Paper 1F-02, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002.* Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

MEASUREMENT OF PCB VOLATILIZATION FROM LAKE HARTWELL SEDIMENTS

Shuang Qi, Makram T. Suidan (makram.suidan@uc.edu, University of Cincinnati, Cincinnati, OH)
Paul de Percin (U.S. EPA, Cincinnati, U.S. EPA, OH)
Victor Magar, James Abbott, Eric Foote and Carole Peven (Battelle, Columbus, OH)

ABSTRACT: There has recently been increased concern regarding the volatility of polychlorinated biphenyls (PCBs) from contaminated soils and sediments. A simple microcosm of sediment, water and air that allows for (pseudo) one-dimensional transport of PCBs was used for a laboratory experiment to conduct PCB transport studies. This bench-scale work determined the rate of PCB volatilization from fully homogenized, uniformly contaminated, and naturally aged Lake Hartwell sediments. Two kinds of sediments were tested in this study: lightly contaminated top layer sediments and highly contaminated deep layer sediments. Experimental results revealed significant volatilization of PCB from the Lake Hartwell sediments. The overall percentages of volatilization in this 80-day study were 2.52% and 6.54% for top layer sediments and deep layer sediments, respectively. Results also indicated higher chlorinated biphenyls had lower volatilization rates.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are persistent in sediments, water and biota due to their very slow biochemical and chemical transformation rates (Erickson, 1997). Recent concerns have been raised about the volatility of PCB from contaminated soils and sediments. The atmosphere is believed to serve as an important pathway for PCB transportation. Activities including landfilling, city dumping, incinerating and accidentally spilling will enhance the PCB transport to the atmosphere. Both experimental (Chiarenzelli *et al*., 1996; 1998) and modeling studies (Harner *et al*., 1995) have shown that PCBs can indeed volatilize from a sediment phase to the atmosphere. A study of PCB concentration and composition of PCBs in the air during the build-up of a landfill of PCB-contaminated sediment indicated that the air was enriched in more volatile PCB congeners compared to the deposited sediment, suggesting volatilization as the major transport pathway in addition to particle transport (Bremle and Larsson, 1998). The sampling results at a Native American reservation in upper New York State by the State University of New York showed that PCB ambient air concentrations occurred in far higher amounts than expected. It was surmised that the elevated concentrations of PCBs in air might have been caused by volatilization of PCBs from sediment. U. S. EPA National Risk Management Resource Laboratory (NRMRL) funded this investigation to evaluate the potential for PCB volatilization from sediments.

PCB contaminated sediment and water were collected from the Lake Hartwell Superfund Site. The Lake Hartwell area consists of 730 acres that were once used for capacitor manufacturing. Some plants used dielectric fluids containing PCB in their manufacturing processes. Between 1955 and 1977, approximately 400,000 lbs of PCBs

were discharged into Town Creek and an unspecified amount was buried in six off-site disposal areas. A more detailed site description is provided in Magar *et al.* (2001).

The rate of PCB volatilization from fully homogenized, uniformly contaminated, and naturally aged sediments was studied at bench-scale in this project. The primary objective of this study was to experimentally quantify the rate at which the various PCB congeners are transported from sediment uniformly contaminated with PCBs to overlaying air in a controllable environment. A secondary objective was to assess if there is a relationship between the rate of volatilization and the extent of substitution of the PCB with chlorine.

MATERIALS AND METHODS

Experimental Setup. A schematic diagram of the air-natural water-contaminated sediment reactor system is shown in Figure 1. Gas washing bottles (250 ml) were set up to obtain PCB transport rates from the contaminated sediment to the air. For each test, four such bottles were set up at the beginning. Two bottles were sacrificed immediately to determine initial concentrations of the PCBs in the sediment while the remaining two bottles were operated to obtain PCB volatilization rates. The air stream exiting the glass-washing bottle passed through stainless steel tubing into a moisture trap. The moisture trap consisted of a stainless steel tube packed with 5 g of anhydrous sodium sulfate. The air exiting the moisture trap was conducted through stainless steel tubing to another stainless steel trap packed with 10 g of florisil (60x100 mesh, Sigma Chemical Co.). A more detailed description of the experimental apparatus can be found in Qi *et al*. (2000).

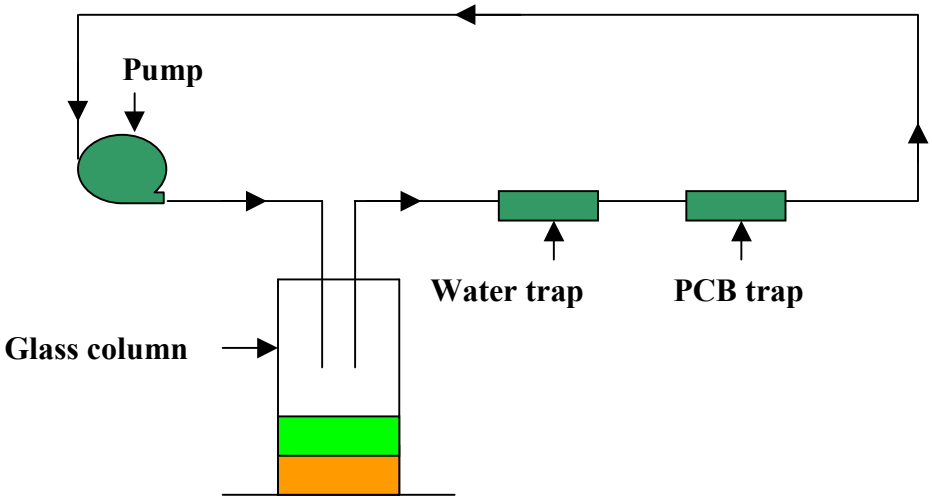


FIGURE 1. Schematic of Experimental System

Sediment Tested. All experiments were performed on two naturally occurring contaminated sediments. One of the first two samples from Lake Hartwell was collected to represent the top or "native" layer occurring at depths of between 0 and 6 inches from the surface. The second sample represented the deeper and, therefore, older contamination occurring at depths between 7 and 12 inches from the surface. The native,

or top, layer was lighter in color than the deeper layer suggesting differences in organic content and perhaps in redox conditions as well.

Characterization of the sediment was performed to identify the physical and chemical properties of the sediment that can impact adsorption/desorption and volatilization characteristics. The moisture contents of the top and deep layer sediments were 47.66% and 47.92% respectively. The sediment characterization performed by Agvise Laboratories (North Dakota) is summarized in Table 1. The results demonstrated that top layer sediment and deep layer sediment had very similar characteristics except for pH and organic matter content. The pH of the deep layer sediment was lower than that of top layer, possibly because anaerobic conditions in the deep layer provided an appropriate environment for reductive dechlorination of the PCBs with hydrochloric acid as a by-product.

Experimental Design. Every volatilization experiment was conducted for a total period of 80 days. Sampling during the 80 days was carried out on days 0, 1, 3, 10, 20, 40, 60, and 80. The content of the gas washing bottles was analyzed on day 0 and on day 80. Analyses for volatilized PCBs were carried out on days 1, 3, 10, 20, 40, 60, and 80 in order to be consistent with the sampling schedule of the previous fundamental studies. On those days, the tubing, the florisil trap, and the moisture trap from every reactor system were removed and extracted.

TABLE 1. Sediment Characteristics.

		Top Layer (LH)	Deep Layer (LH)
Bulk Density (g/cm^3)		0.76	0.71
Particle Density (g/cm^3)		2.53	2.54
pH (water)		5.3	4.9
Porosity (%)		69.8	72.2
% organic matter (Walkley-Black)		3.0	3.7
Particle Size Distribution (μm)	<4	13	41
	4-63	48	50
	63-2000	39	9
Heavy Metal Content (ppm)	Zinc	2.77	2.96
	Iron	269.3	250.2
	Copper	1.54	1.50
	Manganese	129.9	129.1

PCB Extraction and Analysis. Hexane and an acetone/hexane mixture (1:1) were used to recover PCBs from the glass columns, PCB and water traps and the tubing connecting the system. A rotating tumbler was used to facilitate the extraction process. The surrogate internal standards (SIS) compounds added were PCB14, PCB34, PCB112 and PCB104. Activated copper powder was added to sediment samples to complex any sulfur that might be present in the samples.

One each of a laboratory control sample (LCS), blank spike (BS), procedural blank (PB), and matrix spike (MS) was processed along with the sediment samples on day 0 and 80. A procedural blank (PB) was processed along with the air samples on day 3, 60 and 80.

Extracts were sent to Battelle-Duxbury for sample cleanup and analysis. Fifty-one PCB congeners (Table 2) were identified and quantified by using gas chromatographic/mass spectroscopic (GC-MS).

TABLE 2. Monitored PCB congeners.

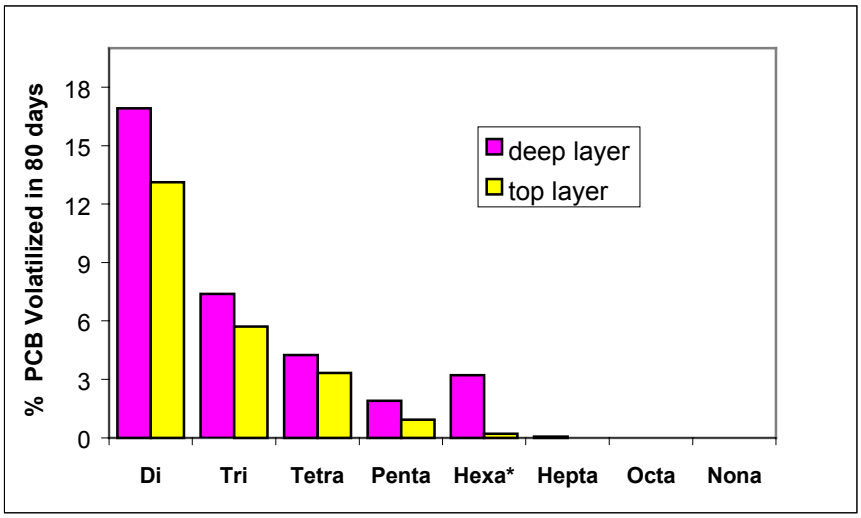
	PCB Congeners
Di	PCB8/5
Tri	PCB18, PCB28, PCB31, PCB33/20
Tetra	PCB41/64/71, PCB42, PCB44, PCB49, PCB52, PCB56/60, PCB66, PCB70/76, PCB74
Penta	PCB84, PCB85, PCB87/115, PCB92, PCB95, PCB97, PCB99, PCB101/90, PCB105, PCB110, PCB118
Hexa	PCB128, PCB132, PCB135/144, PCB136, PCB137, PCB138/160/163, PCB141, PCB146, PCB149, PCB151, PCB 153, PCB156, PCB158, PCB167
Hepta	PCB170/190, PCB174, PCB177
Octa	PCB180, PCB183, PCB184, PCB187/182, PCB194, PCB195
Nona	PCB203/196, PCB206, PCB209

RESULTS AND DISCUSSION

Experiments were performed in duplicate sets. The data were not reported corrected for surrogate recovery. The mass of total PCB (ΣPCB) was determined by summing contributions of individual congeners. The extent of volatilization for ΣPCB and PCB congeners groups were calculated.

Figure 2 presents volatilization rates of various PCB congeners in this 80 days study. A strong correlation between degree of chlorination and the volatilization rate was observed: the higher chlorinated congeners had lower volatilization rates. It should be noted that congener PCB153 was excluded from hexachlobiphenyl calculations, because the amount of PCB153 collected on the florisil trap was dramatically higher than the original content of the sediment. The source of this discrepancy is under investigation.

Volatilization process is dependent on the organic compound's water solubility, vapor pressure and Henry's law constant. Generally speaking, lower and ortho substituted chlorinated biphenyls have higher water solubility and Henry's law constant, thus are more volatile. The 51 PCB congeners investigated in this project have varied properties: low to high chlorinated, low to high ortho chlorine substitution, low to high air-water partitioning coefficients. All these factors can affect the rate of PCB released from sediments.



*: PCB 153 is excluded from Hexachlorobiphenyl.

FIGURE 2. Volatilization of PCB Congeners from Lake Hartwell Sediment

Figure 2 also demonstrates that PCB volatilized faster from deep layer sediment than from top layer sediment. The overall volatilization percentages are 2.52% and 6.54% for top layer and deep layer, respectively.

CONCLUSIONS

This bench-scale study was conducted to investigate the volatilization of PCBs from sediments using two types of Lake Hartwell sediments, one from a lightly contaminated top layer, and one from a highly contaminated deep layer. The data revealed significant volatilization of PCBs. Results also indicated that higher chlorinated biphenyls had lower volatilization rates.

ACKNOWLEDGEMENTS

Funding for this study was provided by the U.S EPA National Risk Management Research Laboratory.

REFERENCES

Bremle, G., and P. Larsson. 1998. "PCB in the Air During Landfilling of A Contaminated Lake sediment." *Atmosphere Environment 32*(6): 1011-1019.

Chiarenzelli, J., R. Scrudato, M. Wunderlich, and D. Rafferty. 1996. "Volatilization of Poly-chlorinated Biphenyls from Sediment during Drying at Ambient Conditions." *Chemosphere 33*(5): 899-911.

Chiarenzelli, J, R. Scrudato, K. Jensen, T. Maloney, M. Wunderlich, J. Pagano, and J. Schneider.1998. "Alteration of Aroclor 1248 in Foundry Waste by Volatilization." *Water, Air and Soil Pollution 104*:113-124.

Erickson, M. 1997. *Analytical Chemistry of PCBs*. Lewis Publishers, New York.
Harner, T., D. Mackay, and K.C. Jonea. 1995. "Model of the Long-Term Exchange of PCBs between Soil and the Atmosphere in the Southern U.K." *Environ. Sci. Technol. 29*: 1200-1209.

Magar, V., J. Icker, J. Abbott, R. Brenner, G. Durell, G. Johoson, E. Crecelius, C. McCarthy, and L. Bingler. 2001. "Natural Recovery of PCB-Contaminated Sediments at the Sangamo-Weston/Lake Hartwell Superfund Site." *The Sixth International In Situ and On-Site Bioremediation Symposium*, pp. 231-236. San Diego, CA.

Qi, S., C. Alonso, M. Suidan, and G. Sayles. 2000. " Investigation of PCB Volatilization from Sediment." 73rd WEF Annual Conference Proceedings.