
Toxic Substances



Sampling and Analysis of Selected Toxic Substances

Task 1: Polybrominated Biphenyls in Air and Soil at User Sites



SAMPLING AND ANALYSIS OF SELECTED TOXIC SUBSTANCES
TASK 1: POLYBROMINATED BIPHENYLS IN AIR AND SOIL AT USER SITES

by

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ABSTRACT

Field sampling for air and soil was conducted in the vicinity of two Borg Warner Co. facilities, one in Oxnard, CA and the other near Parkersburg, W.V.

Polybrominated biphenyls (PBBs) were found in all of the soil samples from Oxnard with the highest levels (36,000 $\mu\text{g/kg}$) nearest the facility and the lowest (5 $\mu\text{g/kg}$) upwind the greatest distance. No PBBs were found in any of the air samples ($<3 \text{ ng/m}^3$).

Polybrominated biphenyls were confirmed in seven of the thirteen soil samples from West Virginia, (up to 12 $\mu\text{g/kg}$) traces detected but not confirmed in three, and no PBBs were detected in the other three. The highest levels were from samples collected in the Ohio River basin especially along the eastern bank. No PBBs were confirmed in the air samples ($<4 \text{ ng/m}^3$).

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SECTION 1

SUMMARY AND CONCLUSIONS

A field trip to collect air and soil samples in the vicinity of Borg-Warner Co., Oxnard, CA was executed January 22 through 28, 1979. Access to suitable sampling locations was severely limited for the air monitoring and somewhat limited with respect to soil sampling. In all, 14 air samples were collected over 4 days. The meteorological conditions varied over the 4 days with strong winds on January 24, 1979. Soil samples were taken along an ENE transect upwind and downwind near (within a block) and far (1 km) from the facility. Soil was also collected ~1 km in either direction at right angles to the first transect.

Polybrominated biphenyls (PBB's) were found in all of the soil samples with the highest levels (36,000 µg/kg) nearest the facility and the lowest (5 µg/kg) upwind the greatest distance. No PBBs were found in any of the air samples (<3 ng/m³).

A second field trip to collect air and soil samples in the vicinity of Borg-Warner Co., Parkersburg, WV was executed March 26 through March 30, 1979. Access to sampling sites was again limited however in this case it was due to the sparsely populated areas adjacent to the facility for which no power drops were available and the Ohio River which blocked access to one side of the facility. In spite of these limitations air sampling sites were located in an upwind-downwind orientation. Thirteen soil samples were taken at several distances in all directions up to 3 km from the facility. In all, 16 air samples were collected over 4 days. The meteorological conditions were somewhat more severe than normal for March with temperatures ranging from -1 to 24°C and westerly winds from calm to moderate. Light snow flurries were encountered during the first sampling period.

Polybrominated biphenyls were confirmed in seven of the thirteen soil samples, traces detected but not confirmed in three and none were detected

in three other soils. The location of the PBB's follows the Ohio River basin especially along the eastern bank. No PBB's were confirmed in the air samples ($<4 \text{ ng/m}^3$).

SECTION 2

INTRODUCTION

Polybrominated biphenyls (PBBs) have been used extensively as flame retardants for polymers, textiles, and other materials.⁽¹⁾ Although previous environmental studies have centered around facilities manufacturing PBBs, little attention has been given to their impact on the environment via user facilities. Questions about their environmental distribution through widespread use have been aroused by the recent major environmental catastrophes in Michigan.⁽²⁾ The extent to which generalized pollution results from normal usage of PBBs throughout the United States is still undefined.

The subject of this report is an assessment of the environmental contamination in the vicinity of a user facility, Borg Warner Co. in Oxnard, CA. To assess the contamination two types of environmental samples were collected, soil and air. The former represents an environmental sink which for persistent compounds such as PBBs gives a historical picture of PBB contamination. Since air is the most probable transport medium, air samples were also taken.

SECTION 3

METHOD VALIDATION

SAMPLING

Air

Air samples were collected using a custom designed rotary vane pump (Nutech Corp., Durham, NC), Figure 1, and a glass sampling head, Figure 2, which holds a glass fiber filter (GFF) and 2 polyurethane foam (PUF) plugs.

The pressure drop imposed by the glass fiber filter and sorbent material is such that flow rates greater than 300 l/min are not practical. For this reason, pumps which could operate continuously at about 300 l/min with an estimated pressure drop of 130 mm of Hg were investigated. Gast rotary vane pumps satisfied this requirement.

These air samplers have been used for the collection of chloronaphthalenes in ambient air.⁽¹¹⁾ The sampler shown schematically in Figure 1 uses a Gast oilless rotary vane vacuum pump model No. 1022. This pump is rated to deliver 280 l/min air flow at no pressure drop and 250 l/min air flow at 130 mm Hg. The selection of this model was based in part on the fact that it has a motor mounted drive rather than belt drive which results in a more compact, lighter unit for field sampling.

The flow rate is monitored at the pump exhaust to avoid the problems associated with correcting for pressure changes during the sampling period. The pressure at the pump was monitored with a vacuum gauge which serves to signal possible malfunctions.

The sorbent material, PUF, was prepared from Olympic 2315[®] polyether type polyurethane foam (Olympic Products Company, Greensboro, NC). These plugs, 5 cm diameter x 13 cm long were cut from sheets of polyurethane foam with an electric knife. The plugs were cleaned by five successive extractions with toluene at 100°C for approximately 10 min per extraction. After

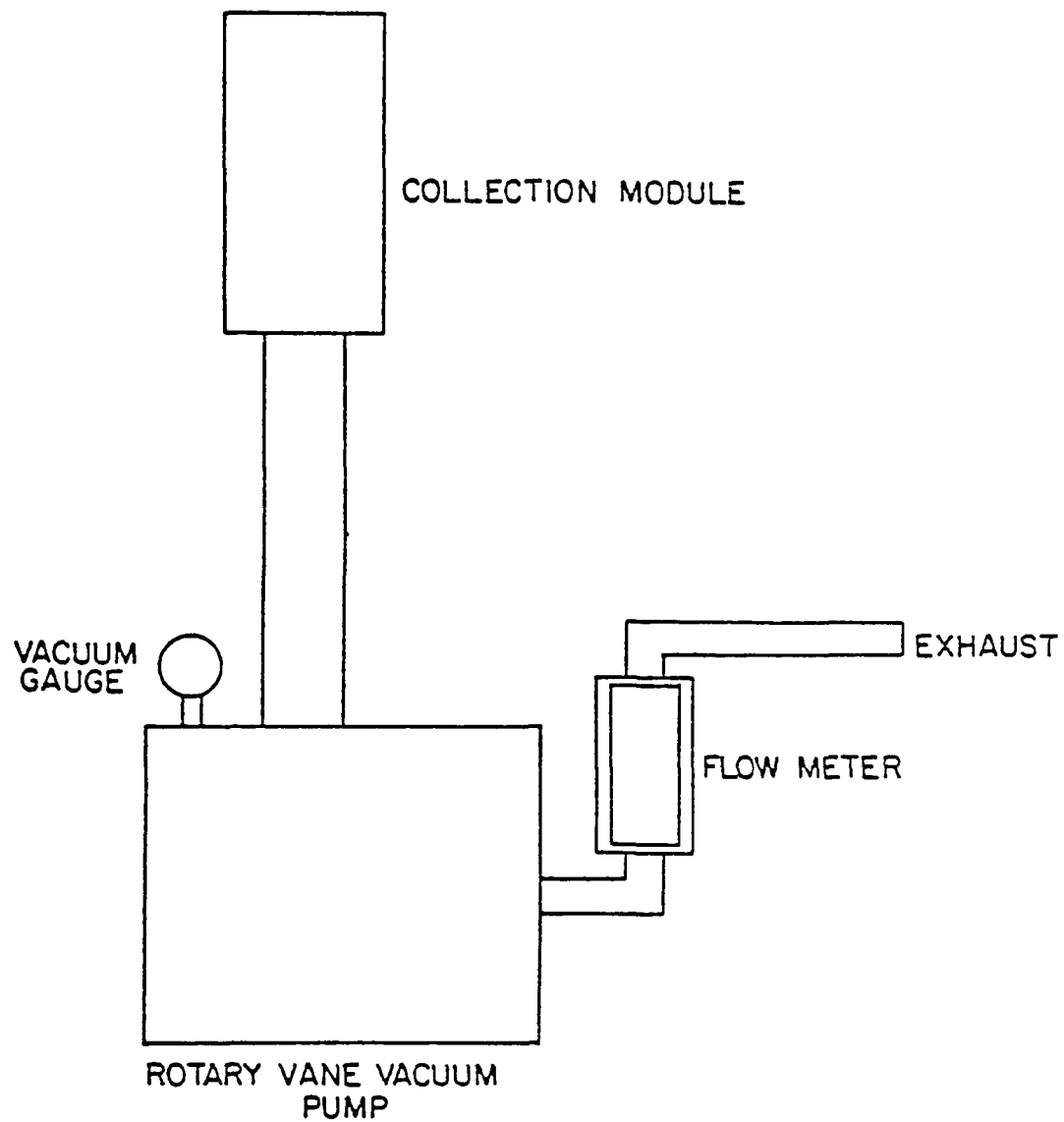


Figure 1. Air sampler.

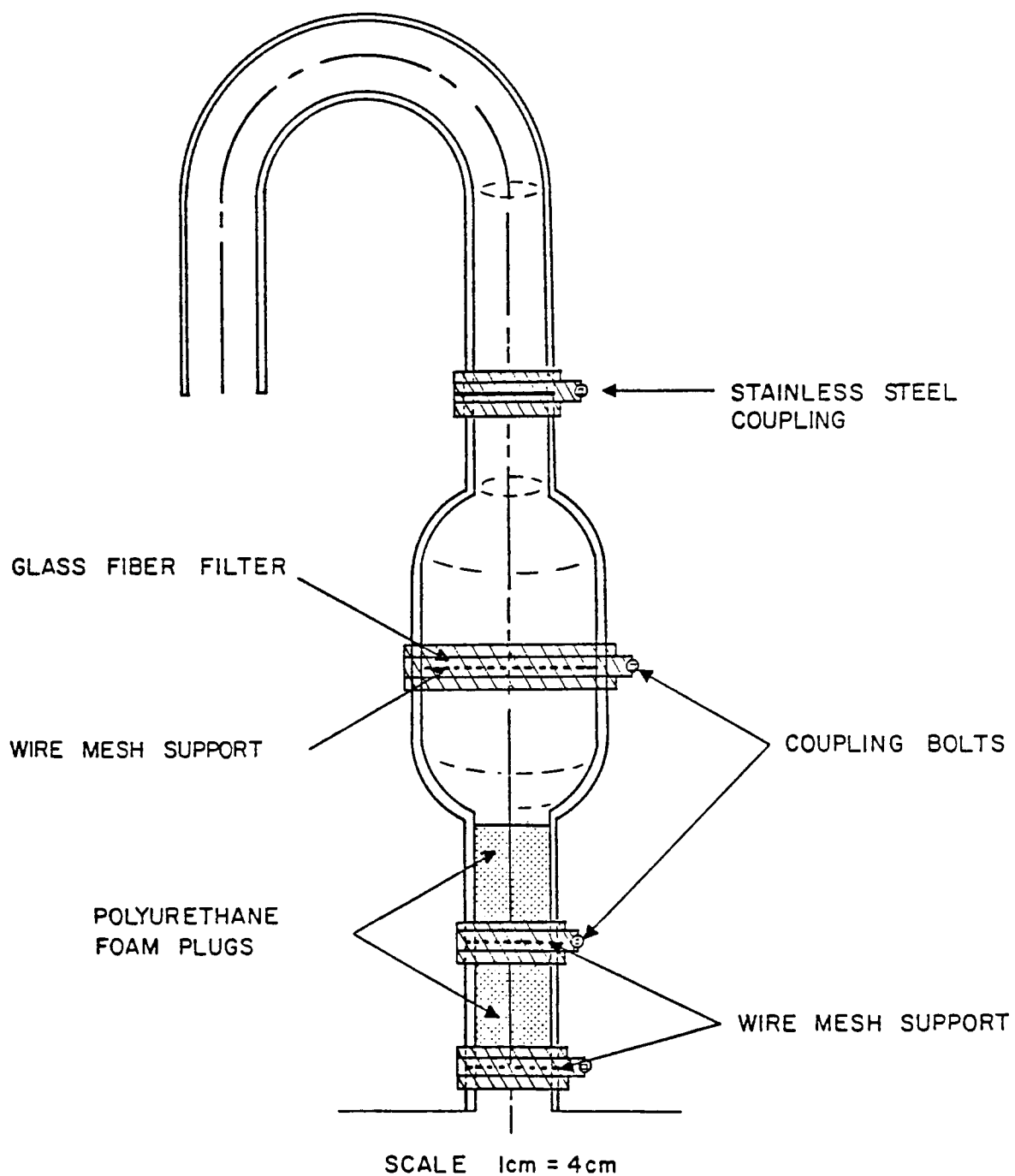


Figure 2. Sampling apparatus configuration for collection of polychlorinated naphthalenes.

extraction individual plugs were placed in 9 oz. glass jars and dried in vacuo at 50°C for ~12 hr. After drying, the jars were capped and wrapped with aluminum foil to prevent photodegradation of the foam. This procedure was shown to give a relatively low background when used for polychlorinated naphthalene (PCN) sampling and analysis.⁽¹¹⁾

The performance of this sampling medium was previously evaluated for PCNs which as a group are more volatile than the PBBs analyzed here. The highest molecular weight PCN, octachloronaphthalene, has a volatility between that of pentabromobiphenyl and hexabromobiphenyl based on gas chromatographic elution times. Monobromobiphenyl has a volatility similar to di- or trichloronaphthalene. In the previous validation experiment, all of the PCNs were well retained on the tandem PUF plugs with the exception of the monochloronaphthalene.⁽¹¹⁾

Control and blank samples for both the GFF and PUF media were prepared and analyzed. That data is included in Section 5.3.

Soil

Soil samples are collected using a common garden bulb planter. A 2.5 cm deep core of soil was taken in 5 points approximately 5 m apart and arrayed so as to represent an area ~10 M in diameter. Each such area is referred to as a location. The soil was placed in precleaned glass jars, capped with foil-lined caps and labeled. The arrangement of these locations is discussed in Section 4.1. The cores from each location were composited before analyzing.

The extraction procedure used for soils was an adaptation of a method reported for pesticides, PCBs and PCNs^(12,13) and tested for its applicability to PBBs.⁽¹⁴⁾

EXTRACTION AND WORKUP

The extraction and work-up procedures had previously been validated for other halogenated compounds (i.e. polychlorinated naphthalenes⁽¹¹⁾). These procedures were validated in this work by the use of controls and blanks prepared in each media, GFF, PUF, and soil. These controls and blanks were analyzed by the protocol in Appendix A. The results are given in Section 5.0 along with the field controls and blanks.

GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) ANALYSIS

Analytical methodology was validated by GC/MS by a consistent policy of use of standards. Each day the mass spectrometer was tuned using perfluorotributylamine (FC-43) as a reference compound. Peak resolution was checked daily, as were relative abundances of peaks in the reference compound. This provided a check only for the mass spectrometer, however. To monitor the performance of the entire system, a solution containing known quantities of pure isomers of certain of the polybrominated biphenyls (2-bromobiphenyl, 4.99 ng/ μ l; 4,4'-dibromobiphenyl, 4.56 ng/ μ l; 2,4',5-tribromobiphenyl, 10.08 ng/ μ l; 2,2',5,5'-tetrabromobiphenyl, 9.90 ng/ μ l; 2,2',4,5',6-pentabromobiphenyl, 10.03 ng/ μ l; and 2,2',4,4',6,6'-hexabromobiphenyl, 9.98 ng/ μ l) and internal standards (octachloronaphthalene, 3.72 ng/ μ l; and decachlorobiphenyl, 3.96 ng/ μ l) was used. The standard was used as the first and last analysis of the day. Also, during the course of the day, every fifth injection was an analysis of the standard solution. Samples were analyzed by the selective ion monitoring (SIM) technique. Ratios of peak areas were calculated and standard deviations of these ratios observed to monitor stability of the system. Also, each sample contained two internal standards, octachloronaphthalene and decachlorobiphenyl, at a level of approximately 2 ng/ μ l each. These standards were monitored in every determination. A second standard mixture (containing decachlorobiphenyl, 88 ng/ μ l; 2,2',4,4',6,6'-hexabromobiphenyl, 116 ng/ μ l; and 2,2',3,3',5,5',-6,6'-octabromobiphenyl, 80 ng/ μ l) was used in the analysis of the hepta- through deca-isomers.

The columns used in the analyses were a 180 cm x 0.2 cm i.d. glass column, 2% OV-101 on 80/100 Gas Chrom Q for monobromo-through hexabromobiphenyl and a 42 cm x 0.2 cm i.d. glass column with the same packing for hexabromo-through decabromobiphenyl. The temperature range was 190° to 280°C, programmed at 12°/min with a helium flow rate of 30 cc/min for the longer column. For the shorter column, a temperature range of 240° to 280°C programmed at a rate of 8°/min was employed. The separator was maintained at 250°C, the injector at 280°C.

Intensities of isotopic peaks relative to a molecular ion (calculated for ^{79}Br) for polybrominated compounds are shown in Table 1.

Table 1. INTENSITIES OF ISOTOPIC PEAKS RELATIVE TO THE MOLECULAR ION FOR
POLYBROMINATED COMPOUNDS

Degree of Bromination	M	M + 2	M + 4	M + 6	M + 8	M + 10	M + 12	M + 14	M + 16	M + 18	M + 20
Br	100	97.8									
Br ₂	100	195	95								
Br ₃	100	293	286	93							
Br ₄	100	391	575	375	92						
Br ₅	100	489	958	937	459	90					
Br ₆	100	587	1436	1875	1376	539	88				
Br ₇	100	685	2011	3280	3210	1885	615	86			
Br ₈	100	783	2682	5249	6421	5027	2460	687	84		
Br ₉	100	881	3440	7873	11557	11310	7379	3095	757	82	
Br ₁₀	100	979	4310	11247	19262	22620	18447	10315	3786	823	81

Using this table as a guide, the most intense ion of a given isotope cluster was selected to monitor for the presence of a given isomer. An approximate time window for elution could be derived from the elution times of the known isomers comprising the standard solution. The ions monitored in PBB analysis are shown in Table 2.

When a primary ion was observed at an appropriate time, identification of the compound as a polybrominated biphenyl was confirmed by a subsequent determination monitoring both the primary and secondary ions. An identification was considered "confirmed" when both ions were present, maximized at the same point, and occurred in the correct intensity ratio.

Table 2. IONS SELECTED FOR PBB ANALYSIS BY SIM

PBB Isomers	M ^a	SIM Ions ^b
C ₁₂ H ₉ Br	232	232, 234
C ₁₈ H ₈ Br ₂	310	312, 310
C ₁₂ H ₇ Br ₃	388	390, 392
C ₁₂ H ₆ Br ₄	466	470, 472
C ₁₂ H ₅ Br ₅	544	548, 550
C ₁₂ H ₄ Br ₆	622	628, 630
C ₁₂ H ₃ Br ₇	700	706, 708
C ₁₂ H ₂ Br ₈	778	788, 784
C ₁₂ HBr ₉	856	866, 862
C ₁₂ Br ₁₀	934	942, 946

^aM = nominal molecular weight based on Br = 79.

^bIons listed in order of "primary" and "secondary".

SECTION 4

FIELD SAMPLING

SAMPLING NEAR THE BORG-WARNER FACILITY IN OXNARD, CA

General Description of the Meteorology of the Area

An excerpt from the Local Climatological Data - Annual Summaries for 1974 is included as Appendix B. This excerpt describes the climatological conditions of Los Angeles, CA. Since Oxnard is on the coastal plain west and a little north of Los Angeles (~75 km), the same influences of ocean (west and south) and mountains (north and east) are operative and determine the climatology of Oxnard. Winds are usually light and variable depending on time of day and season. The predominant wind direction in spring, summer and early fall is on-shore (westerly). In the fall, winter and early spring months, strong winds descend from the mountains to the northeast. These are referred to as the Santa Ana winds and can pick up considerable amounts of dust. Thermal inversions during periods of low air movement at times extends air pollution outward from Los Angeles to Oxnard.

Sampling Protocol

The sampling protocol is given in Table 3 for both air and soil samples. The locations of each of these samples is shown in Figure 3. The local inhabitants were in general not inclined to cooperate and security was very poor. Almost all residences and business establishments had high fences or walls around any private yards. We were informed at the fire station that even with personnel present nearly 24 hours a day they could not assure the security of their fenced areas. Despite these problems, samplers were deployed in nearly the desired array for 4 days as indicated in Table 3.

Discussions with local inhabitants highlighted a factor which may be important in the dispersion of PBBs from such an apparently innocuous source as the Borg-Warner facility in Oxnard. That is the Santa Ana winds which blow out of the mountains in November and December at speeds of 55-80

Table 3. SAMPLING PROTOCOL FOR BORG-WARNER, OXNARD, CALIFORNIA

Period	Cycle	Location	Sampling Time (PST)	Sample Volume (m ³)	Type of Sample	Meteorological Conditions		
						T(°C)	Wind Dir./Speed (kmph)	Other
1/23,24/79 P1	C1	L1	1442-1223	257	air ^a	4-18 ^d	31/2-3 (2 hrs) ^e	overcast-broken clouds in a.m.
		L2	1740-1253	215	air		calm (13 hrs)	
		L4	1620-1314	226	air		2/2-3 (2 hrs)	
							32/2-5 (3 hrs)	
1/24,25/79 P2	C1	L1	1245-1205	271	air ^{a,b}	19 ^f 8-19	32-26/3-7 ^h (9 hrs)	scattered clouds-clear
		L2	1308-1234	264	air		unknown (8 hrs)	
		L3	1205-1136	260	air		31°/8-10 (7 hrs)	
		L4	1344-1302	241	air			
		L5	-	- ^c	soil			
		L6	-	- ^c	soil			
		L7	-	- ^c	soil			
		L8	-	- ^c	soil			
1/25,26/79 P3	C1	L1	1224-1134	260	air ^b	19 ^f 3-10 ^g	27°/8-10 G16 (8 hrs)	clear
		L2	1245-1155	254	air		29/6-9 ^h (4 hrs)	
		L3	1151-1102	254	air		unknown (8 hrs)	
		L4	1317-1213	247	air		2-3/3 (3 hrs)	
							6/3-4 (3 hrs)	
1/26,27/79	C1	L2	1207-1120	262	air	4-16 ^d 3-21 ^g	27/4-5 (6 hrs)	clear
		L3	1118-1055	253	air		2-6/3 ⁱ (4 hrs)	
		L4	1232-1134	250	air		unknown ^l (8 hrs)	
							1-4/5-7 (6 hrs)	
1/28/79	C1	L9	-	- ^c	soil			
		L10	-	- ^c	soil			

^a Nutech Corporation custom designed high volume samplers were used. Sample intake 1-2 m elevation except as noted.

^b Sampler placed on roof ~5 m elevation.

^c Each soil sample was comprised of 5 cores 5.5 cm in diameter and 2.5 cm in depth.

^d From the National Weather Service.

^e From the Oxnard Airport Weather Station. 8 hrs from 2145 to 0600 PST were not recorded.

^f Manual temperature reading at location 4.

^g MRI monitor at location 4.

^h MRI readings indicated calm.

ⁱ MRI readings indicated wind direction was NNE under light winds.

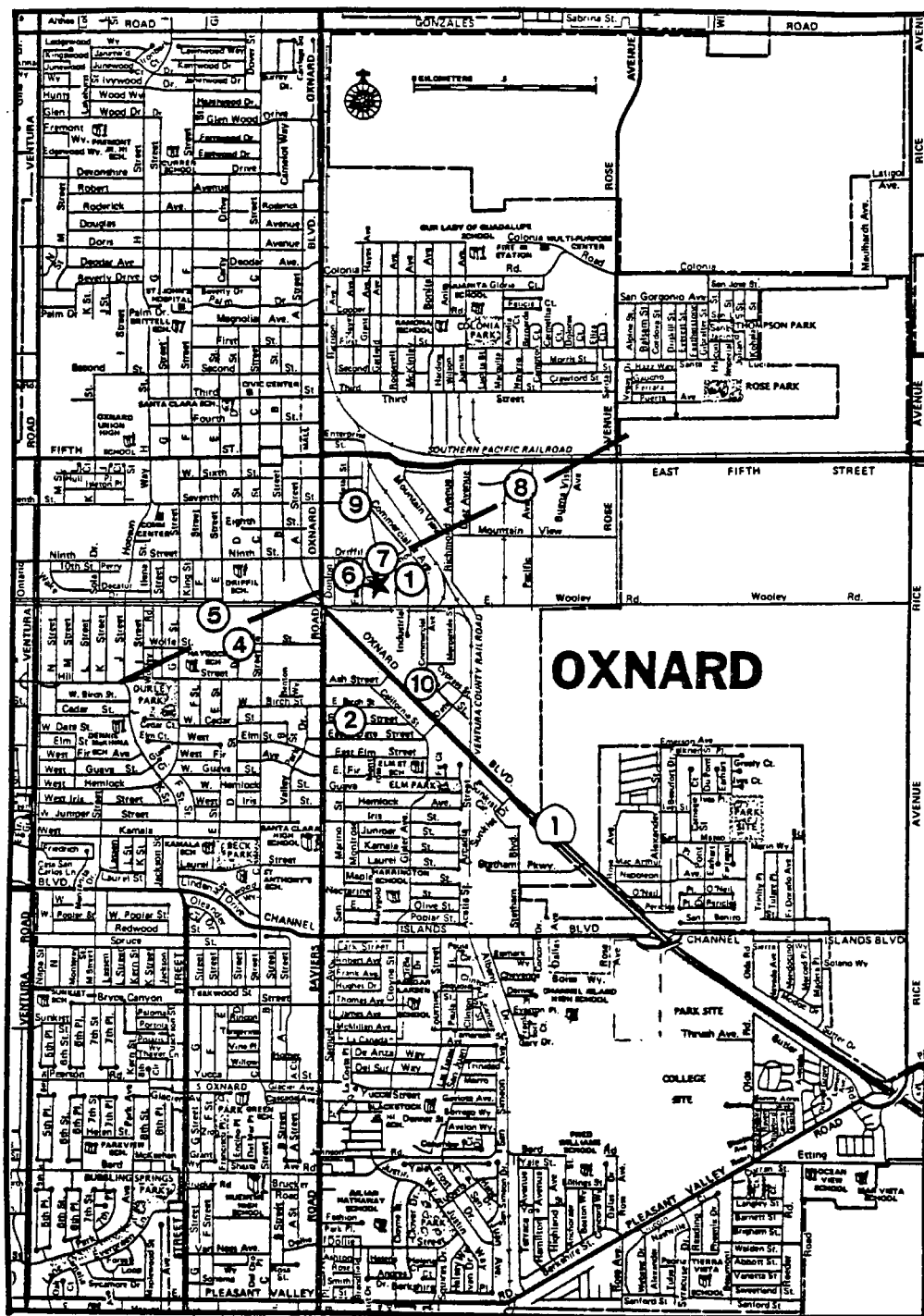


Figure 3. Map of sampling locations Oxnard, CA 1/23-28/1979.

kmph. These winds frequently fuel brush fires in the surrounding hills filling the coastal region where Oxnard is located with dense particulate from the smoke. Similarly dust and other particulates may be transported by these winds.

The meteorological recording instrument (MRI) was set up at Location 4 on 1/24/79. The wind run indicator was operating erratically and hence airport data was used. Wind directions between the two sources were identical

SAMPLING NEAR THE BORG-WARNER FACILITY IN PARKERSBURG, WV

General Description of the Meteorology of the Area

An excerpt from Local Climatological Data - Annual Summaries for 1974 (Part II) is included in Appendix C which describes the average climatological conditions of Parkersburg, WV. The Borg-Warner facility is located in a low, flat area known as Washington Bottom situated on the inside of a right-angle bend in the Ohio River approximately 10 kilometers west of Parkersburg. Weather in the Parkersburg area is generally mild for the region, presumably moderated by the proximity of the Ohio River. For the month of March, average temperatures are in the range 5-8°C and light winds (~12 KMPH) are prevalent. During the actual sampling period (3/26-30/79) the weather was less mild than normal with temperatures from -1 to 24°C and westerly winds from calm to moderate (up to 22 KMPH). Light snow flurries were also encountered during the first sampling period (3/26,27/79). Despite the below freezing temperatures encountered early in the trip, the ground remained thawed thus posing no difficulty in the collection of soil samples. Although an MRI Meteorological Weather Station was set up close to the Borg Warner facility at Location 1, the unit functioned erratically. Specific weather data for the sampling period was therefore obtained from the National Weather Service office located in downtown Parkersburg, WV.

Sampling Period

The sampling protocol is given in Table 4 for both air and soil samples. A map showing the locations of these samples is given in Figure 4. Four air samples (24 hr period) were collected at each of four separate locations (total of 16 air samples) under a variety of meteorological conditions. A

Table 4. SAMPLING PROTOCOL FOR BORG-WARNER, PARKERSBURG, WV

Period	Cycle	Location	Sampling Time (PST)	Sample ₃ Volume(m ³)	Type of Sample ^{a,b}	Meteorological Conditions ^c			Other
						T(°C)	Wind Dir./Speed(KMPH)		
3/26, 27/79 P1	C1	L1	1055-1035	282	air	-1-2 ^d	W/21-22 ^e	(2 hr)	Heavy cloud, snow
		L2	1155-1100	252	air		SW/5-21	(22 hr)	
		L3	1315-1225	185	air				
		L4	1400-1300	247	air				
3/27, 28/79 P2	C1	L1	1050-1035	284	air	-3-8	SW/8-14	(10 hr)	cloudy-clear
		L1	-	-	soil		NW/5	(1 hr)	
		L2	1110-1055	265	air		Calm	(3 hr)	
		L2	-	-	soil		N/5	(1 hr)	
		L3	1240-1140	196	air		E/5-8	(3 hr)	
		L3	-	-	soil		Calm	(4 hr)	
		L4	1315-1200	249	air		SE/5-11	(2 hr)	
		L4	-	-	soil				
		L5	-	-	soil				
		L6	-	-	soil				
		L7	-	-	soil				
		L8	-	-	soil				
		L9	-	-	soil				
3/28, 29/79 P3	C1	L1	1045-1000	277	air	11-23	SE/10-14	(4 hr)	clear
		L2	1110-1035	246	air		S/16	(1 hr)	
		L3	1150-1125	198	air		SW/14-21	(3 hr)	
		L4	1220-1140	225	air		S/13	(1 hr)	
		L10	-	-	soil		SE/14-18	(2 hr)	
		L11	-	-	soil		S/14-16	(2 hr)	
		L12	-	-	soil		SE/14-16	(2 hr)	
		L13	-	-	soil		S/11-16	(4 hr)	
							SW/16-21	(5 hr)	
3/29, 30/79 P4	C1	L1	1025-0940	264	air	17-24	SW/19-22	(7 hr)	clear
		L2	1055-1010	253	air		SE/2-8	(6 hr)	
		L3	1135-1045	186	air		S/11-18	(8 hr)	
		L4	1155-1055	233	air		SW/14-21	(3 hr)	

^a Air samples were collected with a Nutech Corporation custom designed high volume samplers. Sample intake 1-2 M elevation.

^b Each soil sample was comprised of 5 cores 5.5 cm in diameter and 4 cm in depth.

^c From the National Weather Services, Parkersburg, WV given in 24 hr periods from 1000-1000 EST.

^d Manual temperature reading at location 1 was 0° at 1100 EST.

^e MRI readings taken at location 1 indicated wind direction was WSW at 5 KMPH from 1100-1530 EST during this period.

total of thirteen composite soil samples were collected with each composite made up of 5 samples plugs taken approximately 2 meters apart.

The Borg-Warner facility is located 10 kilometers west of Parkersburg at a bend in the Ohio River known as Washington Bottom. The hilly terrain and sparse population near the facility severely limited the choice of adequate air sampler locations. We were able to locate one sample site approximately 0.2 kilometers east of the facility corresponding to the general downwind transect. A second sampling site was also located in the river bottom area directly across the Ohio River from the facility (~1 kilometer west). The third and fourth sample sites were located on ridges overlooking the river bottom from the east and west in the residential areas of Washington, WV and Little Hocking, OH, respectively.

Composite soil samples were taken at each air sample site as well as sites distributed around the Borg-Warner facility in all directions up to a distance of 2 kilometers. The 5 core samples from each location were composited immediately upon collection. Each composite was mixed thoroughly before removal of a portion for extraction and analysis.

SECTION 5
RESULTS OF THE ANALYSIS OF PBB's

SAMPLES FROM OXNARD, CA

Soils

The results for the analysis of soil samples taken in Oxnard are given in Table 5. Only hexabromobiphenyl was found in all of the soil samples. Small (~10% of the total PBBs) amounts of pentabromobiphenyl were found in the two samples containing the largest amount of PBB's. Heptabromobiphenyl (3% of the total PBBs) was found in the sample containing the greatest amount of PBB's. No nona- or decabromobiphenyl was detected in any sample. In two samples P2/C1/L5 and P2/C1/L7, material with a retention time similar to that of monobromobiphenyl and possessing the two ions characteristic of this compound in the proper ratio was observed. In this mass range, one cannot be certain that these GC/MS peaks are due to monobromobiphenyl, and the amounts observed were treated as upper limits of PBB concentration.

Air

All of the glass fiber filters from the air sampling in Oxnard were analyzed for all of the PBB's (1 through 10 bromines) and none were confirmed to be present. The limit of detections, exclusive of collection efficiency and recovery, are given in Table 6 by isomer. Table 6 also contains the limit of detection for the analysis of PUF samples for PBB's (1 through 6 bromines). The analysis of the actual samples is given in Table 7. Where "not confirmed" is listed, the two ions monitored for confirmation showed peaks(s) at the same retention time in the appropriate retention window for that isomer, but the intensity ratio was different from theoretical values. Such a finding does not preclude the presence of a PBB isomer, but fails to confirm its presence. There is a high frequency of interference in the determination of monobromobiphenyl especially in the PUF samples. The highest possible concentration of monobromobiphenyl was 3.4 ng/m^3 in the

Table 5. POLYBROMINATED BIPHENYLS IN SOIL SAMPLES COLLECTED IN OXNARD, CA
1/23/79 - 1/28/79

Sample	Compound (µg/Kg)										Total µg/kg
	C ₁₂ H ₉ Br ₁	C ₁₂ H ₈ Br ₂	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₃ Br ₉	C ₁₂ H ₂ Br ₈	C ₁₂ HBr ₉	C ₁₂ Br ₁₀	
P2/C1/L5 ^a	<7.2 ^b ±0.8 ^d	ND ^c	ND	ND	ND	26 ±4	ND	ND	ND	ND	26 ±4
P2/C1/L6	ND	ND	ND	ND	2100 ±500	33,000 ±6,000	1,100 ±200	ND	ND	ND	36,000 ±6,000
P2/C1/L7	<11 ^b ±1	ND	ND	ND	105 ±9	1,000 ±150	NC	ND	ND	ND	1,100 ±150
P2/C1/L8	ND	ND	ND	ND	ND	5.4 ±1.4	NC	ND	ND	ND	5.4 ±1.4
P5/C1/L9	ND	ND	ND	ND	ND	26 ±4	ND	ND	ND	ND	26 ±4
P5/C1/L10	NC	ND	ND	ND	ND	27 ±6	ND	ND	ND	ND	27 ±6

^aRefer to Table 3 and Figure 3.

^bValues reported for C₁₂H₉Br are indicated as maximum values since there is an appreciable background at the low mass of this compound.

^cNot detected - generally less than 1 µg/kg.

^dThe deviations given are standard deviations of 3 to 6 injections.

Table 6. LIMITS OF DETECTION FOR PBB'S IN AIR SAMPLES

Compound	L/D GFF (ng/m ³)	L/D PUF (ng/m ³)
C ₁₂ H ₉ Br	0.03	0.5
C ₁₂ H ₈ Br ₂	0.02	0.01
C ₁₂ H ₇ Br ₃	0.02	0.01
C ₁₂ H ₆ Br ₄	0.08	0.04
C ₁₂ H ₅ Br ₅	0.15	0.07
C ₁₂ H ₄ Br ₆	0.6	0.3
C ₁₂ H ₃ Br ₇	0.6	-
C ₁₂ H ₂ Br ₈	0.6	-
C ₁₂ H ₁ Br ₉	0.6	-
C ₁₂ Br ₁₀	0.6	-
Total	3.3	0.44 ^a

^a1-6 bromines.

Table 7. POLYBROMINATED BIPHENYLS IN AIR SAMPLES COLLECTED IN OXNARD, CA
1/23/79 - 1/28/79

Sample	Compound (ng/m ³)									
	C ₁₂ H ₉ Br ₁ ^a	C ₁₂ H ₈ Br ₂ ^b	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₃ Br ₇	C ₁₂ H ₂ Br ₈ ^c	C ₁₂ HBr ₉	C ₁₂ Br ₁₀
P1/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	NC	ND	ND	ND	ND				
P1/C1/L2 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	NC	ND	ND	ND	ND				
P1/C1/L4 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P2/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P2/C1/L2 - GFF	NC	ND	ND	ND	ND	ND	ND	NC	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P2/C1/L3 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P2/C1/L4 - GFF	ND	ND	ND	ND	ND	ND	ND	NC	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P3/C1/L1 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	NC	ND	ND	ND	ND				
P3/C1/L2 - GFF	NC	ND	ND	ND	ND	ND	ND	NC	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P3/C1/L3 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	ND	NC	ND	ND	ND	ND				
P3/C1/L4 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P4/C1/L2 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				

(continued)

Table 7 (cont'd.)

Sample	Compound (ng/m ³)									
	C ₁₂ H ₉ Br ₁ ^a	C ₁₂ H ₈ Br ₂ ^b	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₃ Br ₉	C ₁₂ H ₂ Br ₈ ^c	C ₁₂ HBr ₉	C ₁₂ Br ₁₀
P4/C1/L3 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				
P4/C1/L4 - GFF	NC	ND	ND	ND	ND	ND	ND	NC	ND	ND
- PUF	NC	ND	ND	ND	ND	ND				

ND - not detected.

NC - not confirmed.

^aNo value could exceed 3.4 ng/m³.

^bNo values could exceed 0.03 ng/m³.

^cNo values could exceed 0.6 ng/m³.

P4/C1/L3 PUF. Polyurethane foam blanks gave backgrounds equivalent to 0.5 ng/m³. Occasional interference in the determination of the dibromobiphenyl occurred. However the maximum concentration which could be present is \leq 0.03 ng/m³. Octabromobiphenyl is noted as not confirmed in several of the GFF samples, however it must be noted that the maximum that could possibly have been present was below the stated limit of detection.

Quality Control/Quality Assurance

In preparation for the field sampling, control and blank samples were prepared for each medium sampled. Half of the samples were stored in the laboratory and the other half sent to the sampling site and returned in order to evaluate the rigors of transportation. These controls and blanks were intermingled with the samples and analyzed along with the samples. The results of the analysis of the soil samples is given in Table 8. The instrumental sensitivity to the higher brominated compounds drops off rapidly and octabromobiphenyl could not be detected at 23 µg/kg either in the soil control samples or in a reference standard prepared from the spiking solution.

Determinations were all performed at least in duplicate. A standard mixture of known pure polybrominated biphenyl isomers was analyzed at the start and end of each day. In the course of the day, every fifth injection was a determination of the standard solution. Every sample contained two internal standards at a level of 2 ng/µl each, and these standards were monitored with every determination. Solvent washes were done between sample and standard injections.

Blank and control PUF and GFF samples were analyzed; the results are given in Table 9. The absence of hexabromobiphenyl in the control samples was due to technical difficulties in preparing the spiking solution. Subsequent analysis of control samples from the Parkersburg sampling trip showed adequate recoveries of hexabromobiphenyl.

RESULTS OF THE ANALYSIS OF SAMPLES TAKEN NEAR PARKERSBURG, WV

Soils

The results of the GC/MS analysis of soil samples taken near Parkersburg, WV are given in Table 10. Hexabromobiphenyl was confirmed and quantitated in seven of the thirteen soil samples and traces detected but not confirmed in three additional samples. Three samples contained no detectable levels

Table 8 . ANALYSIS OF CONTROL AND BLANK SOIL SAMPLES FOR THE OXNARD, CA SAMPLING TRIP
1/23/79 - 1/28/79

		Compound, µg/Kg (0/0)						Total
Sample		C ₁₂ H ₉ Br ₁	C ₁₂ H ₈ Br ₂	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	
Laboratory Control	1	2.8 ± 0.6 ^c	90 ± 2 (76 ± 2)	105 ± 0.4 (81 ± 0.3)	174 ± 14 (85 ± 8)	196 ± 60 (108 ± 31)	118 ± 70 (120 ± 71)	686 ± 93 (89 ± 25)
	2	ND	78 ± 10 (66 ± 8)	102 ± 10 (80 ± 8)	178 ± 18 (87 ± 8)	218 ± 16 (120 ± 9)	168 ± 16 (172 ± 17)	744 ± 32 (105 ± 42)
Blank	1	NC ^e	ND	ND	ND	ND	ND	<1
	2	NC	ND	ND	ND	ND	ND	<1
Field Control	1	NC	44 ± 14 (36 ± 12)	44 ± 12 (34 ± 9)	64 ± 36 (32 ± 18)	52 ± 26 (36 ± 18)	ND	204 ± 48 (34 ± 2)
	2	NC	68 ± 22 (58 ± 19)	90 ± 10 (69 ± 8)	154 ± 8 (75 ± 4)	202 ± 22 (111 ± 12)	178 ± 60 (182 ± 62)	692 ± 69 (99 ± 50)
Blank	1	ND	ND	ND	ND	ND	ND	<1
	2	ND	ND	ND	ND	ND	ND	<1

^aPercent recovery in parenthesis.

^bThis compound was added at 23 µg/kg and could not be detected in either the control sample or the calibration standard at that level.

^cNone added.

^dND = not detected at more than 1 µg/kg.

^eNC = not confirmed by proper ion ratios.

Table 9. ANALYSIS OF CONTROL AND BLANK POLYURETHANE FOAM (PUF) AND GLASS FIBER FILTER (GFF)
SAMPLES FOR THE OXNARD, CA SAMPLING TRIP, 1/23/79 - 1/28/79

		Compounds							
		C ₁₂ H ₉ Br ng	C ₁₂ H ₈ Br ₂ ng (0/0)	C ₁₂ H ₇ Br ₃ ng (0/0)	C ₁₂ H ₆ Br ₄ ng (0/0)	C ₁₂ H ₅ Br ₅ ng (0/0)	C ₁₂ H ₄ Br ₆ ng (0/0)	Total ^a	
<hr/>									
PUF									
Laboratory	1	≤32 ^b	94 + 4 ^c (78 + 3)	110 + 17 (85 + 13)	156 + 8 (76 + 4)	229 + 34 (127 + 19)	ND ^d (^{<} 17)	589 + 39 (91 + 24)	
Control									
Blank	1	≤128	NC ^e	ND	ND	ND	ND		
25	Field								
	Control	1	≤44	93 + 6 (78 + 4)	101 + 5 (78 + 4)	144 + 16 (71 + 8)	183 + 16 (102 + 9)	ND (^{<} 17)	521 + 24 (82 + 14)
	Control	2	≤2	6560 + 360 (111 + 6)	7050 + 440 (107 + 7)	10,150 + 480 (100 + 5)	12,900 + 550 (142 + 6)	216 (4)	36,660 + 900 (115 + 18)
	Blank	1	≤48	NC	ND	ND	ND	ND	
	Blank	2	≤115	NC	ND	ND	ND	ND	
GFF									
Laboratory	1 QI	ND	38 + 5 (32 + 4)	77 + 2 (59 + 2)	160 + 10 (79 + 5)	100 + 0 (56 + 0)	ND (^{<} 2)	375 + 12 56 + 19	
Control									
	QIII	ND	960 + 130 ^f (16 + 2 ^f)	2100 + 30 ^f (32 + 1 ^f)	6,460 + 100 ^f (63 + 1 ^f)	3,980 + 10 ^f (44 + 1 ^f)	ND (^{<} 2)	13,500 + 167 39 + 20	
Blank	1	ND	ND	ND	ND	ND	ND		

(continued)

Table 9 (cont'd.)

Sample		Compounds						Total ^a
		C ₁₂ H ₉ Br ng	C ₁₂ H ₈ Br ₂ ng (0/0)	C ₁₂ H ₇ Br ₃ ng (0/0)	C ₁₂ H ₆ Br ₄ ng (0/0)	C ₁₂ H ₅ Br ₅ ng (0/0)	C ₁₂ H ₄ Br ₆ ng (0/0)	
Field Control	1 QI	ND	116 \pm 25 (97 \pm 21)	250 \pm 14 (192 \pm 11)	193 \pm 21 (96 \pm 10)	171 \pm 18 (95 \pm 10)	ND	730 \pm 40 120 \pm 48
	QIII	NC	948 \pm 17 (16 \pm 0.3)	2027 \pm 250 (31 \pm 4)	5457 \pm 444 (54 \pm 4)	3830 \pm 218 (42 \pm 2)	ND	12,262 36 \pm 16
Blank	1	ND	ND	ND	ND	ND	ND	

^aExclusive of C₁₂H₄Br₆.

^bLimit of detection due to background interferences.

^cStandard deviation of 3 or more determinations.

^dND = not detected - Technical difficulties in the preparation of the spiking solution.

^eNC = not confirmed in ion ratios of 2 or more ions not correct for this compound.

^fDeviation of a measured value from the average of two determinations.

Table 10. POLYBROMINATED BIPHENYLS IN SOIL SAMPLES COLLECTED NEAR PARKERSBURG, WV
3/26/79 - 3/30/79

Sample	Compound (µg/kg)										Total
	C ₁₂ H ₉ Br ₁	C ₁₂ H ₈ Br ₂	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₃ Br ₇	C ₁₂ H ₂ Br ₈	C ₁₂ HBr ₉	C ₁₂ Br ₁₀	
P2/C1/L1 ^a	ND	ND	ND	ND	ND	35 ± 3 ^b	ND	ND	ND	ND	35 ± 3
P2/C1/L2	ND	ND	ND	ND	ND	<0.3 ^c	ND	ND	ND	ND	<0.3
P2/C1/L3	<5 ^d	ND	ND	ND	ND	<0.8 ^c	ND	ND	ND	ND	<0.8
P2/C1/L4	ND	ND	ND	ND	ND	<0.5 ^c	ND	ND	ND	ND	<0.5
P2/C1/L5	ND	ND	ND	ND	ND	3.2 ± 0.3 ^e	ND	ND	ND	ND	3.2 ± 0.3
P2/C1/L6	ND	ND	ND	ND	ND	1.9 ± 0.1 ^b	ND	ND	ND	ND	1.9
P2/C1/L7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P2/C1/L8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P2/C1/L9	ND	ND	ND	ND	ND	0.73 ± 0.03 ^b	ND	ND	ND	ND	0.73
P3/C1/L10	ND	ND	ND	ND	ND	1.86 ± 0.02 ^b	ND	ND	ND	ND	1.86
P3/C1/L11	ND	ND	ND	ND	ND	2.4 ± 0.1 ^b	ND	ND	ND	ND	2.4
P3/C1/L12	NC	ND	ND	ND	<0.4 ^c	10.6 ± 0.4 ^e	1	ND	ND	ND	12.0 ± 0.4
P3/C1/L13	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

^a Refer to Table 4 and Figure 4 .

^b Trace detected but not confirmed.

^c ± indicates range of duplicate measurements.

^d Not confirmed, may be background.

^e ± indicates standard deviation of three or more measurements.

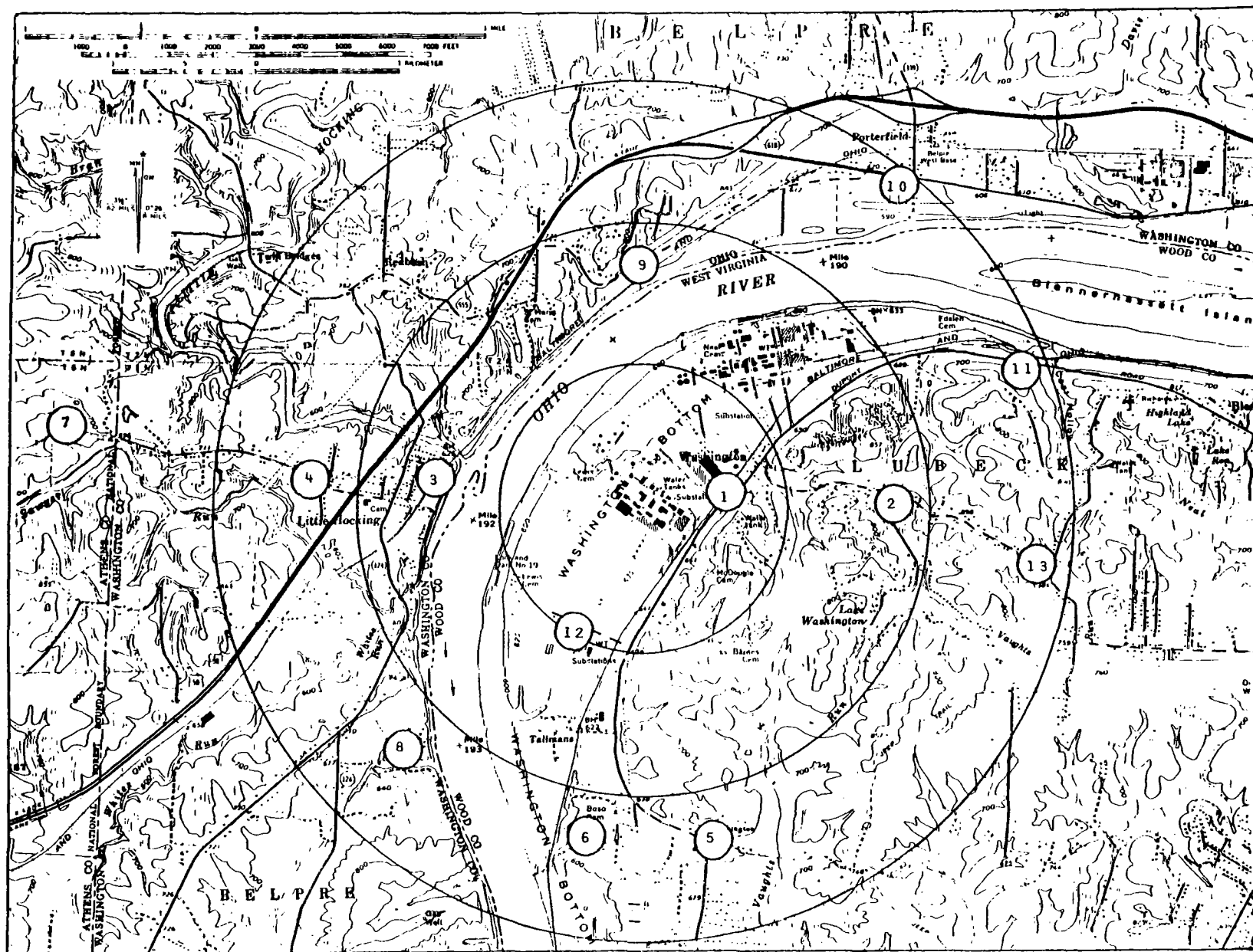


Figure 4. Map of sampling locations, Parkersburg, WV (3/26-30/79).

of any PBB. One sample, P3/C1/L12, showed small proportions of pentabromobiphenyl and heptabromobiphenyl along with the hexabromobiphenyl. The soil extracts from those samples were submitted to the optional Florisil column cleanup (see Appendix A). This clean-up reduced the background interference with the detection of monobromobiphenyl as well as shortening instrumental analysis time. In only two samples were the m/z, 232 and 234 ions observed and in neither case was the ratio near the theoretical for monobromobiphenyl.

Air

No air samples could be confirmed to contain PBB's (Table 11). Some trace amounts may have been detected but could not be confirmed. Where this occurred the upper limit of the quantity is listed as a \leq amount. For the limits of detection see Table 6. There was some background interference with the detection of monobromobiphenyl however the maximum amount which could have been present in any sample was $<0.1 \text{ ng/m}^3$.

QUALITY CONTROL/QUALITY ASSURANCE

Control and blank samples were prepared for each medium sampled. Half of the samples were stored in the laboratory (laboratory controls and blanks) and half were sent to the field and returned (field controls and blanks). The controls and blanks were intermingled with the samples and analyzed along with the samples. The results of the soil samples are given in Table 12. Octabromobiphenyl was added at $104 \text{ } \mu\text{g/kg}$ and could be detected but quantitation was not possible.

Determinations were all performed at least in duplicate. A standard mixture of known pure PBB isomers was analyzed at the start and end of each day. In the course of the day, every fifth injection was a determination of the standard solutions. Every sample contained two internal standards at a level of $2 \text{ ng/}\mu\text{l}$ each, and these standards were monitored with each determination. Solvent washes were performed between standard and sample injections.

Blank and control PUF and GFF samples were analyzed and the results are given in Table 13.

Table 11. POLYBROMINATED BIPHENYLS IN AIR SAMPLES COLLECTED NEAR PARKERSBURG, WV
3/26/79 - 3/30/79

Sample	Compound (ng/m ³)										Total
	C ₁₂ H ₉ Br ₁ ^a	C ₁₂ H ₈ Br ₂ ^b	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₃ Br ₇	C ₁₂ H ₂ Br ₈	C ₁₂ HBr ₉	C ₁₂ Br ₁₀	
P1/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P1/C1/L2 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P1/C1/L3 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	≤0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
P1/C1/L4 - GFF	NC	≤0.03	ND	ND	ND	≤0.01 ^c	ND	ND	ND	ND	≤0.04
- PUF	NC	ND	ND	≤0.02	ND	ND	ND	ND	ND	ND	≤0.02
P2/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P2/C1/L2 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P2/C1/L3 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	≤3.7 ^c	ND	ND	ND	ND	≤3.7
P2/C1/L4 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	≤0.03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P2/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P3/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P3/C1/L2 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P3/C1/L3 - GFF	NC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

(continued)

Table 11 (cont'd)

Sample	Compound (ng/m ³)										Total
	C ₁₂ H ₉ Br ₁ ^a	C ₁₂ H ₈ Br ₂ ^b	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₃ Br ₇	C ₁₂ H ₂ Br ₈	C ₁₂ HBr ₉	C ₁₂ Br ₁₀	
P3/C1/L4 - GFF	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P4/C1/L1 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P4/C1/L2 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	<0.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P4/C1/L3 - GFF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
P4/C1/L4 - GFF	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
- PUF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected.

NC = not confirmed.

^aNo values could exceed 0.4 ng/m³.

^bNo values could exceed 0.03 ng/m³.

^cTrace detected but not fully confirmed.

Table 12. ANALYSIS OF CONTROL AND BLANK SOIL SAMPLES FOR THE PARKERSBURG, WV SAMPLING TRIP,
3/26/79 - 3/30/79

Sample		Compound, µg/Kg (0/0) ^a						Total
		C ₁₂ H ₉ Br ₁	C ₁₂ H ₈ Br ₂	C ₁₂ H ₇ Br ₃	C ₁₂ H ₆ Br ₄	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	
Laboratory								
Control - 1	ND ^{cd}	284 ± 12 [*]	182 ± 7 [*]	ND ^c	46 ± 4	444 ± 18	>27	956 ± 23
	-	(95 ± 4)	(107 ± 4)	-	(90 ± 8)	(73 ± 3)		(91 ± 14)
- 2	ND	242 ± 4 [*]	144 ± 4 [*]	ND	47 ± 6	466 ± 16	>37	899 ± 18
	-	(81 ± 1)	(85 ± 2)	-	(92 ± 12)	(76 ± 3)		(84 ± 7)
Blank - 1	ND	ND	ND	ND	ND	ND	ND	ND
	- 2	ND	ND	ND	ND	ND	ND	ND
Field								
Control - 1	ND	500 ± 16 [*]	270 ± 0 [*]	ND	60 ± 5	484 ± 30	>66	1314 ± 34
	-	(168 ± 5)	(159 ± 0)	-	(118 ± 10)	(79 ± 5)		(131 ± 41)
- 2	ND	403 ± 10 [*]	251 ± 6 [*]	ND	84 ± 3	799 ± 56	>53	1537 ± 56
		(135 ± 3)	(148 ± 4)	-	(165 ± 6)	(131 ± 9)		(145 ± 15)
Blank - 1	ND	ND	ND	ND	ND	ND	ND	ND
	- 2	ND	ND	ND	ND	ND	ND	ND

^aPercent recovery in parenthesis.

^bThis compound was added at 112 $\mu\text{g/kg}$ the values listed are lower limits of the amount recovered based on the M-Br ($m/z = 706$) ion and an estimate of the RMR.

^cNone added.

^dND = not detected.

Table 13. ANALYSIS OF CONTROL AND BLANK POLYURETHANE FOAM (PUF) AND GLASS FIBER FILTER (GFF) SAMPLES FOR THE PARKERSBURG, WV SAMPLING TRIP 3/26/79 - 3/30/79

Compound, ng (0/0) ^a							
Sample	C ₁₂ H ₉ Br	C ₁₂ H ₇ Br ₂	C ₁₂ H ₇ Br ₃	C ₁₂ H ₅ Br ₅	C ₁₂ H ₄ Br ₆	C ₁₂ H ₂ Br ₈	Total ^b
<u>PUF</u>							
Laboratory							
Control - 1	NC ^c	48 ± 6 ^c (21 ± 2.5)	96 ± 2 ^c (73 ± 2)	12 ± 5 ^c (25 ± 10)	390 ± 1 ^c (81 ± 1)	ND	456 ± 8 (50 ± 31) ^d
Blank - 1	<16 ^f	ND	ND	ND	ND	ND	ND
-2	<4	ND	ND	ND	ND	ND	ND
Field							
Control - 1		92 ± 2 ^e (40 ± 1)	148 ± 2 ^c (113 ± 2)	46 ± 1 ^c (96 ± 1)	707 ± 39 (147 ± 8)	NQ ^g	993 ± 39 (99 ± 44) ^d
- 2	Trace	4000 (27)	5240 (62)	1620 ± 65 (63)	17,000 (56)		27,860 ± 65 (56 ± 17) ^d
Blank - 1	<7	ND	ND	ND	ND	ND	
-2	<6	ND	ND	ND	ND	ND	
<u>GFF</u>							
Laboratory							
Control - Q1	ND	10 (4)	21 (16)	ND 0	ND 0	ND	30 3
- Q3	ND	2080 (14)	1510 (18)	700 (27)	10,000 (33)	NQ ^g	14,390 (23 ± 7) ^d
Blank	ND ^d		ND	ND	ND	ND	
Field							
Control - Q1	NC	66 ± 2 ^c (28 ± 1)	160 ± 6 ^c (122 ± 4)	30 ± 1 ^c (62 ± 2)	302 ± 11 ^c (63 ± 2)	ND	558 ± 14 (69 ± 39) ^d
- Q3	NC	1880 (13)	2120 ± 8 ^c (25)	960 ± 50 ^c (38)	14500 ± 900 ^c (48 ± 3)		19,460 ± 900 (31 ± 15) ^d
Blank - 1	<0.4	ND	ND	ND	ND	ND	ND

^aPercent recovery in parenthesis.

^bTotal exclusive of C₁₂H₂Br₈ which could not be quantitated.

^cThe deviation of the mean from the measured values for two measurements.

^dStandard deviation of the percent recoveries for each isomer.

^eNC = not confirmed by ion ratio.

^fMaximum amount which could be present given the background of the sample.

^gDetected but not quantitated.

SECTION 6

DISCUSSION

OXNARD, CA

The soil samples all contained some detectable hexabromobiphenyl. The highest concentration (P2/C1/L6) was found across the street from a loading dock storage area at the Borg-Warner facility. This was downwind with respect to the Santa Ana winds (from the mountains ENE). The second highest (P2/C1/L7) was taken ~1 block NNE of the Borg-Warner facility, however this sample showed a 30 fold lower PBB concentration. The samples L5 and L8 were nearly equidistant from the facility yet there is a 5 fold difference in PBB levels. This would tend to indicate the Fall and Winter northeasterly winds have a larger role in the dispersion of the PBB's than the prevailing Westerlies. Residents mentioned the large amount of airborne particulate during the winter wind storms. It would appear that these winds may play a role in the spread of PBB contamination.

The mass of the soil PBB burden may be estimated by converting $\mu\text{g}/\text{kg}$ to g/km^2 . The conversion factor for the Oxnard soil samples is 4.64. The estimation of soil burden may best be done in two stages using the average level of the 2 "near" samples as representative of the first 0.1 km and the remaining samples for the area from 0.1 to 1.0 km. This gives a burden of ~2,500 g for the first 0.1 km and ~400 g for the 0.1 to 1.0 km distance for a total of approximately 3000 g of PBB's. Obviously this is only an order of magnitude estimate since it assumes a step change in concentration between the two circles where very large concentration differences are observed.

No air samples were found to contain PBB's. This is not surprising since airborne PBB's at this time would be expected to arise from the suspension of contaminated soil. Even at the highest soil contamination (33,000 $\mu\text{g}/\text{kg}$), the PBB's would not be detected at a particulate level of 100 $\mu\text{g}/\text{m}^3$ (values for Los Angeles of 93 $\mu\text{g}/\text{m}^3$ have been reported⁽¹⁵⁾).

PARKERSBURG, WV

The polybrominated biphenyl levels in the soil samples from Parkersburg, WV ranged from 35 $\mu\text{g/kg}$ to not detectable. The distribution of the PBB's is not as straight forward as is the case for Oxnard due in part to the hilly terrain and the Ohio River. The detection of PBB's follows the river contours both upstream and downstream (N and NE and S of the Borg-Warner facility). The highest levels were found due east of the facility before a ridge blocks the air flow. No PBB's were found west of the facility. The closest access west of the facility was across the river however PBB's were found more distant in other directions. East winds are uncommon in this area relative to the NW, W, and SW winds and that may account for the distribution of the PBB's. Another factor which must at least be considered when interpreting this data are the transportation routes which may have been used to bring PBB's to the facility. Several of the samples were taken on road sides although only P2/C1/L1 and P3/C1/L11 are the only ones which are clearly on trucking routes. The other roadside samples were taken on back roads with little or no trucking traffic.

The concentration of PBB's in the soil may be converted to concentration per unit soil surface area by multiplying by 4.64 kg/m^2 . If one estimates the area contaminant as 5 to 10 km^2 and takes the average PBB level found, 8 $\mu\text{g/kg}$, (disregarding trace and not detected samples) convert it to g/km^2 to obtain 37 g/km^2 . The total soil burden may be estimated to be on the order of 180-400 g.

No PBB's could be confirmed in any of the air samples. The same considerations apply here as in Oxnard concerning resuspension of PBB laden particulate with even lower soil levels of PBB's.

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APPENDIX A
SAMPLE PREPARATION PROCEDURES

PROCEDURE FOR CLEANUP OF POLYURETHANE FOAM PLUGS

1. Cut 5 cm diameter x 13 cm long plugs from sheet of Olympic[®] 2315 polyurethane foam.
2. Mark each plug with an identification number in the top using a hot wire.
3. Place four plugs in bottom of clean four liter beaker, add 500 ml hot toluene (100°C).
4. Compress the plugs 10 times using a one liter Erlenmeyer flask.
5. Let sit five minutes on steam bath.
6. Repeat Steps 4 and 5.
7. Compress the plugs and decant the toluene.
8. Add 250 ml fresh, hot toluene and repeat steps 4 through 7.
9. Repeat Step 8 three times (total of five extractions).
10. Using clean tweezers, transfer each plug into a foil-wrapped wide-mouthed jar and cover loosely with a foil-lined cap.
11. Dry in vacuo at 50° for 12 hours.
12. Remove from oven, tighten cap and store away from potential contaminants.

PROCEDURE FOR EXTRACTION OF POLYBROMINATED BIPHENYLS FROM POLYURETHANE FOAM PLUGS

1. Using cleaned tongs, remove foam plugs from storage jars and place them in 400 ml beakers.
2. Add 150 ml of toluene to beakers containing foam plugs.
3. Compress the foam plugs 10 times to the bottom of the beakers with a 125 ml Erlenmeyer flask, soak for five minutes and compress an additional 10 times.

4. Squeeze the toluene out of the plug and decant into a flat bottom boiling flask.
5. Repeat steps 2 through 4 two more times.
6. Concentrate in a flat bottom boiling flask topped with a Snyder column to approximately 15 ml.
7. Transfer and concentrate to 1 ml under nitrogen stream.
8. Add internal standards and submit to GC/MS analysis.

PROCEDURES FOR EXTRACTION OF FILTERS

1. Cut filter in 2 equal pieces and analyze one piece as below.
2. Cut with a clean scalpel into pieces which will fit into a micro Soxhlet extractor (extractor volume 10 ml).
3. Place a small plug of glass wool in the bottom of the extractor and insert filter pieces.
4. Fill a 50 ml round bottom flask with 30 ml of solvent. Assemble Soxhlet extractor and extract overnight.
5. Evaporate to 1 ml under nitrogen stream.
6. Add internal standards and submit to GC/MS analysis.

PROCEDURE FOR EXTRACTION OF POLYBROMINATED BIPHENYLS BIPHENYLS FROM SOIL SAMPLES*

1. Weigh 50 g of soil into a 1 quart screw cap jar.
2. Add 50 ml of diethyl ether, shake and allow to stand overnight.
3. Remove diethyl ether in vacuo at room temperature.
4. Add 5 ml of distilled-deionized water to dampen soil.
5. Add 40 ml of acetone and shake for 20 minutes.
6. Add 80 ml of toluene and shake an additional 10 minutes.

*Procedure adapted from D. F. Goerlitz and L. M. Law, J. Assoc. Offic. Anal. Chem., 57, 176-181 (1974).

7. Decant acetone-toluene extract through glass wool into a one liter separatory funnel.
8. Repeat Steps 5 through 7 two more times.
9. Extract combined organic fractions with 500 ml water.
10. Back extract water three times with 25 mL portions of toluene.
11. Dry combined organic extracts with sodium sulfate.
12. Concentrate to 15 mL in a flat bottom boiling flask topped with a Snyder column. Evaporate to 1 mL under nitrogen.
13. Add internal standards and submit to GC/MS analysis.

OPTION COLUMN CLEANUP

Reagents

Hexane - suitable for use in pesticide residue analysis or distilled in glass

Florisil (60/100 mesh) PR grade - store at 130°C until used

Sodium sulfate - anhydrous, granular, Mallinckrodt No. 8024 or equivalent. Store at 130°C in glass stoppered bottle.

Procedure:

1. Prepare columns in Chromoflex glass columns with 6 mm i.d. Plug with a small wad of clean glass wool and add 1.6 g of Florisil. Top Florisil with a 2 cm layer of anhydrous sodium sulfate.
2. Prewash column with 5 mL of hexane. Drain, but do not let liquid level drop below the top of the sodium sulfate.
3. Transfer concentrated extract, in hexane solvent, to top of column and follow with three hexane rinsings of ~0.5 mL each. Drain until liquid level is near top of the sodium sulfate. At no point allow the liquid level to drop below the top of the sodium sulfate. Elute PBB's with 15 mL of hexane.

4. Concentrate sample in Kuderna-Danish evaporator to a small volume ~0.5 mL. Transfer sample to a conical vial with hexane rinses, add 10 µl toluene and evaporate to ~0.1 mL under a nitrogen stream.

NOTE: The column cleanup may be performed after the internal standard is added since both octachloronaphthalene and decachlorobiphenyl coelute with PBB's on Florisil.

APPENDIX B
LOCAL CLIMATOLOGICAL DATA
OXNARD, CA

Local Climatological Data

Annual Summary With Comparative Data

1974

LOS ANGELES, CALIFORNIA
CIVIC CENTER



Narrative Climatological Summary

The climate of Los Angeles is normally pleasant and mild through the year. The Pacific Ocean is the primary moderating influence, but coastal mountain ranges lying along the north and east sides of the Los Angeles coastal basin act as a buffer against extremes of summer heat and winter cold occurring in desert and plateau regions in the interior. A variable balance between mild sea breezes, and either hot or cold winds from the interior, results in some variety in weather conditions, but temperature and humidity are usually well within the limits of human comfort. An important, and somewhat unusual, aspect of the climate of the Los Angeles metropolitan area, is the pronounced difference in temperature, humidity, cloudiness, fog, rain, and sunshine over fairly short distances.

These differences are closely related to the distance from, and elevation above, the Pacific Ocean. Both high and low temperatures become more extreme and the average relative humidity becomes lower as one goes inland and up foothill slopes. On the coast and in the lower coastal plain, average daily temperature ranges are about 15° in summer and 20° in winter, but in foothill and inland valley communities these ranges increase to about 30° in summer and 25° in winter. Relative humidity is frequently high near the coast, but may be quite low along the foothills. During periods of high temperatures, the relative humidity is usually below normal so that discomfort is rare, except for infrequent periods when high temperatures and high humidities occur together.

Like other Pacific Coast areas, most rainfall comes during the winter with nearly 85 percent of the annual total occurring from November through March, while summers are practically rainless. As in many semiarid regions, there is a marked variability in monthly and seasonal totals. Annual precipitation may range from less than a third of the normal value to nearly three times normal, while some customarily rainy

months may be either completely rainless, or receive from three to four times the average for the month. Precipitation generally increases with distance from the ocean from a yearly total of around 12 inches in coastal sections to the south of the City up to over 20 inches in foothill areas. Destructive flash floods occasionally develop in and below some mountain canyons. Snow is often visible on nearby mountains in the winter, but is extremely rare in the coastal basin. Thunderstorms are infrequent.

Prevailing winds are from the west during the spring, summer, and early autumn, with northeasterly wind predominating the remainder of the year. Average wind speeds are rather low. At times, the lack of air movement, combined with a frequent and persistent temperature inversion, is associated with concentrations of air pollution in the Los Angeles coastal basin and some adjacent areas. In fall, winter, and early spring months, occasional foehn-like descending (Santa Ana) winds come from the northeast over ridges and through passes in the coastal mountains. These Santa Ana winds may pick up considerable amounts of dust and reach speeds of 35 to 50 m.p.h. in north and east sections of the City, with higher speeds in outlying areas to the north and east, but rarely reach coastal portions of the City.

Sunshine, fog, and clouds depend a great deal on topography and distance from the ocean. Low clouds are common at night and in the morning along the coast during spring and summer, but form later and clear earlier near the foothills so that average annual cloudiness and fog frequencies are greatest near the ocean, and sunshine totals are highest on the inland side of the City. The sun shines about 75 percent of daytime hours at the Civic Center. Light fog may accompany the usual night and morning low clouds, but dense fog is more likely to occur during the night and early morning hours of the winter months.

noaa

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

ENVIRONMENTAL
DATA SERVICE

NATIONAL CLIMATIC CENTER
ASHEVILLE, N.C.

APPENDIX C
LOCAL CLIMATOLOGICAL DATA
PARKERSBURG, WV

Local Climatological Data

Annual Summary With Comparative Data

1974

PARKERSBURG, WEST VIRGINIA



Narrative Climatological Summary

The climate of Parkersburg can well be described as moderate. Located on the south bank of the Ohio River and in the extreme north of the "upper south," Parkersburg is in the farthest north area where tender vegetation, such as magnolias, is able to survive most of the winters. In summers, prolonged hot weather is infrequent. During the period of record, there have been only 24 days with a temperature of 100° or more. Likewise, prolonged cold weather is infrequent; temperatures of -10° or lower have occurred on only 13 days. Precipitation is usually ample for the locality's needs; the Ohio is a well-watered valley. The heaviest rains are in June and July. The lightest amounts are in October. On the average of once every four or five years, a dry spell in July or August does some damage to crops in the vicinity. Frequent rainfall in late May and in June may cause difficulty in harvesting early hay. Days with measurable snowfall average about 25 for the year; the average annual snowfall is about 24 inches. However, total snowfall amounts vary greatly from winter to winter, ranging from over 55 inches to less than 4 inches.

Within 2 miles of the Weather Service Office, there is a locally-famous early vegetable-producing district. Presumably because of the moderating influence of the nearby Ohio River, the character of the soil and its southern exposure, the district produces vegetables about three weeks earlier in the spring than do other places in the Parkersburg area. Since 1950 the mean latest and earliest occurrences of 32° are April 18 and October 23. Lower temperatures are prevalent in the area on clear, calm nights.

Parkersburg is not a windy City, the winds being light most of the time. However, once in a while a winter storm may be accompanied by winds up to gale force and, also infrequently, the squall winds of a summer thunderstorm may blow about as hard.

Parkersburg is located at the confluence of the Little Kanawha with the Ohio River. A rather closely spaced series of wooded ridges more or less paralleling the Ohio or Little Kanawha River, and rising to as much as 100 to 150 feet above the valley floor, gives the local terrain a hilly character. There are two principal hills near the station; one about 0.6 mile to the southwest and rising to an elevation of about 820 feet m.s.l., and the other about 1/4 mile east-northeast and rising to an elevation of about 765 feet m.s.l.

Situated near the path taken by the average storm moving eastward across the country, Parkersburg is subject to the stimulating influence of rather frequent changes in weather. During warm periods in the summer with the circulation from the Gulf, the humidity may be depressingly high with dew points in the mid-seventies. Being relatively free from extremes of temperature, precipitation, and wind, Parkersburg's moderate climate is very favorable to man and his varied activities in this area.

TECHNICAL REPORT DATA <i>(Please read Instructions on the reverse before completing)</i>		
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16. ABSTRACT Field sampling for air and soil was conducted in the vicinity of two Borg Warner Co. facilities, one in Oxnard, CA and the other near Parkersburg, WV. Polybrominated biphenyls (PBBs) were found in all of the soil samples from Oxnard with the highest levels (36,000 µg/kg) nearest the facility and the lowest (5 µg/kg) upwind the greatest distance. No PBBs were found in any of the air samples (<3 ng/m ³). Polybrominated biphenyls were confirmed in seven of the thirteen soil samples from West Virginia (up to 12 µg/kg) traces detected but not confirmed in three, and no PBBs were detected in the other three. The highest levels were from samples collected in the Ohio River basin especially along the eastern bank. No PBBs were confirmed in the air samples (<4 ng/m ³).		
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