved phase sample components were collected by using 45g of XAD-2 adsorbent packed in a glass column (2 mm i.d.) directly downstream of the filter. When the filter and XAD-2 cartridge were collected every fourth week, a funnel rinse of 500mL dichloromethane or acetone was also collected for analysis. A 20L graduated carboy was used for to measure the volume of precipitation collected. A standard precipitation gauge was used to measure the true sample depth.

Sample Preparation. The sample preparation procedure employed is described elsewhere[4].

Each sample was comprised of three separate portions: a glass fibre filter, a glass cartridge which contained the XAD-2 resin, and a solvent rinse of the collection funnel. The glass fibre filter was extracted by Soxhlet using toluene, and PCDDs/PCDFs were recovered from the XAD-2 resin by simple elution with acetone/hexane. The concentrated extracts then underwent a multi-stage chromatographic cleanup. For the filters and XAD-2 sample portions, final extracts for consecutive 28-day sampling events were combined, to give a final sample for GC/MS analysis equivalent to a 56-day sampling period.

GC-MS Analysis. Samples were analyzed by gas chromatography-tandem mass spectrometry using a Finnigan MAT 70 triple quadrupole mass spectrometer coupled to a Varian 3400 GC equipped with splitless injection, or by GC-high resolution mass spectrometry using a Fisons/VG AUTOSPEC mass spectrometer operated at 10,000 (10% valley) resolution. The GC was a HP5890 II equipped with a splitless injection system. Both instruments employed a 60m fused silica, 0.25 mm i.d./0.25 micron film thickness DB-5 column. The use of the isotope dilution method for quantitation was similar to the method described by U.S. EPA Method 1613. For each 56-day sampling period the combined filter and XAD-2 cartridge, and two 28-day sample funnel rinses, were analyzed separately.

3. Results and Discussion

Table 1 shows the results for PCDD/PCDF TEQs and for total PCDDs/PCDFs (tetra to octa congeners) deposition via precipitation at two Ontario sites over an approximate 2-year period. There were 17 sampling events from March, 1992 to August, 1994. Concentrations shown in Table 1 are total nanograms of PCDD/PCDF TEQs, or total nanograms PCDDs/PCDFs (tetra to octa congeners) deposited per square meter over a 56-day equivalent sampling period.

On average, the deposition rate at the urban location is greater than that of the rural site (14 ± 19 ng/m^2 vs. 11 ± 10 ng/m^2) per 56-day sampling period. However, this difference is a result of only one "high" result of 70 ng/m^2 (April 13, 1993 sample). On examination of individual results, it seems that there is little difference between the urban and rural deposition rates. Concentrations in precipitation are low enough at both sites that many more analyses would be required to establish statistically significant differences. If we exclude the "high" result from the data set, and only consider the other nine sampling dates where results are available for both the urban and rural sites, then the average 56-day deposition is 8.3 ng/m^2 (std. dev. 3.9) for the urban site, and 13 ng/m^2 (std. dev. 11) for the rural site. Likewise, there is no significant difference between summer and winter samples (although deposition seems to be greater in the Winter months at the rural location).

Because the sample filter, XAD cartridge, and funnel rinse were analyzed separately, we could determine the distribution of the PCDDs/PCDFs in the sampling apparatus used. It was observed that 70-90% of all PCDDs/PCDFs detected were found in the funnel rinse. About 10-20% of analytes were detected on the filter extract, and only 1-8% of analytes were in the XAD-2 cartridge extract. It is well-known that PCDDs/PCDFs are prone to being strongly adsorbed onto surfaces, but these results may seem unusual because a very short contact time would be expected between raindrops and the funnel surface. Considering the overall imprecision of the sampling and analysis methods employed - simply analyzing the funnel rinse

Table 1: **Total PCDD/PCDF (tetra to octa) and Total TEQ Deposition in Ontario via Precipitation (56-day equivalent sampling period)**

Sampling Date	Total TEQ and Total PCDD/PCDF Deposition (ng/m^2)					
	Urban Location (Toronto)		Rural Location (Dorset)			
			Total TEQ		Total PCDD/PCDF	
	Total TEQ	Total PCDD/PCDF	A	B	A	B
Mar. 17, 1992	0.11	11	0.10	0.14	20	34
May 12, 1992	0.053	13	0.14	0.028	9.5	11
July 7, 1992	no data	no data	0.041	0.0063	7.4	2.7
Sept. 1, 1992	0.048	8.7	0.046	0.042	7.0	18
Oct. 27, 1992	no data	no data	0.015	0.016	7.3	7.2
Dec. 22, 1992	0.11	16	no data	0.071	no data	9.8
Feb. 16, 1993	0.10	15	0.061	0.22	18	42
April 13, 1993	0.20	70	0.080	0.084	13	27
June 8, 1993	0.0077	5.8	0.034	0.012	6.4	5.5
Aug. 3, 1993	0.030	6.7	0.040	0.0055	3.2	2.5
Sept. 28, 1993	0.0088	4.0	0.0069	0.0071	3.2	3.2
Nov. 23, 1993	0.051	8.1	0.10	0.065	15	18
Jan. 8, 1994	no data	no data	0.049	0.041	21	17
Mar. 15, 1994	no data	no data	0.039	0.095	13	19
May 10, 1994	0.0034	2.1	0.0024	0.0032	1.1	1.4
July 5, 1994	no data	no data	0.0042	0.0045	2.6	2.8
Aug. 30, 1994	no data	no data	0.0093	0.015	4.7	3.3

each sampling period would have given a fair indication of the overall PCDD/PCDF precipitation deposition rate. The large proportion of PCDDs/PCDFs found in the funnel rinse may be a result of air locks that sometimes occurred in the sampling train, which sometimes caused precipitation to pool in the funnel - and resulted in a much greater contact time between the raindrops and the funnel surface.

In this study, estimates of overall method precision can be made, because collocated samplers were employed at one of the sampling sites. The overall relative standard deviation for replicate measurements was 22%. The average per-cent relative standard deviations of replicate measurements of individual 2,3,7,8-substituted congeners were 10%-11% for hepta- and octachlorinated PCDDs/PCDFs, and ranged from 14% to 39% for the tetra-to-hexachlorinated congeners (congeners where fewer than three sets of replicate were available for comparison were excluded from this analysis).

Average annual deposition rates for total PCDDs/PCDFs in this study were 95 ng $m^{-2}yr^{-1}$ for the urban site, and 74 ng $m^{-2}yr^{-1}$ at the rural site. These results are comparable to annual deposition rates of 92 ng $m^{-2}yr^{-1}$ for Bloomington, Indiana rain reported by Hites^5)^. Expressed as PCDD/PCDF TEQs, the average annual deposition rates were 0.43 ng $m^{-2}yr^{-1}$ and 0.32 ng $m^{-2}yr^{-1}$ for the Ontario urban and rural sites, respectively.

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5. References

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