PCB Concentrations in Fish Following Partial Remediation of a Small Hazardous Waste Site

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Abstract

A small, PCB-contaminated hazardous waste site at the downstream end of the Sherman Island Pool of the upper Hudson River (New York) was partially remediated in 1996. Remediation included removal of contaminated on-site soil and adjacent sediment along the river shoreline that was exposed while the water level in the pool was lowered by four feet during the remediation.

Annual fish monitoring over a ten year period from several locations within the pool, including stations downstream and directly across the pool from the site, demonstrated that PCB contamination in fish in the immediate vicinity of the site was reduced following remediation. However, PCB contamination remains in the river sediment adjacent to the site and elevated PCB concentrations continue to be observed in fish collected at the station adjacent to the site, particularly in small fish. We used a multiplicative equation to model PCB concentrations in several species of fish as a function of collection location and time period, lipid content, and length. Multiple linear regression techniques were used to examine differences in geometric mean PCB concentrations among locations and species and to further describe and test for differences in temporal trends among locations and species.

PCB concentrations in several fish species declined following remediation, particularly in the station adjacent to the site, and differed among locations for each species within the relatively small spatial scale of the pool. Mean concentrations in fish from the station directly adjacent to the site, except for large yellow perch, were much higher than other locations within the pool during the same time-step. The results of our analysis suggest that long-term monitoring strategies that do not adequately consider spatial and temporal differences in concentration may mask the importance of localized contamination and reduce the ability to discern temporal changes in fish concentrations following remediation or natural recovery.

Introduction

The Sherman Island Pool, the reservoir created by the Sherman Island Dam on the Upper Hudson River, is approximately 210 miles upstream of the Battery in New York Harbor and 3.6 miles (5800 m) long by 700 to 800 feet (230 m) wide. The "Queensbury" site, a 0.75 acre area near the downstream end of the Sherman Island Pool with approximately 150 meters of shoreline, was designated by New York State Department of Environmental Conservation (NYSDEC) as a hazardous waste site in 1989 (Parsons 1994). The contaminated area resulted from the disposal of PCB-laden dielectric fluid from capacitors and cooling oil from transformers on the ground. Subsequent runoff and discharge from the disposal practices led to significant contamination of the soils on-site and adjacent sediments of the river. Interim remedial measures for on-site soils were conducted at the site prior to 1992; however, sediment and fish samples collected in the vicinity of the site in 1992 and 1993 showed highly elevated PCB concentrations.
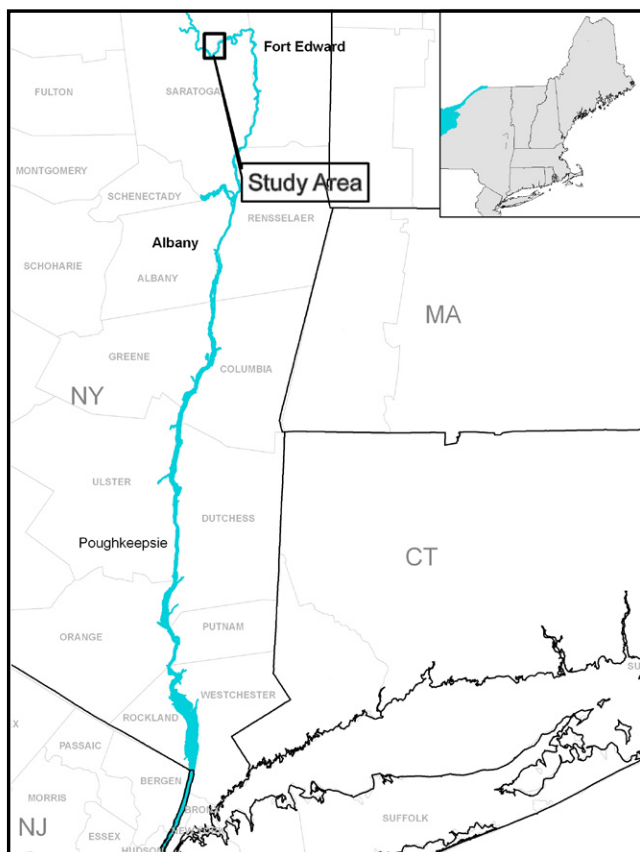
Remedial action took place in the summer of 1996. Cleanup levels for soil of one ppm in the top foot and ten ppm in subsurface soil resulted in the removal of 3,500 cubic yards. Nearshore sediments were excavated in the dry to a depth of two feet and backfilled with clean fill while the reservoir was lowered about four feet for a period of two weeks. The excavation included an area of PCB-contaminated sediment near the mouth of a culvert that exceeded 50 ppm. Remaining contaminated sediment areas, including approximately 0.05 acres exceeding 50 ppm and 4.4 acres exceeding one ppm, were designated as a second Operable Unit (Foster Wheeler 2003).

Species		Queensbury			Sherman Island Pool		
Fillet	Time-Step	Total PCB (mg/kg, wet wt.)	Total PCB (mg/kg, Lipid)	Number of Samples	Total PCB (mg/kg, wet wt.)	Total PCB (mg/kg, Lipid)	Number of Samples
Smallmouth Bass	1	0.86 (0.32-1.21)	93 (37-159)	5	0.20 (0.01-0.91)	22 (0.72-152)	28
Smallmouth Bass	2	0.40 (0.05-1.57)	43 (3.13-224)	23	0.08 (0.02-0.77)	7.20 (2.90-26)	60
Smallmouth Bass	3	0.22 (0.02-0.64)	43.75)	25	0.05 (0.01-0.20)	5.96 (1.25-30)	47
Rock Bass	1	1.49 (0.05-5.60)	167 (3.57-560)	8	0.07 (0.01-0.26)	8.27 (1.89-21)	35
Rock Bass	2	0.33 (0.05-2.52)	46 (4.27-381)	21	0.05 (0.02-0.12)	5.87 (0.52-14)	72
Rock Bass	3	0.20 (0.02-0.70)	17.4 (0.81-74)	25	0.05 (0.01-0.20)	5.11 (0.49-18)	52
Yellow Perch	1	0.18 (0.02-0.84)	34 (2.00-205)	15	0.18 (0.05-0.84)	32 (3.13-220)	31
Yellow Perch	2	0.18 (0.02-0.97)	20 (3.47-156)	27	0.05 (0.02-0.15)	5.70 (1.15-22)	83
Yellow Perch	3	0.09 (0.02-0.34)	12.5 (2.27-71)	33	0.02 (0.01-0.13)	3.24 (0.67-24)	54
Whole Body							
Smallmouth Bass	1	6.87 (2.04-11.3)	471 (102-870)	4	0.13 (0.09-0.16)	8.31 (4.45-10.9)	4
Smallmouth Bass	3	0.35 (0.05-0.96)	16.4 (2.36-55)	21	0.09 (0.03-0.32)	4.88 (1.88-19.7)	33
Rock Bass	1						
Rock Bass	3	0.40 (0.04-0.94)	14.3 (1.19-33)	38	0.09 (0.02-0.30)	3.65 (0.46-11.8)	59
Yellow Perch	1	10.5 (2.39-19.3)	253 (80-470)	4	0.14 (0.10-0.20)	3.47 (3.10-3.74)	4
Yellow Perch	2	9.76 (0.15-33.7)	495 (7.13-1696)	5	0.09 (0.07-0.12)	3.64 (2.85-4.11)	3
Yellow Perch	3	0.35 (0.03-1.02)	18.3 (1.16-54)	16	0.07 (0.01-0.11)	3.87 (0.91-11.9)	28
Sunfish	1	23.76	766	1			
Sunfish	2	5.26	289	1	0.08 (0.07-0.10)	3.58 (3.00-4.45)	3
Sunfish	3	0.27 (0.26-0.28)	9.5 (9.1-9.9)	2			
Forage Fish	1	6.24 (4.72-7.48)	371 (196-502)	3	0.10 (0.09-0.12)	2.95 (2.89-3.06)	3
Forage Fish	3	0.58	11	1			

Objective

Our objective is to evaluate temporal and spatial changes in PCB concentrations in several species of large and small fish from multiple sampling locations following partial site remediation.
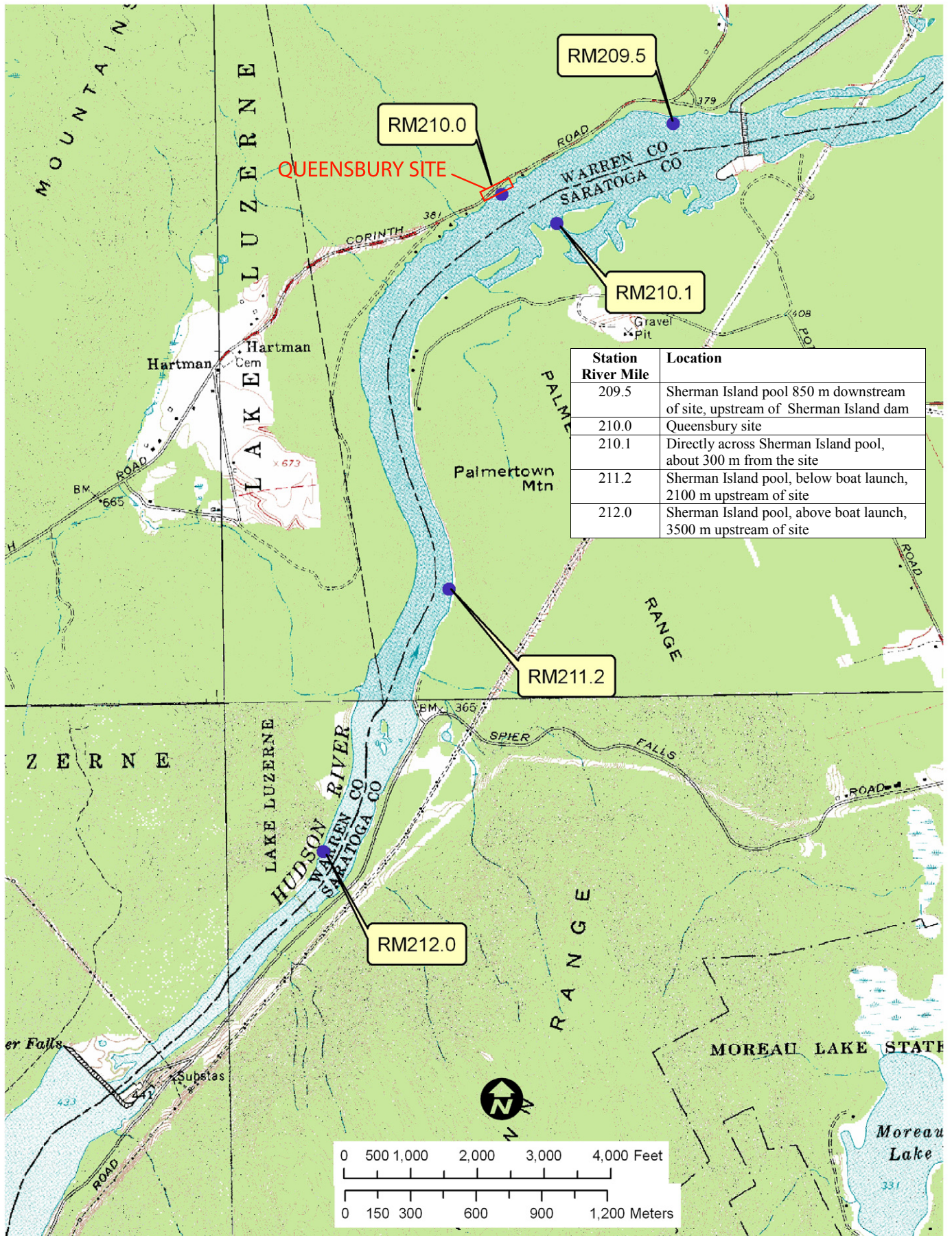
Overview of approach

Polychlorinated biphenyls (PCBs) and other lipophilic organic contaminant concentrations in fish tissues are typically "normalized" by dividing PCB concentration (C_f) by percent lipid (Fat). This approach relies on two assumptions:

- PCB concentrations in fish tissue from a given area are expected to be proportional to lipid content; and
- Lipid-normalized PCB concentrations are expected to have lower variability.

Hebert and Keenleyside (1994) found that neither of these assumptions held for their sample data and proposed an alternative procedure based on linear regression. In this paper we apply a modification of this approach that does not require either a linear relationship between PCB concentration and lipid or a normal distribution.

Figure 1

RM209.5

RM210.0

QUEENSBURY SITE

RM210.1

RM211.2

RM212.0

Station River Mile	Location
209.5	Sherman Island pool 850 m downstream of site, upstream of Sherman Island dam
210.0	Queensbury site
210.1	Directly across Sherman Island pool, about 300 m from the site
211.2	Sherman Island pool, below boat launch, 2100 m upstream of site
212.0	Sherman Island pool, above boat launch, 3500 m upstream of site

0 500 1,000   2,000   3,000   4,000 Feet

0   150 300   600   900   1,200 Meters

Methods

Most fish were collected under contract to Niagara Mohawk Power Company (NMPC) by Parsons Engineering Company personnel with assistance from NYSDEC. Methods for fish collection and sample processing followed standard protocols for sample handling and maintaining chain-of-custody as outlined by NYSDEC (Sloan et al. 2002, 2005) and Parsons (2006). Principal target species included smallmouth bass (Micropterus dolomieui), rock bass (Ambloplites rupestris), and yellow perch (Perca flavescens). Other species used in the analysis to supplement the available small fish, whole body sample data include two species groups: sunfish, which include pumpkinseed (Lepomis gibbosus) and bluegill (Lepomis macrochirus); forage fish, which include several minnow and darter species (Cyprinid spp., Notropis atherinoides, Notropis hudsonius, Luxilus cornutus), fallfish (Semotilus corporalis), and logperch (Percina caprodes)]. Fish were captured primarily with variable mesh gill nets and electro-shocking.

Fish samples were collected in the summer from five stations in the Sherman Island Pool between 1992 and 2005 (Figure 1; Table 1). Large fish (individual fillet samples) were collected annually at three stations (RM209.5, RM210.0, RM210.1) from 1995-2005 and two additional upstream stations (RM211 and RM212) from 1995-2000. Small fish (whole body, mostly individual samples but some composites of similarly-sized fish to ensure sufficient tissue mass for analysis) were collected in 1993 and annually from the three principal stations from 2001-2005. The target sample size was five samples per location for each species. Target sample size was not always achieved; also, additional samples were analyzed by NYDEC in some cases. To take into account the changes in sample collection strategy and to increase sample size for the statistical comparisons, data were grouped into three time-steps: "Baseline" (pre-removal) 1992-1996 (note that sediment remediation in 1996 took place in late August, after fish collections were completed for the year); "Post_1" 1997-2000; and, "Post_2" 2001-2005.

Chemical analysis

Most of the fish in the database were collected by NMPC contractors and analyzed for PCBs using standard Aroclor analytical methods (SW-846 Method 8082) and percent lipids ((Parsons 2006). Total PCBs represented the sum of detected Aroclors or congeners. Detection limits were mostly less than or equal to 50 ng/kg.

Mathematical Framework

PCB concentrations are typically normalized by dividing by percent lipid content, but this approach includes some underlying assumptions that are typically not tested.

- Lipid-normalized concentrations can be thought of as a regression between concentration and fat.

$$R = C_f / fat \Leftrightarrow C_f = R \times fat + \varepsilon$$

- In this paper, we use a more flexible multiplicative model that does not require assumption of a linear regression through the origin:

$$\log(C_f) = \beta_0 + \beta_1 \log(fat) + \varepsilon \Leftrightarrow C_f = e^{\beta_0} fat^{\beta_1} e^{\varepsilon},$$

- The null hypothesis: tests the linearity assumption of the usual lipid-normalization method.

$$H_0 : \beta_1 = 1.0$$

- Other factors such as fish length can be included and tested. Lipid- and length-adjusted spatial and temporal comparisons of PCB concentrations in fish tissue are made by adding additional terms to the model:

$$\log(C_f) = \mu + \mu_{Time \times Location} + \gamma_1 \times \log(fat) + \gamma_2 \times \log(Length) + \varepsilon$$

- This is often termed an "analysis of covariance," because effects are adjusted for "covariation" with continuous variables such as lipid and length. Spatial and temporal comparisons were adjusted using the Tukey–Kramer multiple comparison procedure (Kramer, 1956).

Results and Discussion

Data

Limitations in the available data made it necessary to group samples into three time periods: Baseline represented samples collected between 1992 and 1996. The Post_1 time-step represented four years, from 1997-2000. During this period, large fish were sampled annually at five stations within the Sherman Island Pool and small fish were only collected incidentally. The Post_2 time-step represented samples collected between 2001 and 2005. During this period, both large and small fish were sampled at three stations. Table 2 shows the arithmetic mean and range of total PCB concentrations (wet weight and lipid-normalized) number of samples collected and used in this analysis by species, location, and time-step.

Model Results

Lipid: Log-transformed PCB concentrations were positively but nonlinearly associated with percent lipid in smallmouth bass, rock bass, and yellow perch for both large and small fish, although the slopes of the relationships varied. These relationships were significant ($p<0.05$) for all except small yellow perch ($p=0.16$). Because the upper confidence limits for the log-lipid regression coefficients are less than 1.0, the assumption of linearity between PCB and percent lipid does not hold for these species in the Sherman Island Pool.

Length: Log-transformed PCB concentrations were not significantly associated with log length in either large or small fish. Consequently, length was not included in the models used to evaluate temporal and spatial differences.

Predicted versus Observed
Model predictions of total PCB concentrations correlated well with observed results in both large and small smallmouth bass, rock bass, and yellow perch (Figure 2).

Figure 2
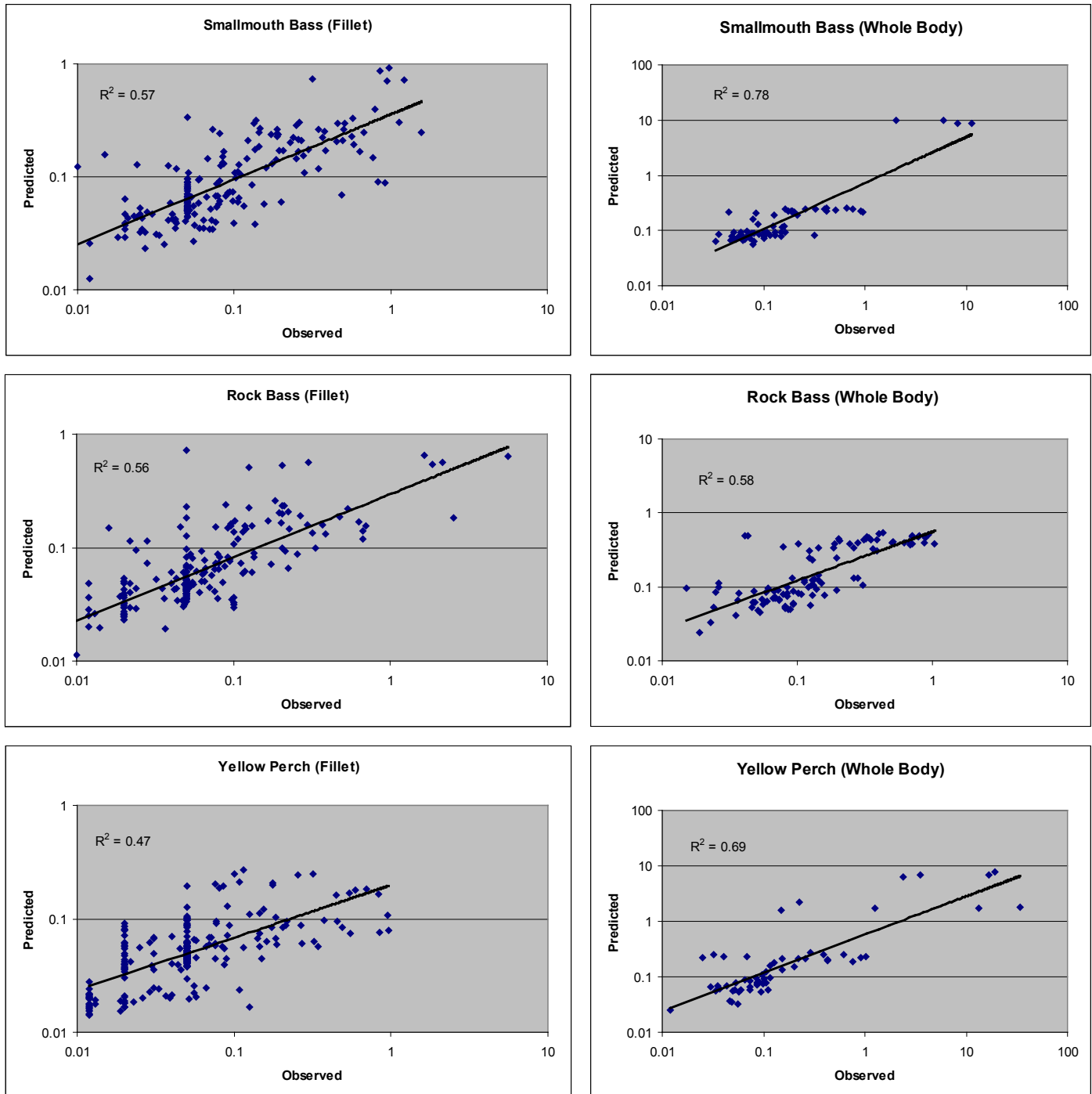
Temporal comparisons within species by station

Large fish: Estimated mean PCB concentrations in large smallmouth bass decreased from baseline with each time-step at the site (RM210.0) and the two stations closest to the site (RM209.5 and RM210.1) (Figure 3). The differences were statistically significant (p<0.05) at the second time-step. No differences were observed at the other two stations (RM211.2 and RM212.0).

Estimated mean PCB concentrations in rock bass decreased significantly (p<0.05) from baseline with each time-step at the site and at the second time-step at the station directly across the reservoir from the site (RM210.1) (Figure 3). No temporal differences were observed for the other three stations.

Yellow perch showed a different pattern than the other two species. Baseline concentrations at the site were lower than for the other two species. Estimated mean concentrations decreased significantly from baseline with each time-step at the station downstream of the site (RM209.5). None of the other stations showed any significant temporal differences.

Small fish: Temporal comparisons were limited by the available data for the small fish (whole body). Smallmouth bass and yellow perch showed significant decrease in concentration at the site between baseline and the Post_2 time period (Figure 4). No baseline samples were available for small rock bass.

Because of the limited data available for small fish, available data for whole body samples of smallmouth bass, rock bass, yellow perch, sunfish (pumpkinseed and bluegill), and forage fish (several species) were combined using a "species smash" approach (Sloan et al. 2005). The results of this analysis showed that estimated concentrations at the site declined during each of the time-steps, but remained higher than the other stations at each time-step (Figure 5). The model showed no differences between species groups when lipid, time-step, and location were included in the model.

Spatial comparisons within species comparisons by station and time-step

Large fish: Baseline (1995-96) estimated, geometric mean PCB concentrations in large fish (fillet samples) adjusted for one percent lipid adjacent to the site (RM210.0) were significantly higher than the other four Sherman Island Pool locations for smallmouth bass and rock bass, but not for yellow perch (Figure 3). For the Post_1 time period (1997-2000), estimated concentrations continued to be significantly higher at the site than the other four stations for smallmouth bass and rock bass. PCB concentrations in yellow perch at the site were slightly higher than other stations. For the Post_2 time period (2001-2005), only two stations other than the site were sampled. In all three species, concentrations at the site remained higher than at the other two stations.

Small fish: Small fish (whole body samples) were collected for baseline for smallmouth bass and yellow perch, but not for rock bass. Except for a few incidental samples during the Post_1 period, small fish were collected from three stations in Post_2. Baseline concentrations at the site were significantly (p<0.0001) higher than baseline concentrations at RM212 in smallmouth bass and yellow perch (Figure 4). No baseline data were available from other stations. Estimated PCB concentrations at the site were significantly (p<0.0001) higher for the Post_2 time-step than concentrations at RM209.5 and RM210.1 in smallmouth bass and rock bass. Post_2 concentrations for yellow perch at the site were similar to Post_2 concentrations at RM209.5 (p=0.16), but were significantly higher than Post_2 concentrations at RM210.1 (p<0.01).

Reach Averaging
Common practice in monitoring fish PCB concentrations in riverine or estuarine environments is to treat a geographic section (e.g., a river reach) – sometimes defined by dams at the upstream and downstream ends – as a single analysis unit. Fish may be collected from single or multiple discrete locations or without regard for location within the reach. Our results suggest that in cases where localized areas of contamination exist within the reach, the potential for bioaccumulation may be underestimated.

To illustrate this issue, estimated PCB concentrations for each species (fillet samples) were compared for the station adjacent to the site (RM210.0) with concentrations from the combined results from the other Sherman Island Pool stations (Figure 7). The results indicate that an average concentration from stations other than adjacent to the site would not capture the elevated concentrations at the site in smallmouth bass and rock bass or the temporal changes following the remediation.

Statistical Modeling Approach
The multiplicative model used to analyze these data provided a framework to test important hypotheses in the presence of potentially confounding factors. When the dependent variable and the continuous independent variables are log transformed, the assumption that PCB concentration is linearly related to independent covariates such as lipid can be tested. The usual linear regression through the origin is a special case of the more general multiplicative model. Using this model framework, we found that lipid content was the primary driver of variation in PCB content and that variation in lipid content tended to mask effects when viewed in terms of unadjusted wet weight concentrations. Subsequent comparisons of PCB content among years and locations were conducted after adjusting for covariation with lipid.

Implications for monitoring

In the database used in our analysis, the numbers of fish in each species group were not always consistent by year and location. Missing data made it necessary to group across years to obtain adequate numbers of fish to estimate averages at each combination of locations and time-steps. Limited baseline data, particularly for small fish, made it impossible to consider annual variability during the baseline period. Our findings suggest that monitoring programs for fish designed to evaluate contaminated sediment sites and the effectiveness of remediation should include multi-year, multi-species baseline and post-remedial sample collection from discrete locations that take into account known areas of sediment contamination.

Conclusions

The on-site soil and partial sediment remediation conducted in 1996 at the Queensbury site resulted in a rapid decline in fish concentrations adjacent to the site and to a lesser degree elsewhere in the Sherman Island Pool.

PCB concentrations of large smallmouth bass and rock bass and all species of small fish collected from the station adjacent to the Queensbury site were consistently higher than other locations. Small fish PCB concentrations remain elevated adjacent to the site.

The multiplicative model provided a useful framework for statistical comparison of fish total PCB concentrations at different locations and time-steps, accounting for lipid and length.

The sampling strategy, which consisted of annual collections of multiple species from discrete locations within Sherman Island Pool, was successful in demonstrating the local impact of contaminated sediment on large and small fish and the reduction in fish concentrations following remediation. Using a reach-averaging approach to assess PCB contamination in fish would likely mask the impact from the contaminated site and recovery following remediation.
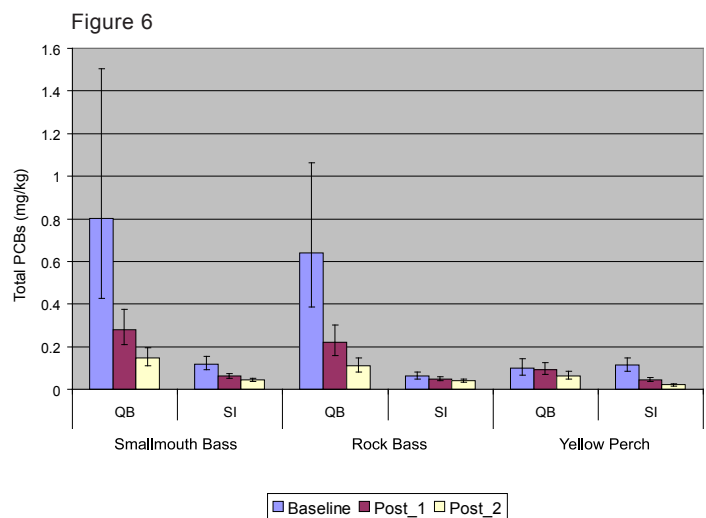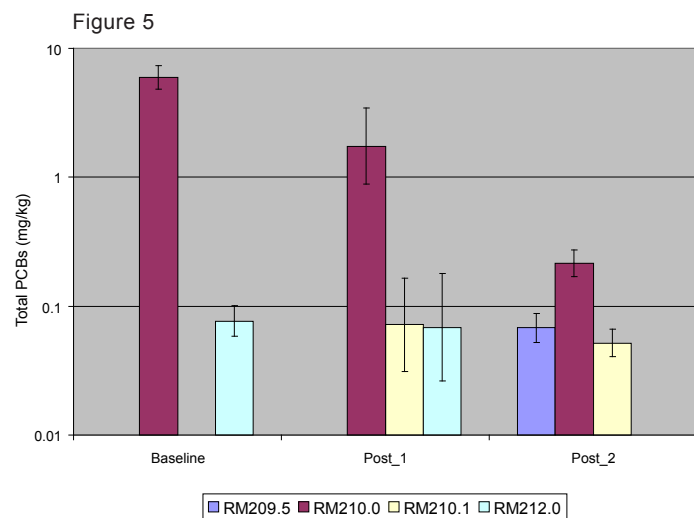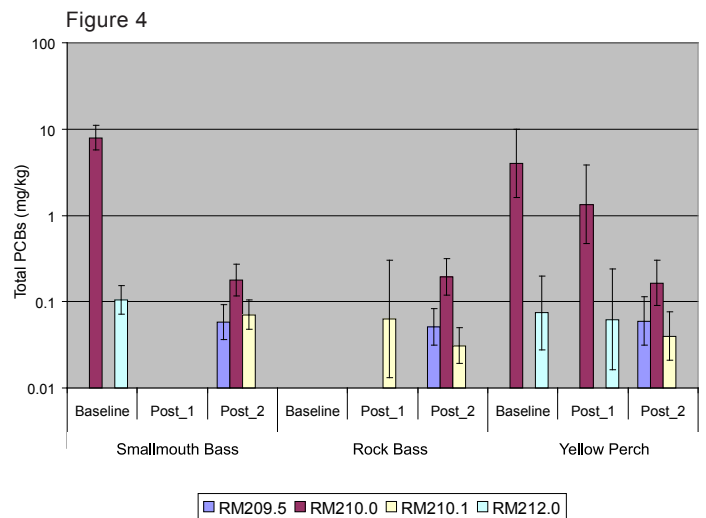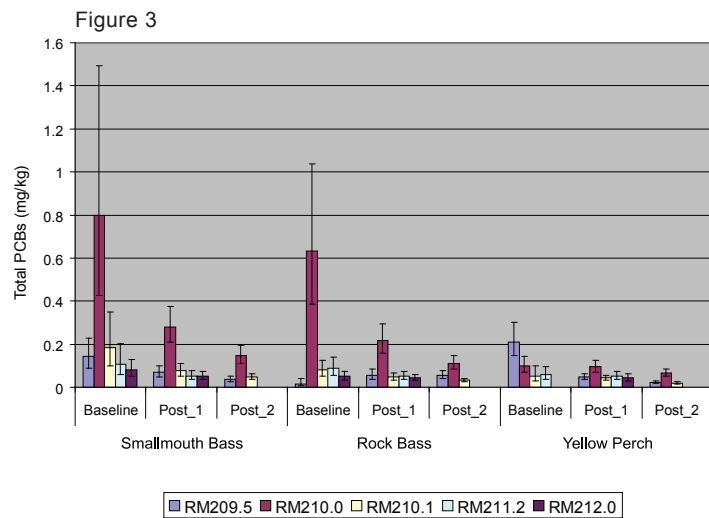
Figure 3

Figure 4

Figure 5

Figure 6

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Figures

Figure 1. Map of Hudson River (inset)

Figure 1. Map of Sherman Island Pool, showing sampling locations

Figure 2a.Observed versus predicted estimated PCB concentration (mg/kg) at 1% lipid in large fish (fillet) samples for smallmouth bass, rock bass, and yellow perch.

Figure 2b.Observed versus predicted estimated PCB concentration (mg/kg) at 1% lipid in small fish (whole body) samples for smallmouth bass, rock bass, and yellow perch.

Figure 3. Estimated geometric mean PCB concentration (mg/kg) and 95% confidence interval adjusted for 1% lipid in large fish (fillet samples) by species, location, and time-step.

Figure 4. Estimated geometric mean PCB concentration (mg/kg) and 95% confidence interval adjusted for 1% lipid in small fish (whole body samples) by species group, location, and time-step.

Figure 5. Estimated geometric mean PCB concentration (mg/kg) and 95% confidence interval adjusted for 1% lipid in small fish (whole body samples), all species combined, by location and time-step.

Figure 6. Estimated geometric mean total PCB concentration (mg/kg, wet wt.) and 95% confidence interval at 1% lipid in large fish (fillet samples) by species and time-step for Queensbury (QB) and other stations in the Sherman Island Pool (SI).

Tables

Table 1. Fish sampling locations within the Sherman Island Pool.

Table 2. Arithmetic mean (min, max) total PCBs (mg/kg wet wt), lipid-normalized PCBs (mg/kg lipid), percent lipid, length, and number of samples by tissue type, species, and time-step for the Queensbury site (QB) and all other stations in the Sherman Island Pool (SI).