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Author Smith, R.

Corporate Author

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CHEMICAL DATA ON AIR SAMPLES COLLECTED IN AND NEAR THE BINGHAMTON
STATE OFFICE BUILDING (FEBRUARY, MARCH 1985) BEFORE AND AFTER
THE HVAC SYSTEM IS RETURNED TO NORMAL

R. Smith, P. O'Keefe, K. Aldous, D. Hilker, G. Eadon

July 17, 1985

Wadsworth Center for Laboratories and Research

New York State Department of Health

Albany, New York 12201

INTRODUCTION

Air samples were collected and analyzed for chlorinated dibenzofurans (CDFs), chlorinated dibenzodioxins (CDDs) and chlorinated biphenylenes (CBPs) to study the effect of BSOB HVAC system operating mode on BSOB indoor and outdoor concentrations. This report describes sampling, analytical procedures and results for the determination of these analytes in air samples collected (1) on 2/15/85 at 3 outdoor locations near the BSOB prior to venting of the HVAC, (2) on 2/22/85 at the same locations after venting and (3) on 3/29/85 at the mechanical room mixing boxes on floors 6 and 14 inside the building after venting. Because Prof. C. Rappe of the University of Umea, Sweden, had produced evidence suggesting detectable contamination in an earlier outdoor air sampling, the outdoor samples were collected in duplicate, extracted, and split for independent analysis by Prof. C. Rappe.

Results of the last sampling prior to the return of the HVAC system to normal (September 1984 samples) showed a mixture of Cl₄-Cl₆ CDFs in air from the 6th and 14th floor mixing boxes (similar to that previously found in building air) at concentrations of 47-260 pg/m³ total TCDFs and 29-185 pg/m³ total penta-CDFs (1). At that time C. Rappe found traces of ~~several~~ Cl₄-Cl₆ CDFs in a single sample (September, 1984) of outside air at concentrations of approximately 0.1 pg/m³/isomer (e.g. 12378/12348 0.14 pg/m³ uncorrected for recovery) (1). To confirm these preliminary findings it was necessary to repeat the outdoor air analyses, improving detection limits if possible.

METHODOLOGY

Air Sample Collection

Sample were collected using a two-stage sampling device (0.3 μ particulate filter, silica gel adsorbent cartridge) specifically designed to collect PCDDs and PCDFs (2). In the laboratory the 140^o activated 25 mm x 45 mm silica gel cartridges were spiked with ¹³C 2,3,7,8-TCDD, ³⁷Cl 2,3,7,8-TCDF, and ¹³C 1,2,3,7,8 penta-CDF internal standards. The sampling device was then assembled and wrapped in foil for transport. At the site, samples were taken by drawing 80 M³ of air through the sampler at approximately 20 L/min using a 1.5 CFM Gast vacuum pump. After sampling, the intact device was wrapped in foil and transported at room temperature to the laboratory for analysis.

Sample Extraction, Compositing, and Splitting

The particulate-containing filter was placed in the associated adsorbent cartridge and subjected to Soxhlet extraction with 80 ml benzene for 16 hrs (samples found to contain large amounts of water were extracted with acetone then benzene). The duplicate sample extracts to be combined (e.g. 50363 + 50364) were concentrated if necessary, combined, (as sample #50744) and split 50/50. Sample extracts to be mailed to Umea, Sweden were concentrated to 100 μ L, transferred to 2 mm i.d. Pyrex capillary tubes, then the volume was reduced to just dryness under vacuum (exchanged standards were similarly handled). The capillary tubes were then sealed and packaged for transport. The sample extracts to be analyzed by WCL R were additionally spiked with ¹³C OCDD and handled as follows:

Sample Clean-up

The benzene extract was passed through a 22 mm i.d. chromatography column packed bottom to top with 4 mm Na_2SO_4 , 4 mm K Silicate, 4 mm silica gel, 30 mm 44% H_2SO_4 silica gel, 4 mm silica gel, 40 mm Na_2CO_3 , 50 mm silica gel and 4 mm Na_2SO_4 followed by hexane solvent. The sample in 50% benzene/hexane was then cleaned up using a microprocessor controlled sequence of acidic alumina, PX-21 carbon, and neutral alumina chromatography followed by concentration to 100 μL for storage in sealed glass capillaries. Just prior to GC/MS analysis, the samples were concentrated to 4 μL under vacuum. The extract at this stage contains all Cl_4 - Cl_1 , CDFs and CDDs.

Capillary GC/LRMS

A portion of the sample extract (0.8 to 1.8 μL) was injected onto either a 60 m 0.25 mm i.d. SP2330 or 50 m 0.2 mm i.d. DB5 fused silica GC capillary column, head pressure 20 psi, directly interfaced to a Hewlett-Packard 5970 Mass Selective Detector. The MSD was used in the EI mode with a 235^oC source temperature and unit resolution. Data acquisition was accomplished using the single ion monitoring mode with m/e values and chromatographic conditions shown in Table 1.

Calculations

The results were calculated by integrating a single ion chromatographic peak (e.g. 2,3,7,8-TCDF) and by summing total area counts for groups of observed peaks (e.g., TCDFs). TCDFs and TCDDs were quantitated by an isotope dilution internal standard method (eq. 1) which inherently corrects for any recovery losses. Detection limits were similarly calculated, substituting nearby MS noise in arbitrary counts (e.g. 1000 area counts) incorporating a detection limit factor of 2.5.

$$C_1 = X C_2 A_1 / A_2 \quad (\text{eq. 1})$$

Where C_1 = the calculated concentration of native CDF (or CDD) in pg/m^3 .

X = a theoretical mass spectral response factor that corrects for differences in isotope abundances (1 for ^{13}C -TCDD, 2.5 for ^{37}Cl -TCDF; a measured response factor may also be used.

C_2 = the known concentration of added, isotopically labeled CDF (or CDD) in pg/m^3 .

A_1 = the measured area under the ion chromatographic peak due to native CDF or CDD (e.g. TCDF at m/z 306) in arbitrary counts.

A_2 = the measured area under the ion chromatographic peak to isotopically labeled standard (e.g. TCDF at m/z 312) in arbitrary counts.

Response factors relative to the internal standards were also obtained for congener groups by running native standards along with internal standards.

These response factors were applied to the quantitation of Hexa CDFs to Octa CDF and Penta CDDs to Octa CDD.

Standards

[^{14}C] 2,3,7,8-TCDD (KOR Isotopes, Cambridge, MA) has been used for air sampler recovery experiments. The sample cleanup procedure has been evaluated using all 22 TCDDs, OCDD (Analabs, North Haven, CT) 2,3,7,8-TCDF (NIEHS), ^{37}Cl penta-CDF mixture of isomers purified by RPLC (KOR), OCDF

(Analabs), and 2367-TC BP (academic source). Internal standards for quantitation included $^{13}\text{C}_{12}$ 2,3,7,8-TCDD (KOR) and $^{37}\text{Cl}_4$ 2,3,7,8-TCDF (KOR) purified by RPLC, ^{13}C 1,2,3,7,8 penta-CDF and ^{13}C OCDD.

Quality Assurance

The following measures ensure the quality of this analysis. Various blanks are run concurrently with samples and strict criteria for the identification of each compound class are observed. An isotopically labeled internal standard is added to each sample prior to sampling or analysis to provide both a qualitative check and accurate quantitation when sample recovery data is variable.

Blanks

Four types of blanks were run: (1) a system blank prior to the use of any glassware to ensure no carryover from prior samples; (2) a method blank, run simultaneously and using the same standards, solvents, adsorbents, and glassware as the actual samples; (3) isotopically-labeled standards; and (4) benzene blanks to check for GC and syringe carryover.

Precision

The best measure of precision is obtained from replicate samples. This is commonly within 20%. The recovery of the internal standard available for each sample will provide a measure of precision; however, this is based on external standardization (requiring manipulation and accurate measurement of sample volumes of 1 to 4 μl) and is known to be less precise than internal standardization.

Criteria for Detection

To be detected as a PCDD or PCDF isomer in a sample all of the following conditions must be met:

1. co-elution on GC with appropriate standard if available.
2. response at a minimum of two ions corresponding to M , $M+2$; response must be in proper ratio $\pm 20\%$; response at additional fragment ions such as $M-COCl$ for greatest reliability when sensitivity permits.
3. adequate recovery of all internal standards.
4. acceptable QC blanks and spikes.
5. negligible mass spectral interference.

RESULTS

Table 2 contains the data generated by the New York State Department of Health from outdoor air samples collected prior to (February 15-18) and after (February 22-25) returning the building's HVAC system to normal operations. Table 3 contains the data generated from indoor air samples collected on the 6th and 14th floors on March 29-April 1.

DISCUSSION

The outdoor air data both before and after returning the HVAC system to normal operation contains no evidence for the presence of any tetrachlorodibenzofuran isomer (detection limit 0.06-0.15 pg/m^3) or any pentachlorodibenzofuran isomer (detection limit 0.2-0.5 pg/m^3). (Doctor C. Rappe's analysis of splits of these samples yielded results consistent with this data (not detected at about 1 pg/m^3 /isomer). (Personal Communication, written report to follow). Since tetra and pentachlorofurans are by far the most abundant compounds among the furans, dioxins and biphenylenes within the BSOB, detection of any such BSOB-induced contamination of the outdoor air in either the pre-venting or current post-venting mode of operation is clearly beyond the capacity of present-day analytical techniques.

The indoor air data of Table 3 demonstrates the presence of tetra-, penta-, and hexachlorofurans in detectable concentrations; Hepta- and octachlorofurans, tetra- and penta-chloro-biphenylenes and tetra-, penta-, hexa-, hepta-, and octachlorodibenzodioxins were all below limits of detection.

There are many cross comparisons possible among the data produced by WCL&R from the September 1984 and the March 1985 samplings. Dibenzodioxins (tetra through octachloro), hepta and octachloro furans, and pentachlorobiphenylenes were not detected in either sampling; tetrachlorobiphenylenes, barely above the limit of detection in 1984, were not detected in 1985, consistent with the

subsequently discussed decrease in overall concentrations. As Table 4 demonstrates, the patterns observed in the tetra through hexachlorofurans (the only compounds present above detection limits during both samplings) are generally maintained. Thus, for the 6th floor, the ratio total TCDF:total PeCDF:total HxCDF was 1:0.37:0.13 in 9/84 versus 1:0.60:0.14 in 4/85; the corresponding 14th floor ratios were 1:0.60:0.09 and 1:0.42:0.14. For the 6th floor, the ratio 2378-TCDF/total TCDF was 0.07 in 9/84 and 0.06 in 4/85; the corresponding 14th floor ratios were 0.05 and 0.06. The largest 2378-substituted PeCDF peak (actually a mixture of 12378 and 12348-PeCDF) constituted 15% of total PeCDF on the 6th floor in 9/84, and 9% in 4/85. The corresponding values for the 14th floor are 15% and 16%.

The most important difference between the two data sets is the significant decrease in concentrations of tetra through hexa CDFs in the April sampling (Table 4). Thus, for example, total TCDF concentration (averaged over the 6th and 14th floors) decreased by a factor of 2.6; the corresponding factors for total PeCDF and total HxCDF were 2.9 and 2.0. These decreases in concentration as well as improvements in detection limits for 2367-tetrachlorobiphenylene and 12367-pentachlorobiphenylene result in a recalculated "2378-TCDD equivalent" concentration of $<4.1 \text{ pg/m}^3$ in April, 1985 versus $<11 \text{ pg/m}^3$ in November, 1984 (Table 5).

REFERENCES

- 1 Aldous, K., Hilker, D., O'Keefe, P., Smith, R. and Eadon, G., Chemical data on air and wipe samples collected from the Binghamton State Office Building-September 1984, New York State Department of Health Report.
- 2 Eadon, G., Aldous, K., Hilker, D., O'Keefe, P. and Smith, R., Chemical data on air samples from the Binghamton State Office Building, New York State Department of Health Report.

TABLE I

DATA ACQUISITION

Rev. 1.3 1-Nov-84

load/store Method : METH:BINGH.M

Description : 2378 ANALYSIS ON 2330 GC COLUMN

SIM ACQUISITION 13 Jun 85 10:19 am METH:BINGH.M

solvent delay 8.00 eM volts 800 relative resulting voltage 2200

Group	1	2	3	4	5	6	7	8	9	10
# of ions	6	18	9	4	5	8	1	1	1	1
start Time	10.00	0.00	0.00	0.00	0.00	0.00				

low ms Resolution NO cycles per second 1.4

ion #	1	2	3	4	5	6
m/z	303.90	305.90	311.90	339.65	341.65	351.90
Dwell	100	100	100	100	100	100

TEMPERATURE PROGRAM & HEATED ZONES

run time 75.00 equilibration time 0.50 splitless on time 0.50

Level	initial tEmp	initial time	Rate (OC/Min)	final tEmp	final time	total time
1	75	1.00	50.0	235	75.00	75.20
2						
3						
4						
5						
6						
7						
8						

	actual	Setpt	Limit		actual	Setpt	Limit
Oven (Standby)	75	75	300	Inj Port A	---	Off	250
Inj Port B	250	250	250	Transfer Line	235	235	300
Detector A	---	Off	425				

TABLE I (continued)

TEMPERATURE PROGRAM & HEATED ZONES

rUn time 95.00 eQuilibration time 0.50 sPlitless on time 1.00

Level	Initial tEmp	initial time	Rate (OC/Min)	final tEmp	final time	total time
1	190	1.00	5.0	220	16.00	23.00
2			5.0	235	7.00	33.00
3			5.0	250	18.00	54.00
4			5.0	270	7.00	65.00
5			5.0	300	24.00	95.00
6						
7						
8						

	actual	Setpt	Limit		actual	Setpt	Limit
Oven (Standby)	190	190	300	Inj Port A	---	Off	250
Inj Port B	250	250	250	Transfer Line	276	275	300
Detector A	---	Off	425				

TABLE I (continued)

DATA ACQUISITION

Rev. 1.3 1-Nov-84

load/store Method : METH:BINGIN.M

Description : CONGENER GROUP ANALYSIS FOR BING INDOOR AIR SAMPLES DB-5

1.00 Valves Splitless Off
 14.00 Group 1
 14.00 Mass Spec On
 47.00 Group 2
 60.00 Group 3
 95.00 Stop Run

SIM ACQUISITION 13 Jun 85 2:07 pm METH:BINGIN.M

solvent delay 14.00 eM volts 800 relative resulting voltage 2400

Group	1	2	3	4	5	6	7	8	9	10
# of Ions	15	9	15	4	4	20	20	20	20	20
start Time	14.00	47.00	60.00							

low ms Resolution NO cycles per second 0.6

Ion #	1	2	3	4	5	6	7	8	9	10
m/Z	270.00	272.00	286.00	288.00	304.00	306.00	312.00	320.00	322.00	334.00
Dwell	100	100	100	100	100	100	100	100	100	100

Ion #	11	12	13	14	15
m/Z	340.00	342.00	352.00	356.00	358.00
Dwell	100	100	100	100	100

Group	1	2	3	4	5	6	7	8	9	10
# of Ions	15	9	15	4	4	20	20	20	20	20
start Time	14.00	47.00	60.00							

low ms Resolution NO cycles per second 1.0

Ion #	1	2	3	4	5	6	7	8	9
m/Z	304.00	306.00	320.00	322.00	340.00	342.00	352.00	356.00	358.00
Dwell	100	100	100	100	100	100	100	100	100

Group	1	2	3	4	5	6	7	8	9	10
# of Ions	15	9	15	4	4	20	20	20	20	20
start Time	14.00	47.00	60.00							

low ms Resolution NO cycles per second 0.6

Ion #	1	2	3	4	5	6	7	8	9	10
m/Z	356.00	358.00	374.00	376.00	390.00	392.00	408.00	410.00	424.00	426.00
Dwell	100	100	100	100	100	100	100	100	100	100

Ion #	11	12	13	14	15
m/Z	444.00	446.00	460.00	462.00	472.00
Dwell	100	100	100	100	100

TABLE I (continued)

TEMPERATURE PROGRAM & HEATED ZONES

rUn time 95.00 eQuilibration time 0.50 sPlitless on time 1.00

Level	initial tEmp	initial time	Rate (OC/Min)	final tEmp	final time	total time
1	190	1.00	5.0	220	16.00	23.00
2			5.0	235	7.00	33.00
3			5.0	250	18.00	54.00
4			5.0	270	7.00	65.00
5			5.0	300	24.00	95.00
6						
7						
8						

	actual	Setpt	Limit		actual	Setpt	Limit
Oven (Standby)	190	190	300	Inj Port A	---	Off	250
Inj Port B	250	250	250	Transfer Line	278	275	300
Detector A	---	Off	425				

TABLE I (continued)

DATA ACQUISITION

Rev. 1.3 1-Nov-84

load/store Method : METH:BINGH.M

Description : 2378 ANALYSIS ON 2330 GC COLUMN

SIM ACQUISITION 13 Jun 85 10:19 am METH:BINGH.M

solvent delay 8.00 eH volts 500 relative resulting voltage 2200

Group	1	2	3	4	5	6	7	8	9	10
# of Ions	5	18	9	4	5	8	1	1	1	1
startTime	10.00	0.00	0.00	0.00	0.00	0.00	-----	-----	-----	-----

low ms Resolution NO cycles per second 1.4

ion #	1	2	3	4	5	6
m/z	303.90	305.90	311.90	339.85	341.85	351.90
Dwell	100	100	100	100	100	100

TEMPERATURE PROGRAM & HEATED ZONES

run time 75.00 equilibration time 0.50 splitless on time 0.50

Level	initial tEmp	initial time	Rate (OC/Min)	final tEmp	final time	total time
1	75	1.00	50.0	235	75.00	79.20
2						
3						
4						
5						
6						
7						
8						

	actual	Setpt	Limit		actual	Setpt	Limit
Oven (Standby)	75	75	300	Inj Port A	---	Off	250
Inj Port B	250	250	250	Transfer Line	235	235	300
Detector A	---	Off	425				

TABLE 3. Indoor Air Samples Collected within the Binghamton State Office Building (pg/MS)

LOCATION	Vol M3	Sample #	F U R A N							
			2378 Te	Total Te	Recov. %	23478 Pe	12378 Pe	12348 Pe	Total Pe	Recov. %
March 29-April 1										
Floor 6-HVAC	77.6	50801	2.5	38	92	0.4	3	20	102	
Floor 6-HVAC	77.6	50802	3.2	59	51	0.5	2.7	42	68	
Floor 14-HVAC	77	50803	3.8	64	40	1.6	4.4	27	45	
Control (Spike)	0	50804	180	-	50	-	330	-	20	
Control	0	50850	ND (0.2)	-	56	ND (0.3)	ND (0.2)	-	24	
Blank	0	51297	ND (0.2)	-	65	ND (0.3)	ND (0.2)	-	86	
SPIKE LEVEL			198		90		618		51	

LOCATION	Vol M3	Sample #	D I O X I N		
			2378 Te	Total Te	Recov. %
March 29-April 1					
Floor 6-HVAC	77.6	50801	ND (0.3)	-	82
Floor 6-HVAC	77.6	50802	ND (0.3)	-	72
Floor 14-HVAC	77	50803	ND (0.4)	-	55
Control (Spike)	0	50804	157	-	87
Control	0	50850	ND (0.2)	-	100
Blank	0	51297	ND (0.2)	-	103
SPIKE LEVEL			79	-	198

PeCDD

Table 4. Comparison of Polychlorinated Dibenzofuran Concentrations (Pg/m³) in Air Samples^(a)

	2378	Total	12378		Total	123478	Total	Total	Total
	-Cl ₄	-Cl ₄	-Cl ₅	-Cl ₅	-Cl ₅	-Cl ₆	-Cl ₆	-Cl ₇	-Cl ₈
<u>6th Floor</u>									
Sept., 1984 ^b	6.0	89	5.0	ND(1) ^c	33	2.0	12 ^c	NA	NA
April, 1985 ^b	2.8	49	2.9	0.5	31	ND(0.6) ^c	6.9 ^c	ND(0.7)	ND(1.5)
<u>14th Floor</u>									
Sept., 1984 ^b	10	215	20.0	1.4	130	3.5	20	NA	NA
April, 1985 ^c	3.8	64	4.4	1.6	27	ND(0.7)	9.1	ND(1.0)	ND(2.1)
<u>GRAND AVERAGE</u>									
Sept., 1984	8.0	150	13.0	1.2	83	2.9	16	NA	NA
April, 1985	3.3	57	3.7	1.1	29	1.2	8.0	ND(1.0)	ND(2.1)

(a) ND indicates not detected (limit of detection); NA = not analyzed for

(b) Average of two samples unless specifically indicated

(c) Based on measurement in one sample

Table 5. Calculation of Average "2,3,7,8-TCDD Equivalents Due to Various Dibenzofurans, Dibenzodioxins and Biphenylenes for 6th and 14th Floor Air Samples

Best Estimate of Average Concentration Equivalents"	X	Relative Activity of Compound Class vs. Dibenzodioxins	X	Relative Activity Due to Chlorine Substitutions	=	"2,3,7,8- TCDD
<u>2,3,7,8-TCDF</u>						
3.3 pg/m ³	X	1/3	X	1	=	1.1 pg/m ³
<u>12378, 12348, 23478-PeCDF</u>						
4.8 pg/m ³	X	1/3	X	1	=	1.6 pg/m ³
<u>HEXA CDFs</u>						
$\frac{8.0 \text{ pg/m}^3}{2^a}$	X	1/3	X	1/30	=	0.04 pg/m ³
<u>2378-TCDD</u>						
<0.4 pg/m ³	X	1	X	1	=	<0.4 pg/m ³
<u>12378-PeCDD</u>						
<0.5 pg/m ³	X	1	X	1	=	<0.5 pg/m ³
<u>HEXA CDDs</u>						
<2.1 pg/m ³	X	1	X	1/30	=	<0.07 pg/m ³
<u>2367-Tetrachlorobiphenylene</u>						
<0.2 pg/m ³	X	1	X	1	=	<0.2 pg/m ³
<u>12367-Pentachlorobiphenylene</u>						
<0.2 pg/m ³	X	1	X	1	=	<0.2 pg/m ³
					Total	<4.1 pg/m ³

(a) Since standards are not available to allow quantitation of all 2378-substituted hexa CDFs, it is conservatively assumed that 1/2 of the "total hexa CDF" is 2378-substituted.