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# Tributary Loadings of Priority Pollutants to Lake Ontario: A Prototype Approach Employing Surrogate Parameters

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TRIBUTARY LOADINGS OF PRIORITY POLLUTANTS TO  
LAKE ONTARIO: A PROTOTYPE APPROACH  
EMPLOYING SURROGATE PARAMETERS

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FINAL PROJECT REPORT  
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## 1. Project Description and Background

This project originated from a need for information on loading of persistent toxic pollutants to Lake Ontario from New York tributaries. The information is specifically required for the Lake Ontario Mass Balance Model, which is an integral part of the long-term Great Lakes research program (Domske, 1999; Swackhamer and Armstrong, 1987). The project was designed to demonstrate a cost-effective approach for estimation of loads of polychlorinated-biphenyls (PCBs) through use of a relatively small number of large-volume whole-water samples for PCB analysis. The Black River basin in north-central New York (Appendix A) was selected to demonstrate the feasibility of the approach because it is the largest New York contributor of PCBs to the Lake (LaMP, 2002; Litten, 1996; Litten et al., 1993; FLOWPA, 2000).

The Lake Ontario LaMP (2002) identified PCBs, mercury, dieldrin, DDT and its metabolites, mirex, and dioxins/furans as priority pollutants that are targeted for reduction to prevent, or reduce to acceptable levels, concentrations observed in the lake and its ecosystem, particularly in fish and in species that eat fish, such as eagles, herring gulls, snapping turtles, and humans. The Lake Ontario mass balance model (LOTOX2) has been developed to guide management of remedial efforts to reduce the priority pollutant concentrations. LOTOX2 predicts in-lake and biotic concentrations based on inputs from multiple sources and on the limnological and ecosystem processes that govern the fate of these pollutants in Lake Ontario.

Tributary inputs are potentially an important source of priority pollutants to Lake Ontario. The Niagara River may be the major source of these contaminants, as it provides more than 86 percent of the water to the lake (Lake Ontario LaMP, 2002, Table 5.2). Accordingly, Environment Canada monitors pollutant loads at the entrance to the lake at Niagara-on-the-Lake, and at the outflow of the lake into the St. Lawrence River at Wolfe Island. Current estimates of the Niagara River contribution to the priority pollutant loadings to Lake Ontario range from 49 to 77 percent, depending on the parameter group (Lake Ontario LaMP, 2002, Table 5.1). Other tributaries (both U.S. and Canadian) contribute between 4 and 45 percent; the lowest loads are mercury and the highest are mirex. U.S. and Canadian tributaries, other than the Niagara River, contribute 31 percent of PCBs, but the estimates are based on minimal data and are significantly uncertain.

The concentrations of priority pollutants for most U.S. tributaries have been characterized by only a few samples; the Canadian tributary database is only slightly better. Concentrations are often in the range of picograms per liter (pg/L), and large-volume samples and specialized analytical techniques are required to produce concentrations above detection limits. Analyses are consequently expensive. Depth- and width-integrated samples are required for parameters that are transported in the particulate phase, such as most of the priority pollutants of interest, but such sampling has not been systematically conducted for the Lake Ontario tributaries. Thus, these data are needed to accurately characterize the spatial and temporal variation in pollutant concentrations for estimates of annual loadings to the lake.

With input loading data of uneven and sparse quality, LOTOX2 is severely compromised as a management tool. It is difficult to justify resource-management actions without specific seasonal and spatial loading information. Thus, effective and efficient remediation of Lake Ontario requires improved estimates of tributary loadings for the priority pollutants.

One major difficulty with any annual load estimation is the cost of obtaining the necessary samples. To address this dilemma, regression models have been used to estimate the concentrations and loads of priority pollutants (such as PCBs) through use of one or more relatively inexpensive surrogate parameters, such as daily streamflow, seasonality variables, and the constituent concentrations of suspended-sediment, dissolved organic carbon, particulate organic carbon, and total particulate nitrogen. The correlations among these variables can be calibrated with environmental data that represent the range of flow and seasonal effects in pollutant transport. Once calibrated, the models are used to estimate concentrations and daily loads for periods when samples were not obtained.

The objective of the project, therefore, was to develop and evaluate an annual load model for PCB transport in the Black River through the use of streamflow data, seasonality variables, and concentrations of suspended sediment (SS), total particulate nitrogen (TPN), dissolved organic carbon (DOC), and particulate organic carbon (POC) concentrations as load predictors. The data and load models will provide a characterization of the occurrence of the specific PCB congeners and the factors that control dissolved and particulate PCB transport in the Black River to Lake Ontario. The organization of the project and the project schedule are described in Appendix B.

## 2. Methods

The Black River drains an area of 1,916 mi<sup>2</sup> in north-central New York adjacent to the western Adirondack Mountains (Waller and Ayer, 1975). The study was conducted on the Black River at Watertown, N.Y. (USGS stream gage 04260500, drainage area 1864 mi<sup>2</sup>; see map of location in Appendix A). The Watertown gage is 10 km upstream from the confluence of the river at Lake Ontario, near Dexter, and flow measured at the site represents 97.5 percent of the basin area that drains to the lake. The gage site is about 30 km downstream from a major source of PCBs at Carthage, where contaminated sediment has entered the river from paper-pulp wastes (Litten *et al.*, 1993).

Eckhardt and his colleagues obtained 50 samples for the surrogate constituents of SS, TPN, DOC, and POC at a range of flows from October 2004 through September 2005 (the 2005 water year). Samples were taken approximately weekly, with additional samples collected during the major periods of high flow, when loading rates are highest. The samples were taken at the USGS gage site on Vanduzee Street in Watertown, which is close to the river mouth and has an accessible bridge that is suitable for representative cross-section sampling with depth-integrated and equal-width increments. Samples were collected during flows that ranged from 1,100 to 26,100 ft<sup>3</sup>/s. The samples were analyzed at USGS laboratories for concentrations of total suspended sediment, particulate and dissolved organic carbon, and total particulate nitrogen (referred to as surrogate constituents). For samples taken when the flow exceeded 4500 ft<sup>3</sup>/s, and for samples taken in conjunction with PCB samples, particle-size fraction of suspended sediment finer than 0.062 mm (silt and clay) was also measured; two samples for suspended sediment were lost due to bottle breakage during shipment. Figure 1 shows when the samples were taken and displays the corresponding flow.

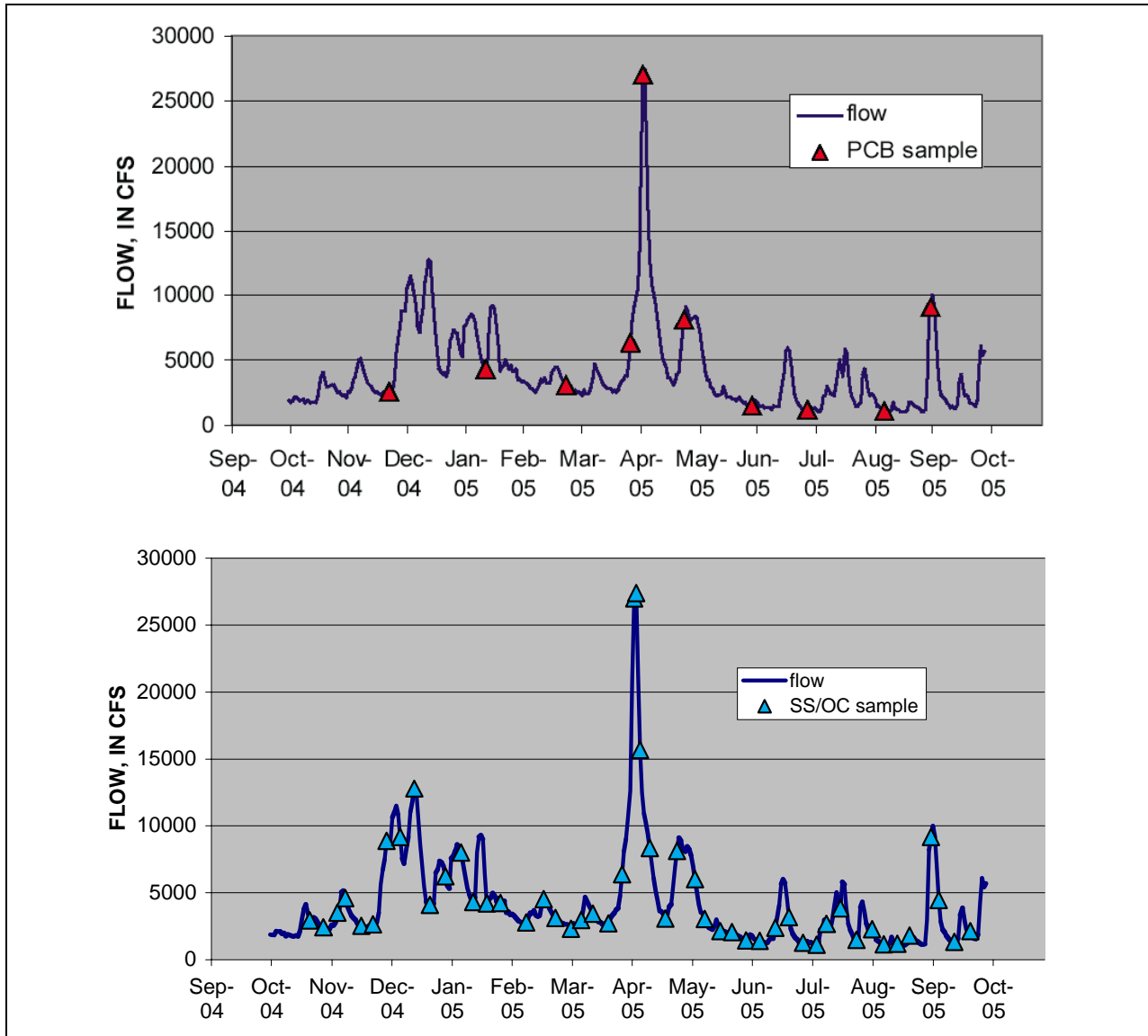


Figure 1. Annual hydrograph for the Black River, showing when samples were taken. [cfs, cubic feet per second]

In addition, 10 large-volume samples were collected for PCB analysis to represent the range of flow conditions in water year 2005, and each sample was collected concurrently with a sample for the surrogate constituents. About 60 liters were collected using cross-sectional and depth-integration sampling methods, placed in organic-free glass containers, and returned to the USGS laboratory at Ithaca. The whole-water sample was filtered through an organic-free glass-fiber filter (1-micron nominal pore size). The filtrate was spiked with isotopically-labeled PCB compounds to allow evaluation of extraction efficiencies. The spiked filtrate was metered through a single 75-gram cartridge of solid-phase-extraction (SPE) XAD resin (Musty and Nickless, 1974; Pankow et al., 1982) at an average extraction rate of about 2.6 L/hr. The extraction period was about 23 hours, depending upon sample volume. The filters were frozen and SPE cartridges were chilled to 4 degrees Celsius and shipped by overnight delivery to AXYS Analytical Services in British Columbia, Canada, for analysis. The solid-phase PCB components on the filters were extracted with toluene (Soxhlet method), and the

liquid-phase components were eluted from the XAD cartridges with dichloromethane. Analysis of the solid- and liquid-phase extracts was done by gas chromatography and high-resolution mass spectrometry (GC/HRMS) according to EPA method 1668A specifications for PCBs. Two field-blank samples of about 7.5 liters of chromatography-grade reagent water were also analyzed, in conjunction with collection, filtration, extraction, and analysis of the environmental samples, to evaluate potential contaminant artifacts. One environmental sample was collected in replicate to give an indication of the variation associated with the sampling and analytical processes. Each large-volume sample was taken concurrently with sample collection for SS, POC, DOC, and TPN to provide data on correlations of these surrogate constituent concentrations to the PCB concentrations.

The method 1668A GC/HRMS analyses through AXYS Analytical Services provided congener-specific results for PCBs, with congener detection limits of 0.001 to 0.050 ng/L (ppt) for a 1-L sample. The AXYS lab was instrumental in the development of this method and is a contract lab for the NYSDEC. A relatively large volume (60 L) coupled with the low detection limits of method 1668A was necessary to achieve acceptable quantification for the expected range and concentration of PCB congeners, particularly for low-flow conditions in the Black River. A summary of the Quality Assurance Project Plan (QAPP) issues and a quality-assurance analysis of the PCB data are in Appendices C and D, respectively.

Separate annual load-estimation models were developed for SS, DOC, POC, and TPN based on the 50 samples and for dissolved and particulate PCBs based on the 10 samples collected during this project. The model approach was based on the load-estimation models developed by Cohn et al. (1992) and Ferguson (1986). Through these models, which utilize the sample concentrations for the load constituents, daily mean flow, and seasonality-fitting factors, we estimated daily, monthly, and annual loads for the 2005 water year. In a second approach to estimate annual PCB loads, a two-stage model used the surrogate constituent loads coupled with the correlations of the surrogate concentrations to dissolved and particulate PCB concentrations. The correlations between DOC and dissolved-phase PCB total-congener concentrations and between SS, POC, and TPN and the particulate PCB total-congener concentrations were used to convert the annual load estimate for the SS, TPN, DOC, and POC constituents into an annual load of dissolved and particulate PCBs for the 2005 water year.

### 3. Data Summary

In this section, the flow conditions and the concentration results for the 50 surrogate constituent samples and the 10 PCB samples are summarized for the 2005 water year. The surrogate-constituent concentrations are plotted with flow, and summary statistics are presented in Table 1. The PCB results are summarized as total dissolved- and particulate-phase concentrations in Table 2, and summaries of selected congener-level results are also discussed. The section concludes with a brief comparison of PCB results from this study with PCB results selected from other Lake Ontario studies.

#### Flow

Figure 2 shows the hydrograph of mean daily flow for the 2005 water year period of study and the daily maximum and daily median flows for the last 30 years. The maximum flow of 27,400 ft<sup>3</sup>/s on April 5,



2005, was due to runoff from rainfall combined with the melting of winter snowpack. The hydrograph peak in early September was associated with rainfall from the remains of Hurricane Katrina.

The study period was one of average flow. The average flow for the study period was 4154 ft<sup>3</sup>/s, which is similar to the average flow of 4180 ft<sup>3</sup>/s for the period of record (1921-2005). The Black River has a substantial base flow component and is highly regulated for flood control and power generation.

Twenty-eight of the fifty surrogate-constituent samples were collected when flows were above the historical median flow of 2890 ft<sup>3</sup>/s, and thirteen were collected when flows were in the upper quartile of historical flows, above 5210 ft<sup>3</sup>/s (Figure 1). Six of the ten PCB samples were collected when flows were above the median flow of 2890 ft<sup>3</sup>/s, and four were collected when flows were in the upper quartile of flows, above 5210 ft<sup>3</sup>/s.

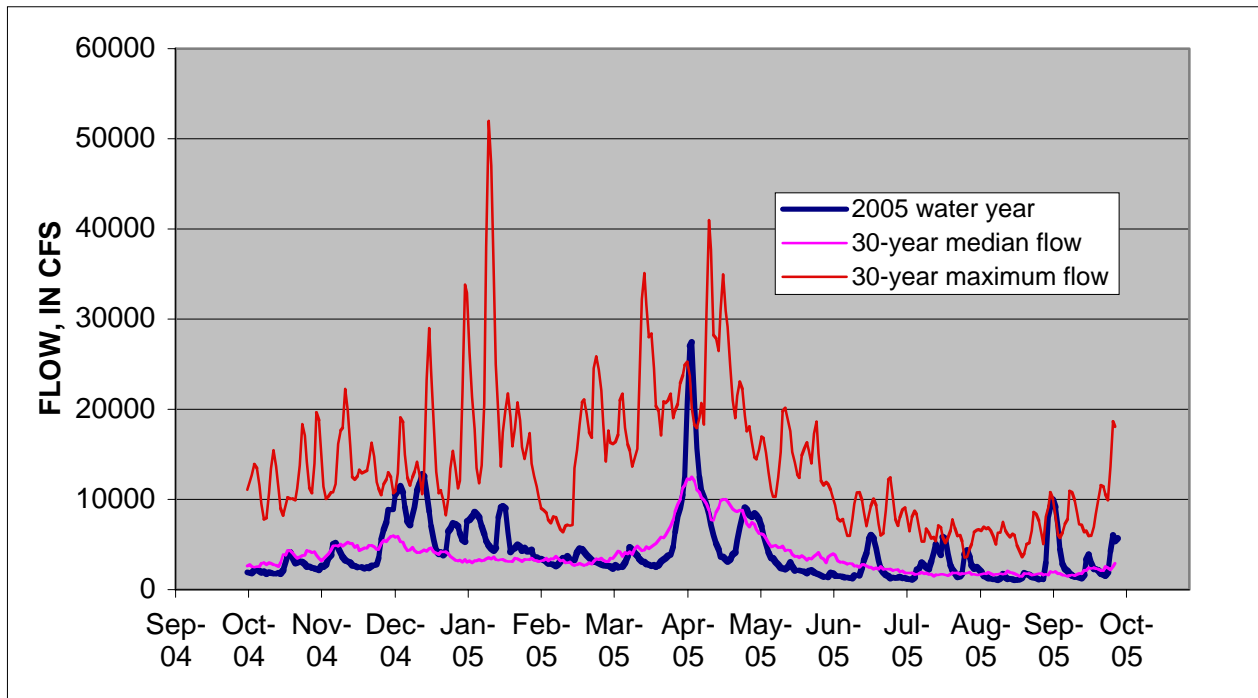


Figure 2. Mean daily flow during the 2005 water year study period compared with 30-year maximum and median flows. [cfs, cubic feet per second]

## Surrogate Constituent Results

Concentrations of the surrogate constituents are summarized in Table 1 and Appendix E, are plotted with the mean daily flow in Figures 3 through 7, and are correlated to flow in Figure 8. The particulate parameters – SS, POC, and TPN – show a moderate correlation with flow, and the highest concentrations occurred in association with the major flow event in April 2005. POC and TPN concentrations were relatively high in two samples from the late summer of 2005, one of which is associated with a minor storm-runoff event, and the other associated with runoff from Hurricane Katrina. Concentrations of these particulate constituents are generally low compared to other rivers that drain to the Great Lakes; for example, SS concentrations in Lake Erie tributaries in Ohio often reach concentrations 10 times the maximum value observed in this study (Richards and Baker, 2002). This probably reflects the forested nature of the Black River watershed and the degree to which it is a regulated river.

Table 1. Summary statistics for flow and surrogate constituent concentrations  
 [in milligrams per liter [mg/L], except where noted).

<b>Parameter</b>	<b>Minimum</b>	<b>25<sup>th</sup> percentile</b>	<b>Median</b>	<b>75<sup>th</sup> percentile</b>	<b>Maximum</b>
Flow (ft <sup>3</sup> /s)	1,060	2,072	3,100	5,010	27,400
Suspended Sediment	1.0	3.0	4.0	7.0	79
Dissolved Organic Carbon	3.1	3.7	4.3	5.05	8.8
Particulate Organic Carbon	0.05	0.2	0.3	0.5	2.5
Total Particulate Nitrogen	0.01	0.03	0.04	0.06	0.24
Silt and Clay (percent)	46	63	80	100	100

Concentrations of dissolved organic carbon were poorly correlated to flow but do appear to vary seasonally, with lower concentrations in the winter when levels of biological activity are lower. The major flow events in April and September did not appear to significantly affect DOC concentration, neither increasing it because of washing of organic matter into the river by runoff, nor decreasing it by simple dilution.

The grain size of the sediment did not show a clear relationship to flow or to time of year. Overall, the suspended sediment is predominantly silt and clay.

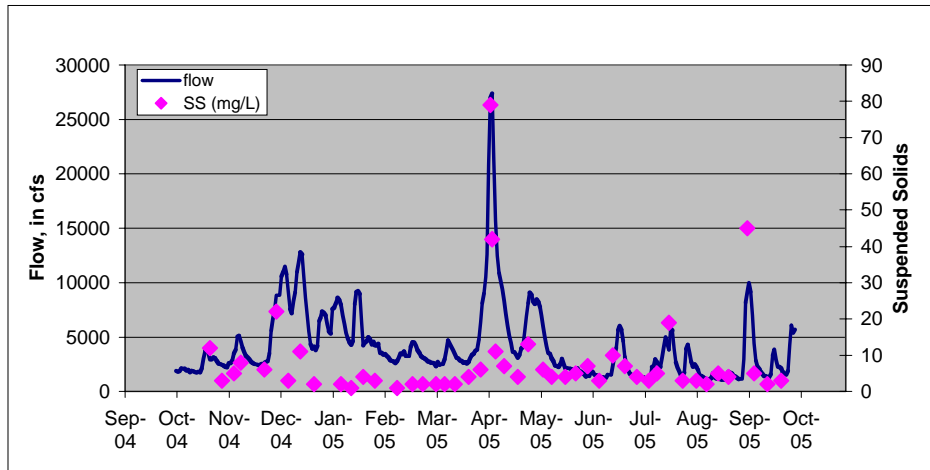


Figure 3. Suspended sediment concentrations.

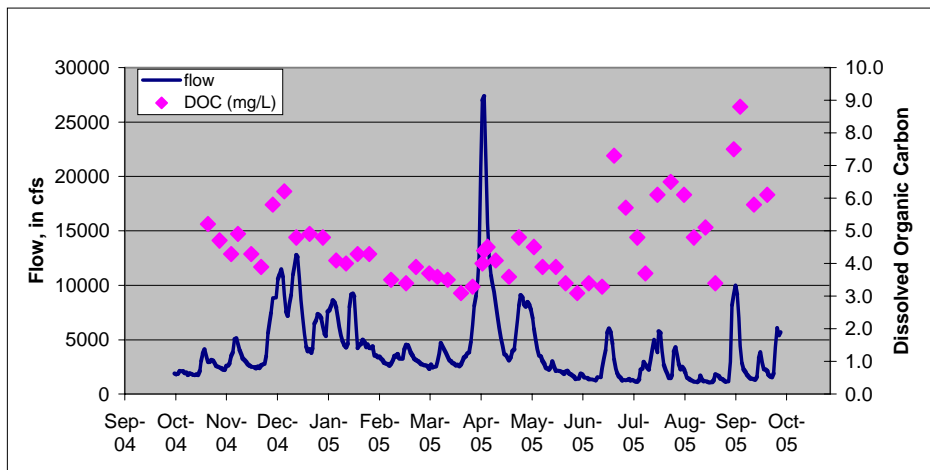


Figure 4. Dissolved organic carbon concentrations.

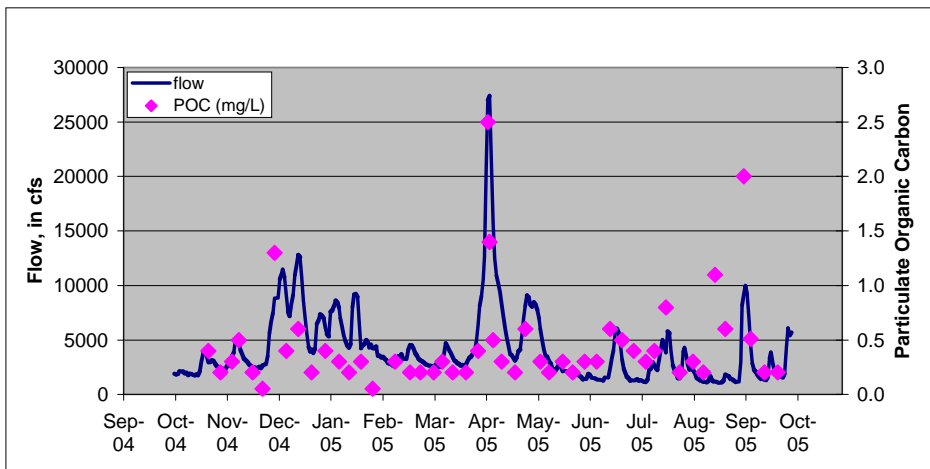


Figure 5. Particulate organic carbon concentrations.

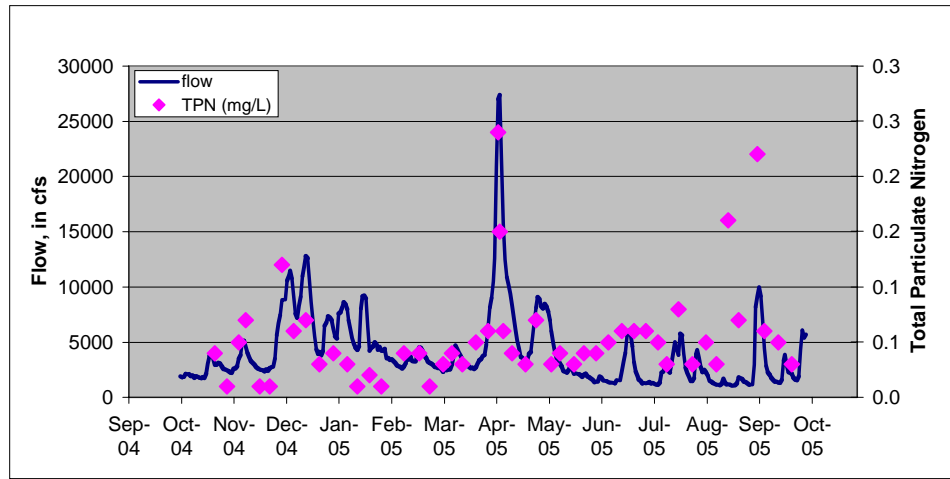


Figure 6. Total particulate nitrogen concentrations.

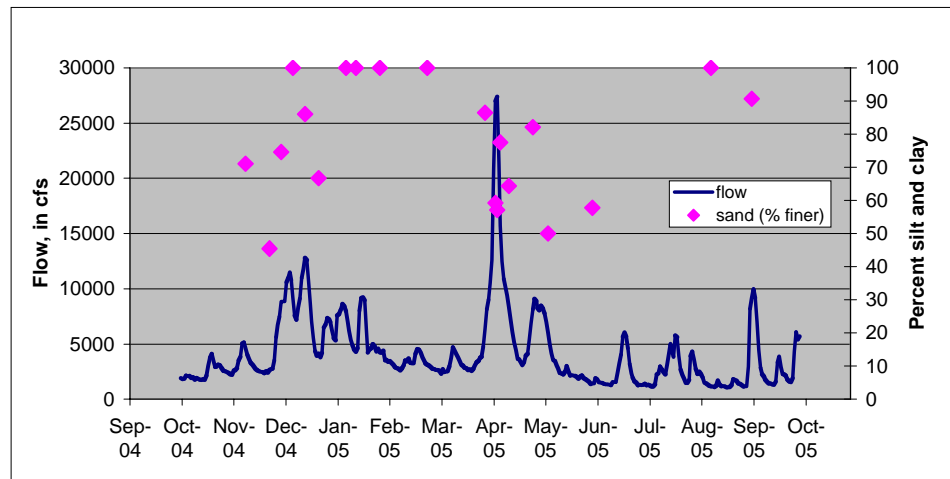


Figure 7. Percent silt and clay (measured for samples when flow exceeded 4500 cfs or when PCB samples were taken).

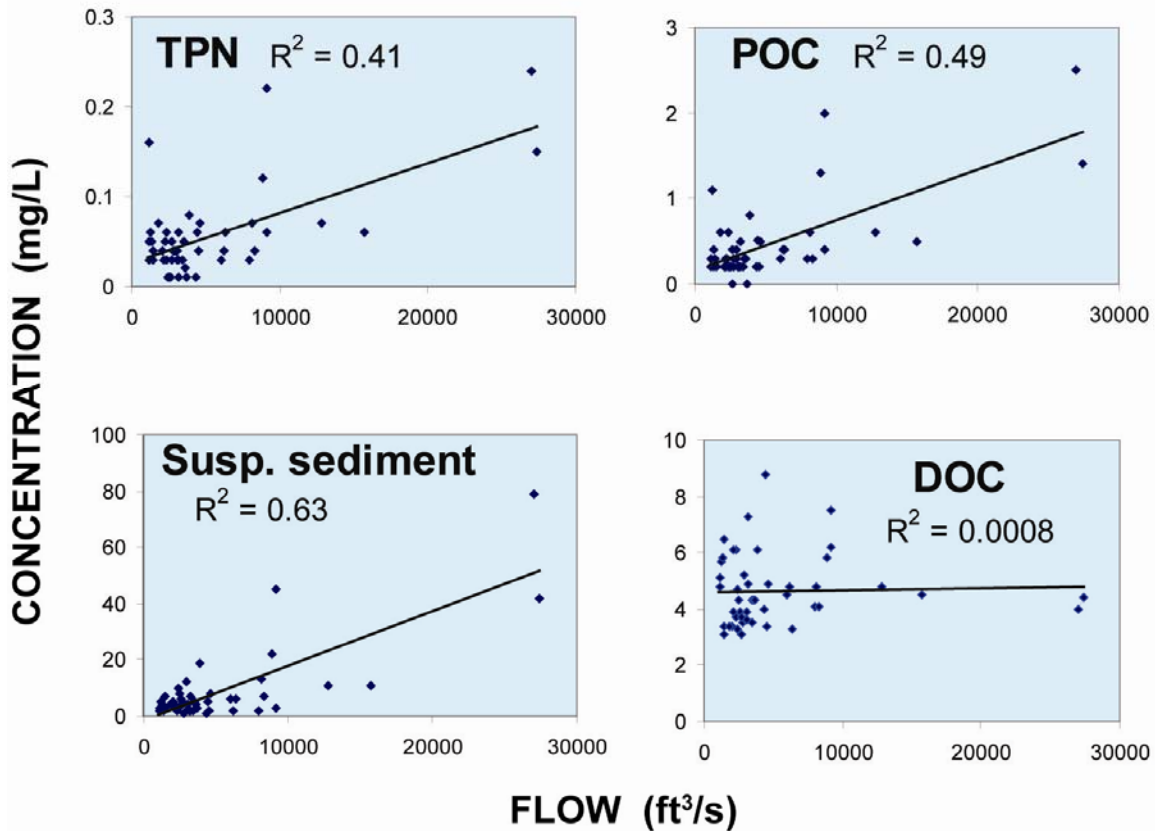


Figure 8. Correlations of total particulate nitrogen (TPN), particulate organic carbon, (POC), dissolved organic carbon, (DOC), and suspended sediment (SS) to mean daily flow,

## PCB Results

Total dissolved and particulate PCB concentrations are summarized in Table 2 and Appendix F, plotted with the annual hydrograph and correlated to mean daily flow in Figure 9, and correlated to the surrogate constituent concentrations in Figure 10. Particulate PCB concentrations had good correlation with flow. Dissolved PCB concentrations were not closely correlated to flow but were less variable than particulate PCB concentrations. The dissolved PCBs, however, appeared to vary seasonally, with higher concentrations in the spring and summer and lower concentrations in the fall and winter (Figure 9). This likely reflects the annual temperature cycle, with greater biochemical activity in the river during warm months and reduced sediment-water exchange during cold months.

Table 2. Summary statistics for total dissolved and particulate PCBs (in picograms per liter [pg/L]).

Parameter	Minimum	25 <sup>th</sup> percentile	Median	75 <sup>th</sup> percentile	Maximum
Dissolved PCBs	333	606	1155	1525	2020
Particulate PCBs	65	210	372	1557	5570

Among the ten PCB homolog groups, the dichlorobiphenyls had the greatest percent of the total dissolved PCB mass in early samples (November 2004 to April 2005). In later samples, the trichlorobiphenyls dominate, or in some cases had about the same mass as the tetrachlorobiphenyls. In most particulate-phase samples, the tetrachlorobiphenyls had the greatest percentage of the total PCB mass.

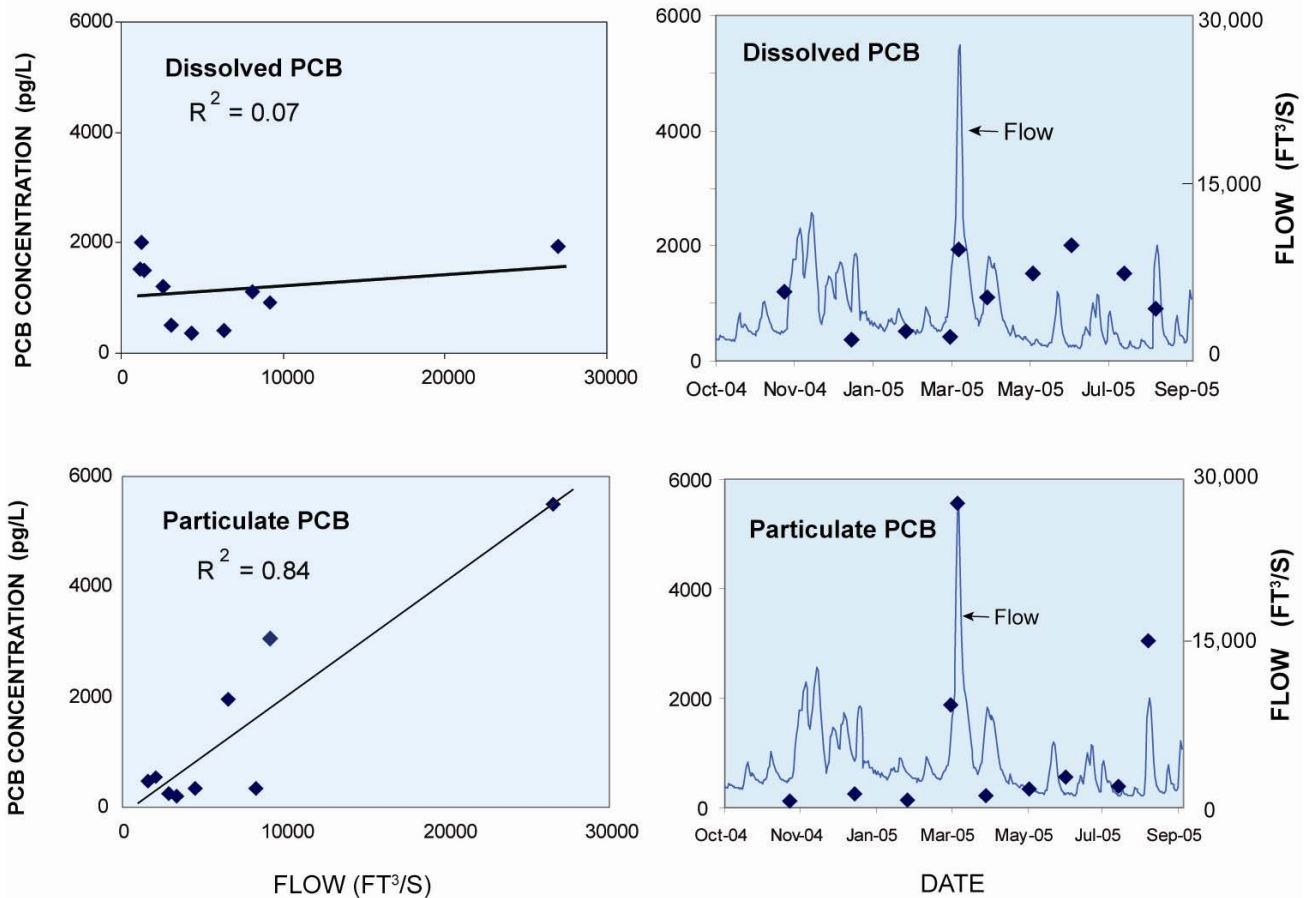


Figure 9. Correlation of concentrations of dissolved and particulate PCBs with mean daily flow. [pg/L, picograms per liter]

The distribution of the PCB mass among the congeners is quite similar in most samples, in both the dissolved and particulate phases. This is reflected in pairwise correlations (Pearson) of congener concentrations among samples that range from 0.79 to 0.99 for the dissolved-phase samples, with 33 of 45 pairwise correlations greater than 0.90, and from 0.71 to 0.99 for the particulate-phase samples, with 36 of 45 pairwise correlations greater than 0.90.

Among the dissolved PCBs, PCB-4 had the highest concentrations, often contributing more than 50 percent of the total dissolved PCB mass in the samples. PCB-1 usually had the second highest concentration, although it ranked lower in later samples. PCB-19 usually ranked third in concentration in early samples, and often second in later samples. PCB-52 also ranked high in the dissolved sample mass. Among the particulate PCBs, the congener group PCB-61/70/74/76 had the highest concentration in all samples but one. Other high-ranking congeners were PCB-31, PCB-20/28 and PCB-52. PCB-52 was the only congener that was significantly present in both the dissolved and the particulate phase in samples.

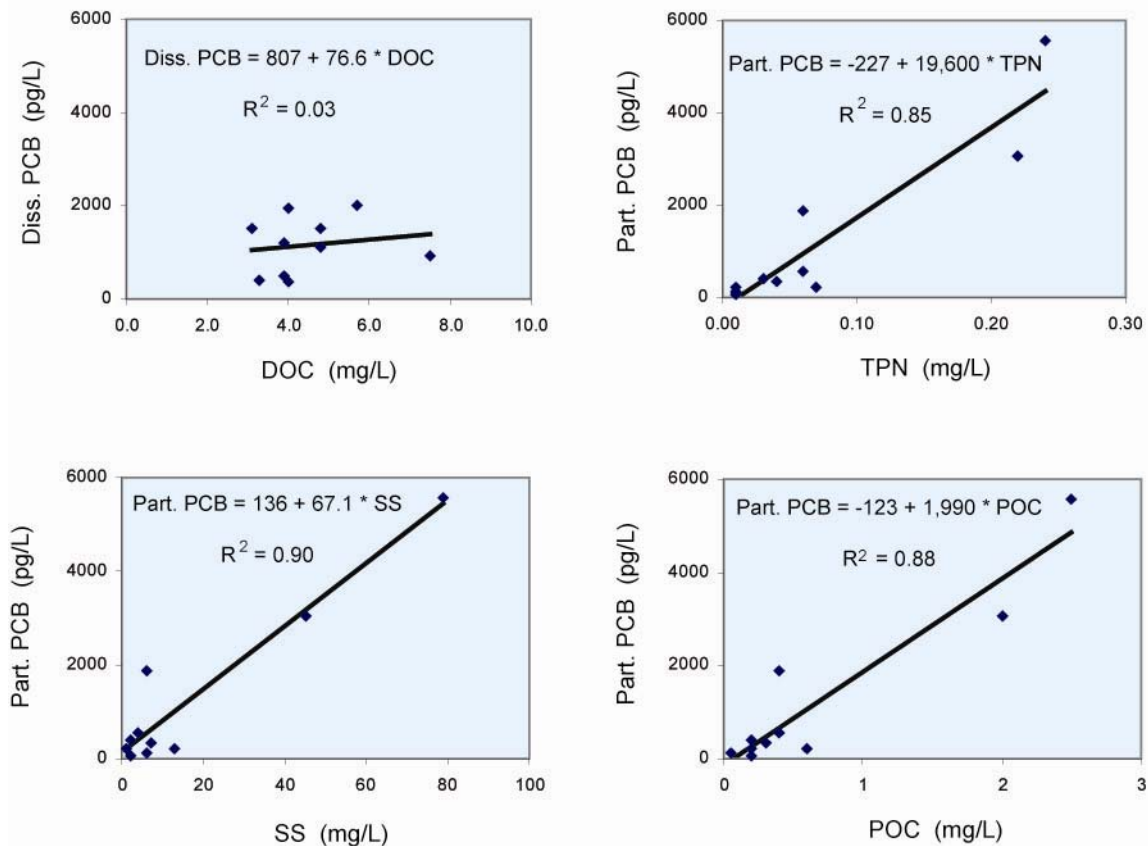


Figure 10. Correlation of concentrations of dissolved PCBs (Diss. PCB) and particulate PCBs (Part. PCBs) with DOC, POC, SS, and TPN.

Dissolved PCB concentrations were poorly correlated to DOC concentrations (Figure 10); a lack of good correlation to the particulate-phase of the surrogate constituent concentrations was also observed. In contrast, the particulate PCB concentrations were well correlated to the SS, POC, and TPN concentrations, which indicates that the transport of these particulate phases is directly related to flow. The fitted regression line for each correlation in Figure 10 provides the intercept ( $b_0$ ) and the slope ( $b_1$ ) coefficients used in the load estimations that are discussed in the next section.

### **Comparison with results of other PCB studies**

Sample results from a study of PCBs in New York tributaries to Lake Ontario, which included the Black River, were provided by USEPA (Richard Coleates, Edison Laboratory, written commun., 2006) and compared to results collected in this study. One paired-sample comparison from these two data sets is shown in Figure 11 for similar conditions of base flow and time of year. Important differences between the samples include: (1) the USEPA samples were collected by boat from water in the mouth of the Black River below the Dexter bridge at its confluence with Lake Ontario 10 km downstream from the Watertown gage, (2) the analyses were conducted by different laboratories (AXYS and the USEPA-Edison), (3) the methods produce slightly different groupings of congeners due to co-elution, (4) the USEPA samples were 1-L volumes compared to the 60-L volumes used in this study, and (5) the USEPA whole-water samples were not separated into dissolved and particulate phases. Despite these differences, the paired samples showed a similar distribution of co-detected congeners (n=28). In particular, both samples confirmed the relatively high concentrations of the PCB-1 and PCB-4 congeners. Notable differences between the samples include: (1) the number of detected congeners and co-eluted groups in the Watertown sample (n=148) far exceeded the number in the USEPA sample (n=28), which is attributed to the lower detection levels for the 60-L relative to 1-L sample sizes, and (2) the congener concentrations were generally larger in the USEPA sample than in the Watertown sample, although each sample had nearly equal total PCB concentrations.



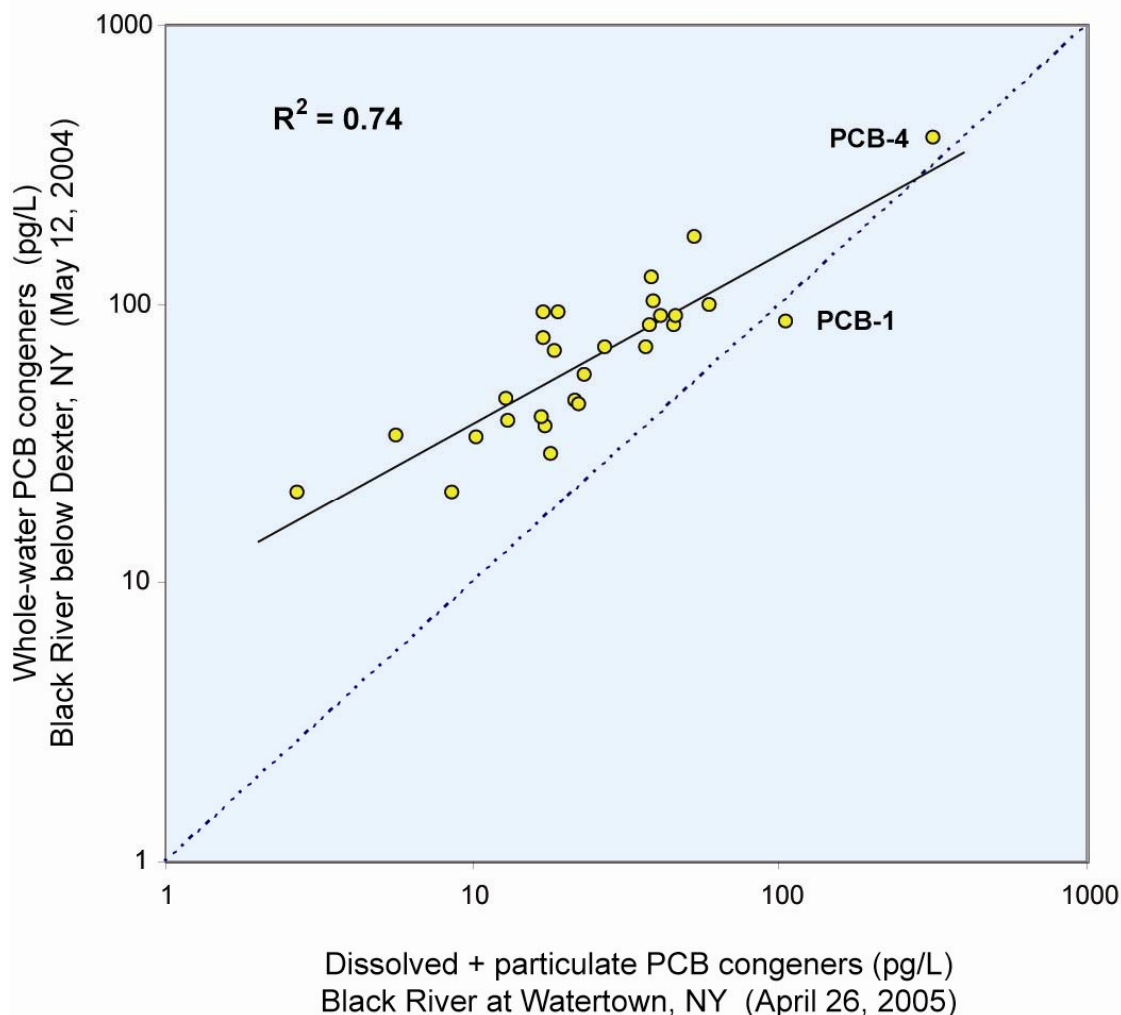


Figure 11. Comparison of congener concentrations for one comparable sample pair from the Black River at Watertown (this study) and the Black River below Dexter (USEPA, Edison, NJ). [non-detected values not shown]

A comparison of dissolved PCB results from this study with the results of Luckey and Litten (2005) for water samples from Lake Ontario showed similarities in congener composition, but some important differences were noted. The comparison was made with dissolved-phase results from the Black River samples because 90 percent of the PCB mass in the Lake Ontario samples was present in the dissolved phase. Luckey and Litten found PCB-4 and PCB-52 to be among the major constituents of the congener mix, but on average no congener dominated the total concentration as PCB-4 did in the Black River samples. PCB-1 ranked 18<sup>th</sup> in their list, and PCB-19 occurrence was not significant. PCB-11, their most abundant congener in the lake samples, was not important in the river samples. PCB-20/28, their second-ranked congener pair, ranked mid-way in the total mass the Black River samples, but the pair ranked high in the Black River particulate-phase samples. Other important congeners in their samples, PCB-31 and PCB-61/70/74/76, were also more important constituents in the particulate phase than the dissolved phase for the Black River samples.

#### 4. Load Models and Results

Two approaches were used to estimate annual loads of dissolved and particulate PCBs from the Black river for the 2005 water year. In the first approach, PCB loads were computed through a direct fit of dissolved and particulate PCB concentration models to flow and seasonal time. In the second approach, the concentrations of the surrogate constituents (SS, TPN, POC, and DOC) were estimated through the model, and these estimates were used to compute PCB loads through the correlation of surrogate concentration to PCB concentration.

In the first approach, a Maximum Likelihood Estimation (MLE) regression approach by Cohn (1992) was used to develop a series of models of annual loads of PCBs (and the surrogate constituents) from the Black River basin to Lake Ontario for the 2005 water year. The approach effectively integrates instantaneous values of flow times constituent concentration over time to achieve monthly and annual summations of load. Continuous values of flow are directly available through the river gage at the sampling site, but continuous estimates of concentrations must be computed through regression of concentration (C) from sample results using flow (Q) and seasonal time (T) variables (Fourier function) as predictor variables. The general form of the natural-log (Ln) concentration model is:

$$\text{Ln } C = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin 2\pi T + a_4 \cos 2\pi T + a_5 \sin 4\pi T + a_6 \cos 4\pi T + \varepsilon_R$$

where  $a_0$  through  $a_6$  are regression coefficients that are fitted through MLE during model calibration, and  $\varepsilon_R$  is residual error. In this study, the regression coefficients were accepted only when probability (p) tests exceeded 95-percent confidence of nonzero values (i.e., alpha = 0.05) and  $\varepsilon_R$  was minimized. The results for the first approach are given in Table 3.

Table 3. Results of concentration model calibrations and the load estimates [ns, non-significant value for alpha = 0.05].

Constituent	Number of samples	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$	$R^2$	Residual error	Load
Total particulate nitrogen (TPN)	50	-0.67	1.62	0.23	-0.22	-0.54	ns	ns	83.3	0.28	230 Mg/yr
Suspended sediment (SS)	48	4.34	1.98	ns	-0.37	-0.71	-0.27	-0.15	88.3	0.29	35,000 Mg/yr
Particulate organic carbon (POC)	50	1.51	1.72	0.18	-0.31	-0.45	ns	ns	89.3	0.19	2,000 Mg/yr
Dissolved organic carbon (DOC)	50	4.02	1.14	ns	-0.26	-0.11	ns	ns	95.9	0.03	17,000 Mg/yr
Dissolved total PCBs	10	2.07	0.99	0.41	-0.30	-0.26	-0.36	-0.10	97.3	0.10	3.3 kg/yr
Particulate total PCBs	10	1.96	2.19	ns	-0.41	-1.20	ns	ns	86.2	1.00	4.0 kg/yr

The loads of dissolved PCBs were not well correlated to the transport of DOC, POC, SS, or TPN, but the good fit of the two flow variables ( $a_1$  through  $a_2$ ) and the four seasonal time variables ( $a_3$  through  $a_6$ ) provided an excellent predictive model of concentration in terms of high  $R^2$  and low residual model error. The loads of particulate PCBs, which were well correlated to the transport of POC, SS, and TPN, had a good model fit only for the log-flow flow variable ( $a_1$ ) and two seasonal time variables ( $a_3$  and  $a_4$ ); correspondingly, the predictive model for particulate PCBs had a lower  $R^2$  and more residual model error than for dissolved PCBs.

In the second approach, the dissolved and particulate PCB loads were estimated through the correlation equations that relate the surrogate constituent concentrations to the PCB concentrations (Figure 10). The following general equation was used:

$$\text{PCB load} = \{b_0 + [b_1 * \text{mean surrogate constituent concentration}]\} * \text{mean annual flow}$$

where the mean surrogate constituent concentration is the surrogate constituent load (from Table 3) divided by the mean annual flow (with appropriate unit conversions), and  $b_0$  and  $b_1$  are the regression coefficients fitted for the concentration correlations (Figure 10); the mean annual flow for the 2005 water year was 4154 ft<sup>3</sup>/s. The  $b_0$  and  $b_1$  coefficients effectively convert the mean annual flow-weighted surrogate concentration to a mean annual flow-weighted PCB concentration. The results are given in Table 4.

Table 4. Results of surrogate constituent concentration correlations to PCB concentration, and the PCB load estimates.

PCB phase	Surrogate constituent	$b_0$	$b_1$	Annual surrogate load (Mg/yr)	Mean surrogate concentration (mg/L)	Annual PCB load (kg/yr)
Particulate	TPN	-227	19,600	230	0.062	3.7
Particulate	SS	136	67.1	35,000	9.44	2.9
Particulate	POC	-123	1,990	2,000	0.54	3.5
Dissolved	DOC	807	76.6	17,000	4.59	4.3

The results of the two load estimation approaches (Tables 3 and 4) show that the direct model computation of PCB loads were similar to loads computed through the correlation models based on surrogate constituent concentrations. The dissolved PCB load in Table 4 is slightly higher than those estimated by the direct approach (Table 3), which is probably due to the poor correlation of dissolved PCB and DOC concentrations. The two load estimation approaches work well mainly because the dissolved and particulate PCB concentrations were strongly related to the flow and time variables. Thus, the surrogate concentrations, although they were correlated to PCB concentrations and to flow, contributed little additional information about PCB transport beyond that described by the direct PCB load model approach. Accordingly, the results given in Table 3 are preferable to those in Table 4 due to the relative simplicity of the direct approach and the documented accuracy of the Cohn (1992) model.

Plots of the monthly dissolved and particulate PCB load estimates (Figure 12) show that the dissolved load exceeded the particulate load during the fall and winter months. Particulate loads exceeded dissolved loads in spring and summer months that had significant runoff, such as the snowmelt in April, several summer thunderstorms, and the remnants of hurricane Katrina in September 2005. An estimate of the annual total PCB load of 7.3 kg/yr thus had nearly equal dissolved and suspended components.

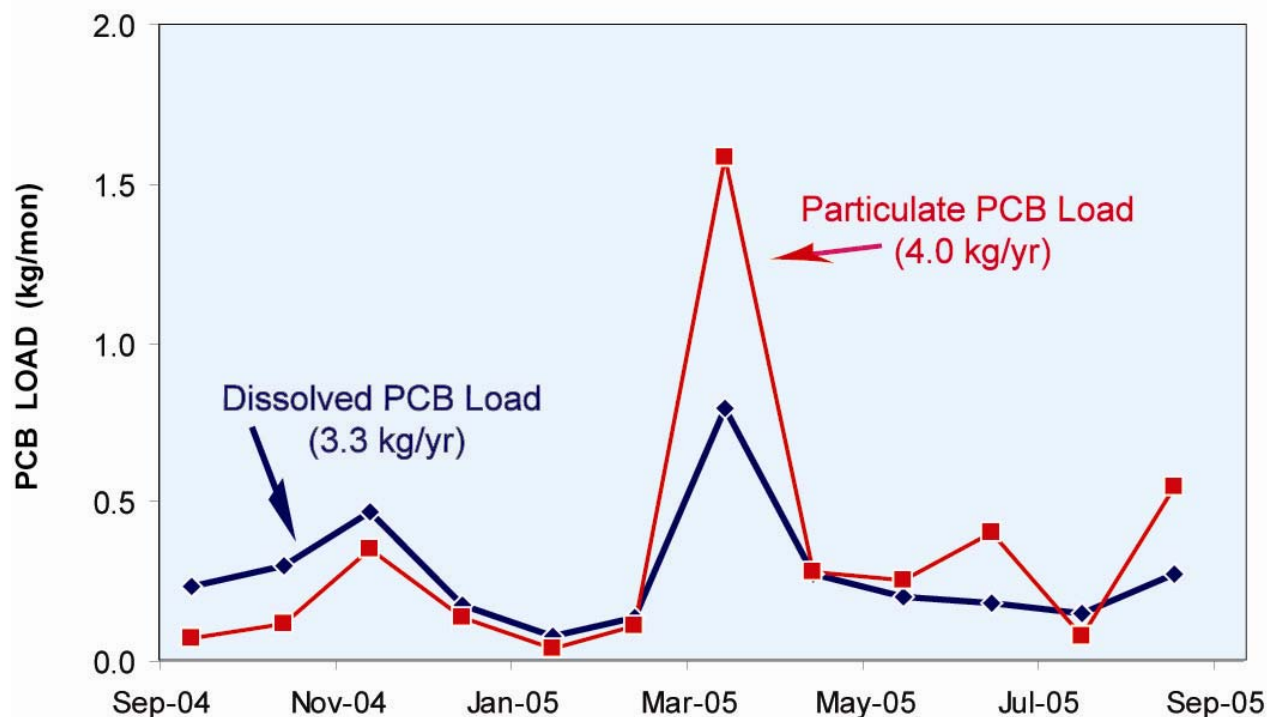


Figure 12. Monthly load estimates of dissolved and particulate PCBs for the Black River at Watertown, 2005 water year.

## 5. Discussion and Future Work

1. Given the similarity of congener masses between the 1-L and 60-L samples (Figure 11), the high-resolution method 1668A and large sample volumes may not be necessary to characterize the bulk of total PCB loads in tributaries to Lake Ontario. An adequate number of depth-integrated and spatially-distributed 1-L samples could thus simplify a sampling design to focus on an expanded characterization of variability in concentrations that result from flow and seasonal effects.
2. The models developed in this study can be used for predictions of PCB loads through flow data for years beyond the 2005 water year. An additional set of PCB results from at the Watertown site would, however, provide useful verification and further calibration of the current load model.
3. The dissolved- and particulate-phase sample extracts from this study are in frozen storage at the AXYS laboratory and may be used for additional GCMS analyses for other persistent priority pollutants in Lake Ontario, such as DDT and its metabolites, mirex, dieldrin, and dioxins/furans.

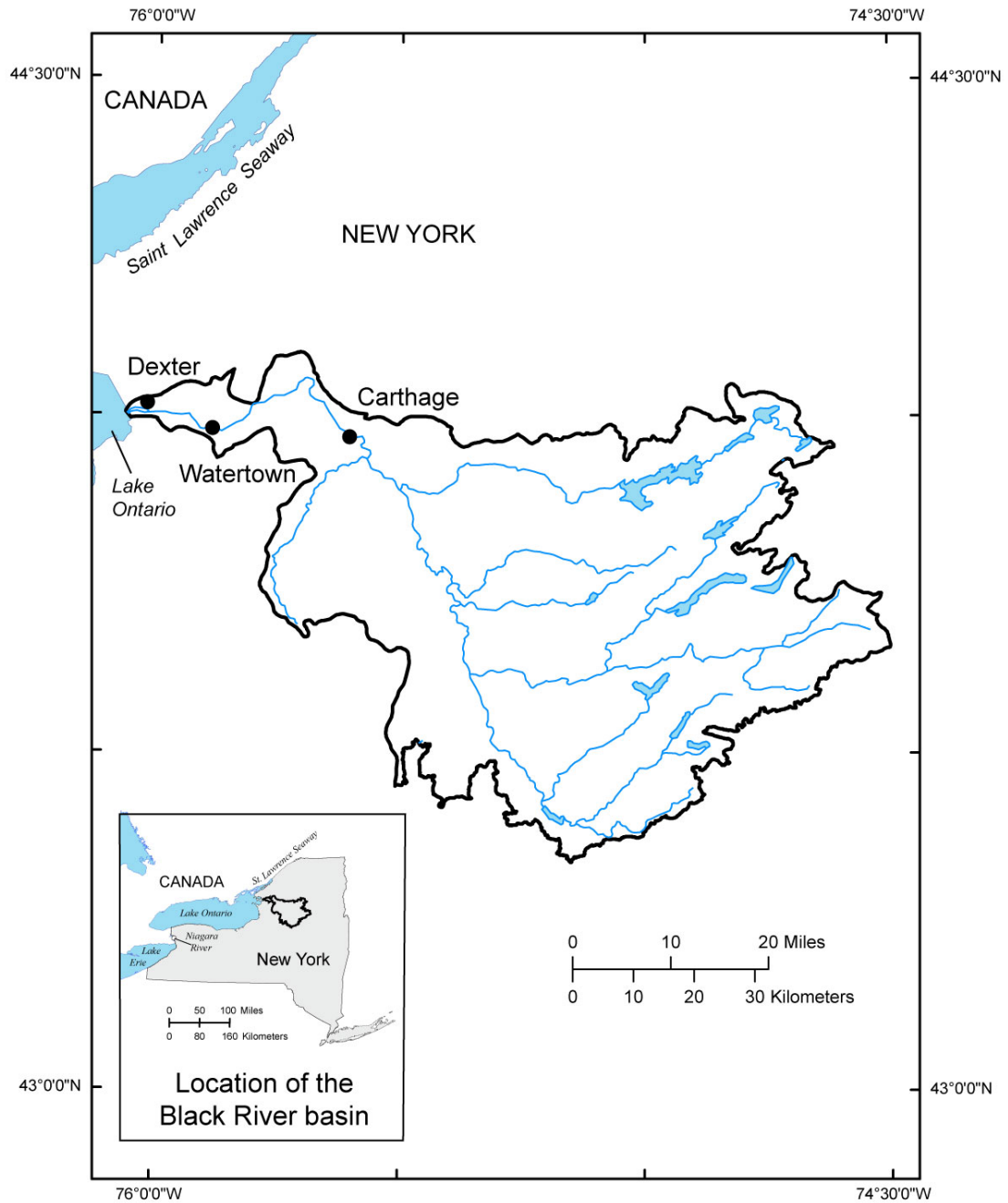
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## **7. List of Appendices**

Appendix A	Map of the Black River Watershed.
Appendix B	Project Organization and Schedule
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Appendix E	Surrogate Data
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### APPENDIX A. MAP OF THE BLACK RIVER WATERSHED



## APPENDIX B. PROJECT ORGANIZATION AND SCHEDULE

### Project Organization and Task Responsibilities

Eckhardt was responsible for streamflow records, field sampling, sample filtration and extraction, and delivery of environmental and QA/QC samples to AXYS and USGS Laboratories, as well as for receipt and evaluation of analytical results.

Richards was responsible for overseeing the project, preparing interim reports, and evaluating the data (especially the PCB data) from a quality control perspective. Statistical applications, including development of the regression loading models and interpretation of the relationships between PCBs and surrogate parameters, were shared between Richards and Eckhardt, with Eckhardt taking the lead in the development of load models. Preparation of the final report and other communications was also shared between Richards and Eckhardt. Luckey was the EPA project manager in Region II and was responsible for project oversight by EPA and for receipt and approval of project deliverables. Our contact at AXYS Analytical Services was initially through Laurie Phillips and later Pam Riley. Brian Wohnsiedler of the Jefferson County Soil and Water Conservation District in Watertown, N.Y., administered the subcontract to USGS.

### Project Schedule

<b>Date</b>	<b>Accomplishment Milestone</b>	<b>Responsible Investigator</b>
October 1, 2003	Project begins	
June 4, 2004	QAPP complete	Richards / Eckhardt
October 21, 2004	Sampling begins	Eckhardt
September 22, 2005	Sampling ends	Eckhardt
December 2, 2005	PCB analytical results received	AXYS / Eckhardt
January 30, 2006	Surrogate parameter analytical results received	USGS / Eckhardt
May 30, 2006	Meeting of project team in Troy NY; PCB data quality and preliminary load results discussed	Richards/Eckhardt
August 31, 2006	Load calculations complete	Richards / Eckhardt
September 27, 2006	Final project report to EPA	Richards / Eckhardt
September 30, 2006	Project ends	



## APPENDIX C. REVIEW OF QAPP GOALS AND PROJECT OUTCOMES

In addition to a statement of the project goals, design, and organization, the QAPP developed for this project contained a number of specific goals related to sample collection and the quality of the analysis performed on the samples. These specific goals are reviewed below, and compared with the results accomplished in the project.

### Field sampling

The following table summarizes the number of samples of various types. Total particulate nitrogen (TPN) was analyzed in the surrogate samples in addition to the SS, POC, and DOC specified in the QAPP.

Sample Matrix	Analyte/Parameter	Number of samples
<u>ENVIRONMENTAL SAMPLES</u>		
ambient water	PCBs	10
ambient water	POC/DOC/TPN	50
ambient water	SS	50
<u>BLANK SAMPLES</u>		
blank water	PCBs	2
blank water	POC/DOC/TPN	2
blank water	SS	2
<u>DUPLICATE SAMPLES</u>		
ambient water	PCBs	1
ambient water	POC/DOC/TPN	4
ambient water	SS	4

The USGS maintains multiple levels of QAQC to ensure that information collected, interpreted and dispersed by the USGS is of high quality and credible. For this project, river samples were depth- and width-integrated to avoid bias due to inhomogeneities in the concentration distribution in the river cross section. All sampling and sample-processing equipment was routinely cleaned immediately after use with a 1-percent solution of Liquinox detergent and adequately rinsed with clean tap water, de-ionized water, and organic-free reagent-grade water. The equipment was rinsed again in the field prior to sample collection with ambient water that was about to be sampled. Field personnel used disposable nitrile-polymer gloves that precluded any direct contact with sampling equipment, bottles, or sampled water. USGS field methods are standardized on the national level and are documented in a series of publications that are continually updated; see <http://water.usgs.gov/owq/Fieldprocedures.html>. Record-keeping of sample collection is standardized through use of standard field forms that allow documentation and tracking of all environmental sampling and QAQC activities. All field personnel receive training in sample collection and processing protocols that are defined through national and New York Water Science Center (NYWSC) USGS programs. The NYWSC QAQC program is periodically reviewed by the national office; see <http://ny.water.usgs.gov>. Additional information on

the USGS National QAQC Program for water-quality data may be found online at <http://water.usgs.gov/owq/quality.html>.

The sediment-sample bottles used in this project were 500-ml glass re-usable bottles. The fiber-glass filters for PCBs, POC, and TPN, and the 125-ml glass bottles for DOC were oven-fired at 450 deg. C. Field samples were immediately chilled to 4 deg. C and transported to the laboratory for processing. DOC samples were preserved to pH less than 2 with 1 ml of 4.5N sulfuric acid, which was certified for DOC use by the USGS-NWQL. All samples were waterproof-labeled with station identification number, date, time, and project account. Documentation of all sample information and Chain-of-Custody requirements were met through standardized procedures, which originate with the Analytical Services request form that allows tracking of all samples from the field to the NWQL.

### **Analytical Methods and Facilities**

**National Water Quality Laboratory (NWQL).** The USGS NWQL in Denver, CO, was utilized for determinations of total particulate nitrogen (TPN), particulate organic carbon (POC), and dissolved organic carbon (DOC); see [nwql.usgs.gov](http://nwql.usgs.gov) for method descriptions. POC and TPN analyses were done by the high-temperature combustion method according to EPA method 440.0 (Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis, Revision 1.4, September 1997, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development). DOC analyses were done by uv-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993). The NWQL maintains multiple levels of internal and external QAQC, which are described in part by documents in <http://wwwnwql.cr.usgs.gov/USGS/Pubs/USGS%20OFR%202005-1263.html>. Tracking of all samples from the field to the NWQL, including Chain-of-Custody documentation, was met through the Analytical Services request form. Analytical data were automatically transferred to the National Water Information System (NWIS) database, which serves as the repository and archive for all environmental and QAQC data collected through this project.

**Missouri Water Science Center Sediment Laboratory.** Analysis of suspended-sediment concentration and the percentage of sand fractions in samples were done by the USGS Missouri Sediment Laboratory in Rolla, MO. The sediment laboratory participates in the USGS Sediment Laboratory Quality Assurance Project (SLQA), which is part of an overall quality assurance program for sediment analyses that combines and augments several existing quality-assurance activities. The SLQA provides quantitative information on sediment-data quality to sediment laboratories and their customers. The focus of this project is on all quantitative analyses done on water-sediment mixtures to derive concentrations, sand/fine splits, and particle-size distribution. The USGS Branch of Quality Systems (BQS) currently distributes standard-reference and double-blind water-sediment samples to participating laboratories, including the Missouri District Sediment Laboratory. Analytical results from all sediment quality-control samples are compiled and statistically summarized by the BQS both on a laboratory-by-laboratory basis and a national basis. Additional information on the laboratory methods and QAQC results of the SLQA project may be found online at <http://sedserv.cr.usgs.gov/>.

**AXYS Analytical Services.** AXYS is a NELAC certified laboratory that uses well-published and documented analytical methods for determination of PCB congeners by the EPA 1668A method. As such the data from this lab is acceptable for entry into USGS-NWIS database, upon successful review of raw data. Supporting information for the methods and QAQC protocols used at the AXYS laboratory is given in <http://www.axysanalytical.com>.

### Precision and accuracy

The anticipated data qualities for the analytical methods used in the project are described in the table below. These values were supplied by the laboratories doing the analyses, and may be considered goals for precision and accuracy. Analytical accuracy for surrogate parameters is estimated as the mean deviation from standard-reference samples; this is part of the on-going quality-control program of the USGS analytical laboratory, and was not specifically evaluated for samples collected in this project. Four replicate samples were collected and analyzed for surrogate parameters. The average precision, as measured by the relative percent difference, is reported in the right-most column of the table.

Analyte/ Parameter	Sample Matrix	Analytical Method Reference	Method Detection Limit	Estimated Accuracy*	Estimated Precision*	Observed Precision
PCBs	water	EPA-1668A	congener specific **	±30%	rpd<20%	see below
SS	water	ASTM-D3977	1.0 mg/L	±5%	rpd<5%	15.2%
POC	water	EPA-440.0	0.12 mg/L	±5%	rpd<5%	7.3%
DOC	water	USGS-1120-92	0.33 mg/L	±5%	rpd<5%	1.1%
TPN	water	EPA-440.0	0.022 mg/L	±5%	rpd<5%	10.9%

\* as validated in the laboratory used for the project;

\*\* MDLs range from 0.001 to 0.050 ng/L (PPT) for a 1-liter sample; 60 liter samples were used.

Precision for surrogate parameters is measured by the relative percent difference (absolute) (rpd) between two duplicate determinations:

$$\text{rpd} = 100 * \frac{|x_1 - x_2|}{(x_1 + x_2)/2} \quad \text{where } x_1 \text{ and } x_2 \text{ represent concentrations in samples 1 and 2.}$$

The observed precision for SS and TPN is poorer than the precision goal. However, the corresponding concentrations are quite low, and relative percent deviations tend to increase with decreasing concentrations.

Precision and accuracy of the PCB analyses were evaluated using the results of spikes of specific congeners (not present in natural waters) metered into each sample after the filter but before the XAD column which traps dissolved PCBs. The mean value of the spike recoveries reflects the accuracy, and the goal was that it should fall in the range 70-130% of the true value. The relative standard deviation of the spike recovery reflects the precision, and the goal was that these values be less than 20 percent. The results calculated from these spikes (n=11) are shown in the following table.

Congener	Mean Percent Recovery	Standard Deviation of Percent Recovery	Relative Standard Deviation
PCB-14	97	11.8	12.2%
PCB-55	76	5.8	7.7%
PCB-104	66	5.4	8.1%
PCB-152	57	6.8	11.8%
PCB-204	36	8.8	24.1%

Results for all congeners meet the precision goal, with the exception of PCB-204. The accuracy goal was achieved only by the lightest two congeners. However, recoveries are known to decrease with increasing chlorination. Consequently, the accuracy goal was unrealistic, except for the lighter congeners. The percent recoveries could be used to develop a gradational scale to adjust the measured congener concentrations, but this was not done for the data obtained in this project.

In addition to adding a spike containing these congeners to each dissolved phase sample, the AXYS lab analyzes one or two separate matrix spike samples with each group of environmental samples. These spikes are placed directly on a clean XAD column prior to extraction, and measure the performance of the extraction and analysis. The samples analyzed for this project were accompanied by a total of six such matrix spike samples; these recoveries are summarized in the following table.

Congener	Mean Percent Recovery	Standard Deviation of Percent Recovery	Relative Standard Deviation
PCB-1	99	8.6	8.7%
PCB-3	100	7.5	7.6%
PCB-4	98	10.7	10.9%
PCB-15	96	12.6	13.1%
PCB-19	104	9.4	9.0%
PCB-37	99	10.3	10.3%
PCB-54	103	7.7	7.5%
PCB-77	97	9.3	9.6%
PCB-81	97	8.6	8.8%
PCB-104	100	6.5	6.5%
PCB-105	99	10.4	10.4%
PCB-114	98	7.9	8.0%
PCB-118	99	10.3	10.4%
PCB-123	99	10.2	10.3%
PCB-126	97	10.0	10.3%
PCB-155	104	10.4	10.0%
PCB-156/157	101	5.6	5.5%
PCB-167	101	7.0	7.0%
PCB-169	99	5.7	5.8%
PCB-188	101	6.4	6.3%

<b>Congener (continued)</b>	<b>Mean Percent Recovery</b>	<b>Standard Deviation of Percent Recovery</b>	<b>Relative Standard Deviation</b>
PCB-189	98	7.8	8.0%
PCB-202	104	11.1	10.7%
PCB-205	99	8.0	8.1%
PCB-206	102	6.7	6.5%
PCB-208	102	5.9	5.8%
PCB-209	101	8.8	8.7%

The results for these matrix spikes all are well within the precision and accuracy goals listed above; in fact none of them differs statistically from 100% recovery. The fact that these percent recoveries remain around 100% regardless of degree of chlorination, combined with the results summarized above, is consistent with the conventional understanding that poorer XAD column trapping efficiencies with the heavier congeners are responsible for reduced percent recoveries, not some aspect of extraction and analysis.

#### **Other data quality indicators**

**Non-detection.** An important data-quality objective is to avoid non-detected values. In other studies, we might choose a goal such as: the detection limit should be no higher than 10% of the typical environmental concentrations, or: no more than 5% of the samples should be non-detects. However, the PCB analyses return results for more than 200 congeners, some of which occur in much smaller environmental concentrations than others. Non-detected values are inevitable and are the typical result for some congeners. The appropriate data-quality objective for this study was that the *particulate and dissolved PCB concentrations (all congeners combined)* be above detection limit in every analysis. For this objective, it was assumed that the total or dissolved PCB concentration would be calculated as the sum of the congener concentrations, with non-detects treated as zero (Sather et al., 2001). This criterion is equivalent to specifying that at least one or more congeners be detected in each sample. This criterion was met for every sample in both the dissolved and particulate phases. In fact, it was met at the level of PCB-homolog groups except for some samples in which all three nonachloro-biphenyls and/or the decachloro-biphenyl were below detection limit.

**Representativeness.** The samples collected for this project needed to be representative of the water transported past the sampling point, and of the water entering Lake Ontario from the Black River. The sampling site at Watertown captures 97.5 percent of the entire drainage area of the Black River basin, and measured loads can be simply extrapolated to represent the entire basin. The sampling program was designed to fully represent seasonality and the range of flows. Surrogate samples were collected approximately weekly, and PCB samples were collected approximately monthly. Samples were obtained during low flow periods, near the peak flow during the largest runoff event of the year, and at a range of flows in between, as shown in Figure 1. Samples were depth and width-integrated across the river cross section to assure adequate integration of lateral and vertical variations in concentration. We believe that the samples were fully representative of the concentration distribution at the sampling location during the course of this project. The main difficulty, however, is that the data represent only one year – the 2005 Water Year; nonetheless, the mean annual flow of 4154 f<sup>3</sup>/s in 2005 was similar to

the mean annual flow of 4180 ft<sup>3</sup>/s for the period of record (1921-2005) at this site, which indicates that study year was representative of average hydrologic conditions.

**Comparability.** Since the goal of this project was to evaluate load estimations that have not been attempted elsewhere, comparability with other studies is an issue for future projects. However, the study employed state-of-the-art sampling, analytical methods, and statistical approaches, and all data are expressed in standard units. This maximizes the potential comparability of our results with other projects that may utilize a similar approach in the future.

PCB analyses for one sample from the Black River were provided to us by the USEPA (Richard Coleates, USEPA, Edison, NJ). We compared these results with those for PCB samples collected under similar conditions of flow and time of year (Figure 11). There are some important differences: the analyses were by different labs (AXYS and the EPA Edison lab), the methods produce somewhat different groupings of parameters due to co-elution, the Coleates samples was only 1 Liter in volume as compared to our 60 Liter samples, and the Coleates sample was not separated into dissolved and particulate phases. In spite of these differences, the two samples showed similar distribution of the detected congeners. In particular, both samples show high concentrations (relative to the other congeners) of PCB-4 and PCB-1. One noteworthy difference between the two sets of results is that a number of congeners were detected in our samples that were not detected in Coleates' samples, which was attributed to the low detections limits associated with the 60-L sample size used in the study.

**Completeness.** Because this is not a compliance project, there was no firm threshold of completeness that would separate an adequate result from an inadequate one. However, adequate evaluation of the relationships between PCBs and surrogates would probably not be possible with less than seven (7) PCB samples, and the completeness goal was to obtain ten samples. Adequate regression models for the SS, POC, and DOC surrogates can be obtained from 24 samples, though results for more samples would produce models with better predictive power (i.e., smaller confidence intervals for predicted concentrations). The most important aspect of completeness for these samples is that they represent the range of seasonal effects and flows. In this respect, the goal for completeness for surrogate samples was that at least 8 samples be collected from each quarter of the calendar year, and that at least 15 samples be collected during periods of flow that exceed the median historical flow, with at least 7 of these associated with flows in the upper quartile.

These completeness goals were met. Ten PCB samples (plus one replicate) and 50 surrogate samples were collected and analyzed. Eleven surrogate samples were collected during the fourth quarter of 2004, 12 during the first quarter of 2005, 15 during the second quarter, and 12 during the third quarter. Twenty-eight of the fifty surrogate-constituent samples were collected when flows were above the historical median flow of 2890 ft<sup>3</sup>/s, and thirteen were collected when flows were in the upper quartile of historical flows, above 5210 ft<sup>3</sup>/s. Six of the ten PCB samples were collected when flows were above the median flow of 2890 ft<sup>3</sup>/s, and four were collected when flows were in the upper quartile of flows, above 5210 ft<sup>3</sup>/s.

## **Peer Review**

Peer review was provided by the EPA Project Manager via on-going dialog by phone and email. In addition, a meeting was held in Troy, NY on May 30, 2006, to review the project data and preliminary interpretations. This meeting was attended by Principal Co-Investigators (Richards and Eckhardt); the EPA Project Manager (Luckey); Simon Litton, New York State Department of Environmental Conservation, and several water-quality specialists of the USGS NYWSC.

We consulted statisticians with expertise in the regression loading approach, including Dr. Timothy Cohn (USGS), about development and evaluation of the load models. We also consulted with the chief scientist involved in developing the LOTOX2 model for Lake Ontario, Dr. Joe DePinto (Limnotech), about useful methods of evaluating and presenting total PCB data given the issues of non-detected values and estimated values at concentrations less than the quantitation limit for some congeners.

Additionally, the USGS conducts internal quarterly project reviews and at completion of research projects, including this one. Finally, we anticipate developing a manuscript for journal publication, presenting the major project results, which will receive anonymous peer reviews through the selected journal.

## **Assessments and Oversight**

Assessments include various reviews and audits conducted by independent individuals, peers, and the EPA project manager to ensure that specified procedures are followed throughout the project, to identify shortcomings or deviations, and to initiate corrective actions.

Quarterly reviews were completed throughout the project by personnel from the USGS District Office in Troy, NY, including the Section Chief, the District water-quality specialist, and the Assistant District Chief. The quarterly review includes audits of project management, field activities, laboratory activities, and database management. Assessment results are immediately communicated verbally to the project leaders (Eckhardt and Richards); followed by written documentation to be incorporated into the project files. Dale Hoover, QA/QC officer at AXYS Analytical Services, was responsible for assuring that the process and performance standards offered by AXYS were met during the analysis of our PCB samples.

The assessment process identified two issues that affected the project. One was a delay in beginning sampling, which caused the project to be extended beyond the original time frame; revisions to the project time line have been negotiated with the Project Manager and reported in Quarterly Reports. The achieved project schedule is in Appendix B. The second issue was potentially more serious, and involved field blank results for PCBs that, when compared with lab blank results, indicated a non-trivial level of contamination. Because of the high cost of PCB analyses, it was not possible to conduct additional blank samples to identify the cause and extent of contamination. This issue, together with the question of how to handle non-detected values and values less than quantitation limit, led to a detailed analysis of the project data to assess the extent and severity of the problem. This analysis is reported in Appendix D; in summary, the analysis showed that these issues had a minor impact on the

determination of total PCB concentrations in the samples, and a negligible impact on the estimates of PCB loads to Lake Ontario.

### **Documentation and Records**

Progress reports have been issued quarterly to the EPA Project Manager (Frederick Luckey) during the project. An article summarizing the project results and findings is being prepared for publication by Eckhardt and Richards in a peer-reviewed scientific journal. The final report to EPA (this document) describes the monitoring activities, data, and interpretation of results.

Analytical data for SS, TPN, POC, and DOC are available through the USGS National Water Information System (NWIS) database, which will serve as the permanent repository and archive for all environmental and QAQC data collected through this project. The data will be available, after final release, for online retrieval through <http://waterdata.usgs.gov/nwis>. The PCB data are summarized in this report, and compilations of all raw data have been forwarded to the EPA project manager as Excel files.



### APPENDIX D. QUALITY ASSURANCE ANALYSIS OF PCB DATA

The PCB data consists of 11 environmental samples, one of them a replicate, two field blanks, seven lab blanks, a lab clean-up blank, and six lab-spiked matrix recovery reports. The environmental samples and the field blanks included paired analysis of the dissolved-phase (XAD-extracted filtrate) and solid-phase (filtered particulate) components.

Results from the first set of samples included the first field blank and two environmental samples. The total PCB concentration (sum of all unflagged congener concentrations) for the dissolved phase of the first field blank was higher than that for one of the environmental samples and much higher than the first lab blank, indicating possible contamination. The second field blank, collected mid-way through sample collection, had a lower total PCB concentration for the dissolved phase but were still comparable to those in some environmental samples. Total PCB concentrations for the samples and field and lab blanks are listed in the following table.

Table 1: Total PCB concentrations (pg/L) in samples and blanks, sorted in descending order.

<b>Sample</b>	<b>Total PCBs, Dissolved Phase</b>	<b>Sample</b>	<b>Total PCBs, Particulate Phase</b>
Sample 8	2020	Sample 5	5570
Sample 5	1940	Sample 10	3050
Sample 9	1530	Sample 4	1890
Sample 7	1510	Sample 8	558
Sample 7 Rep	1350	Sample 7 Rep	437
Sample 1	1200	Sample 9	394
Sample 6	1110	Sample 7	349
Sample 10	913	Sample 6	215
Field Blank 1	519	Sample 2	213
Sample 3	503	Field Blank 2	127
Sample 4	413	Sample 1	124
Sample 2	373	Sample 3	65.4
Field Blank 2	371	Field Blank 1	41.7
Lab Blank 1	10.1	(No Lab Blanks for Particulate Phase)	
Lab Blank 2	4.13		
Lab Blank 6	4.08		
Lab Blank 7	3.23		
Lab Blank 3	1.45		
Lab Blank 4	0.991		
Lab Blank 5	0.927		

In the context of the entire data set of environmental samples, the highest sample concentrations are substantially higher than the highest field blank concentrations, but the total PCB concentration for the field blank is higher than the concentration in several low-flow environmental samples. Also, the concentrations in the two field blanks are much higher than in the lab blanks. Finally, the distribution of congener concentrations in the two field blanks is quite similar to each other, and to those in the environmental samples. These observations suggest that a systematic contamination may exist at

relatively low concentrations. The contaminant patterns are more evident in the dissolved-phase samples than in the particulate-phase samples.

To evaluate the importance of this issue, an analysis of the data was conducted at the congener level. This analysis was conducted using the congener mass in the samples, rather than the concentrations, since all the extracted mass is concentrated into a fixed extract volume for injection onto the chromatographic column.

Three kinds of analytical issues were identified and evaluated. The first of these issues involved results that were reported as less than the congener detection limit (non-detects [ND]). For these results it is uncertain whether the congener was actually present in the sample or not. The result is reported as  $<dl$ , where  $dl$  is the sample- and congener-specific detection limit value.

The second issue involved concentration results that were reported but were less than the quantitation limit. For these results the congener was deemed to be present but the exact concentration is unknown. The result is reported as  $qlK$ , where  $ql$  is the highest value that the result might be (i.e., the quantitation limit). These results were identified as K-flag values.

The third issue involved results that were reported above the quantitation limit, but that were close to values observed in lab or field blanks. For these results, the congener was deemed to be present and the value was confidently established by the analyses, but the presence of the congener may be contamination artifact. Following established practice in this issue, the mass of the congener in environmental samples was compared with the highest mass for that congener in the blank samples. If the mass in a sample was less than three times the highest mass in the blanks, that congener result was deemed suspect because of possible contamination. These results are referred to as  $<3B$ .

For each of these issues, one could assume that each reported result was valid, and the concentration was equal to the detection limit, the quantitation limit, or the reported value respectively. This assumption yields the highest possible total PCB concentration for the sample. At the other extreme, one could assume that if any of these issues affected a congener concentration, the result should be considered as non-detected and set to zero. Lastly, a number of middle positions could be assumed; for example, the non-detected values could be set to equal to half the detection limit, the K-flag values could be set to half the quantitation limit, and the  $<3B$  results set to zero. A specific result could not be both an ND and a K-flag, but it could be one of these and  $<3B$ . In our analyses, we assigned a value based on ND or K-flag before assigning a value based on  $<3B$ .

Seven combinations of assumptions were thus used, as follows:

<i>Case</i>	<i>ND</i>	<i>K-flag</i>	<i>&lt;3B</i>
1.	detection limit	K value	reported value
2.	0.5* detection limit	K value	reported value
3.	0.5* detection limit	K value	0.5*blank value
4.	0.5* detection limit	0.5*K value	0.5*blank value
5.	0.5* detection limit	K value	0
6.	0	0.5*K value	0
7.	0	0	0

Each case was considered in succession for the dissolved and particulate congener masses in each sample, and the resulting masses were summed to obtain the total mass for each sample and phase. The adjusted total PCB concentration was then calculated by dividing the mass by the sample volume. Finally, the PCB concentration for each case was expressed as a percent of the PCB concentration relative to case 1, which by definition is the largest. If contamination were present, the true value is between the maximum value (case 1) and the minimum value (case 7). The results are shown in the following table.

Case	Multipliers for DL, K, <3B cases	Range of sample results , as percent of case 1	
		<u>Dissolved phase</u>	<u>Particulate phase</u>
1	1, 1, 1	(100)	(100)
2	.5, 1, 1	99.8 - 100	99.5 - 100
3	.5, 1, .5	88.5 - 97.7	87.9 - 100
4	.5, .5, .5	88.4 - 97.7	86.5 - 100
5	.5, 1, 0	77.2 - 95.7	76.0 - 100
6	0, .5, 0	77.2 - 95.5	74.9 - 100
7	0, 0, 0	77.2 - 95.5	74.3 - 100

Case 3 was selected as yielding the most reasonable approximation of the true value. The results show that the total PCB concentrations were not strongly affected by any approach to address the uncertainty introduced by non-detects, concentrations less than quantitation limits, and environmental concentrations comparable to blank concentrations. In the worst case, these uncertainties may affect total PCB concentration by about 25 percent.

Samples that were most affected by these issues were those with the lowest concentrations typically associated with low flow. Thus, the impact on annual load estimates is small. In summary, there is evidence of contamination artifacts, which are typical in the quantification of trace-level priority pollutants, but their effect on the annual load estimates is negligible.

**APPENDIX E. SURROGATE CONSTITUENT DATA**

**Sample information for suspended sediment, TPN, POC, and DOC samples**

Date	Time	Flow (cfs)	Sand break	NWIS record	Comment	TPN (mg/L)	POC (mg/L)	DOC (mg/L)	SS (mg/L)	sand (% finer)
10/21/2004	1250	2972		00500098		0.040	0.4	5.2	12	--
10/28/2004	1000	2482		00500114		<.02	0.2	4.7	3	--
11/04/2004	1215	4260		00500188		0.050	0.3	4.3	5	--
11/08/2004	1120	4678	X	00500159		0.070	0.5	4.9	8	71
11/16/2004	1335	2503		00500189	SS broken bottle	<.02	0.2	4.3	--	--
11/22/2004	1200	2560	X	00500202	PCB sample	<.02	<.1	3.9	6	46
11/29/2004	1430	8994	X	00500276		0.120	1.3	5.8	22	75
12/06/2004	1045	9179	X	00500279		0.060	0.4	6.2	3	100
12/13/2004	1030	12800	X	00500383		0.070	0.6	4.8	11	86
12/21/2004	1000	4550	X	00500384		0.030	0.2	4.9	2	67
12/29/2004	1000	6312		00500385	SS broken bottle	0.040	0.4	4.8	--	--
01/06/2005	1410	7927	X	00500386		0.030	0.3	4.1	2	100
01/12/2005	1110	4342	X	00500436	PCB sample	<.02	0.2	4.0	1	100
01/19/2005	1430	3668		00500438		0.020	0.3	4.3	4	--
01/26/2005	1015	4260	X	00500513		<.02	<.1	4.3	3	100
02/08/2005	1340	2756		00500514		0.040	0.3	3.5	1	--
02/17/2005	1110	4376		00500515		0.040	0.2	3.4	2	--
02/23/2005	1130	3139	X	00500631	PCB sample	<.02	0.2	3.9	2	100
03/03/2005	1350	2139		00500632		0.030	0.2	3.7	2	--
03/08/2005	1020	2877		00500634		0.040	0.3	3.6	2	--
03/14/2005	1500	3462		00500635		0.030	0.2	3.5	2	--
03/22/2005	1100	2750		00500636		0.050	0.2	3.1	4	--
03/29/2005	1130	6413	X	00500698	PCB sample	0.060	0.4	3.3	6	86
04/04/2005	1020	26100	X	00500784	PCB sample	0.240	2.5	4.0	79	59
04/05/2005	1010	28140	X	00500786		0.150	1.4	4.4	42	57
04/07/2005	1300	15580	X	00500842		0.060	0.5	4.5	11	78
04/12/2005	1500	8150	X	00500843		0.040	0.3	4.1	7	64
04/20/2005	1230	2671		00500904		0.030	0.2	3.6	4	--

Date	Time	Flow (cfs)	Sand break	NWIS record	Comment	TPN (mg/L)	POC (mg/L)	DOC (mg/L)	SS (mg/L)	sand (% finer)
04/26/2005	1050	8042	X	00500905	PCB sample	0.070	0.6	4.8	13	82
05/05/2005	920	6128	X	00501028		0.030	0.3	4.5	6	50
05/10/2005	730	3069		00501029		0.040	0.2	3.9	4	--
05/18/2005	1215	2244		00501413		0.03	0.3	3.9	4	--
05/24/2005	745	1938		00501414		0.04	0.2	3.4	5	--
05/31/2005	1140	1440	X	00501415	PCB sample	0.04	0.3	3.1	7	58
06/07/2005	1430	1376		00501417		0.05	0.3	3.4	3	--
06/15/2005	740	2961		00501418		0.06	0.6	3.3	10	--
06/22/2005	730	3244		00501419		0.06	0.5	7.3	7	--
06/29/2005	930	1279	X	00501999	PCB sample	0.06	0.4	5.7	4	--
07/06/2005	830	1132		00502000		0.05	0.3	4.8	3	--
07/11/2005	735	2729		00502001		0.03	0.4	3.7	5	--
07/18/2005	615	3389		00502002		0.08	0.8	6.1	19	--
07/26/2005	920	1417		00502004		0.03	0.2	6.5	3	--
08/03/2005	1240	2244		00502006		0.05	0.3	6.1	3	--
08/09/2005	1000	1101	X	00502027	PCB sample	0.03	0.2	4.8	2	100
08/16/2005	740	1190		00502145		0.16	1.1	5.1	5	--
08/22/2005	715	1991		00502144		0.07	0.6	3.4	4	--
09/02/2005	1100	9056	X	00502147	PCB sample	0.22	2.0	7.5	45	91
09/06/2005	1415	3980		00502486		0.06	0.5	8.8	5	--
09/14/2005	720	1376		00502487		0.05	0.2	5.8	2	--
09/22/2005	830	2259		00502488		0.03	0.2	6.1	3	--

**NOTES**

Sand break done when flow exceeded 4500 cfs or if PCB sample was collected

TPN, total particulate nitrogen concentration

POC, particulate organic carbon concentration

DOC, dissolved organic carbon concentration

SS, suspended sediment concentration

sand, percentage of suspended-sediment particles finer than sand (0.062 mm)

--, no data

NWIS, USGS National Water Information System <http://waterdata.usgs.gov/nwis>

## APPENDIX F. PCB DATA SUMMARY

### PCB sample information

Date	Time	Mean daily flow (ft <sup>3</sup> /s)	XAD column ID	AXYS ID	XAD volume (L)	Filter Volume (L)	Extraction rate (L/hr)
11/22/2004	1200	2560	A1127	L7294-3	62.868	65.219	2.80
1/12/2005	1110	4342	A1115	L7294-2	58.611	60.660	2.46
2/23/2005	1130	3139	999	L7294-1	60.268	62.028	2.58
3/29/2005	1130	6413	A1127	L7662-2	62.056	63.309	2.76
4/4/2005	1020	26100	A1115	L7662-1	59.247	59.944	2.42
4/26/2005	1050	8042	A1137	L7662-3	61.225	62.108	2.62
5/31/2005	1140	1440	999	L7804-1	58.363	59.063	2.70
6/29/2005	930	1279	A1115	L7804-2	61.497	62.830	2.70
8/9/2005	1000	1101	999	L7956-1	60.632	61.119	2.71
9/02/2005	1100	9056	A1131	L7956-3	62.221	62.786	2.67
<b>mean:</b>					60.84	61.91	2.64
							(44 ml/min)

### PCB QAQC sample information

Date	Time	Comment	XAD column ID	AXYS ID	XAD volume (L)	Filter Volume (L)	Extraction rate (L/hr)
11/19/2004	1501	Field blank 1	A1131	L7294-4	6.198	7.238	2.22
5/31/2005	1145	Duplicate	A1131	L7804-3	58.589	59.369	2.68
8/31/2005	1101	Field blank 2	A1115	L7956-2	6.325	7.811	2.37

**PCB data summary (concentrations in picograms/Liter)**

**Dissolved phase**

Date	Time	Flow	Total PCB	TEQ*	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
11/22/2004	1200	2560	1200	0.00332	177	551	253	143	51.2	14	4	1.44	0.331	0.199
1/12/2005	1110	4342	373	0.00318	53.9	135	79.9	59	29	11.5	3.47	1.52	0.073	<0.0085
2/23/2005	1130	3139	503	0.00113	58.6	213	116	79.4	28.7	5.72	1.3	0.444	0.093	0.157
3/29/2005	1130	6413	413	0.00165	36.2	130	101	95.5	39.4	8.38	1.73	0.275	0.1	0.115
4/4/2005	1020	26100	1940	0.00325	112	725	555	394	124	23.7	4.72	1.55	0.358	0.2
4/26/2005	1050	8042	1110	0.00210	116	413	284	208	69	15.1	4.15	1.25	0.344	0.158
5/31/2005	1140	1440	1510	0.00915	70.6	383	470	399	142	35.8	8.01	1.54	<0.0188	0.155
6/29/2005	930	1279	2020	0.00732	49.6	424	634	680	178	45.3	8.12	1.87	0.338	0.118
8/9/2005	1000	1101	1530	0.00493	52.9	347	484	445	162	32.9	5.32	1.2	<0.0378	<0.0165
9/02/2005	1100	9056	913	0.00412	25.3	167	278	277	121	35.1	7.59	1.96	0.49	<0.0161

**Particulate phase**

Date	Time	Flow	Total PCB	TEQ*	Mono	Di	Tri	Tetra	Penta	Hexa	Hepta	Octa	Nona	Deca
11/22/2004	1200	2560	124	0.00265	2.15	13.8	28.4	39.9	24.9	10.4	3.14	0.87	0.309	0.177
1/12/2005	1110	4342	213	0.00435	1.17	9.43	29.1	58.1	59.8	34.2	14.3	4.56	1.7	0.4
2/23/2005	1130	3139	65.4	0.00135	0.967	7.16	13.5	21.4	14.6	5.63	1.63	0.511	0.061	<0.0081
3/29/2005	1130	6413	1890	0.01080	14.3	211	625	709	238	64.7	17.6	4.2	0.84	<0.0079
4/4/2005	1020	26100	5570	0.06890	107	744	1390	1680	1120	398	95.9	22.8	6.34	3.34
4/26/2005	1050	8042	215	0.00337	2.39	19.9	44.6	70.9	47.6	19.5	7.24	1.91	0.43	0.433
5/31/2005	1140	1440	349	0.00738	2.68	20.4	67.7	116	74.1	42.8	19.1	5.56	0.899	0.358
6/29/2005	930	1279	558	0.01010	3.76	36.1	120	193	123	58	17.6	5.74	1.19	0.639
8/9/2005	1000	1101	394	0.00683	2.41	29.7	87	124	91.7	42.9	11.1	3.39	1.07	0.69
9/02/2005	1100	9056	3050	0.05960	31.7	255	693	1010	631	288	92.3	31.3	6.73	3.5

\* Toxic equivalents according to World Health Organization definition, calculated with non-detects assigned values of half the detection limit.