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# Volatile Loss of PCB Aroclors from Subaqueous Sand

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A series of experiments were conducted to measure the rate of volatile loss of PCBs from subaqueous quartz sand spiked with Aroclors 1242, 1248, 1254, and 1260 under laboratory conditions (20 °C, 25% relative humidity). Volatilized PCBs were trapped on Florisil columns attached to a 1.5-L evaporation chamber through which 1.2 L/min of filtered air was drawn for a 24-h period. PCB losses ranged from 20 to 65% and were inversely correlated with the chlorine percentage of the aroclors ($R^2 = 0.97$). Congeners with the fewest number of chlorines in each aroclor were preferentially lost. In comparison, sediment from a Federal Superfund site along the St. Lawrence River, originally contaminated with Aroclor 1248, lost 19% of its PCB total during a similar experiment. Several orthochlorinated congeners, produced by anaerobic biodegradation, were preferentially lost, and four of these (2/2; 2/6; 2; 26/2) accounted for >55% of the total loss. This work suggests that under certain conditions the volatile loss of PCBs and other hydrophobic compounds from wet soils and sediments may be rapid and substantial. Further work is needed to elucidate the implications for analytical procedures, remedial actions, and the global mass balance of PCBs.

## Introduction

Numerous studies have documented the occurrence of PCBs and other organochlorine compounds in various media, including moss and lichen (*1−6*), higher plants (*5*), snow and rain (*7, 8*), lake sediments (*9, 10*), and biota (*11, 12*), in locations considerably removed from their use and manufacture. Transfer by atmospheric processes is inferred, and PCBs have been identified in air samples from many locations (*13−15*). Atmospheric deposition and loss through volatilization from water (*13, 16−18*) have been noted as primary factors in the mass balance and transfer of PCBs in the Great Lakes and other water bodies, including the oceans (*19*).

Conflicting information on the rate of volatile loss of PCBs from solid media exists. Larsson (*20*) found only 0.5−0.7% of the PCBs originally spiked into lake sediments in artificial ponds were lost after 15 months, presumably by volatilization, and half-lives of ~10−20 years have been estimated for PCBs in soils (*21*). In contrast, PCB Aroclor (1254 and 1260) half-lives as brief as 1.1 years have been measured from experimental plots in the Canadian Arctic (*22*) despite low temperatures, and Haque et al. (*23*) measured significant volatile losses of Aroclor 1254 (~30% tetrachlorinated congeners; ~20% pentachlorinated congeners) from dry sand after 1 week. Even more rapid rates of loss (half-lives of a few days) have been measured during the drying of small samples (0.25−

1.0 g) of PCB contaminated, anaerobically biodegraded, river sediment under ambient laboratory conditions (*24*). These studies suggest that rapid PCB volatile losses can take place from soil and sediment under some conditions.

Numerous studies have confirmed that PCB concentrations in air and water bodies have declined (*25, 26*) since efforts to reduce their escape into the environment were enacted in the 1970s. With falling PCB fugacities in the air (*21*), soils and sediments may release previously deposited PCBs to water bodies and the atmosphere (*27*). In an effort to learn which PCB congeners are likely to be released from submerged sediment and the potential differences between a range of Aroclors, we have conducted a series of experiments in which the PCBs released from spiked, subaqueous sand were captured and quantitated. Because the results cannot be directly extrapolated to 'real world' scenarios, a comparison is made with the PCB volatile loss from contaminated river sediment.

## Analytical Methods

**Reagents.** All reagents utilized including hexane, sodium sulfate, sulfuric acid (Fisher Scientific), Florisil, and tetrabutylammonium sulfate (Sigma Chemical Company) were reagent grade and checked for contamination before use. Double-deionized water (DDI) was used throughout. Concentrated Aroclor 1248 in hexane was purchased from ChemService. Aroclors 1242, 1254, and 1260 in methanol were purchased from Supelco, Inc. Sediment consisting of ~70% fine-grained sand and containing ~63 ppm PCBs was obtained from the St. Lawrence River adjacent to a Federal Superfund site located near Massena, NY (*24*).

**Experimental Procedures.** A series of four experiments were conducted with Aroclors 1242, 1248, 1254, and 1260. For comparative purposes, a fifth experiment utilized contaminated St. Lawrence River sediment. A 1.5-L jacketed, glass evaporation chamber with two sample ports was utilized for all experiments. A flat glass lid was held securely to the upper flange of the chamber using a Teflon gasket and spring-loaded horseshoe clamp, which allowed rapid opening and air-tight sealing of the chamber. Prior to each experiment, the chamber was cleaned, and a blank consisting of a hexane rinse of all interior surfaces, including the lid, was analyzed. Approximately 0.25 g of dry, precleaned, medium-grained, quartz sand was weighed and placed in a shallow, preweighed, precleaned, glass beaker. A milliliter of aroclor spike with a known PCB concentration in methanol (~20 μg of Aroclors 1242, 1254, and 1260) or hexane (~25 μg of Aroclor 1248) was added to the sand. The solvent was allowed to evaporate to dryness (1−2 h) within the sealed chamber under experimental conditions. After solvent drying, the outlet Florisil column ($t = 0$ h column) was removed and eluted with hexane to monitor the loss of PCBs during spike evaporation. For Aroclors 1242 and 1248, the interior of the chamber was also rinsed with hexane and analyzed. Once the solvent evaporated, 25 mL of double deionized water (DDI) was added to the beaker and allowed to evaporate, under laboratory conditions (25% relative humidity and 20 °C), for a period of 24 h. For the experiment utilizing St. Lawrence River sediment, ~0.25 g of sediment (dry weight) was added to the glass beaker and submersed in 25 mL of DDI water.

Inlet and outlet columns were fitted to ports on the evaporation chamber and filled with sodium sulfate (for water absorption) and 100% activated Florisil (10 g). Air was withdrawn through the outlet column with a vacuum pump at a rate of 1.2 L/min. Outlet Florisil columns were changed after solvent evaporation ($t = 0$) and $t = 1, 2, 4, 8,$ and/or 24

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**TABLE 1. Summary of Aroclor Volatilization Experiments[a]**

| experiment | Aroclor 1242 | Aroclor 1248 | Aroclor 1254 | Aroclor 1260 | St. L. River sediment |
|---|---|---|---|---|---|
| initial loss during spiking (ng) | | | | | |
|   spike drying column | 1 590 | 732 | 84 | 259 | na |
|   post-spike chamber rinse | 56 | 171 | nd | nd | na |
| recovered on columns (ng) | | | | | |
|   1 h | 2 427 | 1 991 | 432 | 153 | 310 |
|   2 h | 1 305 | 1 435 | 432 | 190 | 241 |
|   4 h | 1 493 | 2 455 | nd | nd | 643 |
|   8 h | 2 241 | 2 138 | nd | nd | nd |
|   24 h | 4 467 | 5 257 | 4 317 | 1 987 | 1 998 |
| chamber rinse (ng) | 57 | 106 | 1 545 | 1 368 | 130 |
| remained on sand or sediment (ng) | 3 754 | 9 388 | 9 569 | 13 802 | 12 320 |
| total recovered (ng) | 17 390 | 23 673 | 16 379 | 17 759 | 15 642 |
| amount spiked (ng) | 20 899 | 25 000 | 19 580 | 18 720 | na |
| initial concentration (ppm) | 83.6 | 100.0 | 78.3 | 74.9 | 63.0 |
| mass balance (%) | 83.2 | 94.7 | 83.7 | 94.9 | na |
| PCBs volatilized (%) | 62.3 | 55.5 | 34.5 | 20.0 | 19.2 |

[a] na, not applicable; nd, not determined.

h. During each column change, the beaker containing the sand− or sediment−water mixture was removed and weighed to monitor water loss.

**Data Analysis.** At the end of each experiment, the outlet Florisil columns were eluted with 100 mL of hexane, the entire interior of the chamber was rinsed with hexane, and the sediment or quartz sand and remaining water was extracted. The inlet column was also eluted and analyzed. Initial PCB concentrations spiked onto the sand were determined by GC analysis of Aroclor standards. The total recovered (Table 1) was calculated by adding the amount of PCBs volatilized during spike drying, the amount captured on columns during the experiment, the post-experiment chamber rinse, and the amount recovered from the sediment. The mass balance (Table 1) was determined by dividing the total recovered by the amount spiked. The amount of PCBs volatilized (Table 1) was calculated by summing the amount recovered from the columns and the post-experimental chamber rinse and dividing by the amount spiked minus the amount released during spike drying. For the St. Lawrence River sediment experiment, the amount of PCBs volatilized was calculated by dividing the amount recovered on the columns and in the post-experimental rinse by the total recovered as above; however, no PCBs were added.

**PCB Extraction and Gas Chromatography.** Water was separated from subaqueous sand and sediment by pipetting and was extracted by three sequential liquid/liquid separations with acetone, acetone/hexane (1:1), and hexane. The remaining wet sand and sediment were extracted by three sequential sonications with acetone, acetone/hexane (1:1), and hexane and recombined with the hexane extracts of their respective liquid fractions. Decachlorobiphenyl was added to the sand and sediment samples before extraction as a surrogate standard. The extracts were combined and dried using sodium sulfate, and sediment samples were oxidized with sulfuric acid and cleaned using tetrabutylammonium sulfate and 4% activated Florisil columns. Extracts from precleaned spiked sand samples were analyzed without cleanup. Aroclor standards in methanol were solvent switched to hexane and diluted before GC analysis. The hexane extract was condensed and stored at 4 °C until analyzed. Congener-specific PCB analysis was performed on an HP5890 gas chromatograph using an electron capture detector and an Ultra DB-5 column. The gas chromatograph was calibrated every six samples using a mixed Aroclor standard prepared by the New York State Department of Health Wadsworth Laboratory enabling accurate quantitation of 69 congeners (Table 2). Volatilized PCBs were removed from Florisil columns by elution with hexane. The hexane was concentrated for GC analysis without further treatment. The interior of the glass drying chamber was also rinsed with hexane, condensed, and analyzed.

**Quality Assurance/Quality Control.** Inlet columns and chamber blanks were used to monitor possible contamination by laboratory air or reagents or other organic compounds. PCB accumulation rates on inlet columns ranged from 0.7 to 2.3 ng/h and averaged 1.6 ng/h ($n = 4$), which provided an estimate of laboratory air PCB concentrations during the period that this work was conducted. All possible sources of contamination were found to be insignificant in comparison to the amount of PCBs volatilized during the aroclor experiments ($>2 \mu$g). The initial level of PCB contamination in the drying chamber was estimated by rinsing the interior of the chamber thoroughly with hexane before use. The total recovered before each experiment ranged from 1 to 4 ng of PCBs. The average concentration of the chamber blank was 2.5 ng of PCBs ($n = 5$). A blank experiment utilizing 'uncontaminated' (measured PCB concentration 76 ppb) archived soil obtained from the Geneva Agricultural Experimental Station of Cornell University yielded 6.5 ng of PCBs during a 24-h period. Decachlorobiphenyl (DCB) recovery from sediment and sand ranged from 95% (St. Lawrence River sediment) to 120% (sand spiked with Aroclor 1260) and averaged 108%. The recovery for Aroclor 1260 is elevated because of the presence of DCB in the original aroclor mixture.

## Results

Table 1 summarizes the key parameters of the five experiments conducted with subaqueous sand and St. Lawrence River sediment. The loss of PCBs during each 24-h experiment ranged from 19% (sediment) to 62% (sand spiked with Aroclor 1242). Mass balances for the four Aroclor experiments ranged from 83 to 95%. A table summarizing congener-specific recovery, volatile loss percentage, and normalized volatile loss percentage for each aroclor experiment is available in the microfilm edition of the journal (see paragraph at end of paper on Supporting Information). In general, lower chlorinated congeners show lower recoveries than more highly chlorinated congeners. The loss of PCBs during evaporation of the spike solution (methanol or hexane) ranged from 12% (Aroclor 1242) to 1% (Aroclor 1254) of the total volatilization loss during the experiment. Significantly more PCBs ($>10$ times) were recovered from the final chamber rinse of experiments with Aroclors 1254 and 1260 than from Aroclors 1242 and 1248, suggesting that volatilized higher chlorinated congeners are transported shorter distances than lower chlorinated congeners before redeposition.

TABLE 2. PCB Congener Identification, IUPAC Numbers, and Assigned Peak Numbers for Figures 2 and 3

| congener | IUPAC No. | assigned no. | congener | IUPAC No. | assigned no. |
|---|---|---|---|---|---|
| 2 | 1 | 1 | 34/34+236/34 | 77+110 | 37 |
| 4 | 3 | 2 | 2356/25+34/23 | 151+82 | 38 |
| 2/2+2/6 | 4+10 | 3 | 235/236 | 135 | 39 |
| 24+25 | 7+9 | 4 | 2356/24 | 147 | 40 |
| 2/3 | 6 | 5 | 236/245 | 149 | 41 |
| 2/4+23 | 8+5 | 6 | 245/34 | 118 | 42 |
| HCB | | 7 | 2356/23 | 134 | 43 |
| 26/2 | 19 | 8 | 235/245 | 146 | 44 |
| 25/2 | 18 | 9 | 245/245+234/236 | 153+132 | 45 |
| 4/4+24/2 | 15+17 | 10 | 234/34 | 105 | 46 |
| 236+26/3 | 24+27 | 11 | 2345/25 | 141 | 47 |
| 23/2+26/4 | 16+32 | 12 | 2356/236 | 179 | 48 |
| 25/3 | 26 | 13 | 234/235 | 130 | 49 |
| 24/3 | 25 | 14 | 2346/236+2356/34 | 176+163 | 50 |
| 25/4 | 31 | 15 | 234/245 | 138 | 51 |
| 24/4 | 28 | 16 | 2346/34 | 158 | 52 |
| 34/2 | 33 | 17 | 2345/23 | 129 | 53 |
| 23/4 | 22 | 18 | 2356/245+2345/246 | 187+181 | 54 |
| 236/2 | 45 | 19 | 2346/245 | 183 | 55 |
| 25/25 | 52 | 20 | 234/234+245/345 | 128+167 | 56 |
| 24/25 | 49 | 21 | 23456/25 | 185 | 57 |
| 24/24+245/2 | 47+48 | 22 | 2345/236 | 174 | 58 |
| 23/25 | 44 | 23 | 2356/234 | 177 | 59 |
| 236/2+23/24+34/4 | 59+42+37 | 24 | 2346/234+2345/34 | 171+156 | 60 |
| 236/4 | 64 | 25 | 2346/2356 | 201 | 61 |
| 23/23 | 40 | 26 | 2345/235 | 172 | 62 |
| 235/26+245/4 | 94+74 | 27 | 2345/245 | 180 | 63 |
| 25/34 | 70 | 28 | 23456/236 | 200 | 64 |
| 24/34 | 66 | 29 | MIREX | | 65 |
| 234/4+34/23 | 60+55 | 30 | 2345/234+23456/34 | 170+190 | 66 |
| 245/25 | 101 | 31 | 2345/2356 | 199 | 67 |
| 245/24 | 99 | 32 | 23456/245+2345/2346 | 203+196 | 68 |
| 245/23 | 97 | 33 | 23456/234 | 208 | 69 |
| 234/25 | 87 | 34 | 2345/2345 | 194 | 70 |
| DDE | | 35 | 23456/2345 | 206 | 71 |
| 236/236 | 136 | 36 | decachlorobiphenyl | 209 | 72 |



% PCBs Volatilized

$R^2 = .97$

St. Lawrence River sediment
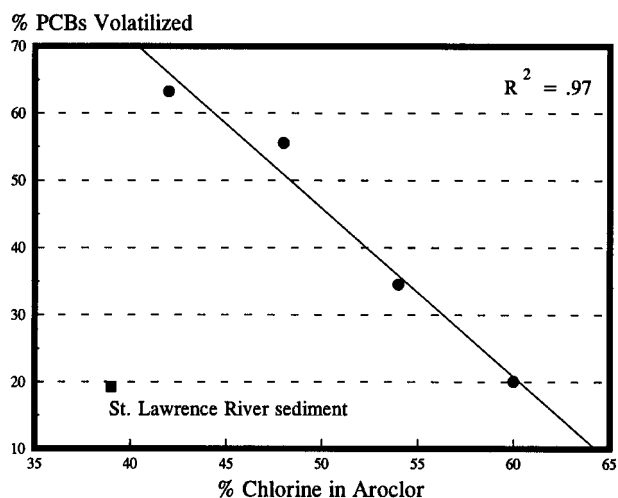
% Chlorine in Aroclor

FIGURE 1. Plot of PCBs lost via volatilization from subaqueous sand versus the chlorine percentage of each Aroclor (1242, 1248, 1254, 1260) during evaporation experiments. Loss from St. Lawrence River sediment shown for comparative purposes. All experiments conducted at 20 °C and 25% relative humidity for a period of 24 h.

## Discussion

**Correlation of PCB Loss with Aroclor Chlorine Content.** Figure 1 shows that the percentage of PCBs lost during each experiment is negatively correlated with the weight percent of chlorine in the spiked aroclor. Note that the St. Lawrence River sediment sample, despite having undergone substantial anaerobic biodegradation as evidenced by its large percentage of lower orthochlorinated congeners (28) and its lower chlorine percentage (~40%), lost the least amount of PCBs

during the experimental period. The retarded PCB loss from river sediment is believed to be related to its age (29), composition (organic rich), and/or grain-size distribution (30% clay and silt); all of which differ significantly from the uniform quartz sand used in the Aroclor experiments. The magnitude of PCB loss from the sediment is analytically indistinguishable from Aroclor 1260, which has 20% more chlorine and more highly chlorinated congeners; however, different congeners were volatilized in each experiment (Table 3).

**Which Congeners Are Volatilized?** Table 3 lists the 10 most abundant PCB peaks collected on the outlet column in each of the experiments by percentage of the normalized volatile loss. Note that many of the peaks are actually composed of two co-eluting congeners that cannot be resolved on the capillary column used for this study (Ultra DB-5). The 10 largest peaks account for 62.0−69.1% of the total volatile loss in each Aroclor experiment. The experiments conducted with Aroclors 1242 and 1248 are dominated by congeners containing only two or three chlorines, whereas the majority of those volatilized from Aroclors 1254 and 1260 have four to seven chlorines. Note that with the exception of congener 24/34, lower chlorinated congeners are either absent or not abundant enough to significantly influence the total volatile loss shown in Table 3 for Aroclor 1260. This progressive shift toward a pattern dominated by higher chlorinated congeners with increasing chlorine percentage is shown schematically in Figure 2 and is thought to be a function of the reduced abundance of lower chlorinated congeners, which would dominate the volatilized fraction if present.

Supporting Information (Tables 1a−1d and Figure 1) indicate that all four Aroclors display a progressive decrease in volatilization of individual congeners with increasing
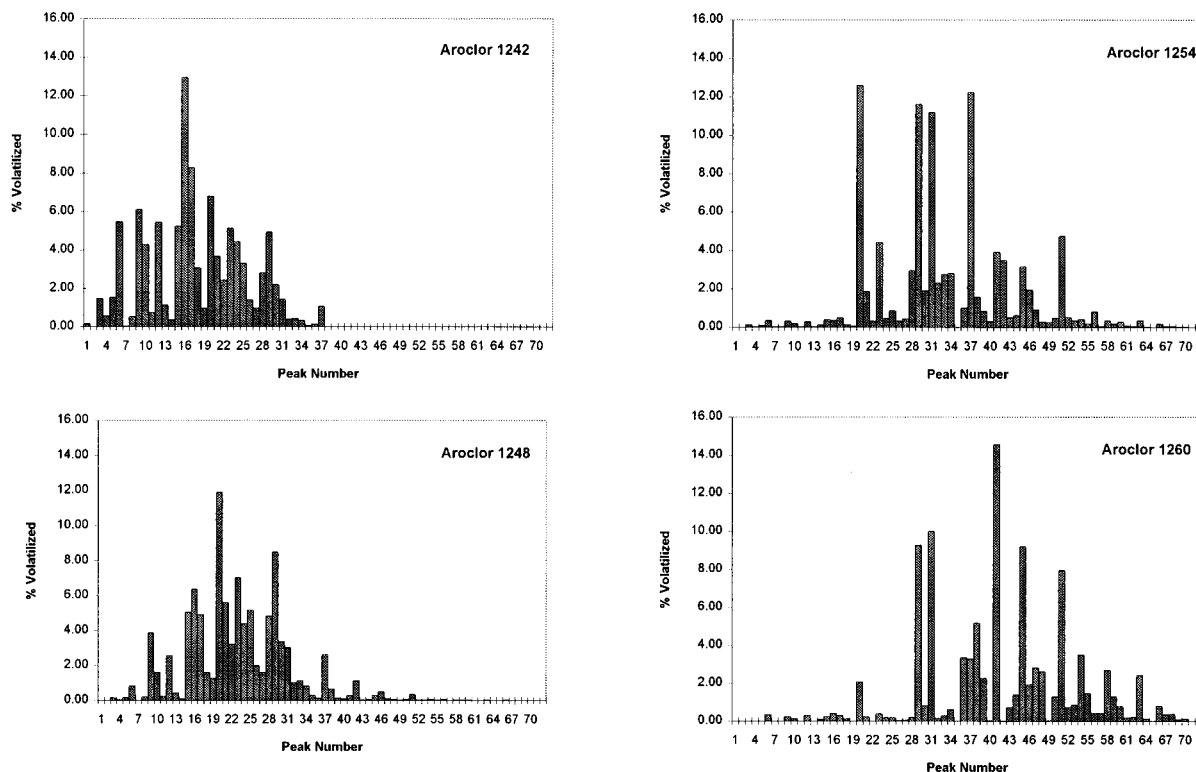
**FIGURE 2.** Percentage of total volatile loss by PCB congener for each aroclor experiment. Note the progressive shift to the right (more highly chlorinated congeners) with increasing levels of Aroclor chlorination and the range of congeners lost in each experiment. See Table 2 for peak identification.

**TABLE 3. 10 Most Abundant (% of Normalized Volatile Loss) Congeners Volatilized in Each Experiment**

| Aroclor 1242 | | Aroclor 1248 | | Aroclor 1254 | | Aroclor 1260 | | St. L. River sediment | |
|---|---|---|---|---|---|---|---|---|---|
| congener | % | congener | % | congener | % | congener | % | congener | % |
| 24/4 | 12.57 | 25/25 | 11.89 | 25/25 | 12.58 | 236/245 | 14.56 | 2/2+2/6 | 35.72 |
| 34/2 | 8.03 | 24/34 | 8.48 | 236/34+34/34 | 12.23 | 245/25 | 10.01 | 2 | 13.07 |
| 25/25 | 6.59 | 23/25 | 7.02 | 24/34 | 11.61 | 24/34 | 9.28 | 26/2 | 7.74 |
| 25/2 | 5.92 | 24/4 | 6.37 | 234/235 | 4.74 | 245/245+234/236 | 9.19 | 236+26/3 | 7.10 |
| 2/4+23 | 5.30 | 236/4 | 5.16 | 23/25 | 4.43 | 234/245 | 7.95 | 4/4+24/2 | 5.50 |
| 26/4+23/2 | 5.29 | 25/4 | 5.03 | 236/245 | 3.92 | 2356/25+2345/23 | 5.16 | 2/4+23 | 4.18 |
| 25/4 | 5.06 | 34/2 | 4.91 | 245/34 | 3.49 | 2356/245+2345/246 | 3.50 | 24/4 | 3.83 |
| 23/25 | 4.98 | 25/34 | 4.82 | 245/245+234/236 | 3.17 | 236/236 | 3.35 | 23/2+26/4 | 3.64 |
| 24/34 | 4.79 | 236/3 | 4.40 | 25/34 | 2.96 | 236/34+34/34 | 3.30 | 4 | 2.18 |
| 236/3 | 4.30 | 25/2 | 3.87 | 234/25 | 2.81 | 2345/25 | 2.83 | 25/25 | 1.90 |
| total | 62.83 | | 61.95 | | 61.94 | | 69.13 | | 84.86 |

retention time (chlorine content). In addition, a progressive steepening of the relative difference in the amount of volatile loss between lower and higher chlorinated congeners is noted as chlorine percentage increases. Aroclor 1260 lost >90% of its lower chlorinated congeners and almost none of the more highly chlorinated congeners, whereas Aroclor 1242 lost between ~60 and 70% of all congeners measured. Shifts in homologue distribution are apparent between the original Aroclor and the volatilized PCBs trapped on the Florisil columns (Table 4). The volatilized PCBs have a progressive increase in chlorine/biphenyl ratio from 3.41 (Aroclor 1242) to 5.65 (Aroclor 1260); however, for Aroclors 1248, 1254, and 1260, the volatilized PCBs are less chlorinated than the original Aroclor, while the converse is true for Aroclor 1242.

**PCB Loss versus Time.** The lower the chlorination of an Aroclor, the faster it lost PCBs via volatilization (Figure 3). Further, as illustrated by Figure 3, the initial rapid PCB loss in experiments with lighter Aroclors (1242 and 1248) begins to slow after several hours. Aroclor 1260, however, had a near linear loss throughout the duration of the experiment (24 h). These data suggest that when the most soluble and volatile PCBs are depleted, other less soluble and less volatile

PCBs begin to dominate the volatilized fraction and the rate of loss via volatilization slows considerably. Further evidence of the influence of PCB aqueous solubility on volatile loss is evident in comparison of the ratio of PCBs (~2−13 $\mu$g) vs water (~7 g) lost in these experiments (equivalent to 0.3−1.9 ppm of PCBs), which varies within the reported range of PCB aqueous solubilities (24). Figure 3 implies that the greatest rate of PCB loss will occur during the first few hours of drying of contaminated media.

**Comparison with PCB Loss from St. Lawrence River Sediment.** As previously mentioned, St. Lawrence River sediment lost considerably less PCBs than would have been predicted based on its PCB chlorine percentage alone. Table 3 shows orthochlorinated congeners with one to three chlorines were lost primarily, and two co-eluting congeners 2/2 and 2/6 account for over 35% of the total loss measured. These orthochlorinated congeners are not found in great abundance in any of the Aroclors and are believed to be produced by anaerobic microbial degradation (28) of the original PCB mixture (Aroclor 1248). The 10 peaks reported in Table 3 account for approximately 85% of the PCB volatile loss from the sediment in this experiment. In Table 4, the

**TABLE 4. Comparison of Homologue, Mole Percentage, and Cl/biphenyl Calculations for Aroclors and Volatilized Congeners in Evaporation Experiments**

| no. of chlorine | Aroclor 1242 | Aroclor 1248 | Aroclor 1254 | Aroclor 1260 | columns 1242 | columns 1248 | columns 1254 | columns 1260 | columns St. L. River |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.73 | 0.00 | 0.00 | 0.00 | 0.15 | 0.00 | 0.00 | 0.00 | 18.32 |
| 2 | 15.15 | 2.16 | 0.26 | 0.12 | 10.84 | 1.99 | 0.67 | 0.40 | 48.08 |
| 3 | 44.58 | 25.12 | 1.21 | 0.56 | 46.06 | 27.59 | 2.48 | 1.82 | 26.82 |
| 4 | 34.63 | 58.65 | 31.91 | 5.52 | 34.47 | 58.02 | 43.57 | 14.98 | 5.63 |
| 5 | 4.34 | 11.79 | 34.43 | 8.25 | 4.23 | 10.09 | 31.66 | 17.23 | 0.51 |
| 6 | 0.50 | 2.10 | 26.34 | 35.42 | 1.81 | 1.98 | 19.11 | 47.88 | 0.54 |
| 7 | 0.06 | 0.19 | 4.98 | 33.63 | 0.43 | 0.32 | 2.33 | 16.46 | 0.10 |
| 8 | 0.00 | 0.00 | 0.84 | 16.16 | 0.01 | 0.01 | 0.19 | 1.22 | 0.00 |
| 9 | 0.00 | 0.00 | 0.03 | 0.35 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |
| Cl per biphenyl | 3.28 | 3.87 | 5.04 | 6.46 | 3.41 | 3.83 | 4.74 | 5.65 | 2.24 |
| ortho | 45.47 | 41.22 | 35.34 | 38.19 | 43.96 | 41.49 | 36.89 | 40.29 | 80.50 |
| meta | 27.56 | 33.58 | 38.87 | 39.42 | 33.58 | 33.18 | 38.81 | 37.22 | 9.26 |
| para | 26.96 | 25.20 | 25.79 | 22.39 | 25.33 | 25.33 | 24.30 | 22.49 | 10.24 |
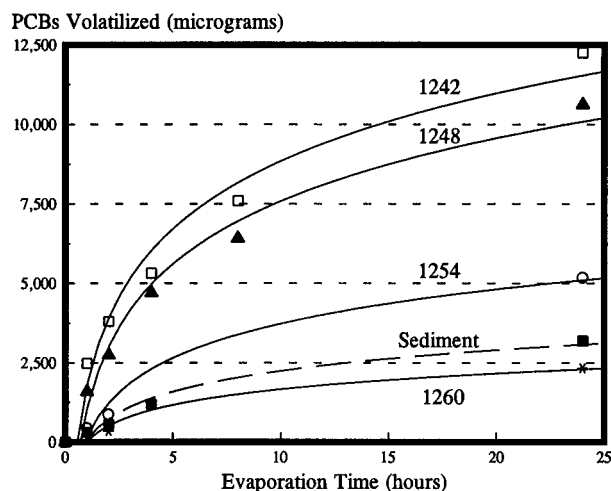


FIGURE 3. Temporal trends of PCB volatile loss in each Aroclor experiment. All regressions are logarithmic and $R^2$ values range from 0.97 to 0.98. Symbols used: (□) Aroclor 1242 (initial concentration 20.9 $\mu$g); (▲) Aroclor 1248 (25.0 $\mu$g); (○) Aroclor 1254 (19.6 $\mu$g); (*) Aroclor 1260 (18.7 $\mu$g); and (■) St. Lawrence River sediment (15.6 $\mu$g).

predominance of the lower orthochlorinated congeners is readily apparent in the volatilized mixture. Congeners with one (18.3%) and two chlorines (48.1%) are enriched in comparison to the Aroclor volatilization mixtures. In addition, the percentage of orthochlorination (80.5%) is higher than the Aroclor experiments that contained 37−44% o-chlorines.

**Possible Implications.** The rate of loss reported in these experiments (half-lives ranging from ~1 day to 1 week) from subaqueous sand is rapid in comparison with other studies on PCB volatilization (20, 21). Our results are approximately an order of magnitude faster than rates of loss reported by Haque et al. (23), who in a similar study found the volatile loss of Aroclor 1254 from dry sand at ambient laboratory conditions (34.5% of total Aroclor in 1 day vs ~30% of tetrachlorinated congeners in 1 week, respectively). The key difference between the two studies is the presence and evaporation of water. Water facilitates the transfer of PCBs from grain surfaces into the aqueous phase and transports the PCBs to the air−water interface where they can be lost by evaporative processes (24). It is therefore likely that the rate of loss will vary with factors that control evaporation (e.g., temperature, air flow, or surface area). By extension, contaminated shallow lakes, rivers, estuaries, harbors, and marine tidal environments may release significant quantities of PCBs and other hydrophobic organics to the air via volatilization enhanced by evaporative processes (30).

This work also suggests that there is a direct correlation between Aroclor chlorine percentage and the amount of PCBs that will be lost during water evaporation. However, despite extensive biodegradation resulting in the production of soluble and volatile orthochlorinated congeners, St. Lawrence River sediment originally contaminated with Aroclor 1248 lost PCBs at a rate similar to Aroclor 1260. This appears to support the work of Hatzinger and Alexander (29) on the effects of aging on contaminant availability in soils; note, however, that recent work by McGroddy et al. (31) suggests that other factors besides age may influence PCB retention. Temporal trends suggest that PCB volatile loss is initially rapid but slows with depletion of the most volatile and soluble congeners, suggesting that the greatest rates of contaminant loss will be during the first few hours of exposure to evaporative processes. The volatilized fraction from anaerobically biodegraded sediment may be dominated by highly volatile orthochlorinated congeners with one to three chlorines which were not part of the original Aroclor mixture (24).

The results of these experiments are thought to be most applicable to PCB analysis of soil and sediment or other media where relatively small quantities are handled in a laboratory setting. Moist media with moderate or high levels of PCBs may experience significant volatile loss during drying, even for short durations at ambient conditions. However, some recent studies indicate that media with low levels of contamination may uptake PCBs during exposure to contaminated laboratory air with greater PCB levels (3). Remedial technologies that employ dewatering of contaminated sediments prior to additional treatment or containment may contribute significant amounts of PCBs and similar compounds to the local environment (24, 30). Further work is needed to evaluate the applicability of this loss mechanism to natural sediments and soils, to estimate the magnitude of the transfer of PCBs from these reservoirs to the air and water, and to determine the potential role in local and global PCB mass balance calculations.

## Supporting Information Available

One figure and four tables detailing the congener-specific recovery, volatile loss percentage, and normalized volatile loss percentage for each Aroclor experiment (5 pp) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $15.00 for photocopy ($17.00 foreign) or $12.00 for microfiche ($13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is available to subscribers electronically via the Internet at http://pubs.acs.org (WWW) and pubs.acs.org (Gopher).

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