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Chemical Data on Air Samples
From the Binghamton State Office Building

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Abstract

Air samples collected at 15 distinct locations and/or times within the Binghamton State Office Building have been analyzed for various chlorinated dibenzofurans, dibenzodioxins and biphenylenes. The average 2,3,7,8-TCDF concentration from twelve locations sampled when the building's internal air circulation system was operative was 15.0 ± 3.6 pg/m^3 . Samples collected at six locations under similar conditions and analyzed using a cleanup methodology designed to recover the full range of compounds of interest had "total TCDF" and total Penta CDF" concentrations of 143 ± 24 pg/m^3 and 42 ± 10 pg/m^3 , respectively. "Total hexa CDF" was measured at 4.8 ± 3.5 pg/m^3 in three samples collected under these conditions. "Total TCDD" concentrations at two locations were 1.0 and 1.3 pg/m^3 , while "total Penta CDD" concentration was < 0.5 pg/m^3 at both locations. Measurement of 2,3,7,8-TCDD at two locations gave concentrations of 0.3 and 0.5 pg/m^3 . "Total tetrachlorobiphenylenes" were estimated at 0.3, 0.5 and 1.3 pg/m^3 at three locations and "total pentachlorobiphenylenes" at 1.5 and 2.6 pg/m^3 in two locations.

A methodology used with apparent success to calculate the "2,3,7,8-TCDD equivalent" concentration in a sample of soot collected in the BSOB was applied to this data to estimate that the overall activity present in the air was ca. 14 pg/m^3 "2,3,7,8-TCDD equivalents."

The air of the Binghamton State Office Building (BSOB) was sampled for various chlorinated dibenzofurans, dibenzodioxins and biphenylenes in November 1982 (Smith et al., 1983), February 1983 (Smith et al., 1983a) and April 1983 (Smith et al., 1983b). Detailed descriptions of the method development and validation, analytical methodologies and quality control data have already been provided; the intent of this paper is to summarize the results obtained from the analysis of BSOB air and to use that data to calculate the approximate "2,3,7,8-TCDD equivalent concentration" (Eadon et al., 1982) that these results correspond to.

Chemical Data

Table 1 contains the analytical data generated during the three samplings of BSOB air. The samples collected in 11/82 were obtained with the internal air circulation system inoperative; therefore, these results will not be referred to in subsequent discussions. Samples collected at 12 different locations on 2/83 and 4/83 had average 2,3,7,8-TCDF concentrations of 15.0 ± 3.6 pg/m³ (error limits represent one standard deviation). The relatively small standard deviation for this large data set for 2,3,7,8-TCDF demonstrates that the compound is fairly uniformly distributed from floor to floor. Since this compound's relevant physical and chemical properties are similar to those of the other analytes discussed in this paper, it is possible that they too are rather uniformly distributed. The more limited data set contained in Table 1 for other classes of compounds is consistent with this proposal.

Because 2,3,7,8-TCDF concentrations were determined using an internal standard technique, all data are considered accurate. However, it is believed that "total TCDF" and "total penta CDF" data produced from the 11/82 and 2/83 samplings may underestimate the actual concentrations of these compounds; for example, during analyses of the 2/83 samples, it was observed that only two of three penta CDF standards were adequately recovered during cleanup of spiked samples (Smith et al., 1983a). The methodology used in the cleanup of the 4/83 samples was modified to permit recovery of a broader range of compounds. These data now provide the most reliable estimate of the concentrations of the remaining compounds and groups of isomers of interest and will therefore be used in subsequent discussions.

Six locations sampled on 4/83 exhibited an average "total TCDF" concentration of 148 ± 24 pg/m³ and a "total Penta CDF" concentration of 42 ± 10 pg/m³. Total Hexa CDF averaged 4.8 ± 3.5 pg/m³ at three of the locations. In three samples collected at two locations, "total TCDD" averaged 1.2 ± 0.2 pg/m³ and 2,3,7,8-TCDD averaged $0.4 \pm .1$ pg/m³; "total Penta CDD" was < 0.5 pg/m³. Since no quantitative standards were available for the biphenylenes, only estimates of their concentrations were generated. However, three locations exhibited "total tetrachlorobiphenylene" concentrations of roughly 0.3, 0.5 and 1.3 pg/m³, and two locations exhibited "total pentachlorobiphenylene" concentrations of 1.5 and 2.6 pg/m³.

Several interesting comparisons can be made between the data produced from these air samples and those produced from soot samples

collected from above the ceiling panels on various BSOB floors (Eadon et al., 1982). In 12 soot samples, the ratio of tetra CDF:penta CDF:hexa CDF was $1.2 \pm 0.2:1:0.5 \pm 0.2$. The corresponding relationship produced from the air data summarized above is $3.5 \pm 0.6:1:0.11 \pm .02$. This increase in the relative concentrations of the less chlorinated and thus more volatile congeners suggests that the air contamination may not be predominantly due to suspended soot particles but may instead be true vapor-phase material. Consistent with this hypothesis, when the particulate material collected using a 0.3 μ glass fiber filter was analyzed separately from the silica cartridge portion of the air sampling apparatus, only minor amounts of PCDFs were detected. For example, three samples in which the glass fiber filter and silica cartridge were analyzed separately, the ratio of "total TCDF" in the two collection media was $0.04 \pm .01$ (Smith et al., 1983a, 1983b).

Air samples collected simultaneously with those used for PCDF analysis exhibited PCB concentrations of $0.16 \pm .02 \mu\text{g}/\text{m}^3$ (Versar, 1983). This concentration corresponds to a PCB:"total TCDF" ratio of 1200; the ratio in soot was 50. Here, too, the relative concentration of the more volatile component has been markedly enhanced.

Calculation of "2,3,7,8-TCDD Equivalents"

The assessment of the biological activity of a complex mixture of chlorinated dibenzofurans, dibenzodioxins, and biphenylenes is complicated by the lack of definitive knowledge of the toxicities of most of the individual congeners, by the inability to accurately analyze

all congeners and by the possibility of synergistic or antagonistic interactions among these compounds. The most straightforward approach to this problem is to utilize the techniques of animal toxicology to compare the biological activity of the mixture to that of a reference compound. This approach, when applied to a representative sample of soot taken from the BSOB led to the conclusion that the acute oral LD₅₀ in guinea pigs of the soot was equivalent to that of an inert matrix containing 58 µg/g of 2,3,7,8-TCDD (Eadon et al., 1982). Because of the differing chemical composition of the contaminants present in the air and in the soot, this number has little direct applicability for estimating the biological activity of compounds present in the air. Further, the concentrations present in the air are so low that performing further animal toxicology experiments to estimate the air's biological activity is impractical.

An alternative approach to this problem is to utilize available analytical and toxicological data together with necessary assumptions and approximations to estimate the number of "TCDD equivalents" due to particular contaminants, and then summing the overall activity over the range of toxic compounds. Although such an approach is obviously only an estimate, it is notable that, when applied to the soot sample used in the animal toxicology experiments, it produced an estimate of the "TCDD equivalent" concentration that agreed remarkably well with the animal toxicology experimentation. (44 µg/g calculated vs. 58 µg/g observed). The important conclusion was reached that the acute oral LD₅₀ of the soot could be estimated without the necessity of postulating major synergistic or antagonistic effects (Eadon et al., 1982).

Use of chemical data to "predict" the 2,3,7,8-TCDD equivalent concentration of the BSOB air is complicated by the fact that no animal toxicology data is available on the effects of inhalation of these compounds. As a consequence, it is necessary to assume that acute oral guinea pig LD₅₀s can be used to relate the air's overall activity to 2,3,7,8-TCDD. Another complication is that only limited data is available on the acute oral guinea pig LD₅₀s of dibenzodioxins and no such data is available on biphenylenes or dibenzofurans other than 2,3,7,8-TCDF. The following assumptions will therefore be made about the LD₅₀s of these compounds:

(1) The ratio of the LD₅₀s of a particular PCDF congener and 2,3,7,8-TCDF or of a particular polychlorinated biphenylene congener and 2,3,6,7-tetrachlorobiphenylene will be the same as the ratio of the LD₅₀s of the corresponding PCDD congener and 2,3,7,8-TCDD. There is presently very little experimental data to support this assumption.

(2) The LD₅₀s of PCDFs, PCDDs and polychlorinated biphenylenes lacking chlorines on at least one of the four lateral positions will be sufficiently high that their influence can be ignored in this calculation. This assumption is based on the LD₅₀s in guinea pigs of 2,8-diCDD, 2,3,7-triCDD, and 1,2,4,7,8-penta-CDD. All have LD₅₀s more than 450 times higher than that of 2,3,7,8-Tetra CDD itself (Table II).

(3) Introduction of a single additional chlorine substituent on a 2,3,7,8-substituted PCDD or PCDF congener or a 2,3,6,7-substituted polychlorinated biphenylene congener has essentially no effect on the congener's guinea pig LD₅₀. This assumption is based on comparison of the LD₅₀s of 2,3,7,8-TCDD and 1,2,3,7,8-penta-CDD (Table II).

(4) Introduction of two additional chlorine substituents on a 2,3,7,8-chlorinated PCDD or PCDF congener or a 2,3,6,7-substituted polychlorinated biphenylene congener raises its LD_{50} by a factor of at least 29. The assumption is based on comparison of the LD_{50} s of 1,2,3,4,7,8-, 1,2,3,6,7,8-, and 1,2,3,7,8,9-hexa CDD and 2,3,7,8-tetra CDD (Table II).

(5) The LD_{50} s of compounds with more than 6 chlorines will be sufficiently large that their influence can be ignored in this calculation. This assumption is based on comparison of the LD_{50} s of 1,2,3,4,6,7,8-hepta CDD and 2,3,7,8-tetra CDD (Table II).

These assumptions require that attention be focused only on 2,3,7,8-substituted tetra, penta and hexa-substituted PCDDs, PCDFs and biphenylenes. Measurements of 2,3,7,8-TCDF concentrations at 12 different locations with the internal air circulation system operative gave average concentrations of 15.0 ± 3.6 pg/m^3 ; since the data in Table II indicate that the LD_{50} of 2,3,7,8-tetra CDF is about three times that of 2,3,7,8-TCDD, the equivalent in terms of acute oral guinea pig toxicity to a 2,3,7,8-TCDD concentration is 5 pg/m^3 (Table III). Measurements at 6 different locations all taken with the interval air circulation system operative and using an optimized analytical methodology yielded total penta CDFs of 42 ± 10 pg/m^3 . Based on earlier soot data, it is conservatively assumed that the most toxic isomers (1,2,3,7,8- and 2,3,4,7,8-penta CDF) together constitute 50% of the penta CDFs and that their LD_{50} s equal that of 2,3,7,8-TCDF; thus, the penta CDFs contribute 7.0 pg/m^3 of 2,3,7,8-TCDD equivalents. Hexa-CDFs were present at total concentrations of 4.8 pg/m^3 in three samples. Based on dioxin studies, the most toxic hexa substituted

dioxins are ca 1/30 as toxic as 2,3,7,8-TCDD; to account for the differing toxicities of 2,3,7,8-TCDD and 2,3,7,8-TCDF it will be concluded that the hexa-CDFs contribute less than 0.1 pg/m^3 TCDD equivalents, a negligible number in comparison to the contributions of the tetra- and penta- CDF.

The PCDDs themselves also make only a small contribution to the "TCDD equivalent" concentrations present in the air of the BSOB. Thus, 2,3,7,8-TCDD was present at an average concentration of 0.4 pg/m^3 , corresponding to a contribution of 0.4 pg/m^3 TCDD equivalent. Total Penta CDD was below detection limit (0.5 pg/m^3); and therefore can make only a negligible contribution to the "TCDD equivalent" concentration.

Total tetrachlorobiphenylenes were roughly estimated at 0.7 pg/m^3 . If the conservative assumptions are made that the toxic 2,3,6,7 congener constitutes 50% of the mixture and that biphenylenes are as toxic as the corresponding dioxins, the tetrachlorinated biphenylenes contribute 0.4 pg/m^3 "2,3,7,8-TCDD equivalents."

Pentachlorobiphenylenes averaged 2.1 pg/m^3 . If similar assumptions are made, this corresponds to 1.1 pg/m^3 "2,3,7,8-TCDD equivalents." Insufficient sample was available to attempt a measurement of hexa-biphenylenes; however, in view of the factor of 30 estimated difference in toxicity between tetra and hexa substituted compounds, the hexa-biphenylenes are unlikely to be major contributors to the "TCDD equivalents" in the BSOB air.

Based on these calculations, the concentration of "2,3,7,8-TCDD equivalents" in the BSOB air is estimated at 13.5 pg/m^3 ; ca. 90% of this estimated activity resides in the tetra and penta CDF isomers (Table III).

Conclusions

The concentrations of the principal compounds of concern in the air of the BSOB have been measured. These experiments have provided evidence suggesting that the contamination in the BSOB air is fairly uniformly distributed throughout the working space of the building in floors 3-17 and is in the gas phase, rather than particulate bound. Based on the results of chemical analysis, literature-derived acute oral guinea pig LD₅₀s and a variety of assumptions, it was estimated that the air contains ca. 14 pg/m³ "2,3,7,8-TCDD equivalents."

References

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Versar New York Inc. (1983). Determination of the Ratios of Toxic Chemicals in the Air in the BSOB: PCB Analysis, Versar New York Report, May 23, 1983.

Table I Concentrations of Polychlorinated Dibenzofurans, Dibenzodioxins, and Biphenylenes
Determined in 11/82, 2/83, and 4/83 Samplings of the BSOD^{1,2}

LOCATION ³	DATE	<u>2,3,7,8-TCDF</u>	<u>"TOTAL TCDF"</u>	<u>"TOTAL PENTACDF"</u>	OTHER
16th, NE	11/82	14 pg/m ³	97 pg/m ³	22 pg/m ³	"TOTAL TCDD" <1.2 pg/m ³
16th, SE	11/82	13 pg/m ³	78 pg/m ³		"TOTAL TCDD" <1.3 pg/m ³
16th, NW	11/82	9.2 pg/m ³	55 pg/m ³		"TOTAL TCDD" <1.3 pg/m ³
16th, SW	11/82	7.0 pg/m ³	52 pg/m ³		
17th, NW	2/83	<u>11.5 pg/m³</u>	71 pg/m ³	17 pg/m ³	
16th, NW	2/83	<u>16 pg/m³</u>	118 pg/m ³	21 pg/m ³	
14th, NW	2/83	<u>11 pg/m³</u>	92 pg/m ³	21 pg/m ³	
14th, NE	2/83	<u>14 pg/m³</u>	185 pg/m ³	13 pg/m ³	
11th, SE & NW	2/83	<u>16 pg/m³</u>	133 pg/m ³	19 pg/m ³	
11th, NW	2/83	<u>23 pg/m³</u>	76 pg/m ³	16 pg/m ³	
11th, NW	4/83	--	--	--	"TOTAL TCDD" <u>1.0 pg/m³</u> ; 2,3,7,8-TCDD <u>0.3 pg/m³</u> "TOTAL PENTACDDs" <0.5 pg/m ³ ; "PENTACHLOROBIPHENYLENES" <u>2.6 pg/m³</u>
9th, SE	4/83	<u>14 pg/m³</u>	<u>150 pg/m³</u>	<u>3.4 pg/m³</u>	"TOTAL HEXACDF" <u>3.7 pg/m³</u>
9th, NW	4/83	<u>16 pg/m³</u>	<u>145 pg/m³</u>	<u>47 pg/m³</u>	"TOTAL TCDD" <u>1.3 pg/m³</u> ; 2,3,7,8-TCDD <u>0.5 pg/m³</u> "TOTAL PENTACDDs" <0.5 pg/m ³ ; "PENTACHLOROBIPHENYLENES" <u>1.4 pg/m³</u>
7th, NW	4/83	<u>11 pg/m³</u>	<u>121 pg/m³</u>	<u>36 pg/m³</u>	"TETRACHLOROBIPHENYLENES" <u>0.5 pg/m³</u>
6th, NW	4/83	<u>11 pg/m³</u>	<u>126 pg/m³</u>	<u>30 pg/m³</u>	"TOTAL HEXACDF" <u>2.0 pg/m³</u> ; 5th, NW; <u>8.7 pg/m³</u> ; 5th, NE
3rd, NW	4/83	<u>16 pg/m³</u>	<u>151 pg/m³</u>	<u>43 pg/m³</u>	"TETRACHLOROBIPHENYLENES" <u>1.3 pg/m³</u>
5th, NE	4/83	<u>20 pg/m³</u>	<u>195 pg/m³</u>	<u>60 pg/m³</u>	"TETRACHLOROBIPHENYLENES" <u>0.3 pg/m³</u>
AVERAGE CONCENTRATION		15.0 ± 3.6 pg/m ³	148 ± 24 pg/m ³	42 ± 10 pg/m ³	"TOTAL HEXACDF" <u>4.8 ± 3.5 pg/m³</u> ; "TOTAL TCDD" <u>1.2 ± 0.2 pg/m³</u> 2,3,7,8-TCDD <u>0.4 ± .1 pg/m³</u> ; "TOTAL PENTACDD" <0.5 pg/m ³ "TETRACHLOROBIPHENYLENES" <u>0.7 ± 0.5 pg/m³</u> "PENTACHLOROBIPHENYLENES" <u>2.1 ± .5 pg/m³</u>

¹Underlined data were collected with the building's internal circulation system operative and analyzed using most current methodology. These results are considered to be the most reliable indicators of the building's current condition and are therefore the basis of all subsequent calculations and discussions.

²Method development and validation, analytical procedures, and quality control/quality assurance procedures are detailed in the papers from which these data were abstracted (Smith et al., 1983, 1983a, 1983b).

³Average concentrations calculated using underlined (best) values only; error limits equal one standard deviation.

Table II. Influence of Structure and Chlorination Pattern on Guinea Pig Oral LD₅₀s (Male, Hartley, 200-250g)

<u>Compound</u>	<u>LD₅₀(ug/kg)</u>
2,3,7,8-Tetra CDD	2.5 ^a
2,3,7,8-Tetra CDF	5-10 ^b
1,2,3,7,8-Penta CDD	3.1 ^c
1,2,3,4,7,8-Hexa CDD	73 ^c
1,2,3,7,8,9-Hexa CDD	60-100 ^c
1,2,3,6,7,8-Hexa CDD	70-100 ^c
1,2,3,4,6,7,8-Hepta CDD	> 600 ^c
1,2,4,7,8-Penta CDD	1,125 ^c
2,3,7-Tri CDD	29,444 ^c
2,8-Di CDD	730,000 ^c

^aJ.B. Silkworth, D. McMartin, A.P. DeCaprio, R. Rej, P. O'Keefe and L. Kaminsky (1982). Acute toxicity in guinea pigs and rabbits of soot from a polychlorinated biphenyl-containing transformer fire, Toxicol. Appl. Pharmacol. 65, 425-39.

^bJ.A. Moore, E.E. McConnell, D.W. Dalgard, and M.W. Harris (1979). Comparative toxicity of three halogenated dibenzofurans in guinea pigs, mice and rhesus monkeys. NY Acad. Sci. 320, 151-163.

^cE.E. McConnell, J.A. Moore, J.K. Haseman, and M.W. Harris (1978). The comparative toxicity of chlorinated dibenzo-p-dioxins in mice and guinea pigs. Toxicol. Appl. Pharmacol. 44, 335-356.

Table III. Calculation of "2,3,7,8-TCDD equivalents," Due to Various Dibenzofurans, Dibenzodioxins and Biphenylenes

Best Estimate of Concentration	X	Relative Activity of Compound Class vs. Dibenzodioxins	X	Relative Activity Due to Chlorine Substitution	=	"2,3,7,8-TCDD equivalents"
<u>2,3,7,8-TCDF</u>						
15 pg/m ³	X	1/3	X	1	=	5 pg/m ³
<u>Penta CDFs</u>						
$\frac{42 \text{ pg/m}^3}{2^a}$	X	1/3	X	1	=	7 pg/m ³
<u>Hexa CDFs</u>						
$\frac{4.8 \text{ pg/m}^3}{2^a}$	X	1/3	X	1/30	=	< 0.1 pg/m ³
<u>2,3,7,8-TCDD</u>						
0.6 pg/m ³	X	1	X	1	=	0.4 pg/m ³
<u>1,2,3,7,8-Penta CDD</u>						
$\frac{< 0.5 \text{ pg/m}^3}{2^a}$	X	1	X	1	=	< 0.3 pg/m ³
<u>2,3,6,7-Tetrachlorobiphenylene</u>						
$\frac{0.7 \text{ pg/m}^3}{2^a}$	X	1	X	1	=	0.4 pg/m ³
<u>1,2,3,6,7-Pentachlorobiphenylene</u>						
$\frac{2.1 \text{ pg/m}^3}{2^a}$	X	1	X	1	=	> 1 pg/m ³
						ca. 14 pg/m ³

^a When isomer-specific data are unavailable, it is assumed that 1/2 of the "total" value corresponds to 2,3,7,8-(dibenzodioxins and dibenzofurans) or 2,3,6,7-(biphenylene) substituted compounds.