

**PCBs IN FRESHWATER AND MARINE SEDIMENTS:
TRANSPORT, TRANSFORMATION AND TREATMENT**

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**TEMPERATURE EFFECTS ON PCB FATE AND TRANSPORT
IN ANAEROBIC NEAR-SURFACE SEDIMENT**

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Introduction

Since the 1970s, General Electric and state and federal agencies have conducted numerous sampling and analysis programs to evaluate polychlorinated biphenyl (PCB) levels in the Upper Hudson River water, sediment and biota. Analysis of this data has shown that there is a high flux of PCBs out of the sediments into the water column during the low-flow summer months as compared with other times of the year^{1,2}. This increased PCB loading from the sediment to the water column during the early summer months under low-flow conditions has been observed at other contaminated river sites^{3,4}, including the Grasse River in Massena, NY, which has been studied extensively by Alcoa⁵. Water temperature appears to have an important role in governing the increased sediment release fluxes. The increased temperature during the summer months can lead to increased physical/chemical processes such as desorption, diffusion and solubility and increased biological processes such as microbial and bioturbator activity.

The release of PCB compounds from the sediment to the water column during low flow conditions in a river system can be facilitated through physical/chemical processes, microorganism activity and bioturbation. Physical/chemical processes include desorption of PCBs from the sediment and diffusion of PCBs through the pore water to the sediment-water interface. Microorganisms can transform PCBs from highly chlorinated compounds to less chlorinated and, therefore, more mobile compounds^{6,7}. Microorganism activity can also generate gas bubbles. Movement of the gas through the sediment can aid in the release of hydrophobic organic compounds out of the sediment by carrying particles attached to the gas bubbles out of the sediment⁸.

Bioturbation can facilitate PCB transport from the sediment to the water column by mixing the sediment, resulting in more contaminated sediment reaching the sediment-water interface^{9,10} and spraying particles from the sediment into the sediment-water boundary layer¹¹, resulting in greater contact of water with PCB contaminated sediments. The increased temperature during the summer months leads not only to increased microbial and bioturbation activity but also to increased rates of physical/chemical PCB release processes such as desorption and diffusion. All of the temperature dependent processes can be contributing to the low-flow, increased release of PCBs from the sediment to the water column during the summer months.

This research aims to elucidate the effects of temperature on the fate and transport of PCBs in anaerobic near-surface sediments. The effects of temperature on PCB diffusion in a clean, homogenous, well-characterized system of sand and kaolinite as well as biologically active and inactive Grasse River sediments are being studied. The results of the clean system experiments will be used to isolate the physical/chemical effects of temperature on apparent PCB diffusion. Observed PCB transport in biologically inactive (autoclaved) Grasse River sediments will be compared to that in biologically active Grasse River sediments to elucidate the additional effects of microbial activity on PCB fate and transport at various temperatures.

Materials and Methods

Three types of solid matrices are being used in the experiments: a sand and kaolinite mixture (synthetic sediment), killed (autoclaved) Grasse River sediment and active Grasse River sediment. The synthetic sediment and the killed Grasse River sediment were autoclaved to suppress microbial activity. Three specific congeners are being used as representative PCBs in this study. These congeners are 2,4,5-trichlorobiphenyl (BZ29), 2,5-dichlorobiphenyl (BZ9) and 2-chlorobiphenyl (BZ1).

Aluminum cylindrical tubes 2.7 cm in diameter and 12.7 cm in height were filled with a spiked sediment layer, a non-spiked sediment layer, water and a semi-permeable membrane device (SPMD) and capped (Figure 1).

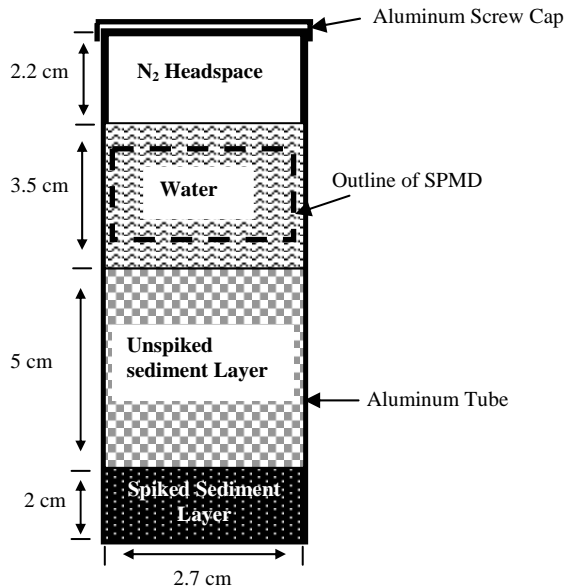


Figure 1. Schematic diagram of the experimental microcosms. The dotted block in the water column section indicates where the SPMD is placed. This drawing is not to scale.

The spiked sediment layer consists of synthetic sediment or Grasse River sediment that was autoclaved and contaminated with 300 mg/kg of BZ29, 300 mg/kg of BZ9 and 300 mg/kg of BZ1 (Accustandard Inc., New Haven, CT). The water was autoclaved with deionized water for all experiments. In order to simulate the low dissolved phase PCB concentrations found in river water and to capture for mass balance purposes any PCBs released to the water, a semi-permeable membrane device (SPMD) was added to the water column to remove dissolved phase PCBs. The SPMD (Environmental Sampling Technologies, St. Joseph, MO) consists of approximately 0.097 grams of triolein enclosed in low-density polyethylene layflat tubing (one inch by one inch). The temperature-dependent diffusion experiments are being run at 15°C, 25°C and 50°C with the microcosm tubes stored in racks inside incubators adjusted to these temperatures.

At each designated sampling time, a synthetic sediment, a killed Grasse River sediment and an active Grasse River sediment microcosm are removed from each of the three incubators, sectioned and analyzed. Once the microcosm tubes are removed from the incubators they are frozen for slicing. A Buehler Isomet 1000 precision saw is used to cut frozen samples into 2 mm thick horizontal sections. The sectioning is done with the sediment still inside of the aluminum tube. The saw cuts through the aluminum and the aluminum ring cut out is extracted with the sediment.

PCBs are extracted ultrasonically from the Grasse River sediment based on USEPA Method 3550b¹². PCBs are extracted from the sand/kaolinite synthetic sediment using a 10 ml acetone:hexane (1:1) mixture and mixing on an end-over-end rotator for 3 days (solvent changed daily). SPMDs are extracted by immersion in 60 ml hexane for 2 days,

changing the hexane each day. Water is extracted by adding 30 ml of hexane to 20 ml of water and rotary shaking for 72 hours. The concentrated extracts from all of the PCB extractions are cleaned with florisil based on USEPA Method 3620B¹³. The PCB congeners of interest, BZ29, 2,3,3'-trichlorobiphenyl (BZ20), BZ9, 2,4-dichlorobiphenyl (BZ7), 2,3-dichlorobiphenyl (BZ5) and BZ1, are quantified using a gas chromatograph with a micro-cell electron capture detector based on USEPA Method 8082¹⁴.

Results and Discussion

The thin sectioning of the laboratory sediment microcosms allows study of PCB transport in river sediment with fine scale resolution. Temperature dependent transport has been observed for each congener in each type of sediment at varying rates. For example, Figure 2 shows that at 32 weeks congener BZ1 was observed to move higher up into the uncontaminated sediment zone in the 50°C microcosm compared to the microcosms being run at 15°C and 25°C.

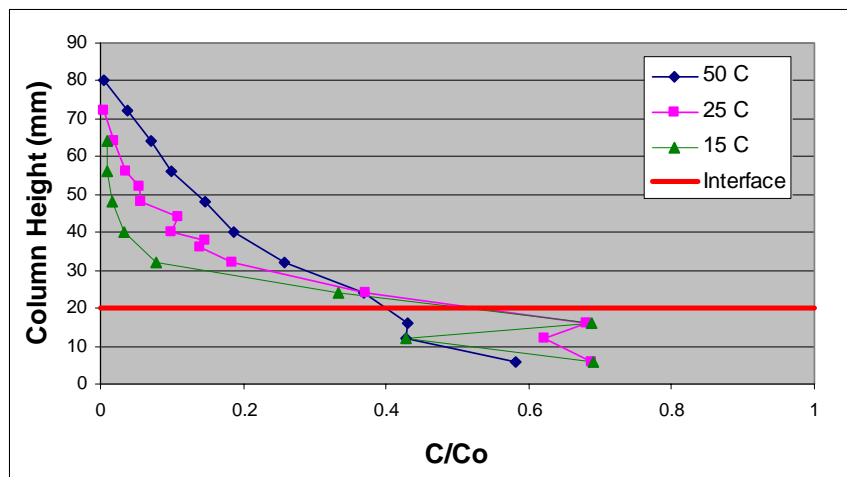


Figure 2. Distribution of PCB congener BZ1 in active Grasse River sediment microcosms (T=15°C, 25°C, 50°C) at 32 weeks. The interface line at 20 mm delineates the point where the spiked sediment layer ends and the unspiked sediment layer begins.

The congener transport is occurring as expected with BZ1 moving the quickest followed by BZ9 and then BZ29. The fastest transport of the congeners is occurring in the active sediment followed by the killed sediment, then the synthetic sand/kaolinite system (Figure 3).

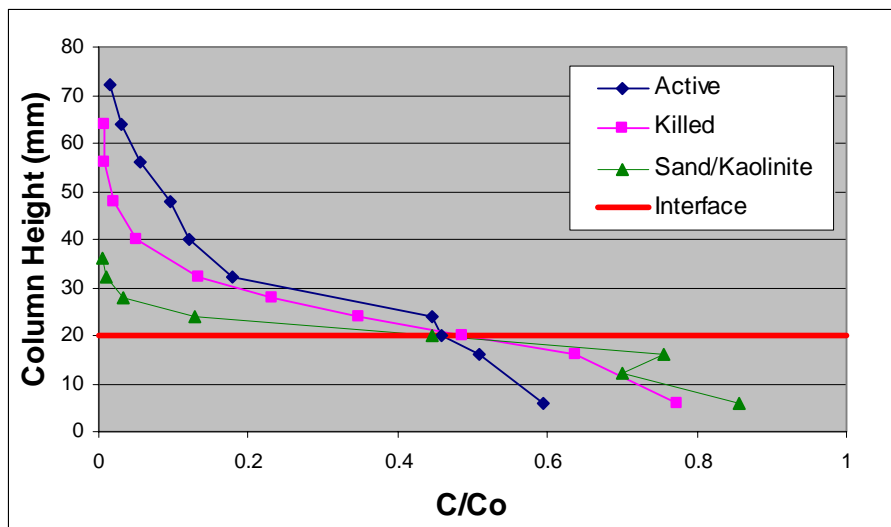


Figure 3. Distribution of PCB congener BZ1 in each type of sediment microcosm at 50°C and 20 weeks. The interface line at 20 mm delineates the point where the spiked sediment layer ends and the unspiked sediment layer begins

The fastest congener transport is occurring in the active sediment likely because of microbial activity. A significant amount of gas formation has been observed in the active sediment microcosms. Movement of the gas through the sediment can create preferential pathways for PCB transport. Movement of the gas through the sediment can also aid in the release of PCBs out of the sediment by carrying particles attached to the gas bubbles out of the sediment. A significant amount of bed expansion has been observed in the active sediment microcosms. This expansion can lead to an increase in porosity of the sediment and, therefore, increased PCB transport. Anaerobic dechlorination of higher chlorinated compounds can lead to lower molecular weight, more mobile compounds. Dechlorination of BZ29 has been observed in the active sediment. The increased transport in the active sediment shows the importance of microbial activity in PCB transport in near surface sediments.

Future work includes completing the experimental portion of the research and modeling the results to obtain temperature-dependent diffusion coefficients for each of the congeners in each type of sediment, at each temperature. Comparing the results of the killed Grasse River experiments and the active Grasse River sediment experiments, the effects of microbial activity on the apparent PCB diffusion coefficients at various temperatures will be assessed.

Acknowledgements

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References

1. Connolly, J.P., et al. (2000). *Environ. Sci. Technol.*, **34**(19), 4076-4087.

2. TAMS Consultants, I., *et al.* (2000). Phase 2 Report - Review Copy Further Site Characterization and Analysis Volume 2D - Revised Baseline Modeling Report Hudson River PCBs Reassessment RI/FS.
3. Bremle, G. and P. Larsson (1997). *Environ. Sci. Technol.*, **31**(11), 3232-3237.
4. Froese, K.L., *et al.* (1997). *Journal of Great Lakes Research*, **23**(4),440-449.
5. Alcoa (1999), Comprehensive Characterization of the Lower Grasse River, Grasse River Study Area, Massena, NY. Vol. I-Main Report.
6. Brown, J.F.J., *et al.* (1987). *Science*, **236**, 709-712.
7. Quensen, J.F.I., J.M. Tiedje and S.A. Boyd (1988). *Science*, **242**, 752-754.
8. Fendiger, N.J., D.D. Adams and D.E. Glotfelty (1992). *The Science of the Total Environment*, **112**, 189-201.
9. Karickhoff, S.W. and K.R. Morris (1985). *Environ. Sci. Technol.*, **9**(1), 51-56.
10. Reible, D.D., *et al.* (1996). *Water Research*, **30**(3), 704-714.
11. Rhoads, D.C. and L.F. Boyer (1982). In *Animal-Sediment Relations*, P.L. McCall, Tevesz, M.J.S., Eds., Plenum Press, New York.
12. USEPA (2003). Ultrasonic Extraction, in *SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, U.S. EPA, Washington, DC.
13. USEPA (2003), Florisil Clean-up, in *SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. U.S. EPA, Washington, DC.
14. USEPA (2003), Polychlorinated Biphenyls (PCBs) by Gas Chromatography, in *SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. U.S. EPA, Washington, DC.