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Over-Water and Over-Land Polychlorinated Biphenyls in Green Bay, Lake Michigan

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■ Air samples were simultaneously collected over water and over nearby land in the Green Bay, Lake Michigan, region and analyzed for 85 polychlorinated biphenyls (PCBs). The concentration and distribution of PCB congeners collected from vapor over water, over land, and dissolved in the water support the hypothesis that volatilization of PCBs from contaminated waters is a major source of PCBs to the local atmosphere. Concentrations of PCB congener ($\sum$PCBs) over the water are higher over southern Green Bay (670–2200 pg/m^3) and lower over the northern bay (160–520 pg/m^3) while $\sum$PCB concentrations over the land ranged from 70 to 760 pg/m^3. The PCB concentration differences over land and over water were statistically significant for congener sums and for homolog groups in southern Green Bay. Regressions of air and water PCB distributions show high correlations (R^2 = 0.73–0.96) in southern Green Bay.

Introduction

It has been hypothesized that large water bodies may act as sources and/or sinks of atmospheric semivolatile

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organic chemicals (SOCs) (1–8). Volatilization to or deposition from natural systems has been estimated from simultaneous measurements of SOCs in air and water. The air and water concentrations are then compared to expected equilibrium values (Henry's law constants) to estimate the direction and magnitude of chemical flux. Polychlorinated biphenyls (PCBs) make good surrogates for predicting the expected behaviors of other organic chemicals because the ~100 PCB congeners detected in the environment encompass a wide range of aqueous solubility, volatility, and molecular weight. Prediction of gas exchange has been corroborated in laboratory studies where the actual chemical uptake or volatilization is measured over time (9). However, direct field measurement of volatilization of PCBs from natural aquatic systems is difficult because (1) the atmospheric and aquatic concentrations are low; (2) volatilization and deposition occur continuously, simultaneously, and often of comparable magnitude; and (3) volatilization of PCBs from natural waters is difficult to distinguish from surrounding terrestrial and industrial sources.

The goal of this study is to address the volatilization hypothesis by employing simultaneous air collection over water and nearby land. Simultaneous measurement of atmospheric concentrations of SOCs directly over water

and over land has not been reported although many estimates of air/water transfer are based on measurements in air and water that are displaced in time and space. If atmospheric concentrations of SOCs over land and over water are significantly different, then water bodies influence regional and global atmospheric concentrations more strongly than previously believed.

In the Great Lakes region, atmospheric concentrations of PCBs have remained virtually constant for more than 10 years despite a ban on all use of these chemicals in the United States and Canada within this period (7, 10). The relatively constant atmospheric level is in contrast to the decrease in PCB concentrations reported in sediments and peat cores but consistent with reported PCB levels in fish (11-13). Volatilization from contaminated aquatic and terrestrial systems coupled with deposition to pristine regions of the Great Lakes may act to buffer atmospheric concentrations of PCBs and limit natural processes from detoxifying the aquatic ecosystem.

Green Bay, Lake Michigan, is an ideal location to examine volatilization of PCBs from a natural system. Green Bay is a large bay fed by the heavily industrialized Fox River in the south and the much cleaner waters of northern Lake Michigan in the north. The water of southern Green Bay and the Fox River are contaminated as PCB-rich sediments are continually resuspended by natural currents and routine dredging (14-16). The discharges from 13 paper mills and 5 municipal wastewater treatment facilities were original sources of PCBs to the Fox River and now affect the bay to an unknown extent. It was expected that the north and south bay would exhibit different aqueous concentrations of PCBs and volatilization rates. Because our study was designed to examine these differences in potential PCB volatilization, over-land and over-water concentration differences were examined in the northern bay as well as in the southern bay.

The direction and magnitude of PCB flux across the air/water interface in Green Bay is predicted by Achman et al. (8). In this paper, we will evaluate the influence of temperature, aqueous PCB concentration, and wind speed on observed atmospheric PCB concentrations and congener distributions.

This study was performed in cooperation with the United States Environmental Protection Agency's Green Bay Mass Balance study of 1989-1991 and is intended to support the atmospheric compartment of the model. Three atmospheric monitoring stations were established at the University of Wisconsin in Green Bay, Peninsula State Park, WI, and Fayette State Park, MI. Our study was intended to complement these measurements and evaluate the appropriateness of using shoreline measurements to describe over-water air concentrations of SOCs.

Sampling Strategy

To compare over-land and over-water PCB concentrations, a series of high-volume air samplers on land were operated simultaneously with a sampler mounted on the bow of the R/V Bluewater (USEPA, Grosse Ile, MI) operating in Green Bay, Lake Michigan.

The samplers on land were placed within 2 km of the shore at three locations surrounding the bay (Figure 1). The first sampler was located on the northern shore of Green Bay at Fayette State Park, MI (FAY, latitude 45°43′33″, longitude 86°38′57″), the second sampler was centrally located at Peninsula State Park in Door County, WI (PEN, 45°07′51″, 87°13′51″), and the third sampler was operated at the eastern edge of the city of Green Bay on the University of Wisconsin—Green Bay campus (UWGB, 44°31′52″, 87°54′30″). Air samples were collected
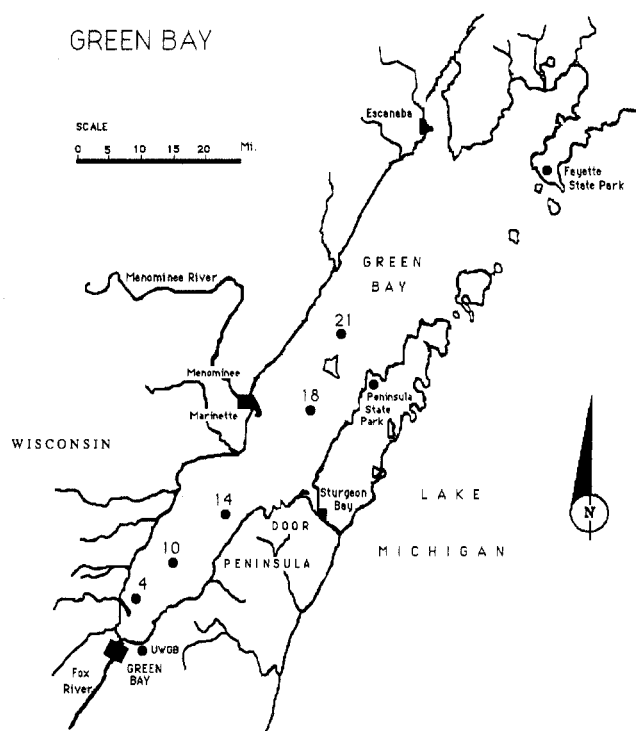

Figure 1. Green Bay, Lake Michigan, air sampling sites.

at the UWGB site each day that air samples were collected over the water aboard the R/V Bluewater. The central and northern samplers operated only when sampling was conducted over the northern bay. All samplers were removed from direct sources of PCBs.

For the over-water samples, an air sampler was mounted on the bow of the R/V Bluewater with the sampler inlet located 2-3 m above the water surface. PCBs in air over the water were collected at sites 4-21 throughout Green Bay (Figure 1). In order to collect discrete samples representative of each site and to eliminate contamination from the vessel, the boat was generally anchored on site into the wind with engines off for the sampling duration. When weather required navigation, the sampler was operated only when the wind was <60° off the bow. Sampling equipment was powered by a generator, and all exhaust was discharged into the water aft of the boat. Water samples were collected and analyzed for PCBs at all stations.

Experimental Methods

Air Sampling: Over Land. Air samples consisted of 200-1300 m^3 of air collected over 5-24 h using General Metal Works high-volume samplers. The land samples were generally collected for 12 h, from 0900 to 2100 h CDT (400 m^3). This sampling time corresponded well to the period of sampling on the RV Bluewater. The samplers were calibrated prior to each sampling trip and operated at 0.45-0.77 m^3/min (TSI hot-film mass flowmeter Model 1352-5g).

Air was passed through a 20 × 25 cm glass fiber filter (GFF) backed up by 40 g of XAD-2 adsorbent or 10.3-cm-thick polyurethane foam. The XAD-2 was provided by DePaul University, Chicago, for the June sampling trip. XAD-2 was cleaned in the University of Minnesota laboratory for the July and October sampling trips. Glass fiber filters were provided and tared by Illinois State Water Survey, Champaign, IL.

XAD prepared in Minnesota was cleaned by two 24-h Soxhlet extractions with pesticide grade acetone (Burdick

and Jackson) followed by one 24-h Soxhlet extraction with petroleum ether (Burdick and Jackson). The XAD was dried in glass jars capped with cleaned polyurethane foam in a 60 °C oven for 2-4 h. XAD resin prepared at DePaul University was cleaned by sequential extraction with methanol, acetone, hexane, and methylene chloride and again in the reverse order. The XAD from DePaul University was stored in water and was wet when loaded into the sampler. Drying time is believed to be much shorter than the total sampling time (10 min vs 10 h).

The XAD was mailed in sealed glass jars from the University of Minnesota to Fayette, MI, for all the sampling at the northern site and to Green Bay, WI, for the June sampling at Peninsula State Park. XAD used at the master site was not mailed. Storing the XAD in water tended to reduce the blank levels in the XAD from DePaul University. At the site, the XAD was transferred to solvent-rinsed stainless steel cartridges which were loaded into the high-volume samplers. The cartridges consisted of screens on the top and bottom so air could flow through freely and the XAD would remain contained. After sampling, the XAD in the cartridges was returned to the University of Minnesota for analysis.

Atmospheric total suspended particulate (TSP) concentration was determined by weighing the tared GFF. Wind speeds and directions were monitored at the meteorological towers at the Peninsula, Fayette, and UWGB sites and provided to us by the Illinois State Water Survey.

Air Sampling: Over Water. A General Metal Works high-volume sampler was mounted on the bow of the R/V *Bluewater*. The sampler was equipped with a 20 × 25 cm glass fiber filter backed by a polyurethane foam plug of dimensions 7.6 cm diameter × 10.3 cm. Air samplers were collected over 5-12-h periods at flow rates of 0.5-0.78 m^3/min (~400 m^3). They were calibrated before each sampling trip.

All PUF was prepared at the University of Minnesota by two 24-h Soxhlet extractions with pesticide grade acetone followed by one 24-h Soxhlet extraction with petroleum ether. The PUF was dried in a heated vacuum desiccator overnight and stored in foil-lined glass jars. The GFF was combusted at 450 °C overnight.

The PUF adsorbent was placed in a solvent-rinsed glass sleeve prior to sampling, and this sleeve was inserted into the high-volume sampler. A silicon o-ring prevented air from flowing around the sleeve, and a stainless steel screen fitted into the sleeve held the PUF in place. To test for chemical breakthrough, several PUF plugs were cut into top and bottom halves prior to cleaning and extracted separately.

TSP concentrations over the water were determined by weighing the tared GFF or from a separate high-volume sampler equipped with a 10-cm tared GFF. The separate sampler was intended to prevent extensive handling of the 20 × 25 cm GFF which would be extracted for PCBs. Wind speeds and directions were measured hourly from the bow of the R/V *Bluewater*. Maximum and minimum air temperatures were recorded daily over the sampling period. The daily over-land and over-water air temperatures did not differ significantly.

Analytical Methods. The PUF air sample plugs and the XAD air samples cleaned in Minnesota were Soxhlet extracted with 150-250 mL of petroleum ether. The XAD from DePaul University was extracted for 24 h, first with acetone and then with methylene chloride. GFF samples were extracted with petroleum ether. All samples were spiked prior to extraction with PCB congeners 3,5-dichlorobiphenyl (IUPAC no. 14), 2,3,5,6-tetrachlorobiphenyl

(no. 65), 2,3,4,4',5,6-hexachlorobiphenyl (no. 166), and deuterated chrysene as surrogates. The solvent was concentrated to 4 mL in a Kuderna-Danish apparatus. Twenty-five percent of the sample extract was then removed for polycyclic aromatic hydrocarbon (PAH) analysis. The exact fraction split was determined by weight. The remaining 75% was subjected to a cleanup procedure that successfully removed polar interferences from the PCBs. A 1.5-cm-i.d. column with Teflon stopcock was packed with 3 g of 100-200-mesh silica gel (Fisher Chemical). The silica was activated overnight at 300 °C in a muffle furnace and deactivated to 6% with deionized Milli-Q water. The silica was overlaid with 10 g of 80-200-mesh neutral alumina (Fisher Chemical). The alumina was activated overnight at 450 °C and deactivated to 10% with deionized Milli-Q water. Clean anhydrous sodium sulfate was added to the top and bottom (1 cm) of the column as well as in between the alumina and silica layers to remove residual water in the sample extract. The column was prewashed with 75 mL of hexane. PCBs, HCB, heptachlor, mirex, and a fraction of the DDT metabolites were eluted in 50 mL of hexane. Dieldrin, HCHs, heptachlor epoxide, and the remaining DDT metabolites were eluted with 50 mL of 10% diethyl ether in hexane. Each fraction was concentrated to ~4 mL with a Kuderna-Danish apparatus.

PCB congeners 2,4,6-trichlorobiphenyl (no. 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (no. 204) were added as internal standards, and the extracts were reduced under a clean nitrogen stream to approximately 100 μL prior to injection. The samples were analyzed by gas chromatography on a 30-m DB-5 bonded-phase capillary column (J&W Scientific) using an Hewlett-Packard 5890 gas chromatograph equipped with a ^{63}Ni electron capture detector. Gas chromatographic conditions were as follows: injector temperature 250 °C, detector temperature 350 °C; oven program, inject at 100 °C (10-min hold), program at 10 °C/min to 160 °C, 0.5 °C/min to 227 °C, 10 °C/min to 260 °C. Chromatographic data were collected, integrated, and manipulated using a Maxima 820D datasystem by Waters. The 610 ng/mL PCB standard solution (610 std) consisted of 25% (v/v) Aroclor 1232, 18% Aroclor 1248, and 18% Aroclor 1262 (Ultra Scientific, North Kingstown, RI). This standard also contained the internal standards and surrogate standards. PCB congeners were identified as designated by Mullin (17). Individual PCB congeners were quantified as follows:

$$\text{congener mass} = (\text{congener area})(\text{RRF})\frac{\text{mass of internal std in sample}}{\text{area of internal std in sample}}$$

$$\text{RRF} = (\text{mass of congener in 610 std/area of congener in 610 std})/(\text{mass of internal std in 610 std/area of internal std in 610 std})$$

RRF is the relative response factor for the congener in the standard. This quantification method requires only that the mass of internal standard injected is known; it is unnecessary to determine extract volume. The total mass was corrected for surrogate recoveries by dividing the sampler congener by the appropriate surrogate fractional recovery. PCBs with two and three chlorines in each sample were divided by the fraction of surrogate no. 14 recovered from that sample. PCBs with four, five, six, and seven chlorines were corrected by no. 65, and PCBs with eight and nine chlorines were corrected by no. 166. When a surrogate recovery was greater than 115% due to interference or contamination, another surrogate was used. The total PCB and individual congener concentrations in

a sample were determined by dividing the total PCB or congener mass by the air volume.

Quality Assurance

Eighty-six PCB peaks were analyzed, and 75 PCB peaks were detected regularly in the air samples. Nine congeners coeluted with contaminants in the solvent blanks or were high and variable contaminants in the travel blanks. In order to compare all the air samples, these congeners were eliminated, leaving 78 peaks and 114 PCB congeners.

Adsorbent travel blanks consisted of clean PUF or XAD stored in aluminum foil lined sealed jars. GFF field blanks were stored in aluminum foil. These blanks were transported to each site but never opened. New travel blanks were cleaned and collected for each sampling trip. Solvent blanks were regularly extracted along with the samples. Mean travel blank values for PUF and XAD adsorbent are reported for each PCB congener in Table I.

Limits of detection (LOD) were determined from analysis of seven consecutive injections of 6 ng of the PCB standard. A mean and standard deviation of the measured mass was calculated. The limit of detection for each congener was calculated as 3 times the standard deviation plus a minimum detectable mass. The minimum detectable mass was estimated from experience as 500 area units for our instrument. Table I lists the LOD for each congener. Since the inclusion of LOD values changed the PCB congener sum in most samples by less than 3%, LODs were not included in the congener sum calculations and all PCB totals represent minimum values.

Extraction Recovery of PCBs. To evaluate analytical recovery of PCB congeners, a complete set of PCB congeners and surrogates (300–600 ng of total PCB) was added to clean solvent or adsorbent and subjected to the same treatment as the samples. The average recovery of all congeners was 83.4 ± 21.8% (Table I). This procedure was repeated seven times throughout the sample extraction period (late 1989 through 1990). Results are summarized in Table I. The average recoveries and standard deviations of PCB congeners no. 14, no. 65, and no. 166 from 75 samples and field blanks were 87 ± 32%, 97 ± 25%, and 97 ± 13%, respectively. Propagated error was estimated at 17% of the total PCB concentration.

Breakthrough of PCBs through Adsorbent. Breakthrough of PCBs was evaluated by cutting three PUF plugs in half prior to cleaning. Each pair of halved PUFs was inserted into the high-volume sampler and the sample was collected and then extracted separately. The results of two pairs of these halved PUFs are plotted in Figure 2. Breakthrough to the second half of the PUF is greater than 50% only for congeners no. 4 and no. 10. From these results we conclude PUF breakthrough was not a problem for quantifying total PCB concentrations in this study. XAD-2 breakthrough is evaluated below by comparison with PUF.

XAD/PUF Comparison. So that the samples collected on XAD-2 resin at the northern land sites could be compared to the samples collected on PUF over the water, two high-volume samplers at the Green Bay master site ran simultaneously on 2 or 3 days during each sampling trip. One sampler was equipped with GFF and PUF, and the other sampler was equipped with GFF and XAD. Results from this comparison study are summarized in Table II and Figure 3ab. The eight XAD/PUF pairs may be compared by absolute concentration differences and by normalized congener pattern differences. The Student's *t*-test showed no significant difference in the PUF and XAD-2 total PCB concentrations ($\alpha = 0.05$). The average concentration difference for the individual congeners is also
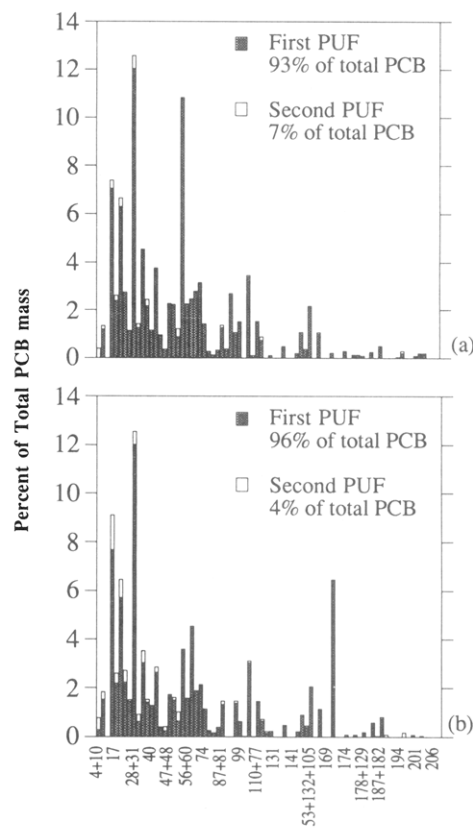
Figure 2. Breakthrough of PCB congeners through polyurethane foam. (a) Collected on October 22, 1989: air temperature 12.2 °C; flow rate 0.67 m³/min; volume 424 m³. (b) Collected on October 23, 1989: air temperature 16.7 °C; flow rate 0.67 m³/min; volume 450 m³.
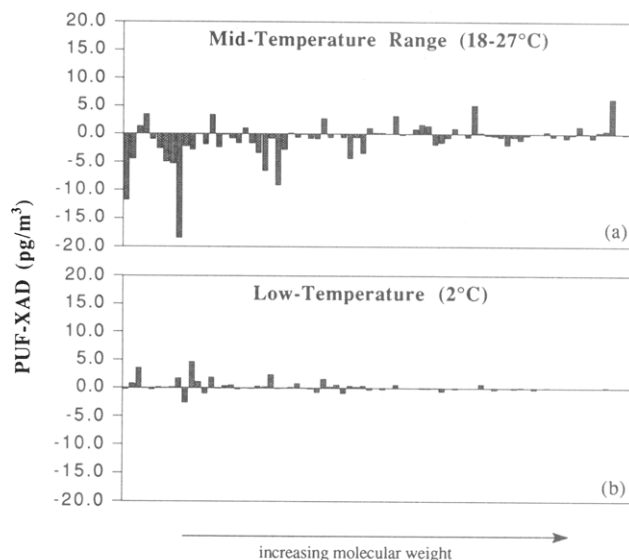
Figure 3. PCB congener concentration retained on XAD-2 subtracted from the concentration retained on polyurethane foam. (a) Bars represent the average difference measured for six sample pairs. (b) Bars represent the difference for one sample pair. Temperatures are daily averages collected during sampling.

not significantly different from zero. There is a large variance about the mean values, however.

In order to detect systematic differences in retention between the XAD and PUF samples, the difference in concentrations for PUF congeners was arranged by increasing molecular weight and plotted. Figure 3a shows a clear trend of higher retention for the lower molecular weight PCBs on XAD compared to PUF. This was especially true for congener nos. 4 + 10, 28 + 31, and 70 +

Table I. Percent Recovery of PCB Congeners, Average Travel Blanks (ng), Average Sample PCB Mass (ng), and Limit of Detection (LOD; ng)

IUPAC congener no.	% rec	% SD	travel bk XAD	travel bk PUF	av sample XAD	av sample PUF	LOD	Cl no.
4 + 10	62.04	22.14	0.91	0.04	2.32	1.85	0.07	2
6	66.40	13.84	0.50	0.03	2.17	3.88	0.08	2
12 + 13	76.38	20.39	0.00	0.00	0.38	3.40	0.03	2
16 + 32	61.79	28.33	0.66	0.72	10.12	16.03	0.05	3
17	73.39	15.06	0.20	2.42	5.52	8.43	0.04	3
18	69.59	13.59	0.30	1.04	11.42	15.47	0.05	3
26	71.30	14.78	0.07	0.93	3.59	5.21	0.04	3
27 + 24	79.02	14.78	0.05	0.28	3.08	3.15	0.03	3
28 + 31	71.5	12.0	1.43	1.77	21.34	36.90	0.15	3
29	70.12	89.58	0.36	0.00	0.76	0.63	0.03	3
33 + 53 + 21	76.91	12.75	0.60	2.75	7.06	11.79	0.08	3
37 + 42	86.67	12.28	0.14	0.17	3.40	8.23	0.06	3
40	73.18	23.79	0.06	0.03	2.24	3.58	0.05	4
44	79.60	12.66	0.25	0.02	5.65	12.30	0.06	4
45	80.15	12.67	0.05	0.00	1.46	3.42	0.04	4
46	82.61	17.76	0.04	0.00	0.54	1.31	0.04	4
47 + 48	77.50	13.88	0.08	0.00	2.88	7.31	0.04	4
49	75.80	14.44	0.43	3.99	3.78	7.50	0.05	4
51	66.99	38.84	1.32	0.02	0.37	1.16	0.03	4
52 + 43	74.42	13.92	0.56	0.04	7.75	14.50	0.05	4
56 + 60	91.56	11.38	0.29	0.00	3.60	6.59	0.09	4
63	99.27	16.37	0.00	0.00	2.90	2.81	0.03	4
66 + 95	84.58	12.55	0.24	0.40	3.47	13.47	0.12	4
70 + 76	82.89	13.18	0.65	1.63	6.62	9.76	0.09	4
74	84.96	13.76	0.26	0.07	2.39	4.08	0.05	4
82	88.32	13.43	0.02	0.00	0.59	0.74	0.02	5
83	127.38	46.81	0.04	0.02	0.39	0.34	0.02	5
85	95.51	11.48	0.00	0.00	0.58	0.91	0.13	5
87 + 81	100.18	22.66	0.17	0.02	2.03	2.55	0.03	5
91	89.43	11.87	0.03	0.00	0.82	1.51	0.03	5
92 + 84 + 89	88.00	11.06	0.47	0.55	2.06	4.51	0.13	5
97	96.70	15.87	0.08	0.00	1.67	1.93	0.02	5
99	88.48	12.83	0.00	0.02	1.30	2.47	0.04	5
100	95.53	19.56	0.00	0.00	0.40	0.83	0.03	5
101	78.29	11.37	0.43	0.09	4.69	5.96	0.04	5
107	73.44	31.83	0.00	0.00	0.14	0.31	0.04	5
110 + 77	82.86	8.80	0.34	0.28	3.43	4.23	0.08	5
118	82.85	7.25	0.14	0.18	1.09	1.76	0.11	5
119	102.88	66.56	0.00	0.02	0.03	0.15	0.05	5
128	100.96	9.49	0.02	0.00	0.82	0.31	0.05	6
131	83.91	17.54	0.00	0.00	0.15	0.39	0.01	6
134 + 114	88.22	11.02	0.06	0.08	1.02	1.66	0.12	6
135 + 144 + 147 + 124	81.21	8.81	0.07	0.00	0.88	0.99	0.04	6
136	84.56	10.08	0.00	0.00	0.00	0.29	0.03	6
141	167.78	211.69	0.00	0.00	0.19	0.46	0.06	6
146	80.53	11.82	0.00	0.00	0.26	0.72	0.04	6
149	75.68	8.11	0.08	0.00	1.64	2.18	0.12	6
151	74.55	7.55	0.21	0.00	0.74	0.82	0.05	6
153 + 132 + 105	77.92	7.37	0.24	0.00	3.65	4.73	0.10	6
158	148.96	98.93	0.39	0.00	0.20	0.24	0.10	6
163 + 138	77.78	7.60	0.00	0.02	1.65	2.69	0.89	6
167	0.00	0.00	0.00	0.00	0.01	0.01	0.01	6
169	0.00	0.00	0.27	0.00	0.06	0.00	0.01	6
170 + 190	86.63	6.36	0.26	0.00	0.56	1.15	0.28	7
172 + 197	94.92	20.10	0.00	0.00	0.03	0.10	0.22	7
173	40.67	50.26	0.00	0.00	0.26	0.01	0.03	7
174	83.01	5.73	0.04	0.00	0.67	0.75	0.09	7
175	102.64	27.15	0.00	0.00	0.08	0.03	0.03	7
176 + 137 + 130	105.35	21.82	0.04	0.10	1.01	0.24	0.03	6
177	69.13	28.76	0.00	0.00	1.25	0.42	0.10	7
178 + 129	82.18	4.71	0.03	0.00	0.54	0.28	0.05	7
180	85.47	5.51	0.00	0.00	0.81	1.28	0.17	7
183	69.46	25.46	0.00	0.00	0.57	0.71	0.13	7
185	84.38	7.64	0.04	0.00	0.04	0.09	0.09	7
187 + 182	77.40	6.82	0.00	0.01	0.91	1.31	0.09	7
189	113.18	18.35	0.06	0.00	0.13	0.00	0.04	7
191	100.75	36.59	0.00	0.00	0.05	0.03	0.06	7
193	96.44	11.81	0.00	0.00	0.10	0.04	0.05	7
194	94.25	17.96	0.00	0.00	0.08	0.09	0.09	8
195 + 208	91.12	6.30	0.00	0.00	0.78	0.68	0.10	9
199	75.32	12.50	0.00	0.00	0.19	0.04	0.05	8
200 + 157	67.12	30.75	0.00	0.00	0.90	0.07	0.03	6
201	84.85	5.21	0.03	0.00	0.15	0.64	0.20	8
202 + 171 + 156	84.05	5.57	0.05	0.00	0.13	0.48	0.05	8
203 + 196	83.87	4.85	0.00	0.00	0.24	1.18	0.22	8
205	81.58	35.01	0.00	0.00	0.40	0.02	0.08	8
206	73.75	30.63	0.00	0.00	0.01	0.02	0.54	9
207	123.73	119.00	0.45	0.00	0.00	0.02	0.09	9
∑PCBS	83.36	22.19	22.97	17.74	155.14	256.15	6.79	

Table II. XAD-2 Resin and Polyurethane Foam (PUF) Comparison[a]

	[PCB] (pg/m³)	flow (m³/min)	air vol (m³)	air temp (°C)
		PUF		
6/4–5	168	0.77	777	10.8
6/5–6	273	0.77	1090	17.1
6/6–7	197	0.77	1092	19.3
6/7–8	493	0.77	1375	19.7
6/9	311	0.77	691	12.8
7/29	278	0.67	449	20.0
7/30	269	0.67	507	21.6
8/1	648	0.67	446	29.8
10/20	262	0.57	395	2.2
10/23	367	0.57	435	16.1
		XAD		
6/5	278	0.54	429	20.0
6/6	266	0.54	415	26.1
6/8	652	0.54	415	20.0
6/10	327	0.54	1434	19.4
7/29	497	0.54	401	20.0
7/30	273	0.54	414	21.6
8/1	390	0.54	408	29.8
10/20	261	0.54	442	2.2
10/23	370	0.54	450	16.1

[a] All samples collected at site UWGB.

Table III. Atmospheric Vapor PCBs ($\sum$PCBs) Collected in Side-by-Side Samplers at UWGB, June 1989[a]

	Cotham		this study	
date	$\sum$PCB (pg/m³)	air vol (m³)	$\sum$PCB (pg/m³)	air vol (m³)
6/4–5	102	888	168	777
6/5–6	244	931	273	1090
6/6–7	152	1183	197	1092
6/7–8	466	799	493	1375
6/8–10	565	1487	311	691

[a] Cotham samples collected at 0.54 m³/min. Samples from this study collected at 0.78 m³/min.

76. This trend indicates that the more volatile PCBs break through the PUF at these flow rates (0.57–0.77 m³/min) and air volumes (400–1400 m³). More halved PUF samples collected at warm temperatures would better delineate this trend. For this set of eight pairs, analysis of variance detected statistically significant differences between the XAD and PUF samples at the 95% confidence level. This is consistent with the XAD/PUF comparison for polycyclic aromatic hydrocarbons of Chuang et al. (18) and the XAD/PUF comparison for PCBs of Billings and Bidleman (19). Volume of air collected, air temperature, and sub-cooled liquid vapor pressure of target compounds affect the ability of PUF to retain PCB congeners (20, 21). The influence of temperature is further described in Figure 3b. At low temperature, PUF and XAD exhibited similar retention behavior. The sample pair plotted, collected on a day when the temperature averaged 2.2 °C, showed that congener concentrations are independent of adsorbent and there is no trend with regard to molecular weight.

The small but significant differences in retention of the lighter PCBs are of concern. These systematic differences prevent the use of all the samples for analysis of the congener distributions. When the distributions of the congeners over land and over water are compared, only samples collected on the same adsorbent may be used.

In early June 1989, we sampled for atmospheric PCBs at the same time and at the UWGB master site with Bidleman and Cotham (22). The high-volume samplers were of similar design, as both were equipped with GFF and PUF, although sampler flow rates varied (0.78 vs 0.54 m³/min). Both samplers were equipped with GFF and PUF. The difference between the two sets of samples was not statistically significant (paired t-test, $\alpha = 0.01$), and there were no systematic differences by congener molecular weight (Table III).

Results and Discussion

Concentrations. Fifty-five air samples were collected over land and over water in the Greey Bay region. A summary of the PCB congener concentrations measured is listed in Table IV. Individual congener concentrations ranged from less than 0.5 to 420 pg/m³ while the PCB

congener sum ($\sum$PCB) concentrations ranged from 65 to 2200 pg/m³. No seasonal variation was observed. The average concentrations of $\sum$PCB in June, July, and August were 580, 535, and 490 pg/m³, respectively. $\sum$PCB concentrations observed varied widely between the different collection sites. There was no statistical $\sum$PCB concentration difference between samples collected in the northern and southern regions of the bay. The average $\sum$PCB concentration and standard deviation measured at the southern sites (UWGB, 10 and 4) is 600 ± 480 pg/m³, and 400 ± 180 pg/m³ at the northern sites (PEN, FAY, 18 and 21).

The values reported here reflect the PCBs collected on the backup adsorbent (PUF, XAD-2) only. Extremely low PCB concentrations were measured on the filters. The PCB masses recorded on the filters were generally lower than our detection limits or close to blank filter values. These very low particle-associated PCBs are expected from gas/particle distribution correlations established by other researchers (10, 23, 24). Using the gas/particle distribution correlations for PCBs of Foreman and Bidleman (25) and congener vapor pressures ranging from about 7×10^{-3} to 3×10^{-8} Torr (26–28), less than 20 pg/m³ particulate PCB was expected for samples collected in Green Bay. This value is close to our detection limit for these sample volumes (300–1000 m³) and TSPs (20–100 µg/m³).

North/South Concentration Gradient. The 35 samples collected over land at UWGB, PEN, and FAY sites did not exhibit any north/south trend. The average atmospheric $\sum$PCB concentrations measured were 370, 420, and 300 pg/m³, respectively. On any one day, the concentrations of atmospheric $\sum$PCB were approximately the same at all three land sites, whether the sample was collected on the outskirts of the moderately industrial city of Green Bay or the remote sites 94 (FAY) and 165 km north (PEN; Table V). This contrasts with the $\sum$PCB concentrations measured by Sweet et al. (29) using 2-week-integrated, wind-directed samplers from the Green Bay region throughout 1988–1989. They reported $\sum$PCB concentrations ranging from 300 pg/m³ at UWGB to 100 pg/m³ at FAY. The concentration gradient they observed appear to be due to more pronounced differences in the winter when volatilization off the water would be lower due to ice cover and low water temperatures.
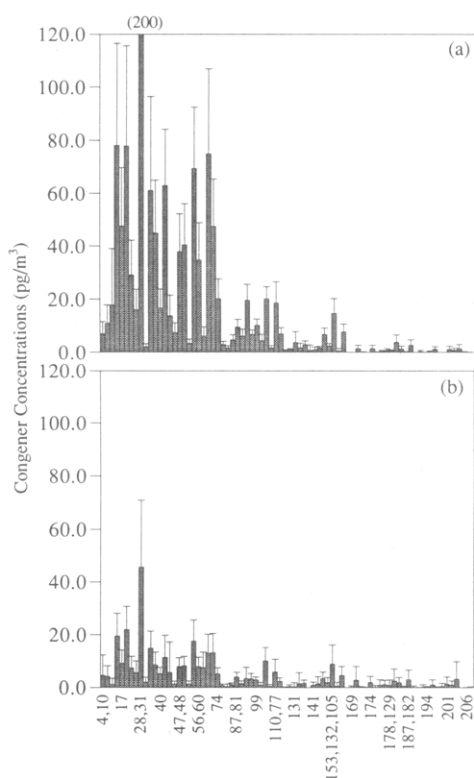
While north/south differences were not evident over the land, the PCB concentration gradient over the water is clear. PCB concentrations measured over the southern bay are 2–5 times higher than the concentrations measured in the north. $\sum$PCBs collected at sites 21, 18, 14, 10, and 4 average 260, 340, 630, 1160, and 1430 pg/m³, respectively. This strong north/south concentration gradient was observed for all three sampling cruises.

The water of Green Bay is contaminated with PCBs at concentration levels that mimic the PCB concentration gradient measured in the air over the bay. $\sum$PCB con-
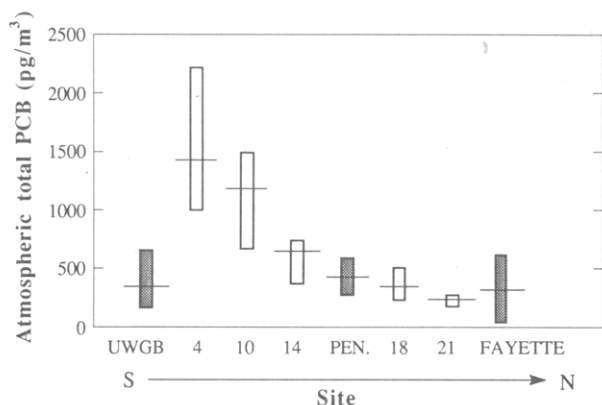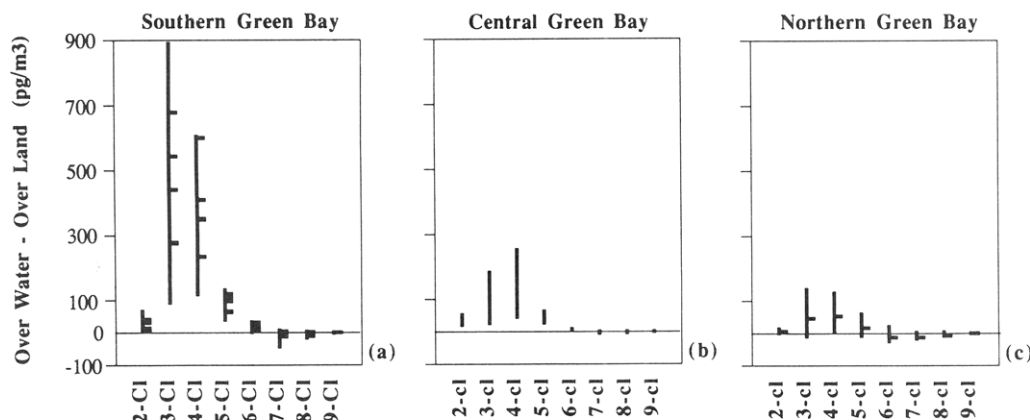
Figure 4. $\sum$PCB vapor concentrations measured in Green Bay, Lake Michigan: dark bars, over land; light bars, over water.

Figure 5. Average PCB congener distributions in the Green Bay, Lake Michigan, atmosphere: (a) over water; southern Green Bay, $n = 9$; (b) over land; southern Green Bay, $n = 25$. Error bars represent 1 standard deviation.

centrations in the water are much higher near the Fox River in southern Green Bay than in the northern Green Bay. $\sum$PCB (particulate and dissolved) concentrations range from 15.6 ± 11.2 ng/L in the southern bay to 1.7 ± 0.6 ng/L in the northern bay (8). The north/south concentration gradient in the dissolved phase and in the gas phase suggests that air and water have the same PCB source or are involved in active exchange. Evidence of this exchange will be examined in more detail below.

Over-Water and Over-Land Atmospheric PCBs. The enrichment of total PCBs over the water relative to over the land was consistent in this study during different sampling periods (Figure 4). Atmospheric concentrations of PCBs measured over land and over water on the same day differ by as much as a factor of 7. Over-land and over-water PCB concentrations are statistically different in the southern bay (comparing over-water sites 4 and 10 to land site UWGB) at the $\alpha = 0.01$ level (paired t-test). When grouped by site, the 9 samples collected at sites 4 and 10 are also statistically different at the $\alpha = 0.01$ level from the 25 samples collected at UWGB (nonparametric rank sum test). Statistical comparisons could not distinguish $\sum$PCB samples collected over land and water in central and northern Green Bay (sites 18 and 21, PEN and FAY).

The distribution of the PCB congeners is reflective of the processes that contribute to atmospheric PCBs. Atmospheric PCBs are dominated by the low molecular weight, most volatile congeners, while sediments show enrichment of the heavier PCBs (5, 12, 30). Atmospheric PCBs that result from volatilization processes have distributions that no longer resemble the original Aroclor mixtures injected in the water (31). Partitioning between air and water, gas phase and aerosol, and aquatic dissolved and particulate phases, as determined by Henry's constants and equilibrium partition coefficients, ultimately favor the burial and removal of the heaviest PCB congeners to the sediments and terrestrial surfaces and the recycling of the lighter PCB congeners via dissolution and volatilization.

Green Bay samples of air, water, and sediment differ in their congener distribution profiles. PCBs from sediment traps deployed near the sediment/water interface in southern Green Bay are almost evenly distributed across molecular weights (32), while vapor-phase PCBs largely consist of the lighter congeners. Panels a and b of Figure 5 are plots of the average congener distribution of vapor samples collected at site UWGB and at sites 4 and 10. The congeners are arranged in order of increasing molecular weight. While both samples are dominated by lighter

Figure 6. Over-water minus over-land PCB homolog concentrations. Horizontal hatch marks represent the concentration difference for a sample pair. All samples were collected on PUF: (a) six sample pairs collected (sites 4, 10, and UWGB); (b) two sample pairs collected (sites 14 and UWGB); (c) four sample pairs collected (sites 18, 21, and UWGB).

Table IV. Average PCB Congener Concentrations Measured by Site[a]

congener no.	Northern bay[b] av	SD	Central bay[c] av	SD	Southern bay[d] av	SD	UWGB[e] av	SD	PEN[f] av	SD	FAY[g] av	SD
4 + 10	2.10	2.35	6.43	12.76	7.01	4.57	4.62	7.83	2.43	4.18	1.19	2.26
6	5.43	4.23	15.02	31.47	10.95	6.99	4.18	4.13	5.99	2.16	1.57	0.83
12 + 13	3.50	4.88	7.65	11.21	17.92	21.14	1.26	2.23	1.30	0.85	0.38	0.76
16 + 32	21.73	4.71	24.89	12.60	78.10	38.46	19.46	8.70	33.21	13.70	9.48	4.97
17	9.35	4.19	10.43	6.23	47.52	22.31	9.29	5.06	16.31	6.20	4.39	2.40
18	18.87	8.41	19.13	9.94	77.86	37.91	21.94	8.85	32.84	11.90	10.06	5.66
26	5.19	2.10	6.46	3.68	29.08	13.17	7.45	4.39	8.75	3.04	2.60	0.74
27 + 24	3.56	1.88	4.06	1.21	16.03	7.70	5.64	4.47	7.44	3.79	4.83	3.08
28 + 31	46.15	24.33	51.23	32.38	199.18	99.58	45.67	25.42	55.54	23.56	20.02	7.66
29	0.89	0.26	1.61	1.25	2.19	1.14	2.02	1.97	0.00	0.00	1.15	1.34
33 + 53 + 21	13.60	5.76	15.47	6.60	61.20	35.31	14.92	6.52	24.25	13.36	6.95	3.99
37 + 42	7.55	3.33	11.80	9.39	44.92	20.10	8.61	4.94	7.49	2.65	4.99	3.42
40	3.99	1.57	5.64	3.10	16.71	7.11	5.23	2.51	5.01	2.93	5.48	3.37
44	16.10	6.85	20.72	13.07	62.99	21.16	11.44	8.39	17.98	6.47	11.78	12.06
45	2.79	2.10	2.68	3.70	13.78	7.78	5.74	11.63	3.98	2.84	0.73	1.45
46	1.33	1.21	1.44	1.47	7.47	3.72	1.33	1.13	2.04	0.97	0.50	0.47
47 + 48	10.34	2.22	11.56	12.77	37.85	14.40	8.04	3.34	6.36	3.13	3.71	5.29
49	8.89	4.30	11.87	11.51	40.48	15.66	8.35	3.58	10.90	4.47	6.99	8.08
51	1.72	0.84	2.38	4.22	3.47	1.63	1.41	1.15	1.17	1.07	0.33	0.67
52 + 43	19.56	9.17	22.05	12.53	69.47	23.06	17.61	8.12	18.61	5.93	20.46	21.46
56 + 60	8.25	4.02	9.88	6.83	34.76	14.05	8.00	3.57	8.79	3.15	7.75	10.02
63	2.62	1.76	5.82	4.53	6.08	3.56	7.67	5.91	3.14	2.75	3.91	1.58
66 + 95	16.22	7.40	20.21	20.40	75.05	31.95	13.13	7.09	1.03	2.51	0.00	0.00
70 + 76	15.34	6.00	16.80	10.57	47.36	18.07	13.30	7.27	14.87	4.44	15.93	20.29
74	5.83	2.43	6.98	4.17	20.13	7.48	5.15	2.37	5.74	2.45	5.67	6.34
82	1.16	0.69	1.36	0.57	3.03	1.16	0.86	0.53	3.33	1.12	0.82	1.30
83	0.33	0.26	0.83	0.76	1.67	0.86	0.41	0.92	1.79	0.57	1.22	1.45
85	1.54	1.11	1.20	1.10	4.70	1.93	1.04	0.71	1.46	1.88	2.16	2.72
87 + 81	4.54	1.88	4.67	1.12	9.57	2.94	3.94	1.88	5.37	0.98	7.29	9.70
91	2.29	1.25	3.38	1.57	6.10	2.70	1.43	1.16	2.38	1.76	2.79	4.51
92 + 84 + 89	6.52	2.06	8.30	5.26	19.61	5.94	3.46	4.28	8.87	3.50	10.55	15.65
97	2.81	1.13	4.03	1.74	6.77	1.67	3.28	2.06	5.36	1.90	4.53	5.58
99	4.40	1.37	4.93	1.82	10.20	2.43	2.86	1.23	2.95	0.74	5.17	6.27
100	1.30	1.68	0.90	1.87	4.39	2.46	0.89	1.09	1.10	1.76	0.43	0.86
101	9.30	3.18	10.77	2.84	20.16	4.50	10.23	5.07	9.05	2.41	15.82	17.42
107	0.11	0.15	0.31	0.19	1.66	0.97	0.45	0.84	0.00	0.00	0.50	0.99
110 + 77	5.72	2.58	7.65	3.32	18.65	7.92	5.91	4.97	12.22	3.62	9.14	10.78
118	2.71	1.29	3.42	1.47	6.97	2.41	2.32	1.45	3.81	1.15	3.84	4.14
119	0.23	0.24	0.19	0.23	0.69	0.39	0.15	0.28	0.09	0.23	0.33	0.56
128	0.43	0.26	0.47	0.53	1.01	0.44	0.52	0.56	3.99	1.13	0.94	1.22
131	0.34	0.76	0.17	0.42	3.71	4.13	0.41	1.47	0.00	0.00	0.00	0.00
134 + 114	1.17	0.50	1.43	2.18	1.81	1.74	1.50	4.25	7.36	5.20	1.59	1.85
135 + 144 + 147 + 124	1.18	0.23	1.52	0.55	3.03	1.32	1.72	1.19	3.25	1.97	3.11	2.90
136	0.00	0.00	0.00	0.00	0.73	2.19	0.00	0.00	0.00	0.00	0.00	0.00
141	0.93	0.95	0.00	0.00	1.01	1.16	0.91	1.28	0.10	0.23	1.36	1.65
146	0.74	0.26	0.62	0.55	1.64	0.68	1.44	2.72	0.60	0.95	0.87	1.11
149	2.94	2.16	3.75	1.63	6.82	2.39	3.44	2.42	5.96	1.27	5.25	7.91
151	1.27	0.58	1.34	0.93	2.45	0.99	1.90	1.95	0.97	0.23	2.38	3.07
153 + 132 + 105	7.74	2.78	7.44	4.03	14.80	5.48	8.95	7.34	8.40	1.39	11.10	11.43
158	0.00	0.00	0.00	0.00	0.50	1.08	0.57	1.48	0.06	0.15	0.94	1.89
163 + 138	4.38	1.51	4.60	2.52	7.72	3.06	4.60	3.55	2.11	3.31	6.43	6.27
167	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.00	0.00	0.08	0.17
169	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.63	0.00	0.00	0.00	0.00
170 + 190	0.82	0.85	0.88	0.96	1.49	1.23	2.82	5.32	1.99	1.05	2.16	2.53
172 + 197	0.10	0.14	0.14	0.22	0.11	0.17	0.21	0.34	0.00	0.00	0.29	0.58
173	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.25	1.02	1.89	0.00	0.00
174	1.10	0.66	0.95	1.04	1.52	1.29	1.88	2.40	2.14	0.80	1.68	1.86
175	0.00	0.00	0.00	0.00	0.07	0.20	0.20	0.68	0.26	0.40	0.00	0.00
176 + 137 + 130	0.10	0.23	0.41	0.78	0.36	0.46	0.89	2.09	4.12	5.84	0.32	0.64
177	0.29	0.30	0.52	0.55	0.88	0.66	1.12	1.61	7.20	2.62	0.66	1.08
178 + 129	0.42	0.48	0.16	0.38	0.59	0.48	0.96	1.92	2.32	1.01	0.52	1.04
180	2.12	1.93	1.17	1.84	3.89	2.74	2.49	4.61	1.10	1.83	4.27	6.76
183	0.92	0.60	0.75	1.07	1.39	1.07	1.80	1.99	1.24	1.08	1.64	1.42
185	0.06	0.14	0.00	0.00	0.12	0.24	0.28	0.47	0.00	0.00	0.17	0.34
187 + 182	1.96	1.21	1.46	1.67	2.74	2.04	3.05	3.69	2.12	1.82	2.42	2.90
189	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.53	0.00	0.00	0.00	0.00
191	0.00	0.00	0.00	0.00	0.24	0.62	0.03	0.13	0.18	0.31	0.00	0.00
193	0.00	0.00	0.00	0.00	0.07	0.14	0.26	0.85	0.23	0.23	0.00	0.00
194	0.22	0.30	0.06	0.10	0.30	0.32	0.19	0.28	0.26	0.64	0.14	0.28
195 + 208	1.97	1.60	1.11	1.60	1.22	1.03	1.05	1.97	3.84	3.06	1.64	2.36
199	0.07	0.15	0.00	0.00	0.02	0.07	0.10	0.27	0.79	1.18	0.00	0.00
200 + 157	0.00	0.00	0.00	0.00	0.00	0.00	0.46	1.23	4.49	4.12	0.00	0.00
201	1.08	1.20	0.62	0.88	1.14	1.35	1.38	2.72	0.00	0.00	0.74	1.21
202 + 171 + 156	0.77	0.63	0.41	0.71	0.90	0.76	1.02	1.48	0.00	0.00	0.62	1.11
203 + 196	0.90	1.21	0.71	1.04	1.42	1.69	3.22	6.75	0.00	0.00	1.00	1.57

Table IV (Continued)

congener no.	Northern bay[b] av	SD	Central bay[c] av	SD	Southern bay[d] av	SD	UWGB[e] av	SD	PEN[f] av	SD	FAY[g] av	SD
205	0.00	0.00	0.00	0.00	0.10	0.29	0.01	0.06	3.56	2.47	0.00	0.00
206	0.00	0.00	0.00	0.00	0.05	0.15	0.05	0.14	0.00	0.00	0.00	0.00
207	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.33	0.00	0.00	0.00	0.00
∑PCBs	328	157	395	298	1206	558	338	248	423	134	268	275
Homologs												
di-Cl	11.0	7.8	29.1	33.3	35.9	23.1	10.1	11.8	10.0	5.5	3.2	3.8
tri-Cl	123.2	51.5	139.3	72.3	534.1	253.9	130.8	55.7	182.2	75.6	62.0	22.9
tetra-Cl	114.8	43.2	141.6	97.6	447.2	166.8	90.9	38.1	105.6	34.6	66.0	65.9
penta-Cl	46.4	19.1	55.9	18.1	127.3	39.2	58.8	26.3	60.2	13.5	86.5	108.3
hexa-Cl	19.6	8.2	19.7	11.0	42.5	16.6	25.1	18.5	28.7	4.7	32.1	36.9
hepta-Cl	8.2	5.9	6.6	8.1	13.8	9.8	15.8	19.7	23.5	8.6	14.0	18.6
octa-Cl	4.5	3.9	2.7	2.7	4.6	4.4	6.9	9.5	12.4	7.6	3.9	4.2
nona-Cl	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.4	0.2	0.2	0.0	0.0
deca-Cl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total	328		395		1206		338		423		268	

[a] Concentrations are in picograms per cubic meter. [b] Sites 18 and 21, northern travel; $n = 5$. [c] Site 14, central travel; $n = 6$. [d] Sites 4 and 10, southern travel; $n = 9$. [e] $n = 25$. [f] $n = 6$. [g] $n = 4$.

Table V. Average PCB Concentrations Over Land (pg/m³) and Average Air Temperatures (°C) during Sampling Period[a]

date (1989)	UWGB	T	PEN	T	FAY	T
6/5	271	20.0	270	18.1	193	17.5
6/6	264	26.1	312	18.7	628	20.0
7/27	196	27.2	516	25.1	184	24.7
7/28	566	20.6	521	21.1		
7/29	492	20.0	588	16.8		
7/30	271	21.6	317	20.5		
10/20	247	2.2			65	2.5

[a] All samples collected on XAD-2 with air flow rate of 0.57 m³/min.

congeners, it appears that the difference in the total concentrations on land and over the water is largely due to the more volatile congeners.

The over-water enrichment in the lighter PCBs is further described in Figure 6. The samples are grouped by collection region: northern sites include sites 18 and 21, site 14 is the central site, and the southern sites includes sites 4 and 10. Each over-water PCB concentration is subtracted by the concentration measured on the same day at the UWGB land site. The over-water/over-land differences are further organized by homolog group. The vertical bars represent the range of concentration difference measured for that homolog group. The horizontal hatches represent the homolog differences for the other over-water/over-land sample pairs collected. The PCB concentration differences over land and over water are most pronounced for the tri- and tetrachlorinated biphenyls. The over-land and over-water difference is not important for those biphenyls with six, seven, eight, and nine chlorine atoms. The less chlorinated congeners account for the ∑PCB differences described in Figure 4 as well as the enrichment of these lighter congeners over the southern bay. This pattern of enrichment of the lighest congeners suggests that volatilization is responsible for the enhancement of PCBs over the bay.

Wind Direction. Prevailing winds during air sampling indicate that the southern region of the bay is a source of atmospheric PCBs. A wide range of over-land/over-water concentration differences were measured in southern Green Bay. Over-land and over-water absolute differences range from 90 to 900 pg/m³ for the trichlorobiphenyls (Figure 6a). The range of differences appears to be related to wind

direction. The largest difference was from samples collected on August 1 (2200 pg/m³ at site 4 and 648 pg/m³ at UWGB), while the smallest difference was from the pair collected on the previous day (670 pg/m³ at site 10 and 430 pg/m³ at UWGB). The four samples that show the largest over-land/over-water difference were collected under the influence of southwesterly winds (August 1, October 23, June 7, and October 22). This is the direction of the contaminated waters of the Fox River, the city of Green Bay, and the more distant industrialized regions of Milwaukee, WI, Chicago, IL, and the Midwest. The remaining sample pairs in Figure 6 do not exhibit any correlation with wind direction as most of the tri- and tetrachlorinated biphenyls are elevated over the water.

We observed little correlation between wind direction and ∑PCB concentration at the UWGB site over land. Below are the average and standard deviations in ∑PCB concentrations and the average wind direction observed on the 17 different days of sampling at UWGB:

wind direction	NE (1–90°)	NW (270–360°)	SE (90–180°)	SW (180–270°)
PCB (ng/m³)	355 (193)	386 (174)	289 (187)	324 (197)
n	3	4	5	5

Although the statistical evidence is not strong, higher average atmospheric PCBs were measured when northwest winds (NW) swept over the bay than when the winds were from the city of Green Bay (SW) and off Lake Michigan (SE). Sweet et al. (29) reported a positive correlation between northwest winds and ∑PCB concentrations. Since this correlation was not significant in winter when ice closed the bay, they concluded that the waters of Green Bay were an important source of PCBs to the local atmosphere.

Back-trajectories of the sampled air mass 5 days before sampling were provided for every sampling day (R. M. Hoff, Atmospheric Environment Service, Egbert, ON, Canada). Although long-range transport of PCBs is considered an important mechanism of regional and global dispersion of the chemicals, the travel path of the air mass prior to the Green Bay region did not affect the concentrations measured in this study. The 10-m wind direction measured during the sampling period and the proximity to the water of southern Green Bay are more important factors affecting atmospheric PCB levels.

Evidence for Flux of Chemicals from the Water. Achman et al. (8) calculated potential net flux of PCBs out
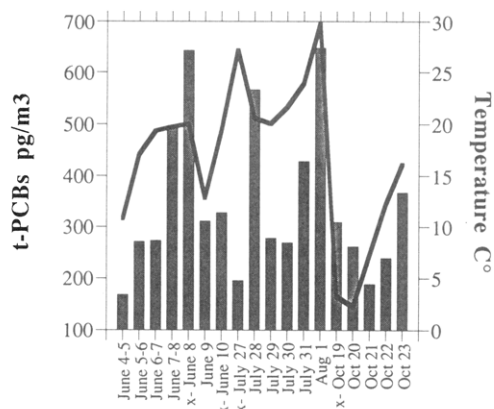
Figure 7. Total PCBs measured at UWGB site (bars) and average air temperature during sampling (line). Samples collected on PUF unless noted with an x, then sample collected on XAD-2 resin. Approximate water temperature at site 4 in June was 12 °C, in July, 15 °C, and in October, 7 °C.

the bay (10–1300 ng/m²·day) using paired air and water samples collected in Green Bay. The calculated flux of PCBs out of water surfaces increases directly with temperature, wind speed, and dissolved-phase PCB concentration and inversely with gas-phase PCB concentration.

Temperature may affect the atmospheric PCB concentration by changing the Henry's law constants and therefore volatilization from natural waters and terrestrial surfaces. Manchester-Neesvig and Andren (10) and Hoff et al. (33, 34) reported significant increases in atmospheric PCB concentrations in the summer. It is not clear whether the summertime increase is due to southerly winds or warmer temperatures. Our study found no relationship between atmospheric PCBs over the water and the temperature of the air or water. In this study, only the samples collected on the shoreline show a relationship between PCB concentration and temperature (Figure 7). This relationship is most evident for those samples collected in October. However, the fall and rise of atmospheric PCB may be more a response to an October 19–21 sleet and snow storm than simply lower air temperature. Snow is an efficient scavenger of PCBs (35). The relationship between air temperature and atmospheric sources of PCBs deserves more study.

Wind speed is expected to increase volatilization by increasing mass transfer across the air/water interface. However, high wind speeds also increase turbulence and dispersion of volatilized chemical so that the effect of wind speed on measured PCB concentrations over Green Bay was not evident.
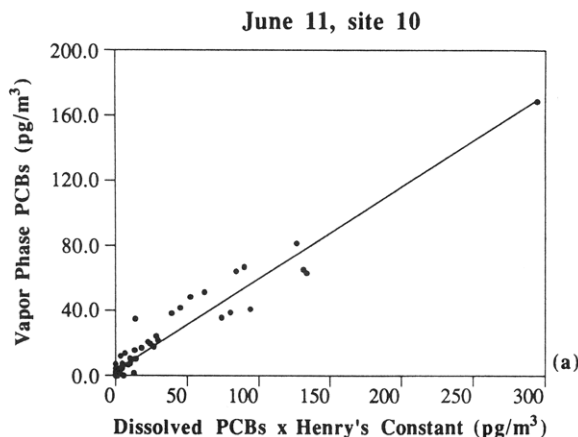
Table VI. Regression Parameters for Vapor PCBs vs Dissolved PCBs times Henry's Law Constant: $C_a = a(c_w H) + b$

date	R^2	a	SD a	b	SD b
		Site 21			
7/29	0.18	0.05	0.013	2.17	0.43
		Site 18			
6/4	0.47	0.30	0.037	0.58	0.69
6/5	0.40	0.25	0.034	0.96	0.64
7/28	0.53	0.06	0.006	1.81	0.73
		Site 14			
7/30	0.74	0.004	0.004	1.69	0.86
10/21	0.93	0.21	0.006	0.15	0.97
		Site 10			
6/6	0.79	0.22	0.013	3.48	0.89
6/7	0.96	0.57	0.014	−0.45	0.98
6/11	0.94	0.57	0.016	−0.87	0.97
7/31	0.86	0.03	0.001	2.82	0.94
10/22	0.96	0.13	0.003	−0.37	0.98
		Site 4			
6/10	0.90	0.05	0.002	0.79	0.95
8/1	0.86	0.08	0.004	6.44	0.94
10/23	0.91	0.34	0.013	−0.62	0.95

While the volatilization hypothesis is supported by the over-land/over-water PCB measurements, direct comparison of air and water confirm the importance of air/water exchange. The aqueous dissolved-phase PCB, C_w, is the most important factor affecting measured atmospheric PCBs over Green Bay. Air and water comparisons by site make this clear. For each air/water sample pair, C_a, is regressed against the water concentrations, C_w, multiplied by the Henry's constant, H, from Brunner et al. (36), for each congener and water temperature:

$$C_a = a(C_w H) + b$$

where a is the slope and b is the intercept of the regression line. At chemical equilibrium, $a = 1$ and $b = 0$. Fourteen air/water pairs were plotted in this manner. The resulting correlation coefficients, slopes, and intercepts in Table VI may help us better understand how volatilization affects the local air PCB concentration.

The correlation coefficients, R^2, are less than 0.60 for air/water pairs collected at sites 18 and 21, in northern Green Bay. Figure 8b is a plot of the congener concentrations measured at our most northerly site. The R^2 for the pairs collected at sites 14, 10, and 4 are much higher; correlation coefficients range from 0.73 to 0.96. While this trend is striking, a note of caution must be added. Several
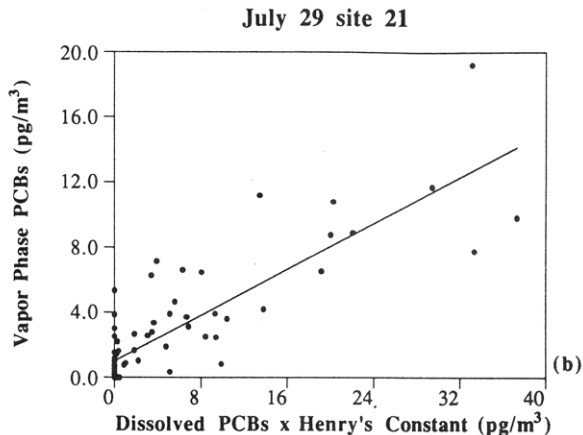
Figure 8. PCB congener concentration measured in gas phase vs PCB congener concentration in dissolved water phase. Slope and intercept for regression lines listed in Table VI.

of the regression lines are highly influenced by the high concentration of congeners no. 28 and no. 31 (Figure 8a is an example of this).

The slopes of the regression lines are always less than 1, suggesting that the atmosphere is undersaturated with respect to the water. Analysis of fugacity gradients (37) is essentially the same as the treatment described here.

The correlation coefficient, R^2, and the slope of the regression line, a, are measures of different phenomena. R^2 is a measure of the similarity between the air and water PCBs, while a is a measure of closeness to equilibrium. For example, the two phases may be very similar yet not close to equilibrium because the water concentration is very high but not volatilizing into the air at a fast enough rate relative to turbulent dispersion.

Conclusions and Implications

This work confirms the hypothesis that volatilization from natural waters is an important source of PCBs to the atmosphere. We found that (1) atmospheric PCB concentrations are higher over contaminated water than over nearby land, (2) atmospheric PCBs over water tend to increase with increasing dissolved PCB concentrations, and (3) the congener distribution of PCBs in the atmosphere correlates linearly with the congener distribution in the adjacent water.

Many organic chemical exchange models assume well-mixed air and water phases (4, 7, 8, 38). This is supported by PCB samples collected by plane at altitudes higher than 300 ft (39). Our work, however, describes a dependence of atmospheric PCB on the adjacent water surface and therefore a poorly mixed local atmosphere. This dependence on surface concentrations suggests a concentration gradient over PCB-contaminated water. This vertical gradient has never been reported for PCBs, although flux models have been proposed for this scenario (40). Without chemical data to verify a measurable vertical gradient, the two-film model remains the best estimate of regional and local flux of PCBs from natural waters.

This study has important implications for mass balance modeling efforts, airborne pollution modeling, and future siting of atmospheric deposition sites. Use of shoreline measurements is not appropriate when air/water exchange is modeled in contaminated systems. Wet and dry deposition to the water body may be underestimated, and the direction and magnitude of flux may be calculated incorrectly. Shoreline measurements may also underestimate contaminated water as a source of chemicals and the water's impact on the local atmosphere. This may provide an inaccurate picture of the water's impact and therefore reduce impetus for cleanup. The linear correlation between air and water also suggest that pairs of air and water measurements separated in time and space may be poor comparisons for exchange modeling. Accurate air/water exchange modeling must use sample pairs proximate in space and time. Shoreline sampling, however, is appropriate for air/water exchange modeling of less contaminated systems and systems that are near equilibrium with bulk air and water. Additionally, results of this study should not affect siting designed for regional estimates of atmospheric concentrations, deposition, and air/water exchange. Samples collected away from direct sources represent the average regional conditions.

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Atmospheric Chemistry of Automotive Fuel Additives: Diisopropyl Ether

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■ To quantify the atmospheric reactivity of diisopropyl ether (DIPE), we have conducted a study of the kinetics and mechanism of reaction 1: OH + DIPE → products. Kinetic measurements of reaction 1 were made using both relative (at 295 K) and absolute techniques (over the temperature range 240–440 K). Rate data from both techniques can be represented by the following: $k_1 = (2.2^{+1.4}_{-0.8}) \times 10^{-12} \exp[(445 \pm 145)/T]$ cm^3 molecule^{-1} s^{-1}. At 298 K, $k_1 = 9.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The products of the simulated atmospheric oxidation of DIPE were identified using FT-IR spectroscopy; isopropyl acetate and HCHO were the main products. The atmospheric oxidation of DIPE can be represented by i-C$_3$H$_7$O-i-C$_3$H$_7$ + OH + 2NO → HCHO + i-C$_3$H$_7$OC(O)CH$_3$ + HO$_2$ + 2NO$_2$. Our kinetic and mechanistic data were incorporated into a 1-day simulation of atmospheric chemistry to quantify the relative incremental reactivity of DIPE. Results are compared with other oxygenated fuel additives.

Introduction

Currently there is a large research effort within the automotive and petroleum industries to develop new, oxygenated, low atmospheric reactivity, liquid fuel formulations for automobiles and light-duty trucks (*1, 2*). Highly branched ethers such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) are components of many of the new formulations. These ethers improve the octane rating of the formulation and, by virtue of their oxygenated nature, have the added advantage of reducing CO emissions (*3*). In addition to MTBE and ETBE, diisopropyl ether (DIPE) has been and is being explored as a possible fuel additive (*4–6*). The potential use of substantial quantities of DIPE in gasoline renders its emission to the atmosphere an important consideration. By analogy to other ethers, the main atmospheric fate of DIPE will be reaction with OH radicals, since photolysis (*7*), reaction with O$_3$ (*8*), and reaction with NO$_3$ radicals (*9*) are expected to be negligibly slow. To assess the atmospheric impact of release of DIPE, accurate kinetic and mechanistic data concerning its reactivity toward OH radicals are needed.

As part of an ongoing program in our laboratories to elucidate the atmospheric chemistry of new fuels and fuel additives (*10–16*) we have studied the kinetics and mechanism of the reaction of OH radicals with DIPE (reaction 1) and report herein those results.

$$\text{OH} + \text{DIPE} \rightarrow \text{products} \qquad (1)$$

While the oxidation of oxygenated hydrocarbons in the atmosphere is initiated by the OH radical, in the mechanistic studies we make considerable use of Cl atom initiated oxidation. Our reasons for employing Cl atoms as surrogates for OH radical attack are as follows: (i) Cl atoms are more easily generated in our reactor than OH radicals; (ii) product analysis is simpler in Cl-initiated systems since there are no complications due to organic reactants and products associated with the usual modes of OH radical formation (e.g., methyl nitrite or ethyl nitrite photolysis); (iii) Cl atoms are, in general, less selective in their attack of organics, hence reducing problems frequently encountered with OH radicals, which preferentially attack the products leading to their consumption rather than the reactants; (iv) the modes of attack by Cl and OH are expected to be the same for saturated organics.

Experimental Section

Three distinct experimental systems were utilized in the present work. Kinetic measurements were made by both absolute rate (flash photolysis resonance fluorescence) and relative rate (Teflon bag + GC-FID) techniques. Products of the simulated atmospheric oxidation of DIPE were identified using FT-IR spectroscopy coupled to a smog chamber facility.

Absolute Rate. Hydroxyl radicals were produced by the vacuum ultraviolet ($\lambda > 165$ nm) flash photolysis of H$_2$O ($\approx$0.1 Torr) and monitored as a function of time by their fluorescence at $\approx$308 nm (A$^2\Sigma^+ \rightarrow$ X$^2\Pi$, O–O band) excited by a microwave discharge resonance lamp. Fluorescence signals from 15 to 100 flash photolytic experiments were averaged to generate a kinetic decay curve suitable for least-squares analysis.

Reaction mixtures consisting of water vapor, reactant, and Ar diluent were prepared manometrically in 5-L pyrex bulbs. To avoid the accumulation of photolysis or reaction products, experiments were conducted by flowing the gas mixtures through the reaction cell at a flow rate of 0.36 cm^3 s^{-1} and operating the flash lamp at a discharge energy of 100 J per flash and at a repetition rate of 0.25 Hz. The total pressure in the reaction cell was 35 Torr [1 Torr = 133.33 Pa = 9.66 $\times$ 10^{18}/T (K) molecule cm^{-3}]. Temperature regulation of the mixtures was achieved by the passage of cooled methanol or heated oil between the outer