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A SOURCE OF PCDDs/PCDFs IN THE ATMOSPHERE OF PHOENIX, AZ

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Abstract

Ambient PCDDs/PCDFs were measured at a metropolitan Phoenix site in December 1994. The sampling site was located near a heavily traveled road in Phoenix in order to assess the influences of motor vehicle emissions. Four sets of 24-hour integrated samples were collected during the period December 15 through 20, 1994. Total PCDDs/PCDFs concentrations (pg/m^3) for the four-sample set and corresponding TEF sum data are higher than wintertime values reported in the open literature for other U.S. urban locations. PCDDs/PCDFs congener profiles suggest primarily combustion source influences. Activity in the vicinity of the sampling site, in concert with companion data collected at the site, strongly suggest influences primarily from mobile sources or vehicular emissions.

Introduction

An ambient monitoring program was conducted at a number of sites in metropolitan Phoenix, AZ during the period 1994-95. The program was conducted under the sponsorship and direction of the Arizona Department of Environmental Quality (ADEQ). Ambient PCDDs/PCDFs measurements were collected at one of the sites, Indian School Road, in December 1994. These data represent the first set of ambient PCDDs/PCDFs data reported for metropolitan Phoenix as well as the State of Arizona.

Experimental Methods

Results are reported for each of six samples. The sample set consisted of four ambient air samples and two field blanks. Each ambient sample represented an approximate 24-hour sampling period at the Indian School Road site situated in metropolitan Phoenix, AZ. The Indian School Road site was situated in close proximity to a heavily traveled roadway in metropolitan Phoenix so as to assess influences from motor vehicle emissions. Sampling was conducted during winter months on days when inversion conditions were expected. Ambient PAHs data (polynuclear aromatic hydrocarbons) were used to prioritize ambient samples to be submitted for PCDDs/PCDFs analyses. PCDDs/PCDFs data for each sample consisted of pg and pg/m^3 values for each of fifteen 2,3,7,8-substituted PCDDs/PCDFs and ten congener class sums (Cl_4 - Cl_6). Each of the two field blanks were examined and found to be free of detectable quantities of PCDDs/PCDFs. (Detection limits in the range of 1-2 pg were reported for each of the blanks.) The only exception was OCDD, which was present in each of the two blanks at concentrations

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of 9.4 and 68 pg respectively. Such trace quantities of PCDD commonly occur in field and laboratory blanks subjected to HRGC/HRMS analysis for PCDDs/PCDFs. As a consequence, no blank correction was made in deriving the ambient concentration data for each of the samples.

Results

Ambient Concentration Data. PCDDs/PCDFs data for the four-sample set are provided in Table 1. Results are provided for each of fifteen 2,3,7,8-substituted PCDDs/PCDFs and ten congener class sums (Cl_4 - Cl_8) on a sample-specific basis. All data are reported in units of pg/m^3 .

Results for the PCDDs/PCDFs congener class sums (Cl_4 - Cl_8) are graphically plotted in Figure 1. The figure presents average concentrations (arithmetic mean) in units of pg/m^3 , and represents a composite profile of the four-sample set.

Ambient concentration data for total PCDDs/PCDFs are also provided in Table 1. These data are plotted in Figure 2 on an average concentration basis.

Toxic Equivalency Factor (TEF) Data. TEF data were generated for each of the four ambient samples, employing the international TEF model. These data are reported in units of pg/m^3 on an isomer/congener-specific basis, as well as TEF sum basis, for each sample in Table 1. A composite or mean value for all four samples is also provided. These same TEF data are plotted in Figure 3.

Discussion

Ambient Concentration Data. As shown in Table 1 measured values are reported for all of the PCDDs/PCDFs isomers and congener class sums examined in each of the four samples. The highest total PCDDs/PCDFs concentrations were observed on December 16 and the lowest concentrations on December 15, 1994. There was a great degree of variability in the total concentrations measured over the calendar period December 15-20, 1994. The average total PCDDs/PCDFs concentrations, though somewhat higher, are consistent with those reported previously by Hunt and Maisel for other U.S. urban locations in wintertime.^{1) 2) 3) 4)} Figure 2 provides a comparison of the Phoenix data to ambient PCDDs/PCDFs data for urban locations in Southern California and Connecticut. Data for comparison are also provided for Fresno, CA which represent some of the highest ambient concentrations for PCDDs/PCDFs measured to date in North America.

Results for December 15/16 indicate a predominance of PCDDs over PCDFs. This observation is consistent with numerous studies reported previously by these authors (Hunt and Maisel) and others in the open literature. Both days the profile is predominated by $Cl_6 < Cl_7 < Cl_8$ PCDDs. The principal isomer as shown in Figure 1 is OCDD, while the principal isomer of toxicological significance is 1,2,3,4,6,7,8-HpCDD.

The predominance of 1,2,3,4,6,7,8-HpCDD as the most persistent 2,3,7,8-substituted PCDDs congener is consistent with the observations of others in the open literature. This particular

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trend is prevalent at sites known to be influenced by stationary or mobile combustion source emissions.

Conversely, results for December 19 and 20 indicate a predominance of PCDFs over PCDDs. This is atypical of data reported for PCDDs/PCDFs in ambient air. The December 20 profiles, for example, report a concentration of 2.16 pg/m³ for the 1,2,3,4,6,7,8-HpCDF isomer, in contrast to a value of 1.30 pg/m³ for the typically most predominant 1,2,3,4,6,7,8-HpCDD isomer.

The predominance of the 1,2,3,4,6,7,8-HpCDF isomer in concert with PCDFs > PCDDs may provide some indication on the nature of sources contributing the atmospheric burdens of PCDDs/PCDFs in metropolitan Phoenix. Further analyses beyond examination of PCDDs/PCDFs data alone is warranted to provide a more conclusive source determination.

Toxic Equivalency Factor (TEF) Data. TEF data presented in Table 1 indicate the highest value of 0.448 pg/m³ was measured on December 20, 1994, while the lowest values of 0.092 and 0.093 pg/m³ were measured on December 15 and 19, respectively. Further analyses of the Phoenix TEF data are provided in Figure 3. As shown, the Phoenix TEF value ($\bar{X} = 0.25$ pg/m³) is higher than TEF sums data for selected U.S. urban locations in Southern California (Los Angeles) and Connecticut.

Regulatory limits or guidelines for acceptable TEF values in ambient air do not currently exist in the majority of U.S. states and/or Air Districts. Standards and/or guidelines do exist, however, in Connecticut, Ontario (Canada), Massachusetts and Pennsylvania. In 1988 the Conn. DEP adopted an AAQS for PCDDs/PCDFs of 1.0 pg/m³ expressed as a TEF sum (based upon EPA 1987 model). Several U.S. states have adopted PCDDs/PCDFs standards based upon predictive dispersion modeling of source emissions. Pennsylvania and Massachusetts, for example, have adopted standards of 0.030 pg/m³ and 0.045 pg/m³, respectively, expressed as a TEF sum for such purposes.

Specific conclusions and observations that can be derived from the results and discussion contained herein are as follows:

- PCDDs/PCDFs were detected in each of the four ambient air samples collected at the Indian School Road site during December 1994.
- Measured values as opposed to ND values were measured for each of the fifteen 2,3,7,8-substituted PCDDs/PCDFs isomers and ten congener class sums (Cl₄ - Cl₆).
- Average total PCDDs/PCDFs concentrations (pg/m³) are higher than wintertime values reported in the open literature for other U.S. urban locations.
- Due to the site-specific bias likely introduced by vehicular traffic at the Indian School Road site, the ambient PCDDs/PCDFs measured should not be construed to be representative of ambient PCDDs/PCDFs burdens in metropolitan Phoenix, as a whole.

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- Results for the December 15/16 samples indicate a predominance of PCDDs over PCDFs. The profile is predominated by (Cl₄ - Cl₈) PCDDs with concentrations increasing with chlorine substitution (Cl₆ < Cl₇ < Cl₈). Such profiles are indicative of combustion source influences.
- Each of the four sampling days strongly suggest combustion source influences in the vicinity of the Indian School Road site.
- The actual type of combustion source(s) influencing the site cannot be determined from the limited amount of PCDDs/PCDFs data currently available. Companion data collected at this same site by DRI (e.g., PAHs) strongly suggest that mobile sources or vehicular emissions represent the most significant influence on air quality at the Indian School Road site.
- Congener profiles for the December 19/20 ambient samples are distinctively different from those evident on December 15/16. The profiles are predominated by PCDFs > PCDDs; atypical of the majority of data in the open literature for U.S. urban settings.
- TEF data for the Indian School Road site are much higher than TEF data for other U.S. urban locations.

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TABLE 1.
PHOENIX, AZ - INDIAN SCHOOL ROAD SITE

AMBIENT PCDDs/PCDFs TEQ DATA - WINTER 1994
SAMPLING PERIOD: 12/15, 12/16, 12/19, 12/20 1994

SAMPLE ID		P1941215 12/15/94 P30X14F7 274.26			P1941216 12/16/94 P32X14F8 299.98			P1941219 12/19/94 P32X14F8 292.12			P1941220 12/20/94 P32X14F8 254.11			Average
Parameter	TEF	pg	pg/m ³	TEQ pg/m ³	pg	pg/m ³	TEQ pg/m ³	pg	pg/m ³	TEQ pg/m ³	pg	pg/m ³	TEQ pg/m ³	TEQ pg/m ³
2,3,7,8-TCDD	1	2	0.0073	0.0073	4.5	0.0150	0.0150	ND	0.0000	0.0000	2.2	0.0087	0.0087	0.0077
1,2,3,7,8-PeCDD	0.5	7.7	0.0281	0.0140	34	0.1133	0.0567	8.8	0.0228	0.0113	10	0.0384	0.0197	0.0254
1,2,3,4,7,8-HxCDD	0.1	15	0.0547	0.0055	70	0.2333	0.0233	7.5	0.0257	0.0028	18	0.0708	0.0071	0.0098
1,2,3,6,7,8-HxCDD	0.1	28	0.0948	0.0095	170	0.5667	0.0567	18	0.0548	0.0055	42	0.1653	0.0165	0.0220
1,2,3,7,8,9-HxCDD	0.1	5.7	0.0786	0.0077	15	0.5000	0.0500	11	0.0377	0.0038	78	0.1141	0.0114	0.0182
1,2,3,4,6,7,8-HpCDD	0.01	0	1.3491	0.0135	0	8.8672	0.0867	0	0.4793	0.0048	0	1.2887	0.0130	0.0285
2,3,7,8-TCDF	0.1	4	0.0146	0.0015	2.7	0.0090	0.0009	5.7	0.0195	0.0020	23	0.0905	0.0091	0.0033
1,2,3,7,8-PeCDF	0.05	4.1	0.0149	0.0007	6	0.0200	0.0010	7.7	0.0284	0.0013	37	0.1456	0.0073	0.0026
2,3,4,7,8-PeCDF	0.5	7.1	0.0259	0.0129	13	0.0433	0.0217	18	0.0616	0.0308	81	0.3188	0.1594	0.0582
1,2,3,4,7,8-HxCDF	0.1	8.3	0.0303	0.0030	17	0.0567	0.0057	20	0.0685	0.0068	110	0.4329	0.0433	0.0147
1,2,3,6,7,8-HxCDF	0.1	8.1	0.0295	0.0030	16	0.0533	0.0053	19	0.0650	0.0065	91	0.3581	0.0358	0.0127
2,3,4,6,7,8-HxCDF	0.1	14	0.0510	0.0051	26	0.0867	0.0087	27	0.0924	0.0092	160	0.6296	0.0630	0.0215
1,2,3,7,8,9-HxCDF	0.1	3.5	0.0128	0.0013	8.7	0.0290	0.0029	7.8	0.0287	0.0027	62	0.2440	0.0244	0.0078
1,2,3,4,6,7,8-HpCDF	0.01	1300	0.2005	0.0020	8100	0.3667	0.0037	740	0.3218	0.0032	1000	2.1644	0.0216	0.0078
1,2,3,4,7,8,9-HpCDF	0.01	0	0.0208	0.0002	0	0.0500	0.0005	0	0.0377	0.0004	0	0.3070	0.0031	0.0010
TOTAL TCDD	0	0	0.0547	0.0000	0	0.2033	0.0000	0	0.1369	0.0000	0	1.7315	0.0000	0.0000
TOTAL PeCDD	0	4	0.1823	0.0000	2.7	0.9687	0.0000	5.7	0.2088	0.0000	23	0.9051	0.0000	0.0000
TOTAL HxCDD	0	270	0.9845	0.0000	1700	5.6670	0.0000	150	0.5135	0.0000	830	2.4782	0.0000	0.0000
TOTAL HpCDD	0	710	2.5888	0.0000	4600	15.3344	0.0000	290	0.9927	0.0000	870	2.6387	0.0000	0.0000
OCDD	0.001	1300	4.7400	0.0047	8100	27.0018	0.0270	740	2.5332	0.0025	1000	3.9353	0.0039	0.0098
TOTAL TCDF	0	0	0.1896	0.0000	0	0.4000	0.0000	0	0.5820	0.0000	0	5.1159	0.0000	0.0000
TOTAL PeCDF	0	15	0.3245	0.0000	61	0.3334	0.0000	40	0.7189	0.0000	440	4.3288	0.0000	0.0000
TOTAL HxCDF	0	93	0.3391	0.0000	210	0.7000	0.0000	2230	7.6338	0.0000	1300	5.1159	0.0000	0.0000
TOTAL HpCDF	0	110	0.4011	0.0000	220	0.7334	0.0000	170	0.5820	0.0000	920	3.8205	0.0000	0.0000
OCDF	0.001	24	0.0875	0.0001	59	0.1987	0.0002	43	0.1472	0.0001	240	0.9445	0.0009	0.0003
TOTAL TEQ				0.0920			0.3659			0.0935			0.4481	0.2488

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