# ANALYSIS OF PROCESSES AND ENVIRONMENTAL FACTORS GOVERNING POLYCHLORINATED BIPHENYL TRANSPORT FROM THE SEDIMENT TO THE WATER COLUMN UNDER LOW-FLOW CONDITIONS IN THE UPPER HUDSON RIVER

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## ABSTRACT

Numerous sampling and analysis programs have been conducted to evaluate polychlorinated biphenyl (PCB) levels in the Upper Hudson River water, sediment, and biota. Analyses of these data have shown that there is a high flux of PCBs out of the sediments into the water column during the low-flow late spring to early summer months as compared with other times of the year. Using available water column and sediment data as well as current literature, this paper analyzes a number of hypotheses regarding environmental factors that could be affecting the processes involved in the low-flow release of PCBs from sediments in the Thompson Island Pool (TIP) in the Upper Hudson River. The release of PCB compounds from the sediment to the water column during low-flow conditions in a river system can be facilitated through a number of processes including physicochemical processes, microorganism activity, and bioturbation. Environmental factors such as temperature, organic matter, and essential nutrients were evaluated to assess their possible effects on the low-flow release processes. The results of this analysis indicate that elevated water and near-surface sediment temperature is an important factor governing the increased release of PCBs from the sediment to the water column during the late spring to early summer months. The higher water and near-surface sediment temperatures during this period increase the rate of the physical, chemical, and biological processes responsible for PCB release from sediments.

## INTRODUCTION

Polychlorinated biphenyl (PCB) contamination of river sediment is a long-term environmental management challenge in many rivers of the United States, including the Hudson River in New York. Release of PCBs from the sediment to the water column is a primary source of human and ecosystem exposure in PCB-contaminated aquatic systems (Connolly, 1991; NRC, 2001). Understanding the mechanisms responsible for the release of PCBs into the water column will help decision makers choose appropriate remediation and management strategies for PCB-contaminated river sediments.

Since the 1970s, General Electric Company and state and federal agencies have conducted numerous sampling and analysis programs to evaluate PCB levels in the Upper Hudson River water, sediment, and biota. Analyses of these data have shown that there is a high flux of PCBs out of the sediments into the water column under low-flow conditions during the late spring to early summer months as compared with other times of the year (Quantitative Environmental Analysis, 1999; Connolly et al., 2000; TAMS Consultants et al., 2000; Erickson et al., 2005). Much of this analysis has been done with field data from the Thompson Island Pool (TIP), a six-mile stretch of the Upper Hudson River bounded upstream by Fort Edward and downstream by the Thompson Island Dam (Figure 1). TIP is ideal for evaluation of sediment-to-water PCB flux because (1) tributary influences are small, (2) upstream sources of PCB contamination are well measured and mostly non-depositional so the load gain across TIP can be measured, (3) a large data set for PCB contamination in the sediment and water column exists for the pool, and (4) the PCB congener signature from the sediment source has been established (Erickson et al., 2005).

Using non-filtered, water-column PCB data and flow data from Ft. Edward and the Thompson Island Dam sampling locations (Figure 1), the TIP PCB loading from the sediment can be calculated through mass balance analysis as the difference between the PCB mass flux at the upstream and downstream boundaries. Figure 2 is a plot of the low-flow (<283 $m^3$/sec (10,000 cfs)) total PCB loading from TIP sediment in 1998 and 1999. As the plot shows, there was an increased loading in May and June (late spring to early summer months) in both years. The plot shows that PCB loading increased as water temperature increased but then decreased while the water temperature remained elevated. In order to gain further insight into the low-flow release processes, the TIP homolog loading in 1998 was graphed (Figure 3). As the plot shows, the dominant homolog group was the di-chlorinated biphenyls, followed by the mono- and tri-chlorinated biphenyls. The loading of each homolog group closely resembles the total PCB loading, indicating that during the increased seasonal release, the PCB release processes were occurring at elevated rates.

Connolly et al. (2000) used field data to calculate the diffusive mass transfer rate coefficient for PCB loading from TIP sediment to the water column under low flow conditions:

$$J = k(C_{out} - C_{in}) \tag{1}$$

where J is the flux of PCBs from the sediment to the water column ($M/L^2T$), k is the diffusive mass transfer coefficient (L/T) and C is the water column PCB concentration ($M/L^3$) for water entering (in) and exiting (out) the TIP. The calculated diffusive mass transfer coefficient was minimum in the winter, peaked in the late spring to early summer months, and declined through the late summer and fall. The timing of the increased PCB water column loading and subsequent decline was hypothesized to be linked to biologically-mediated mixing in the surface sediments.

Erickson et al. (2005) analyzed mass transfer rate coefficients for PCB loading from the sediment to the water column in TIP and reported that approximately 65% of the observed sediment-to-water PCB flux occurred during low flows that did not resuspend sediments. Sediment-water mass transfer coefficients for PCBs in TIP were found to be one to two orders of magnitude larger than the effective mass transfer coefficients expected for molecular diffusion. The seasonal trend in PCB loading was hypothesized to be attributable to a combination of physical and biological factors in the sediment that vary seasonally as a function of flow velocities, temperature, bioturbation, and fish activities.

Butcher and Garvey (2004) analyzed congener-specific PCB loading from the sediment in TIP during the summer months and found that the mixture of congeners released was consistent with a mixed loading source consisting of pore water flux (diffusion) and low-flow suspension of contaminated sediments and re-equilibration with the water column.

The low-flow suspension of contaminated sediments was attributed to a variety of biological and anthropogenic processes including bioturbation, uprooting of macrophytes, and mechanical scour by boats and floating debris. The predicted fraction of the mass flux for the pore water ranged from 5 to 50% for 2-chlorobiphenyl. For tri- and tetrachlorobiphenyls in TIP sediments, the predicted average contribution by pore water flux was less than 10%.

Studies have thus shown that the seasonal increased release of PCBs from the sediment to the water column under low-flow conditions in TIP is not merely a diffusion-based process. However, these studies have not analyzed in detail a range of possible causes for the increased release.

This paper identifies and evaluates a number of processes potentially involved in the low-flow release of PCBs from river sediments, and environmental factors that could be affecting these processes in TIP. The paper provides a review of available data and literature for the Upper Hudson River, in particular the TIP, in an attempt to understand the most important factor or factors responsible for the increased release of PCBs from the sediment to the water column under low-flow conditions in the late spring to early summer months.

## LOW-FLOW PCB RELEASE MECHANISMS

The release of PCBs from the sediment to the water column under low-flow conditions in a river system can be facilitated through a range of physicochemical and biological processes. Figure 4 shows some low-flow release mechanisms known to be active in river sediment. This section describes some of the major release mechanisms hypothesized to be responsible for the transport of PCBs from the sediment to the water column under low-flow conditions in the Upper Hudson River.

Physicochemical release mechanisms include desorption of PCBs from the sediment, diffusion of PCBs through the pore water and across the sediment-water interface, and the advection of groundwater across the sediment-water interface. Quantitative Environmental Anaysis, Inc. (1999) estimated that groundwater advection accounted for 4% of the average PCB loading within TIP between 1993 and 1996, indicating that groundwater advection is not a significant source of water column PCBs.

Microorganisms can transform PCBs from highly chlorinated compounds to less chlorinated, and therefore more mobile, compounds by dechlorination under anoxic conditions (Brown et al., 1987; Quensen et al., 1988; Abramowicz et al., 1993; Rhee et al., 1993; Fish and Principe, 1994; Bedard and Quensen, 1995; Wu et al., 1996; Cutter et al., 2001). Dechlorination of PCBs in Hudson River sediment has been observed in the laboratory and in the field (Brown et al., 1987; Quensen et al., 1988; Abramowicz et al., 1993; Rhee et al., 1993; Fish and Principe, 1994; Bedard and Quensen, 1995). Aerobic microorganisms can degrade the less chlorinated (mono-, di-, tri-) PCBs by the destruction of the biphenyl ring (Harkness et al., 1993). The majority of the PCB inventory in the Hudson River is in anoxic sediment, so aerobic degradation is not a dominant mechanism for PCB removal from the sediment (TAMS Consultants et al., 1997).

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 sediment (Fendiger et al., 1992) and by making the sediment more porous through the creation of bubble tubes (Martens and Klump, 1980) and preferential pathways within the sediment (McDonough and Dzombak, 2005). PCBs can also partition into the gas phase of the bubble and be transported out of the sediment in the gas phase (Fendiger et al., 1992).

Benthic organisms that live on or within the sediment, known as bioturbators, 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 (Karickhoff and Morris, 1985; Reible et al., 1996) and spraying particles from the sediment into the sediment-water boundary layer (Rhoads and Boyer, 1982), resulting in greater contact of water with PCB-contaminated sediments. Bioturbators can also change the stability, porosity, and density of surface sediment through burrowing, ingestion, and excretion (Bosworth and Thibodeaux, 1990). The TIP benthic macroinvertebrate community is dominated by isopods (sow bugs), chironomids (midge larvae), oligochaetes (aquatic worms), amphipods (scuds and sideswimmers), and pelecypods (mussels and clams) (TAMS Consultants and Menzie-Cura & Associates, 2000). Quantitative Environmental Analysis, Inc. (1999) reported that based on the structure and abundance of the benthic invertebrate community it is likely that bioturbation contributes to the sediment-water exchange of PCBs in the Upper Hudson River.

Other mechanisms can be contributing to the low-flow release of PCBs from the sediment to the water column, including scour of surficial sediment by boats, disturbance of sediment due to fish grazing and activities, and uprooting of aquatic plants. The mechanisms discussed here are those hypothesized to be probable causes for the seasonal increased release of PCBs from sediment to the water column.

## ENVIRONMENTAL FACTORS THAT MAY INFLUENCE LOW-FLOW RELEASE MECHANISMS IN THE UPPER HUDSON RIVER

The low-flow PCB release mechanisms can be affected by environmental factors such as temperature, organic matter, and essential nutrients. Hypotheses about how these factors may influence PCB release were developed and evaluated, in a preliminary manner, to assess the relative importance of each on the increased release of PCBs from the sediment to the water column in the late spring to early summer months in TIP.

### Organic Matter

The first hypothesis that was analyzed was that organic matter abundance in the sediment is seasonally variable and that PCB release flux is correlated with sediment organic matter content. Organic matter is a food source for micro- and macroorganisms in the sediment and can also affect physicochemical release processes. Available information on plant growth and organic matter distribution in the sediments of the Hudson River, particularly TIP, and information on the effects of organic matter on physicochemical, microbial, and bioturbator activity was evaluated to examine this hypothesis.

Organic matter in sediments affects the physical-chemical partitioning and transport of PCBs in a number of ways. Decomposition of organic matter and subsequent sediment diagenesis processes form colloidal-sized organic particles within sediment pore water (Valsaraj et al., 1996) that preferentially sorb PCBs. These colloidal-sized particles then diffuse through the pore water and across the sediment-water interface, thus increasing the transport of PCBs from the sediment to the water column (Valsaraj et al., 1996). On the other hand, organic matter fixed on immobile sediment solids can decrease the transport of PCBs from the sediment to the water column due to the preferential sorption of PCBs to organic matter. Ghosh et al. (2003) analyzed PCB-contaminated sediment from Hunters Point (San Francisco Bay, CA) and Milwaukee Harbor (WI) and found that even though organic matter contributed only 5-7% of the total sediment mass, the fraction of total PCBs associated with the organic matter portion of the sediment was 68 and 58% respectively.

Freshly deposited organic matter is an energy source for microbes in the sediment. A number of studies in fresh water sediments have observed a positive correlation between sediment bacterial abundance and quantity and quality of sediment organic matter (Dale, 1974; Bott and Kaplan, 1985; Cole et al., 1988; Schallenberg and Kalff, 1993; Sinsabaugh and Findlay, 1995). In Hudson River surface sediments, microbial abundance and productivity have been related to quantity, quality, and size distribution of particulate organic carbon (Cole et al., 1988; Sinsabaugh and Findlay, 1995).

The effect of organic matter on bioturbator abundance and activity is not well understood. The abundance of macrobenthic biomass has been positively correlated with sediment bacterial biomass which has been positively correlated with organic matter quantity and quality (Schallenberg and Kalff, 1993). Rhoads and Boyer (1982) and Wheatcroft and Martin (1996) report that increasing proximity in time or space to an organic matter source decreases species diversity but increases the total number of macroinvertebrates. Wheatcroft and Martin (1996) found that maximum bioturbation occurs in sediments of intermediate organic carbon content (1.4% organic carbon) and that increased bioturbation is negatively correlated with the total number of species present.

Available data were analyzed to assess the seasonality of the organic matter content of TIP sediment. Most of the organic carbon in the Hudson River comes from allochthonous sources, mainly nonpoint terrestrial sources (Howarth et al., 1992; Howarth et al., 1996). Allochthonous carbon inputs to the Hudson River are highest in the spring due to high flow events (Gladden et al., 1988). Sediment organic matter content is spatially variable in the Hudson River, including TIP, and dependent on the physical make-up of the sediment (Exponent, 1998; TAMS Consultants et al., 2000). Figure 5 shows near-surface (0-5 cm) sediment total organic carbon (TOC) data at various locations in TIP in the late spring and fall of 1992, revealing significant spatial variability in the TOC content of TIP sediment. Comparison of the TIP sediment TOC data from late spring and fall 1992 (Figure 5) indicates that sediment TOC was seasonally variable with an average sediment TOC in the spring of 2.8% and in the fall of 5.9%.

Sediment organic matter can affect all of the PCB release mechanisms including the physicochemical and biological processes. Physicochemical transport processes can be both enhanced and impeded by increased sediment organic matter. Increased transport can occur due to increased colloidal-sized organic particles in the pore water which sorb and transport PCBs through the pore water and across the sediment-water interface. Decreased transport can occur due to increased sediment organic matter available to sorb PCBs. Quantity and quality of sediment organic matter has also been positively correlated with microbial abundance and activity. Increases in sediment organic matter will not necessarily lead to increased bioturbation as studies show that maximum bioturbation occurs in sediment with intermediate organic carbon content (Wheatcroft and Martin, 1996).

The increased organic matter loading from the spring high flow period could lead to an increase in sediment organic matter during the late spring to early summer months but TIP sediment TOC data indicate that it does not (Figure 5). TIP sediment organic matter content is seasonally variable with higher levels in the fall than in the late spring. Thus, it is unclear whether or not sediment organic matter is a factor controlling the increased release of PCBs from the sediment to the water column in the late spring to early summer months but available data suggest that organic matter is not a primary controlling factor.

### Essential Nutrients

The second hypothesis analyzed was that essential nutrient abundance in the sediment is seasonally variable and that PCB release flux is correlated with nutrient availability. Nutrients such as nitrogen and phosphorus are important for cell synthesis and growth and therefore affect microbial and bioturbator abundance and activity. Available information on essential nutrient concentrations in sediment, pore water, and the water column of the Hudson River, particularly TIP, was evaluated to examine this hypothesis.

Water column and sediment studies in areas south of TIP indicate that nitrogen and phosphorus are not limited in the river system. Templer et al. (1998) found that plant species can greatly affect phosphorus levels in the pore water of Hudson River marsh sediment (study site located at Tivoli Bay, south of TIP) but that sediment pore water phosphorus levels remained high year round indicating rapid replenishment from other sediment phosphorus pools. The study found that nitrogen levels in the pore water are high in the spring and drop significantly in the summer months, and that nitrogen demand from plants and microbes exceeds mineralization rates indicating that nitrogen is a limiting nutrient in these systems. Studies on a 70 km stretch of the Hudson River south of TIP have shown that for all seasons and at many locations in the river, nitrogen and phosphorus water column concentrations are quite high with an average total nitrogen concentration of 0.8 mg/l and an average total phosphorus concentration of 0.05 mg/l (Lampman et al., 1999; Cole and Caraco, 2001).

Water quality data from the USGS (2001) for Ft. Edward (the northern most sampling location in TIP) were reviewed for total nitrogen and total phosphorus levels in the water column. For all seasons over a five year period from 1971-1975, total nitrogen levels were quite high with an average concentration of 1.2 mg/l. Total phosphorus data were only available for 1972 but levels were high over the entire year with an average concentration of 0.1 mg/l.

No data were found for phosphorus concentrations in the pore water or sediment in TIP, but sediment total nitrogen (TN) data from TIP were available and analyzed for spatial and seasonal trends. Figure 6 shows that TN is spatially variable in the TIP near-surface sediment. From the data in Figure 6, the average sediment TN in the late spring sampling period was 0.15% and in the fall sampling period was 0.39%, indicating that sediment TN content was higher in the fall than in the spring.

The Redfield ratio refers to the molar ratio of carbon, nitrogen, and phosphorus in phytoplankton (106:16:1) and is reflected in fresh particulate organic matter (DiToro, 2001) in sediment. Therefore, based on the Redfield ratio, the ratio of carbon to nitrogen (C/N) in TIP sediment should be 6.63 mol/mol (DiToro, 2001). Sediment carbon and nitrogen ratios (C/N) were calculated from TIP sediment data for the late spring and fall, 1992 (Figure 7). Figure 7 shows sediment C/N ratios in TIP varying from 10 to 60 mol/mol, indicating that nitrogen is limited in the sediment. From the data presented in Figure 7, the average C/N ratio in the late spring sampling period was 26 mol/mol and in the fall sampling period was 18 mol/mol, indicating that nitrogen was more limited in TIP surface sediment in the late spring than in the fall.

Data for essential in the TIP water and sediment are limited. Based on the TN data and calculated C/N ratios in TIP sediment, nitrogen is spatially and seasonally variable within TIP, with higher concentrations in the fall than in the late spring thus, its seasonality does not coincide with the increased PCB release in the late spring to early summer months.

## Temperature

The final hypothesis analyzed was that near-surface sediment and pore water temperature, which varies seasonally, governs rates of a number of PCB release mechanisms and hence overall PCB release rates. Temperature can affect the physicochemical processes as well as microbial and bioturbator processes. If nutrients and food sources are not limiting, the increased temperature will lead to increased microbial activity (Findlay et al., 1991; Schallenberg and Kalff, 1993) and increased bioturbation (Schaffner et al., 1997). Potential effects of temperature on the physicochemical and biological processes involved in PCB flux out of TIP sediments were examined based on current knowledge about the processes involved in PCB release from sediment, and available data for the Hudson River.

Near-surface sediments (0-5 cm) closely follow the temperature profile of the overflowing water (Lenk and Saenger, 1998; Clark et al., 1999). The Hudson River water varies in temperature from 0°C in the winter to 25°C in the summer months

(Ashizawa and Cole, 1994), and correspondingly the near-surface sediment temperature varies approximately from 0 to 25°C. Temperature variations over this range can significantly affect physicochemical processes such as solubility, desorption, and diffusion, as well as microbial and macrobenthic organism processes.

PCBs become more soluble in water as temperature increases (Burkhard et al., 1985; Dickhut et al., 1986; Shiu et al., 1997). Dickhut et al. (1986) observed significant effects on PCB solubility over the ambient temperature range (4 to 32°C). For example, 3,3',4,4'-tetrachlorobiphenyl solubility increased by an order of magnitude from 4 to 32°C. Shiu et al. (1997) measured aqueous solubilities for mono, di, tri, tetra, and hexa chlorinated PCB congeners and found that from 5 to 25°C aqueous solubilities increased by an average of 50%.

The rate and extent of desorption of PCBs from the sediment to the pore water will be higher at 25°C than at 0°C. Congener-specific PCB desorption studies have found that from 10 to 40°C desorption rate coefficients can increase by up to one order of magnitude (Ghosh et al., 1999). Butcher et al. (1998) found the desorption rate coefficients increase consistently with temperature from 0 to 35°C, by a factor of 3-4 in Hudson River sediment.

Diffusion of PCBs through sediment pore water and across the sediment water interface can increase significantly over the ambient temperature range. The Wilke-Chang equation (Wilke and Chang, 1955) for estimating diffusion coefficients for small concentrations of a dissolved chemical in water has a strong temperature dependence.

$$D = 7.4E - 8\frac{(\Psi M_w)^{\frac{1}{2}}T}{\mu V^{0.6}} \tag{1}$$

In this equation, D is the diffusion coefficient in $cm^2$/sec, $\Psi$ is an association parameter for the solvent, $M_w$ is the molecular weight of the chemical, T is the absolute temperature in K, $\mu$ is viscosity of the solution in centipoise, and V is the molar volume of the solute in $cm^3$/mol. From Equation 1 it is apparent that as temperature increases, the aqueous diffusion coefficient increases. For a mono-chlorinated biphenyl (molecular weight = 189 g/mole) in water, the aqueous diffusion coefficient will double from 0 to 25°C. McDonough and Dzombak (2005) found that from 15 to 25°C in autoclaved (no biological activity) Grasse River sediment the average effective diffusion coefficient in sediment for 2,5-dichlorobiphenyl increased from 6.7 to 10.0 x $10^{-9}$ $cm^2$/sec, an increase of 33% for a 10°C temperature increase.

Microbial abundance and activity in freshwater sediments are temperature dependent. Bacterial abundance in freshwater sediment shows a strong correlation with temperature (Schallenberg and Kalff, 1993). Bacterial production and abundance in the Hudson River are maximum in the summer (July and August) and show a strong correlation with water column temperature (Findlay et al., 1991).

As mentioned previously, microbial activity can produce gas bubbles that can aid in the transport of PCBs through the sediment and across the sediment-water boundary layer. Gas bubble transport through and release from the sediment, referred to as ebullition, has been observed to be temperature dependent and to follow closely the sediment temperature profile (Martens and Klump, 1980; Kipphut and Martens, 1982). Martens and Klump (1980) observed gas bubble ebullition at temperatures between 17 and 27°C, and Kipphut and Martens (1982) observed gas bubble ebullition at temperatures between 14 and 30°C. McDonough and Dzombak (2005) found that at 25°C in Grasse River sediment the average effective diffusion coefficient for 2,5-dichlorobiphenyl was significantly higher in sediment with microbial activity ($57 \times 10^{-9}$ $cm^2$/sec) than in sediment with no microbial activity ($10 \times 10^{-9}$ $cm^2$/sec). McDonough and Dzombak attributed the increased effective diffusion coefficient to the significant amount of gas generation observed in sediment with microbes present.

Aerobic biodegradation of lower molecular weight PCBs in Hudson River sediment has been observed over the ambient temperature range. In laboratory sediment microcosms, aerobic biodegradation of PCBs was observed in the temperature range of 22 to 25°C (Fish and Principe, 1994). Williams and May (1997) spiked Hudson River sediment with Aroclor 1242 and found many of the di- and tri-chlorinated congeners were aerobically degraded at 4°C in Hudson River sediment, but were degraded 3 to 4 times faster at 25°C. In the Hudson River, in-situ aerobic PCB biodegradation in the sediment was observed over a temperature range of 10 to 28°C (Harkness et al., 1993).

Anaerobic dechlorination of PCBs in fresh water sediment is temperature dependent (Tiedje et al., 1993; Bedard and Quensen, 1995; Wu et al., 1996; Wu et al., 1997). Wu et al. (1997) found that the optimal temperature range for dechlorination in Woods Pond Sediment (Lenox, MA) was 20 to 27°C. Wu et al. (1996) also found profound differences in PCB dechlorination rate and extent as a function of temperature in two freshwater sediments, Woods Pond and Sandy Creek Nature Center Pond (Athens, GA). In Sandy Creek sediment, the maximum observed rate of dechlorination occurred at 30°C and decreased by 46% at 27°C, 70% at 18°C, and 87% at 12°C. In Woods Pond sediment, the maximum observed rate of dechlorination remained within 15% of the highest observed value (at 30°C) over the broad temperature range of 20 to 34°C but then decreased by 72% at15°C and 93% at 8°C. Dechlorination of PCBs in Hudson River sediment occurred roughly twice as fast at 25°C than at 12°C (Tiedje et al., 1993).

Bioturbator abundance and activity depend upon many factors of the ecological habitat including temperature. Macroinvertebrate abundance in Hudson River sediment has been correlated with temperature with the peak abundance occurring in July or August (Strayer and Smith, 2000). Bioturbation activities have been observed to decrease in the colder temperatures observed during winter months (Dellapenna et al., 1998). In a laboratory study, Schaffner et al. (1997) found bioturbation to be temperature dependent with no mixing of the sediment at 12°C and significant sediment mixing due to bioturbation at 22°C.

Increased water and near-surface sediment temperature leads to increased microbial abundance and activity, increased gas bubble ebullition, and increased PCB dechlorination and degradation. The increased temperature during the late spring and early summer months also leads to increased bioturbation and increased rates of physicochemical PCB release processes such as solubilization and diffusion. Thus, all of the temperature-dependent processes governing PCB release from sediments contribute to the low-flow, increased release of PCBs from the sediment to the water column during the late spring to early summer months.

## DISCUSSION OF THE FACTORS INFLUENCING LOW-FLOW PCB RELEASE

Results of the evaluation of environmental factors potentially influencing the processes responsible for the increased flux of PCBs out of Hudson River sediment into the water column during the low-flow late spring to early summer months as compared with other times of the year are summarized in Table 1. Physicochemical transport processes can be both enhanced and impeded by increased sediment organic matter. Microbial abundance increases with increased sediment organic matter. However, maximum bioturbation occurs in sediment with intermediate organic carbon content (1.4% organic carbon). The seasonality of sediment organic matter levels (higher levels in the fall then in the late spring) does not coincide with the increased PCB release in the late spring to early summer months and its effects on PCB release from the sediments may not lead to an increased PCB water column loading in the late spring to early summer months. Nitrogen is limited in TIP but its seasonality (higher levels in the fall than in the late spring) does not coincide with the increased PCB release in the late spring to early summer months.  From the data on nutrients and organic matter it is does not appear that they are controlling the increased release of PCBs from the sediment to the water column in the late spring to early summer months. The seasonal variation of sediment temperature does coincide with the increased PCB release in the late spring and early summer months, as temperature affects most of the processes involved in the release of PCBs from the sediment to the water column. Temperature data indicate that elevated water and near-surface sediment temperature is the primary factor governing increased release of PCBs from the sediment to the water column in the TIP under low-flow conditions in the late spring to early summer months.

The increased sediment-water column PCB loading in TIP initially follows the temperature profile and then decreases while the temperature remains elevated (Figure 2). This profile suggests that temperature has a strong influence on the increased loading during the late spring to early summer months. The reason that the loading does not remain elevated throughout the summer months is not clear but the data indicate that a depletion process is occurring. One possible explanation is that spring high flow events redistribute the PCBs in the sediment, re-contaminating the depleted surface sediment with PCBs, and as the temperature increases the rates of biological and physicochemical release processes increase, resulting in an increased loading of PCBs to the water column. After the initial release, the surface sediment is again depleted and the loading returns to the levels observed during the rest of the year.

## CONCLUSIONS

Multiple, inter-related processes occur in river sediments and influence PCB release, and environmental factors, including temperature and availability of organic matter and nutrients, govern the rates of these processes. From analysis of current knowledge related to the PCB release processes and how they are affected by environmental factors, and from analysis of data for the Upper Hudson River, it appears that the near-surface sediment temperature is the primary environmental factor governing the increased loading of PCBs from the sediment to the water column under low-flow conditions during the late spring to early summer months in the TIP. The supply of essential nutrients and a food source, such as phosphorus, nitrogen, and organic matter affects biological activity in sediment and associated PCB transformation and transport. From the available data it appears that sediment organic matter and total nitrogen are seasonally variable in TIP, with higher concentrations in the fall than in the late spring, but their seasonal variability does not coincide with the increased release of PCBs from the sediment to the water column in the late spring to early summer months.

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Table 1. Environmental factors and their effects on the physicochemical, microbial, and bioturbator processes contributing to the increased release of PCBs from the sediment to the water column under low-flow conditions in the Thompson Island Pool, Hudson River.

| **Environmental Factors** | **Seasonal Variability** | **Effects on PCB Release Mechanisms** |
|---|---|---|
| Organic Matter | Limited data, significant spatial variability in TIP sediment data with higher TOC levels in the fall than in the late spring | Increased organic matter leads to:<br>Physicochemical Processes<br>• Increased pore water colloidal particles increasing PCB transport<br>• Increased sediment bound organic matter, decreasing PCB transport<br>Microbial Processes<br>• Increased activity and abundance<br>Bioturbator Processes<br>• Max bioturbation rates occur in sediment of intermediate levels |
| Essential Nutrients | Limited data, sediment data indicate that nitrogen is limited in the surface sediments with higher levels in the fall than in the late spring | Essential for cell synthesis and growth: affects microbial and bioturbator abundance and activity |
| Temperature | Varies from 0°C in winter to ~25°C in summer months | Increased temperature leads to increased:<br>Physicochemical Processes<br>• Solubilization<br>• Diffusion<br>• Desorption<br>Microbial Processes<br>• Activity and abundance<br>• Gas bubble ebullition<br>• PCB biodegradation<br>Bioturbation<br>• Activity and abundance<br>• Mixing rates |

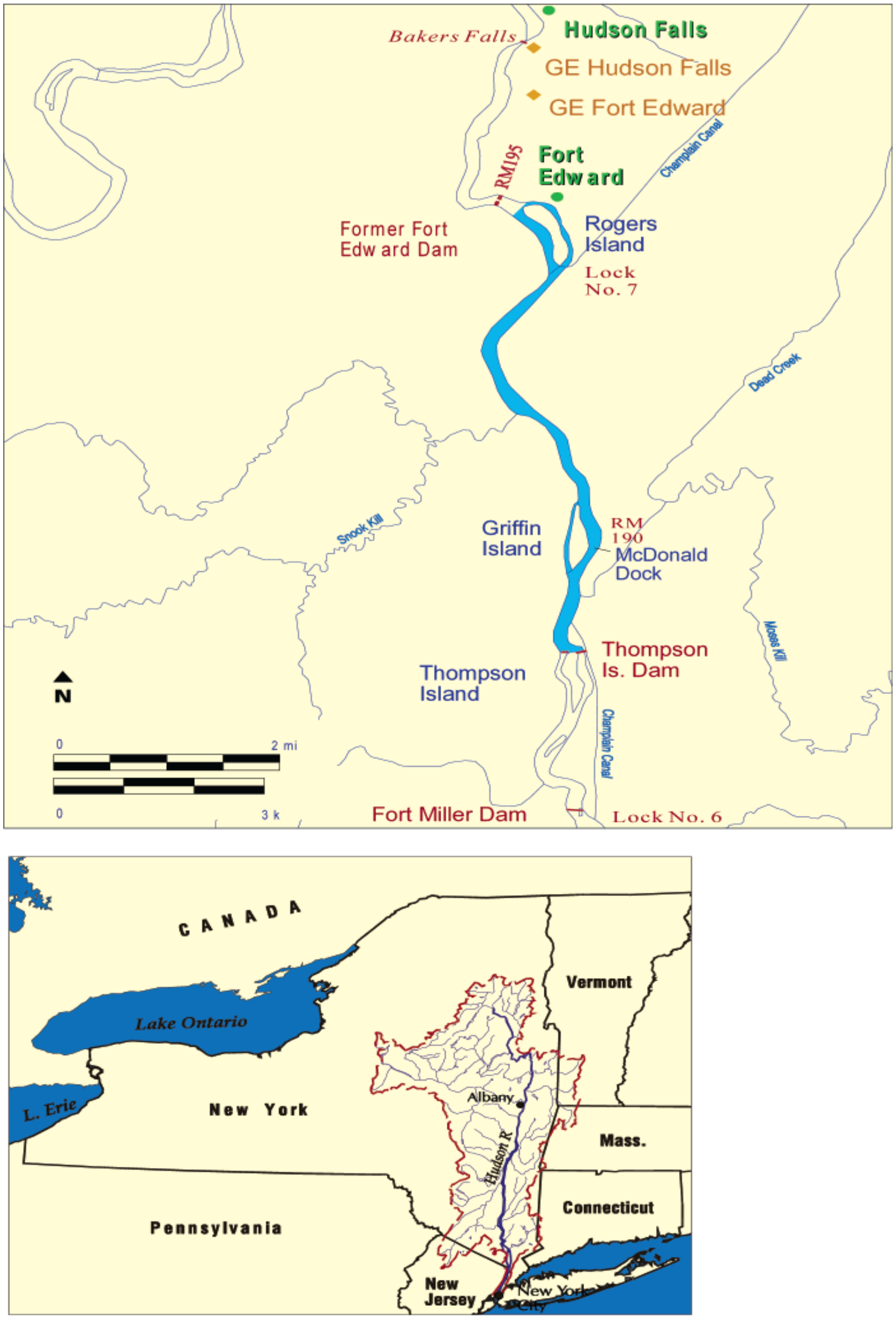

Figure 1. Site map of the Thompson Island Pool, Hudson River, New York. Reprinted with permission from Erickson et al., 2005 (Erickson et al., 2005). Copyright 2005 American Chemical Society.

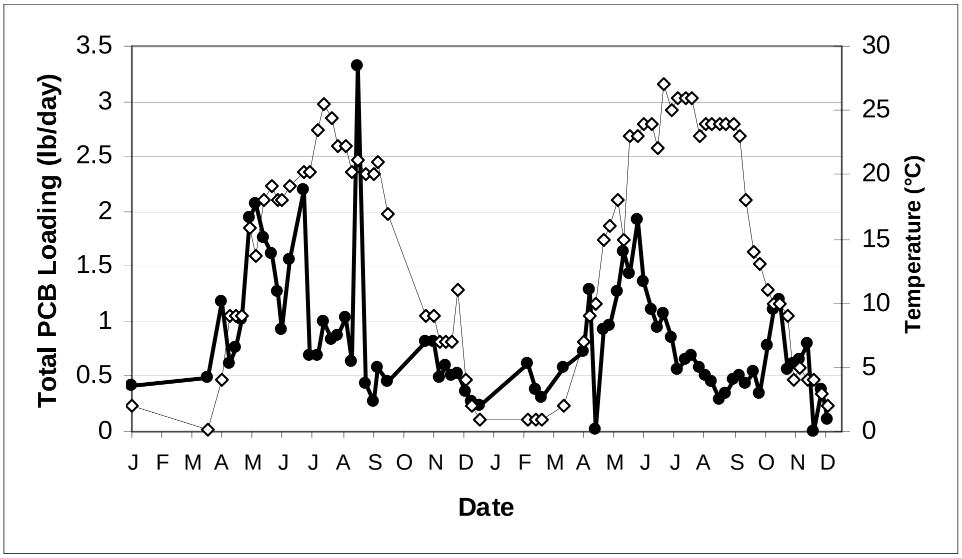

Figure 2. Total PCB loading (●) from the Thompson Island Pool sediment (based on non-filtered water column data) under low-flow conditions (<283 $m^3$/sec (10,000 cfs)) and water column temperature (◊) in 1998 and 1999. The plot shows increased loading of PCBs under low-flow conditions in May and June. Data from General Electric's Hudson River database obtained from Quantitative Environmental Analysis, Liverpool, NY, 2001.

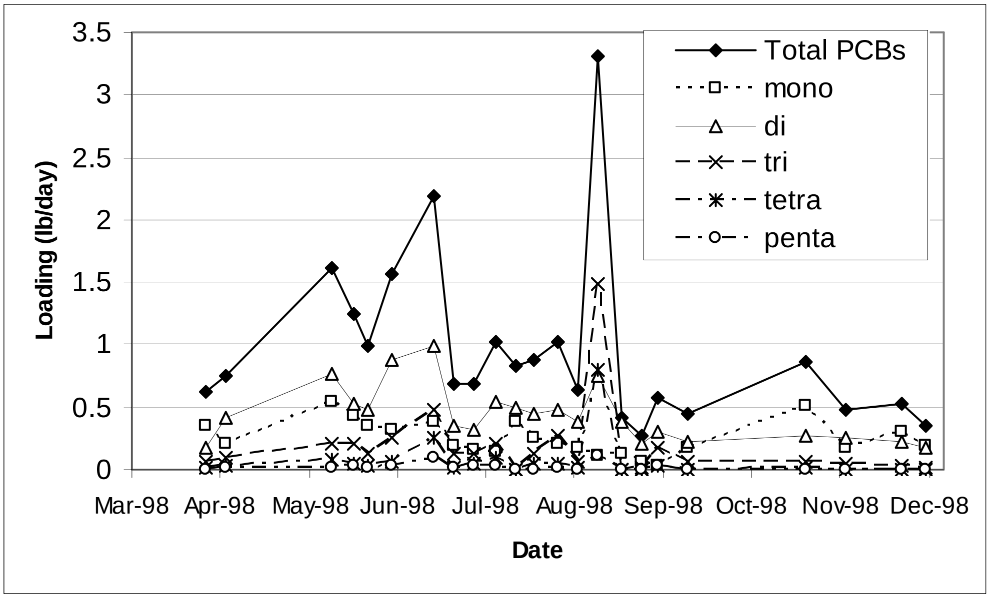

Figure 3. Total PCB and homolog loading from the Thompson Island Pool sediment under low-flow conditions (<283 $m^3$/sec (10,000 cfs)) in 1998. Data from General Electric's Hudson River database obtained from Quantitative Environmental Analysis, Liverpool, NY, 2001.

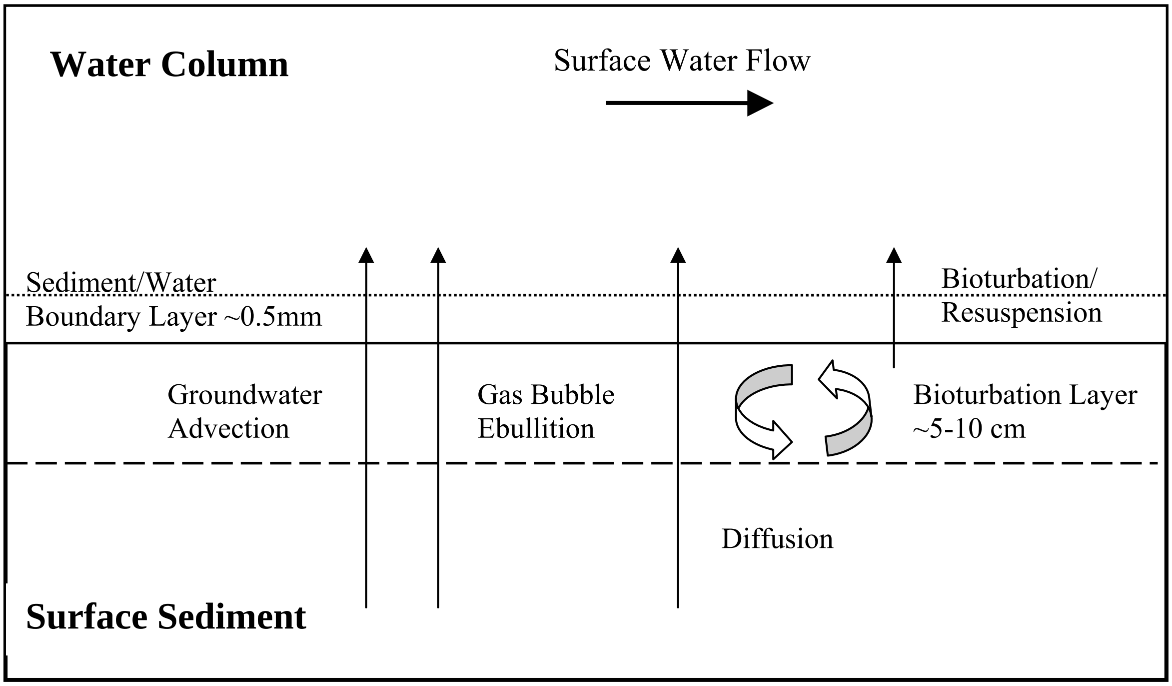

Figure 4. Some possible PCB transport processes from the sediment to the water column under low-flow conditions. Drawing not to scale.

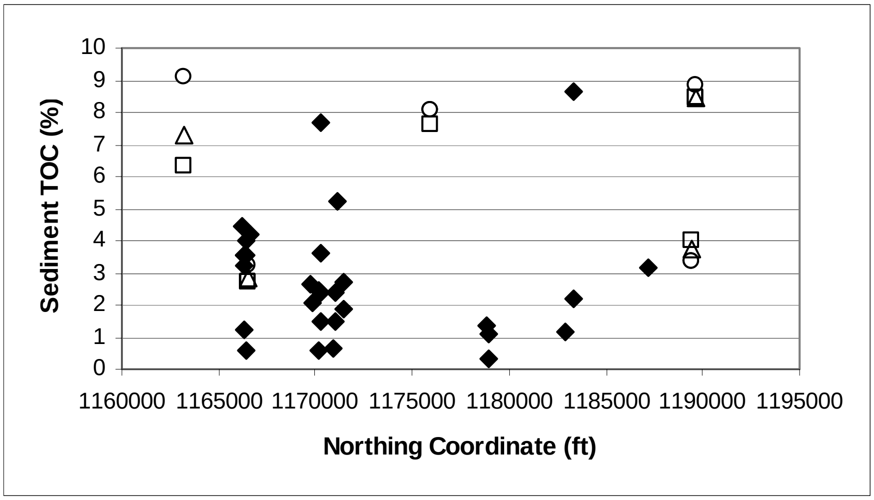

Figure 5. Surface sediment total organic carbon (TOC) data for various locations in Thompson Island Pool (TIP), Hudson River, NY. Data from two studies: May 27 to June 2, 1992 (♦) 0-5 cm samples and Oct. 21 to Nov. 4, 1992 (samples analyzed in 0-2 cm (○), 2-4 cm (□), and 4-6 cm (Δ) segments. Northing coordinates according to the 1927 NY State Plane Coordinate System. Data from EPA Hudson River Database v 5.0 obtained from Quantitative Environmental Analysis, Liverpool, NY, 2001.

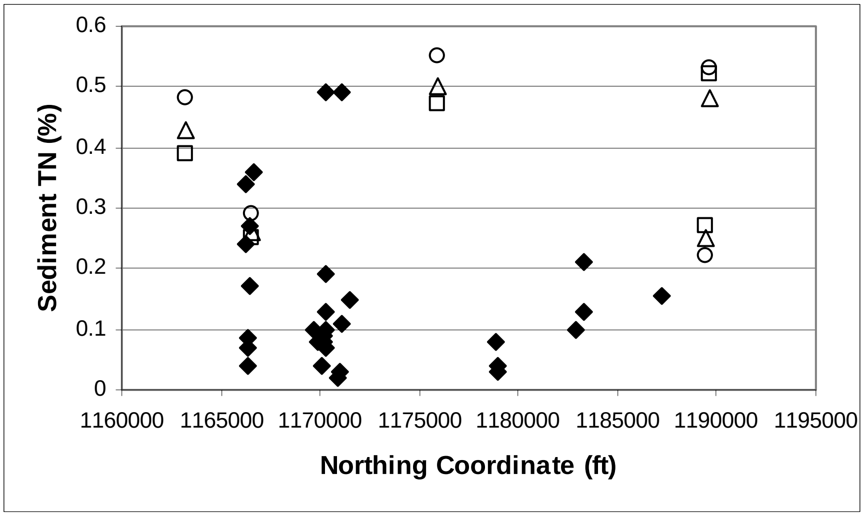

Figure 6. Surface sediment total nitrogen (TN) data for various locations in Thompson Island Pool (TIP), Hudson River, NY. Data from two studies: May 27 to June 2, 1992 (♦) 0-5 cm samples and Oct. 21 to Nov. 4, 1992 (samples analyzed in 0-2 cm (○), 2-4 cm (□), and 4-6 cm (Δ) segments. Northing coordinates according to the 1927 NY State Plane Coordinate System. Data from EPA Hudson River Database v 5.0 obtained from Quantitative Environmental Analysis, Liverpool, NY, 2001.

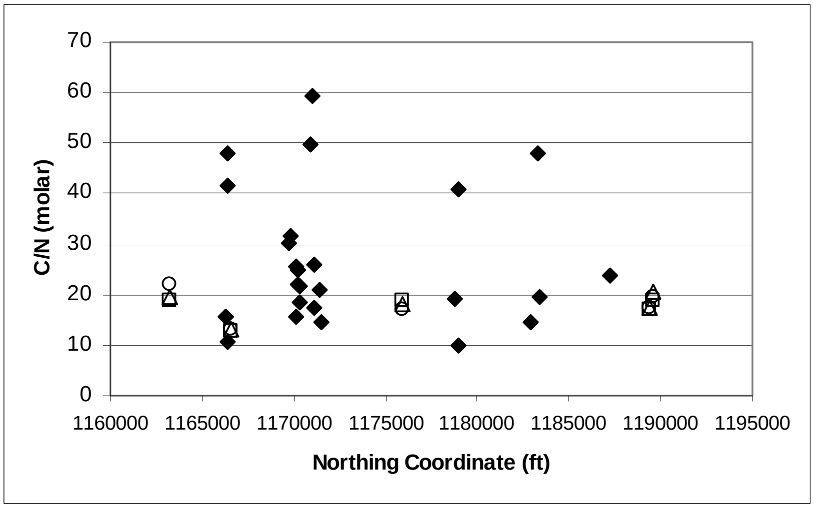

Figure 7. Surface sediment carbon to nitrogen ratio (C/N) data for various locations in Thompson Island Pool (TIP), Hudson River, NY. Data from two studies: May 27 to June 2, 1992 (♦) 0-5 cm samples and Oct. 21 to Nov. 4, 1992 (samples analyzed in 0-2 cm (○), 2-4 cm (□), and 4-6 cm (Δ) segments. Northing coordinates according to the 1927 NY State Plane Coordinate System. Data from EPA Hudson River Database v 5.0 obtained from Quantitative Environmental Analysis, Liverpool, NY, 2001.