

**Enhanced Toxics Monitoring from Final Chlorinated Wastewater
Effluents and Surface Waters Using the Trace Organics Platform
Sampler (TOPS)**

August 1997

New York State Department of Environmental Conservation

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Acknowledgments

The author wishes to thank the operators of the wastewater treatment plants for the many courtesies and items of practical assistance extended to us. Particularly, I want to thank Mike Diehl, Peter Sharkey, and Cynthia Tudor-Schultz at Lockport, Mike Schifano at Monroe County, Bob Holtz at Alden, Ken Maving and John Camilleri at Tonawanda, and Ron Novak at Carthage. Adele Fadel gave us permission to sample at Sauquoit. Tony Ethier of the Axys Group demonstrated the practicality of the filter/XAD system. Georgina Brooks, Dale Hoover, and Lauri Phillips, also of the Axys Group performed the organics analyses. Colin Davies and his staff at Brooks Rand performed the metals analyses. The overall design of the project was a cooperative effort including Cynthia Leece at NYSDEC and John Bourbon of USEPA. Mr. John Donlon built the TOPS and was responsible for its cleaning and operation. Valuable editorial suggestions were given by Fred Luckey at EPA, Region II. Alice Yeh, EPA Region II, was the EPA project officer.

Introduction

The New York State Department of Environmental Conservation, Division of Water (NYSDEC, DOW) received a grant from United States Environmental Protection Agency (EPA) to develop enhanced methods for the measurement of toxic substances in treated wastewater. Results of this project provide the department with the following benefits:

- a) field and laboratory method improvement;
- b) data to help in making contaminant load estimates to Lake Ontario; and
- c) data to better understand aspects of wastewater treatment that affect toxic loadings.

Target substances of interest are metals - mercury, arsenic, and lead- and organics - polychlorinated dioxins (PCDDs) and furans (PCDFs), polychlorinated biphenyls (PCBs), chlorinated pesticides, and polynuclear aromatic hydrocarbons (PAHs). Secondary parameters include total suspended solids (TSS), total organic carbon (TOC), and dissolved organic carbon (DOC). Both sampling and analysis were conducted using the best methods available for the attainment of low detection levels. A major goal has been the development of methods that eliminate non-detections.

NYSDEC has been exploring the use of innovative field methods to sample dilute (low concentration) organic chemicals in water. Over the past eight years NYSDEC personnel have been gaining experience with passive samplers, particularly the Passive In-Situ Chemical Extraction Sampler (PISCES) to collect PCBs from the low nanogram/L concentration range. PISCES are easy to deploy, inexpensive, reasonably sensitive, and useful for locating contaminant sources.

However, it is not clear exactly what PISCES samples. They were originally believed to capture chemicals freely dissolved in water and not substances bound to suspended solids or to large natural macromolecules. More extensive experience indicates that PISCES has some capacity for removing chemicals from other environmental compartments. The uptake rate of target chemicals by PISCES is believed to be a factor of water temperature (which is usually known only at placement and retrieval and used in calculating uptake rate) and by turbulence (which is not quantified and not incorporated in calculating uptake rates). PISCES have not been calibrated for substances other than PCBs and may not be appropriate for work with extremely dilute chemicals such as the chlorinated dioxins and furans.

This report deals with an alternative sampling tool, the Trace Organics Platform Sampler (TOPS). In many ways TOPS is the opposite of PISCES. TOPS is heavy (about 60 lbs versus less than two lbs for PISCES), complicated, expensive (roughly \$5,600 for parts plus two weeks of labor for assembly versus \$20 for PISCES and a few minutes of labor), and TOPS requires AC power. But TOPS is also quantitative in that the operator knows how much water it samples and it produces separate samples for the dissolved and for the suspended solids-bound compartments. PISCES is best used for finding chemical sources in situations where the loss of units through storms or vandalism is tolerable and precise

quantitation is not required. TOPS is best used for obtaining accurate phase-specific concentrations where physical security and electrical power are available. TOPS can process thousands of L of water enabling the quantitation of extremely dilute organic contaminants. It can be modified to sample precisely defined conditions such as particular flow or turbidity conditions. TOPS may also be set up to run over a prolonged period of time in order to obtain temporal and flow integrated samples.

This project has demonstrated the utility of TOPS to collect water samples of a sufficient volume to detect consistently PAHs, PCBs, many pesticides, and dioxins in finished wastewaters from five different communities in the Lake Ontario basin and from surface waters at seven sites. Also, metals - mercury, arsenic and lead, were taken by grab sampling and were also detected consistently. PCBs, dioxins, dieldrin, DDTs, and mercury usually occur at concentrations above the Great Lakes Initiative (GLI) guidelines for effluents. Variability between sampling events was large and upsets in wastewater treatment plant operation appear to have an extremely deleterious effect on the quality of discharge with respect to trace organics.

Tests for break-through showed that at least 85% of the dissolved phase of dioxins, PCBs, and PAHs were retained on the XAD column. Comparisons between TOPS and PISCES were not definitive. While some comparisons show a close correspondence, others don't. This may be due to differences in the period of exposure for the different sampling systems. While TOPS has been demonstrated to be a powerful tool, there is still ample scope for improvement and for further testing. The greatest operational problem encountered in this study was premature filter clogging. Some environments, such as untreated or poorly treated wastewater, contain sticky solids which rapidly plug the filter and cause the TOPS to shut off after a pre-determined back-pressure occurs. Premature shut down causes loss of control over the duration of sampling. Waters containing high concentrations of chemicals competing for attachment sites on the XAD resin may reduce the efficiency of the sampling system for very dilute target substances. The possibility for displacement of chemicals from the XAD when very large volumes of water were pumped was also not evaluated. Waters containing droplets of non-polar solvents would reduce the efficiency of XAD to trap and retain target chemicals.

Methods - metals

Sampling

Metals were taken by grab sampling. Sample bottles (150 mL Teflon bottles for mercury and arsenic) were initially cleaned in the laboratory by soaking in warm high purity 4 N HCl for 48h. After soaking, the bottles were flushed three times with reagent water, refilled with acidified reagent water, and kept warm overnight. They were flushed again and again filled with acidified water. For shipping, they were double bagged in Ziploc bags. Lead was collected in two 500 mL polyethylene bottles that were not acid filled and were shipped single bagged. In the field the bottles were removed from the bags, taped onto a polypropylene line weighted with an epoxide coated grapple, and emptied, if necessary, of acid. The bottles were then submerged in the wastewater, retrieved, capped,

re-bagged, iced, and air shipped to the lab later that same day. During shipping, the samples were cooled by Blue Ice packs.

Mercury analysis

Mercury was analyzed by a modification of Draft USEPA Method 1631¹. In summary, the sample is collected into pre-cleaned Teflon bottles and shipped to the lab within 48 hours. In the lab, 5 mL/L of 12 N pre-tested HCl are added. Before analysis, 0.2 N BrCl are added to oxidize all Hg compounds to Hg(II). After oxidation the sample is UV irradiated for the photo-oxidation of Hg bound in microbial cells. Then the sample is reduced with SnCl₂ to convert Hg(II) to Hg(0). The Hg(0) is separated from the solution by purging with N₂ onto a gold-coated sand trap. The trapped Hg is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection. The method is designed for measurement of total Hg in the range of 0.2 to 100 ng/L.

Arsenic analysis

Arsenic was analyzed by hydride generation flame atomic absorption, Draft USEPA Method 1632². The water sample is collected into pre-cleaned Teflon bottles and shipped to the lab within 48 hours. In the lab the sample is preserved with 5 mL/L of pre-tested 10% HNO₃. Before analysis 6 M HCl and 4% NaBH₄ are added to convert organic and inorganic arsenic to volatile arsines. The arsines are purged from the sample onto a cooled glass trap packed with 15% OV-3 on Chromasorb WAW-DMMS0. The trapped arsines are thermally desorbed, in order of increasing boiling points, into an inert gas stream that carries them into the flame absorption spectrophotometer for detection. The first arsine to be desorbed will be AsH₃, which represents total inorganic arsenic in water. This method is designed for measurement of dissolved and total arsenic in the range of 10-200 ng/L.

Lead analysis

Lead was analyzed by inductively coupled mass-spectrometry, Draft USEPA Method 1638³. An aliquot of sample is accurately measured. Analytes are first solubilized by gentle refluxing with nitric and HCl. After cooling, the sample is made to volume, mixed, and centrifuged or allowed to settle overnight prior to analysis. The digested sample is introduced into a radiofrequency plasma where energy transfer processes cause

¹ USEPA, April 1995. Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, Draft. EPA 821-R-95-027. US Environmental Protection Agency, Office of Water. Engineering and Analysis Division, Washington, DC 20460.

² USEPA, April 1995. Method 1632: Determination of Inorganic Arsenic in Water by Hydride Generation Flame Atomic Absorption, Draft. EPA 821-R-95-028. US Environmental Protection Agency, Office of Water. Engineering and Analysis Division, Washington, DC 20460.

³ USEPA, April 1995. Method 1638: Determination of Trace Elements in Ambient Water by Inductively Coupled Plasma-Mass Spectrometry, Draft. EPA 821-R-95-031. US Environmental Protection Agency, Office of Water. Engineering and Analysis Division, Washington, DC 20460.

desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer having a minimum resolution capability of 1 amu peak with at 5% peak height at m/z 300. Ions transmitted through a mass analyzer (m/z s are 206, 207, and 208) are detected by an electron multiplier or Faraday detector and the resultant current is processed by a data handling system. For lead, the MDL and ML are 15 and 50 ng/L respectively.

Methods - organics

Organics sampling was performed under the assumption that the key to obtaining loading information is to sample a sufficiently large volume of water and use of high quality GC/MS analytical methods. For the sampling system to be practical, it must concentrate suspended solids and dissolved organics in the field. Otherwise, the large volumes of water that would be necessary to achieve low, part per quadrillion detection levels would become unwieldy. A sampling device, called Trace Organics Platform Sampler (TOPS), was designed and built under this project. TOPS pumps water through a glass fiber filter cartridge to collect suspended solids and sends some of the water through a Teflon column containing beads of the synthetic resin XAD-2.

A key aspect of TOPS is its mutability. It can be operated to only collect suspended solids; XAD columns may be arranged in parallel (to process more water); or in series (to determine if break-through is occurring). It is operationally simple. Pumping rates can be changed. It can be readily modified to pump water from environmental clues or to repeatedly switch on and off on a schedule. This last feature permits it to sample over a longer time span. Future iterations of TOPS may be interfaced with a modem or data logger so that it can collect flow-proportional samples.

Trace Organics Platform Sampler (TOPS)

Figure 1 is a schematic illustration of TOPS. **Table 1** is a parts list. With the exceptions of an eight inch piece of platinum cured silicon tubing in a pump, cleaned XAD resin, and cleaned glass fiber filter material, all water contact surfaces are either stainless steel or Teflon. TOPS has a flow totalizer and a timer which permits measuring the amounts of water filtered and the amounts of water passed through the XAD. The parts list shows two flow meters but the TOPS actually used has but one. The experience of the project suggests two may be preferable. A pressure sensor shuts off power to the TOPS when back-pressure from the filter reaches a set-point. In the earliest deployment that set-point was 20 psi but in samples taken after 7/2/96 the set-point was reduced to 15 psi. The amounts of water filtered are greater than the amounts extracted by the XAD. Filters and XAD columns are shipped to a laboratory specializing in ultra-low level detections using GC/MS.

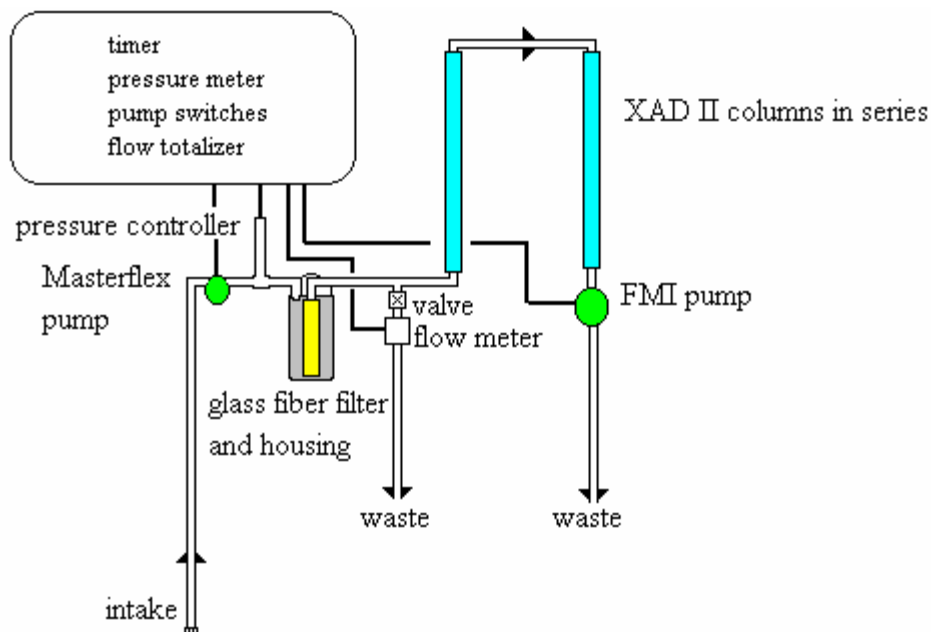


Figure 1. Trace Organics Platform Sampler (TOPS).

The glass fiber filter cartridge (Filterite DFT Classic) has a nominal pore size of 1 μm . Approximately 3/4 of an inch of glass fiber yarn is wound around a hollow perforated stainless steel support. The cartridge is 4 inches long and 2.5 inches in diameter. It is held in a stainless steel housing with Teflon seals. The filter housing has 550 mL of dead space. Raw water was forced through the filter from the outside in. Prior to use, the filter cartridges were baked over-night at 250°C and then solvent cleaned.

Amberlite XAD-2 macroreticular resin (Rohm and Hass Co.) has been a widely used method for the field concentration of polar chemicals, particularly in the Western Great Lakes^{4,5}. Prior to use the XAD was cleaned by a modified version of EPA method 0010A. Raw XAD was sifted through a 297 μm sieve (discard the fines) and then rinsed with Type II water, and allowed to soak over-night in fresh Type II water. Then it was flushed for 8 hours with Type II water. Rinsed XAD was placed in a 2 L Soxhlet and extracted for 22 hours with methanol; 22 hours with methylene chloride; and then another 22 hours with fresh methylene chloride. The cleaned XAD was dried on a fluidized bed of purified nitrogen. The dried XAD was made into a slurry with methanol and poured into Teflon columns 37 cm long and 2.5 cm in diameter. All of these cleaning operations were

⁴ Verbrugge, D.A., J.P. Giesy, M.A. Mora, L.L. Williams, R. Rossman, R.A. Moll, and M. Tuchman. 1995. Concentrations of dissolved and particulate polychlorinated biphenyls in water from the Saginaw River, Michigan. *J. Great Lakes Res.* 21(2) 219-233.

⁵ Swackhammer, D.L., D.E. Armstrong. 1987. Distribution and characterization of PCBs in Lake Michigan water. *J. Great Lakes Res.* 13(1) 24-36.

Table 1. TOPS parts list.

Equipment	Supplier	Part #	Quantity	Price	Total
Masterflex IP pump w/IP 82 head	Cole Parmer	07591-00	1	\$1,320	\$1,320
XAD pump	FMI	QD	1	\$275	\$275
XAD pump head	FMI	Q1CSC	1	\$220	\$220
Flow Indicator	Cole Parmer	E-32704-40	2	\$225	\$450
Flow Sensors	Cole Parmer	E-32704-20	2	\$335	\$670
Power Supply	Cole Parmer	E-32705-55	2	\$50	\$100
Pressure Meter	Cole Parmer	E-07350-66	1	\$279	\$279
Pressure Transmitter	Cole Parmer	E-07356-53	1	\$231	\$231
Gauge Guard	Cole Parmer	E-07359-12	1	\$70	\$70
SS Filter Housing with Teflon gasket	Filterite	LMO4S-1/2	1	\$500	\$500
Aluminum Enclosure24x24x8	Hoffman		1	\$446	\$446
Fiberglass Enclosure12x18x6	Hoffman		1	\$175	\$175
Swagelock Valve	Albany Valve & Fitting		1	\$175	\$175
Swagelock fittings	Albany Valve & Fitting		8	\$20	\$160
Teflon Fittings	Cole Parmer		12	\$20	\$240
Teflon Tubing	Cole Parmer		1	\$70	\$70
316 stainless steel seamless pipe	Uncle Sam's Pipe		1	\$50	\$50
Relays	Newark Electronics	46F8140	2	\$37	\$74
Timer	Newark Electronics	96F1906	1	\$80	\$80
Elapsed Time meter	Newark Electronics	96F1859	1	\$25	\$25
				Total	\$5,610
Supplies					
Filter Cartridges	Filterite	G1A4S	case	\$396	\$396
Trace Organics Extraction Column	AXYS		4	\$291	\$1,164
Silicone Tubing	Cole-Parmer	E-95802-24	25 ft pkg	\$116	\$116

performed by a contract laboratory. The columns were sealed and not opened until the TOPS had been cleaned and readied for deployment.

TOPS operation

TOPS was cleaned first by flushing it with tap water with a dummy XAD column (a Teflon column not containing any XAD) and no filter in the filter holder. Then the TOPS was placed in a fume hood, reconfigured by removing the peristaltic pump from the sampling train, and inserting a baked and cooled filter in the filter holder. New silicone tubing for the peristaltic pump was used for each sample after soaking a minimum of 24 hours in methanol. The FMI pump was used alone during the solvent cleaning process. Two different cleaning processes were used. Initial there were three 10 minute rinses with acetone, three ten minute rinses with methylene chloride, three ten minute rinses with toluene, and three 10 minute rinses with methanol. To reduce exposure and consumption of solvents, the protocol was modified on 8/30/96 to have four ten minute rinses with acetone, three ten minute rinses with hexane, and three ten minute rinses with methanol.

At the conclusion of the solvent rinses, a stainless steel plug (which had been rinsed with all the solvents) was screwed in the bottom of the intake to prevent contaminants from entering the TOPS. A stainless steel valve prevented entrance of contaminants from the waste port below the flow meter, and the FMI pump piston prevented entrance of contaminants below the XAD column(s). Prior to going into the field the silicon tube for the peristaltic pump was inserted. An aluminum cover protected the FMI pump from the elements and gave mechanical protection of all the sampling train.

Two methods of deployment were used. At the sites for field blanks (Orenda and Polaris springs in Saratoga State Park, Saratoga NY and Sauquoit water supply in Sauquoit, NY) the TOPS was suspended from a tripod. This procedure was also followed in Eighteenmile Creek below Burt Dam, at both sites in Cayuga Cr. Erie County, and in the Hudson River at North Creek. At the wastewater treatment plants the TOPS was hung from railings around the final treated chlorinated effluent. It was hung with the intake in the water and the pumps not in the water. TOPS was hung from structures when sampling at the Burt Dam and from the two sites in the Hudson River below Glens Falls. Electric power (115 V) was taken off GFI protected outlets at the treatment plants and from a 5,000 watt generator elsewhere. The two pumps were activated and the start time noted. The FMI pump was set to run at 250 mL/min. and the peristaltic pump at a little more. The system is visibly functioning when there is water exiting both waste lines.

Filtration is most efficient at the lowest practical pump rate. In some sampling situations, particularly when waters are very clear (TSS <1 mg/L), higher pump rates are needed to obtain a sufficiently large sample when time is limiting. Normally, we used a peristaltic pump rate of about 3.5 L/min but have used rates as high as 7.5 L/min in surface water sampling. The rate at which water was pumped through the XAD columns is another compromise. More water means more analyte and better detections but excessively high pump rates may result in unacceptably low recoveries or even damage to XAD beads. On three occasions, XAD columns were installed in series. The second column recovers analyte missed in the first column.

At start-up water samples were collected for total suspended solids and total organic carbon. A sampling jar was held under the overflow waste tube to collect a sample for dissolved organic carbon. The three samples were iced and delivered to the New York State Department of Health (NYSDOH) laboratory for analysis.

Sampling terminated when the back-pressure from the filter exceeded 15 psi, when the TOPS was manually stopped, or when an electrical fault caused the GFI to trip. The pressure controller indicated if it caused shut-off. When the unit stops, the timer also stops and indicates the number of hours of run time. The flow totalizer measured the volume of water passing through the overflow. On retrieval of the TOPS the end plug, which had been stored in a Ziploc bag, was reinserted and the valve closed. The TOPS used here required that the unit be brought back to the NYSDEC laboratory in order to remove the XAD column and the cartridge filter. The cartridge filter was removed and placed on a hexane rinsed aluminum foil. The dead space water from the filter housing

(about 550 mL) was placed in a stainless steel nitrogen pressurized filter holder that had been rinsed with acetone. A 142 mm GFF glass fiber filter which had been baked overnight at 250°C trapped particles from the dead-space water. The flat filter was handled with stainless steel forceps which had been rinsed with acetone, folded in quarters (sample side in) and wrapped up in the aluminum foil wrapper that had held the cartridge filter when it was being baked. Both filters were placed in a Ziploc bag and refrigerated if they could not be immediately shipped out for analysis.

The amount of water which passes through the XAD column is the pump rate times the length of time the pump operated. The amount of water filtered is the sum of the amount of water that passed through the overflow totalizer, the amount of water that passed through the XAD column, and the amount of water found in the filter housing.

This set-up was designed to obtain quantitated detections for all target chemicals. Very large volumes of wastewater may be processed. One sample was almost 2,200 L

Passive samplers (PISCES)

PISCES consists of a solvent reservoir and a membrane. PISCES units were suspended in water with the membrane submerged and down. The inner surface of the membrane is covered by 200 mL of hexane. **Figure 2** is a schematic illustration of PISCES. Dissolved hydrophobic molecules like PCBs dissolve through the membrane and accumulate in the non-polar hexane.

PCB concentrations from PISCES were estimated as the total ng recovered divided by the sampling rate times the number of days of exposure. A sampling rate equation, developed through research conducted by Professor John Hassett at SUNY-College of Environmental Science and Forestry at Syracuse, NY, is:

$$\text{sampling rate, } S \text{ (L/cm}^2\text{/day)} = \exp((-6591/\text{absolute temp.}) + 19.269)$$

The effective sample volume (V) is:

$$V = S \times \text{membrane area in cm}^2 \times \text{days of exposure}$$

Prior to going into the field PISCES bodies, Teflon, slip nuts, and "O" rings were cleaned in hot soapy water, rinsed, and washed with tap water. Soxhlet extracted polyethylene was fitted onto the bodies and pressure tested. Passed units were rinsed with a small quantity of hexane and tested for leakage and then wrapped in clean aluminum foil for transportation to the field. Immediately before deployment, the samplers were rinsed three times with hexane and filled with hexane. The identity of each hexane bottle used to fill passive samplers was recorded. PISCES remained in the water for about two weeks. The times of placement and retrieval and the water temperatures at placement and retrieval were also recorded. At retrieval the passive samplers were wiped dry and opened. The contents were quickly poured in pre-cleaned 250 mL amber packer jars with Teflon lids. Samples were kept in a freezer prior to air-shipping.

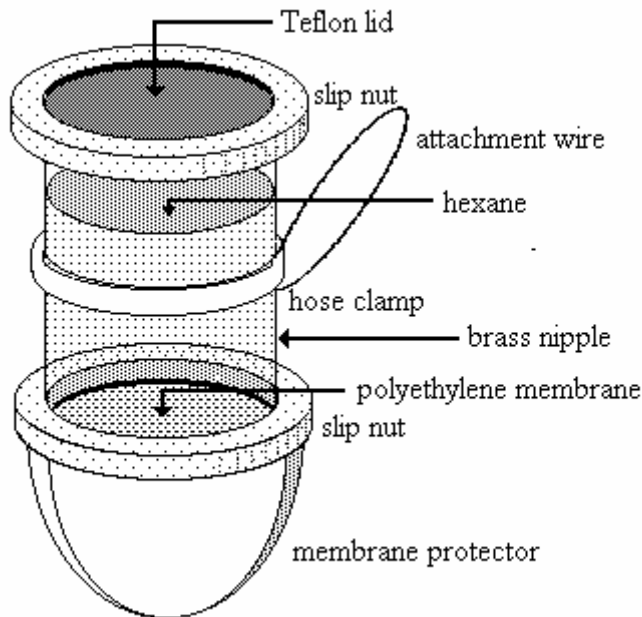


Figure 2. PISCES.

Laboratory - extraction and clean-up

Samples were spiked with perdeuterated PAHs and ^{13}C labeled homologs of dioxins/furans, PCB congeners, and pesticides. Filters were air dried and Soxhlet extracted for 18-20 hours with toluene. XAD was spiked with internal standards and eluted with methanol and dichloromethane (DCM). The combined eluate was backwashed by shaking with solvent extracted distilled water and the organic layer was collected. The aqueous methanol layer was extracted twice more with DCM and the extracts were combined. The DCM layer was backwashed twice with sodium chloride solution and dried over sodium sulfate. The DCM was reduced in volume, transferred to hexane and split four ways.

Samples from wastewater treatment plants were subject to additional clean up using one or more biobead or alumina columns.

PCBs and non-polar pesticides

The extract to be analyzed for PCBs and pesticides were labeled and separated into two fractions (F1 and F2) and F3 on Florisil. (F1 and F2) was eluted with DCM : hexane (15:85) and analyzed by GC/MS for the PCB congeners and non-polar to moderately polar chlorinated pesticides. F3 was eluted with DCM : hexane (1:1) analyzed by GC/ECD for the most polar pesticides (heptachlor epoxide, alpha endosulfan, dieldrin, endrin, and methoxychlor). An aliquot of recovery standard (^{13}C -labeled BZ 153) was added to each fraction prior to instrumental analysis to allow the recovery of the surrogate standards to be monitored.

PCBs and pesticides from the (F1 and F2) fraction were analyzed using a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 G, a CTC autosampler, and a DG 10 data system running INCOS 50 software. The MS detector was operated at a unit mass resolution in the MID mode acquiring two characteristic ions for each target analyte and surrogate. Chromatography was accomplished with a 60 m DB-5 column (0.25 mm id, 0.10 μ m film thickness).

Compounds were identified when the data meet the following criteria:

- i) The retention time of the peak was within 3 seconds of the predicted time.
- ii) Peak responses of both ions was at least 3 times background noise,
- iii) Peak maxima of characteristic ions coincided within 2 seconds.
- iv) Ratio of characteristic ion peak areas was within +/- 20% of the calibration standard.

The concentrations of the identified compounds were calculated by the internal standard method using mean relative response factors determined from the calibration standard runs made before and after each batch of samplers run.

Polar pesticides

Polar pesticides (fraction F3 - heptachlor epoxide, alpha endosulfan, dieldrin, endrin, and methoxychlor) were analyzed by GC/EC using a Hewlett Packard 5890 gas chromatograph with a ^{63}Ni electron capture detector and a 60 m 0.25 mm, 0.1 μ m film DB5 Durabond Fused Silica capillary column. The carrier gas was helium, the makeup gas was 5% methane argon, the injector temperature was 250°C, and the detector temperature was 340°C.

A peak was assigned to a given chlorinated compound if:

- i) The corrected retention time was within +/- 0.02 minutes of that expected.
- ii) the compound was expected in the F3 fraction.
- iii) The GC shape matched that of the authentic compound.

The concentrations of the identified compounds were calculated by the internal standard method using mean relative response factors determined from the calibration standard runs made before and after each batch of samples run.

Polychlorinated dibenzodioxins and dibenzofurans (PCDDs and PCDFs)

The extracts were obtained and spiked as described. The extract was transferred to a separatory funnel and KOH was added. The solution was shaken and the aqueous layer was discarded. Distilled water was added, the mixture was shaken, and the aqueous phase discarded. Concentrated H_2SO_4 was added and shaken. The extraction with distilled water was repeated and the organic layer dried over Na_2SO_4 . The solvent was evaporated to dryness and redissolved in hexane. The hexane extract was transferred to a Biosil A column and eluted with hexane. The extract was then loaded onto an alumina column and eluted with 3% DCM/hexane and that elutant was discarded. The next fraction was eluted with DCM : hexane (1:1) and retained. The alumina column elutant was then loaded

onto a carbon/celite column and eluted with cyclohexane: DCM and discarded. The next fraction of toluene : ethyl acetate was also discarded. Then the column was inverted and eluted with toluene. The toluene fraction was taken to near dryness and redissolved in hexane. The carbon/celite column extract was loaded onto a second alumina column and eluted with 3% DCM : hexane which was discarded. The next fraction of DCM : hexane (1:1) was retained and concentrated to 1 mL. An aliquot of recovery standard (¹³C labeled 1,2,3,4-tetrachlorodioxin and ¹³C labeled 1,2,3,7,8,9-hexachlorodioxin) was added.

PCDDs and PCDFs were analyzed on a VG AutoSpec Ultima high resolution mass spectrometer equipped with a Hewlett Packard gas chromatograph and a CTC autosampler. A 60 m DB-5 chromatography column (0.25 mm x 0.25 μm film thickness) was used for GC separation. Data were acquired in the selected ion monitoring (MID) mode to enhance sensitivity. Two ions were monitored for each group of isomers. Also, two ions were used to monitor each of the ¹³C labeled surrogates standards.

Positive identification of the PCDDs and PCDFs was based on EPA Method 1613. Once identification was made compounds were quantitated by comparing the area of the quantification ion to that of the corresponding ¹³C labeled standard and correcting for response factors. Response factors were determined by twice daily runs of a calibration solution containing all of the authentic and ¹³C labeled PCDDs and PCDFs and must agree within 15% RSD.

Polynuclear Aromatic Hydrocarbons (PAHs)

The portion of extract from XAD and from the filters to be analyzed for PAHs was cleaned up and fractionated on silica gel into polar and non-polar fractions. The polar fraction was analyzed for PAHs by GC/MS. Column clean-up was accomplished with deactivated silica gel slurry packed in pentane. The sample extract retrieved from XAD or filters is loaded onto the column with rinses, eluted with pentane (Fraction 1) and discarded. The column was then eluted with DCM (Fraction 2) which contains the PAHs. The eluate was collected in a small K-D flask. Activated copper was added to Fraction 2 and the extract was reduced to ~1 mL in a 50°C water bath. The sample was quantitatively transferred to a microvial with DCM rinses and concentrated under nitrogen to almost dryness. Lastly, an aliquot of recovery standard solution containing deuterated acenaphthalene, benzo(b)fluoranthene, and fluoranthene was added.

Sample extracts were analyzed using a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 GC, a CTC autosampler, and a DG 10 data system. A 30 m, 0.25 mm x 0.25 μm DB-5 capillary column was directly coupled to the MS source. Data were collected in the MID mode for greater sensitivity.

Compounds were identified if the GC/MS data satisfied the following criteria:

- i) the retention time of the peak was within three seconds of the predicted time.
- ii) Peak response of both ions was at least three times background noise.
- iii) Peak maxima for both characteristic ions coincided within 2 seconds.

iv) The ratio of characteristic ion peak areas were within +/- 20% of the value seen from calibration standards.

The concentration of the identified compounds were calculated by the internal standard method using mean relative response factors determined from the calibration standard runs made before and after each batch of samples run. RRFs must agree to within +/- 10%. Only peaks with responses greater than 3 times the background noise level were quantified. PAH blanks were difficult to keep at "not detected" levels for some of the lighter compounds. This was due in part to PAH sources in the XAD itself.

Table 2 lists the organic chemicals analyzed in this program.

Methods - accessory parameters

Total organic carbon (TOC), dissolved organic carbon (DOC), and total suspended solids (TSS) were analyzed by the New York State Department of Health Environmental Health Lab. TOC and DOC were both acidified in the field and iced and refrigerated prior to analysis. Analysis was by UV-oxidation (USEPA -600/4-79-020 415.2). TSS was determined by method 208 D from Standard Methods.

Sampling Sites

Sampling included blank sites, final chlorinated effluents from five wastewater treatment plants, and surface waters from three sites on the Hudson River, two sites on Cayuga Creek (Erie County) and two sites on Eighteenmile Creek (**Figure 3**).

Blank sites were from ground waters thought to be pristine with no measurable levels of anthropogenic contaminants - Saratoga State Park in Saratoga NY (the Orenda, Polaris wells) and a well from the Town of Sauquoit drinking water system. The particular sites were chosen with advice from NYSDEC geologists. Orenda and Polaris are high volume briny springs whose waters have been deep underground for a long time. It is suggested that the brine may be as old as the Paleozoic (230 million years BP) but diluted with younger waters.⁶ The dilutant waters are geologically young but their source of entrance was far to the east and sufficiently distant in time to exclude man-made chlorinated chemicals.⁷ The Sauquoit site was intensively investigated by NYSDEC under a wellhead protection study and was determined to be "from a confined aquifer, and, as such, is not **Table 2**. Organic chemicals measured from the dissolved and suspended solids phases using TOPS.

⁶ Young, J.R., and G.W. Putman. 1979. Stratigraphy, structure, and the mineral waters of Saratoga Springs - implications for neogene rifting. In Joint Annual Meeting of New York State Geological association 51st Annual Meeting and New England Intercollegiate Geological Conf. 71st Annual Meeting. Tror, NY. Oct 5,6 & 7, 1979. G. M. Friedman, ed.

⁷ Cushing, H.P., and R. Ruedemann. 1914. Geology of Saratoga Springs and Vicinity. University of the State of New York Bulletin. New York State Museum, Albany, NY. Museum Bulletin 169. No. 560. Feb 1, 1914.

PCB congeners		pesticides	PAHs	Dioxins/Furans
8/5	153	hexachlorobenzene	acenaphthalylene	T4CDD total
15	141	alpha HCH	acenaphthene	2,3,7,8
19	130	beta HCH	fluorene	P5CDD total
18	137	gamma HCH	phenanthrene	1,2,3,7,8
17	138/163/164	heptachlor	anthracene	H6CDD total
24/27	158	aldrin	fluoranthene	1,2,3,4,7,8
16/32	129	oxychlorane	pyrene	1,2,3,6,7,8
26	128	trans-chlordane	benz(a)anthracene	1,2,3,7,8,9
25	156	cis-chlordane	chrysene	H7CDD total
31/28	157	o,p'-DDE	benzofluoranthene	1,2,3,4,6,7,8
33	179	p,p'-DDE	benzo(e)pyrene	O8CDD
22	176	trans-nonachlor	benzo(a)pyrene	T4CDF total
45	178	cis-nonachlor	perylene	2,3,7,8
46	175	o,p'-DDD	dibenz(ah)anthracene	P5CDF total
52	187/182	p,p'-DDD	indeno(1,2,3,-cd)pyrene	1,2,3,7,8
49	183	o,p'-DDT	benzo(ghi)perylene	2,3,4,7,8
47/48	185	p,p'-DDT		H6CDF total
44	174	mirex	PAH surrogates	1,2,3,4,7,8
42	177	heptachlor epoxide	acenaphthene d-10	1,2,3,6,7,8
41/71/64	171	alpha-endosulfan	phenanthrene d-10	2,3,4,6,7,8
40	172	dieldrin	chrysene d-10	1,2,3,7,8,9
74	180	endrin	chrysene d-12	H7CDF total
70/76	193	methoxychlor	benzo(a)pyrene d-12	1,2,3,4,6,7,8
66	191		perylene d-12	1,2,3,4,7,8,9
56/60	170/190	pesticide surrogates	dibenz(ah)anthracene d-14	O8CDF
95	189	13C-hexachlorobenzene	benzo(ghi)perylene d-12	
91	201	13C-gamma HCH		dioxin/furan surrogates
84/89	197	13C p,p'DDE		13C-T4CDF
90/101	198	13C p,p'-DDT		13C-T4CDD
99	199	13C mirex		13C-P5CDF
83	196/203	13C PCB 101		13C-P5CDD
97	195	13C PCB 160		13C-H6CDF
87	194	13C PCB 209		13C-H6CDD
85	205	d4-alpha-endosulfan		13C-H7CDF
110	208			13C-H7CDD
107	207			13C-O8CDD
118	206			
114	209			
105				
136	PCB surrogates			
151	13C-BZ101			
144/135	13C-BZ118			
149	13C-BZ105			
134	13C-BZ180			
131	13C-BZ209			
146				

readily susceptible to contamination from the surface in proximity to the well."⁸ Sampling from these wells was intended to assess the adequacy of the cleaning procedures and to serve as practice sites. Before sampling at treatment plants was begun, three sets of samples were taken and analyzed at the ground water sites. After the project began sampling treatment plants three more ground water samples were taken to determine whether there were "memory effects" in the TOPS. Metals, TSS, TOC, and DOC were not measured from the ground water sites.

The treatment plants represented urban and industrial areas, a rural/suburban community, and a plant mostly serving two paper plants. The urban/industrial wastewater treatment plants were in Lockport, Tonawanda, and Rochester (Frank E. VanLare POTW). The largely industrial facility was Carthage and 80% of its influent is from two paper plants. The background rural/suburban community with no known hazardous wastes and downwind from a large industrial urban community (Buffalo, NY) was Alden Village in Erie County.

Besides these wastewater sites, surface water samples were also taken from the Hudson River at North Creek (above the power dams, urban areas, and sites of large scale PCB use; from the Hudson River at Fort Edward (below the sites where PCBs were used industrially), Hudson River at Lock 3 in Mechanicville (below the major PCB deposition areas in the upper Hudson River), Eighteenmile Creek above the Burt Dam, and finally, Eighteenmile Creek below the Burt Dam.

Cayuga Creek (Erie County) has been the subject of PCB trackdown work. TOPS was employed there to obtain large volume suspended solids samples for PCBs. No XAD sampling was attempted in Cayuga Creek.

Figure 4 shows 30 day averaged flows from the five wastewater treatment plants for the period June 1994 to June 1996 and **Figure 5** shows the 7-day mean TSS concentrations in effluents.⁹

⁸ Ground Water Section, Bureau of Watershed Research and Assessment, Division of Water, New York State Department of Environmental Conservation. 1996. Wellhead Protection Area Delineations for Clayville and Seuquoit, Oneida County, New York. Albany, New York.

⁹ SPDES Compliance Information Section, Bureau of Water Compliance Programs, Division of Water, New York State Department of Environmental Conservation, 1996. DMR Data Analysis. Albany, New York.

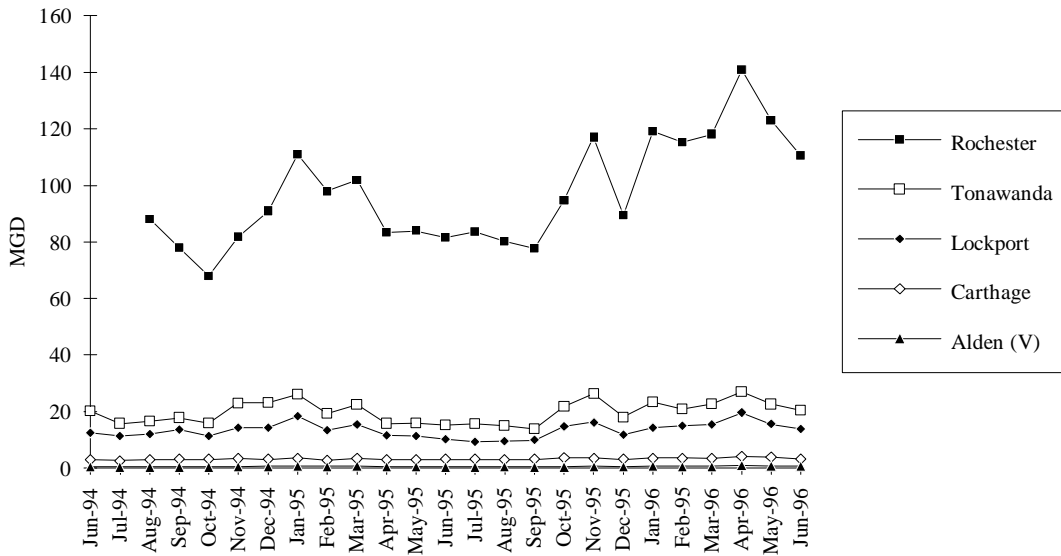


Figure 4. Monthly mean flows (MGD) from the study POTWs.

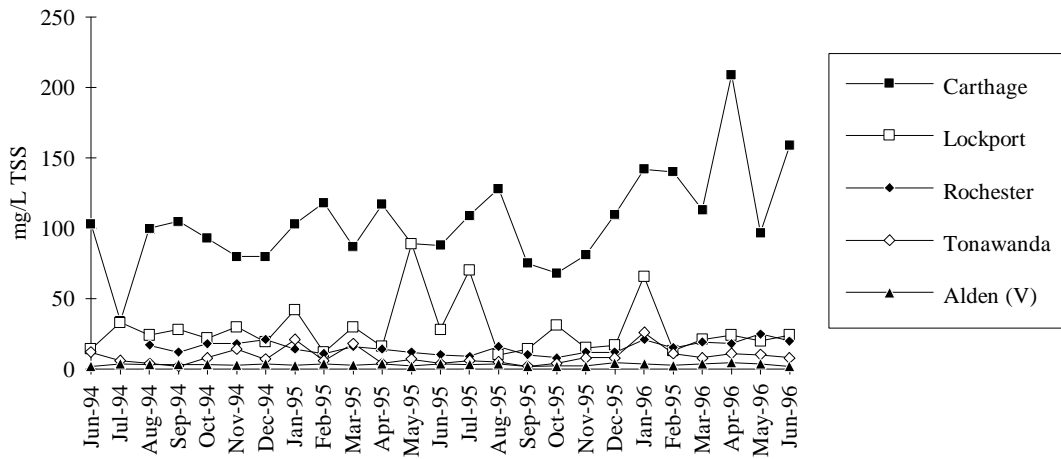


Figure 5. 7-day mean TSS (in mg/L) concentrations in effluents from the study POTWs.

Permitted discharges and TSS levels for the five plants are:

	flow (MGD)	7-day mean TSS (mg/L)
Rochester	135	45
Tonawanda	30	45
Lockport	22	45
Carthage	4.0	153
Alden (V)	0.65	10

Results

TOPS

The TOPS system is capable of extracting trace organic contaminants from large volumes of wastewater and surface water. While the protocol for TOPS operation involves both dissolved phase and suspended solids sampling, on four occasions the dissolved phase was not analyzed. The XAD column from Rochester (7/2/96) was not analyzed due to the very short operation time, less than one hour. Eighteenmile Creek at Burt Dam and the two Cayuga Creek sites were visited without the ability to perform the protocol cleaning. The protocol cleaning was felt to be more significant for the dissolved phase and the purpose of that sampling was the characterization of suspended solids, not total loading.

Table 3 indicates volumes (in L) which passed through the filter and the XAD columns.

Table 3. TOPS sampling dates and L processed by sampling medium.

Site	date	L filtered	L extracted by XAD
Lockport	6/5/96	588	80
Alden	6/12/96	117	104
Tonawanda	6/20/96	1700	747
Rochester	7/2/96	21	
Carthage	7/12/96	126	61
Rochester	7/18/96	121	73
Lockport	8/1/96	120	31
Tonawanda	8/15/96	512	177
Alden	9/17/96	901	294
Hudson R. at North Creek	9/25/96	1370	84
Carthage	9/30/96	4	2
Lockport (two XAD columns)	10/4/96	557	212
Tonawanda (two XAD columns)	10/11/96	1800	365
Carthage	10/17/96	14	6
Alden	10/24/96	2180	240
Rochester (two XAD columns)	10/31/96	110	35
Hudson R. at Lock 3	11/4/96	1160	124
Hudson R. at Ft. Edward	11/15/96	1120	112
18-Mile Cr. below Burt Dam	11/25/96	539	52
18-Mile Cr. above Burt Dam	11/26/96	662	

Given the extreme sensitivity of analytical techniques used to analyze samples from TOPS, a significant effort was devoted to ensuring the cleanliness of the sampling procedure. Three sets of blank samples were collected prior to beginning the visits to targeted facilities and sites. Another set of three blanks were taken after TOPS had been exposed to wastewater. One extra blank XAD column was exposed in order to assess the cleanliness of an alternative and less expensive source of XAD. Two XAD columns were set up in parallel from the 4/25/96 Orenda sampling with XAD from AXYS in one and XAD from Alltech in the other. Contamination levels were slightly elevated in the alternative XAD source column and the practical difficulty in handling XAD was judged to be sufficient to justify the greater expense of have the columns filled by a contractor.

Table 4 displays the dates, sites, and water volumes of blank sampling.

Table 4. Sites, dates of operation, and volumes (L) of system blank water sampled by TOPS.

Site	date	XAD	filter
Orenda	3/14/96	50	555
Orenda	4/25/96	24	440
Sauquoit	5/23/96	41	425
Polaris	7/26/96	43	496
Polaris	8/5/96	27	249
Orenda	9/4/96	170	343

TOPS was an experimental system and the 1996 sampling was not without mishap. Particularly, work in Carthage and on two occasions from Rochester, was partially unsuccessful. Very high levels of suspended matter on those sampling events resulted in rapid plugging of the filter and early shut-down. Because of the early shut-down only a small volume of water was available for flushing traces of cleaning solvent from the TOPS. Filter clogging might be ameliorated by lower pump rates, resting phases in pumping, pre-filtration, or larger filters. A re-design of the system could also permit easier access to the filter and allow the possibility of changing filters in the field. However, an objective of the TOPS system was to minimize field operations to as great an extent as possible. A necessary practical change will be the flushing of cleaning solvent before deployment so that even small volume samples will be adequately trapped.

A major concern in the project was equipment cleaning. Extremely low levels of chemicals are detectable and we were concerned that target analytes would be acquired in the lab or in field manipulation. The cleaning process which originally stipulated three rinses with acetone, methylene chloride, toluene, and methanol was excessive, costly, and unhealthful. Despite the fact that the hood in which the cleaning was conducted met OSHA face velocity standards, the technician doing the work reported headaches and dizziness which ceased when the methylene chloride and toluene were eliminated. The procedure was modified to use acetone, hexane, and methanol. This too may be excessive but further reductions in cleaning intensity have not been tested.

Dioxins and furans

The objective in TOPS sampling was to obtain detections for all analytes in all samples. **Figure 6** shows the frequency of detections for the 17 dioxin and furan congeners among the 18 XAD samples and 20 filters. Our efforts came closer to success for the filters than for the XAD. Some dioxin or furan was detected in all samples.

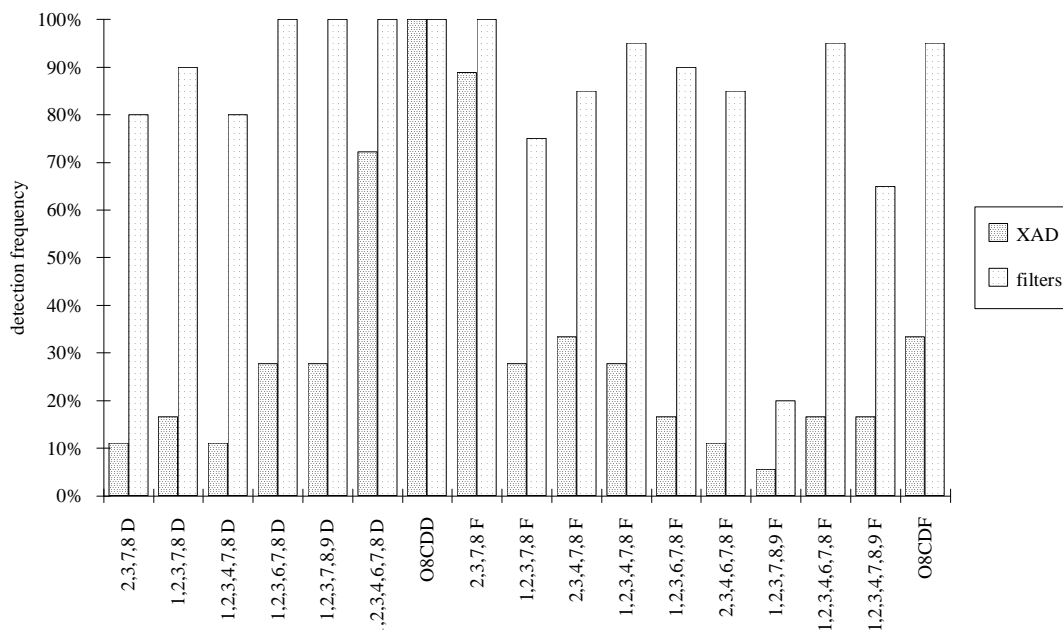


Figure 6. Frequency of Detection of individual PCDD/PCDF congeners by sampling medium.

Differences between concentrations of various dioxin and furan congeners are enormous. Toxicological potencies of the various dioxin and furan congeners are also very different. TEQs (Toxic Equivalents) are factors which permit the summing of concentrations of chemicals that exert the same kind of toxicity as does 2,3,7,8-tetrachlorodioxin but at different potencies.¹⁰ The units, pg/L, are parts per quadrillion.

Table 5 compares dioxin TEQs in effluents from all treatment plants - Alden, Tonawanda, Rochester, Carthage, and Lockport; the five surface water sites; and the six blank samples. It also indicates the percent of TEQ captured by the filters. The Table displays the proposed Great Lake Initiative guidance value (GLI) for total dioxin TEQs.¹¹ None of the observations exceeded the current NYS Guidance Value of 1 pg/L for 2,3,7,8-tetrachlorodibenzodioxin. On an average, 83% of the total dioxin from samples (as opposed to field blanks) was in the suspended solids phase but in some cases just under half of the dioxin was collected by the XAD. The field blanks with a substantial amount of dioxin (Polaris-8/5, Orenda-9/4, and Orenda-4/25) had the overwhelming majority of dioxin in the XAD samples. We do not know if the contaminant originated from

¹⁰ North Atlantic Treaty Organization, Committee on the Challenges of Modern Society. 1988. Pilot Study on International Information Exchange On Dioxins and Related Compounds. International Toxicity Equivalency Factor (I-TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. p. 12.

¹¹ USEPA, 1995. Final Water Quality Guidance for the Great Lakes System; Final Rule. Federal Register. Vol 60, No. 56. Thursday March 23, 1995. p 15392.

inadequate cleaning/transportation or from the site itself. On three occasions XAD columns were set in series to check for break-through. For the dioxins, 83% of the dissolved phase mass was trapped on the first column at a pump rate of 250 mL/min.

Rochester-7/2 was taken during an upset condition brought about by dilute mixed liquor suspended solids. The normal TSS at the plant is 15 mg/L but on the day of sampling Rochester -7/2, TSS was 53 mg/L. Rochester-7/18 was sampled, according to the operator, during typical conditions. Rochester-7/2 is also an underestimate; all other blank and treatment plant concentrations were obtained as the sums of the concentrations found on XAD (dissolved phase) and glass fiber filters (suspended solids phase). Very rapid filter plugging resulted in insufficient dissolved phase sample.

Table 5. 2,3,7,8-TCDD equivalents from suspended solids plus dissolved phases.

	pg/L dioxin TEQs	% on solids
Sauquoit-5/23/96	0.0000	0%
Polaris-7/26/96	0.0001	100%
Orenda-3/14/96	0.0001	100%
Polaris-8/5/96	0.0020	4%
North Creek 9/25/96	0.0036	67%
GLI guidance	0.0086	
Orenda-9/4/96	0.0096	2%
Hudson R. at Ft Edward-11/15/96	0.021	93%
Alden-9/17/96	0.022	60%
Alden-10/24/96	0.023	92%
Alden-6/12/96	0.027	86%
Hudson R. at Lock 3-11/4/96	0.034	29%
Tonawanda-10/11/96	0.058	38%
Lockport-6/5/96	0.059	100%
Tonawanda-8/15/96	0.061	30%
Carthage-7/12/96	0.069	87%
Orenda-4/25/96	0.12	8%
Tonawanda-6/20/96	0.12	83%
Lockport-10/4/96	0.23	87%
18-Mile at Burt Dam-11/26/96	0.26	no XAD
Lockport-8/1/96	0.39	95%
18- Mile below Burt Dam 11/25/96	0.84	68%
Rochester-10/31/96	1.0	100%
Carthage-10/17/96	1.0	99%
Rochester-7/18/96	1.4	98%
Carthage-9/30/96	2.5	96%
Rochester-7/2/96	4.8	no XAD

Figure 7 compares mean relative abundances of 2,3,7,8-substituted dioxin and furan congeners denominated in TEQs from Rochester and Lockport. Data are from the sums of dissolved phase and suspended solids samples.

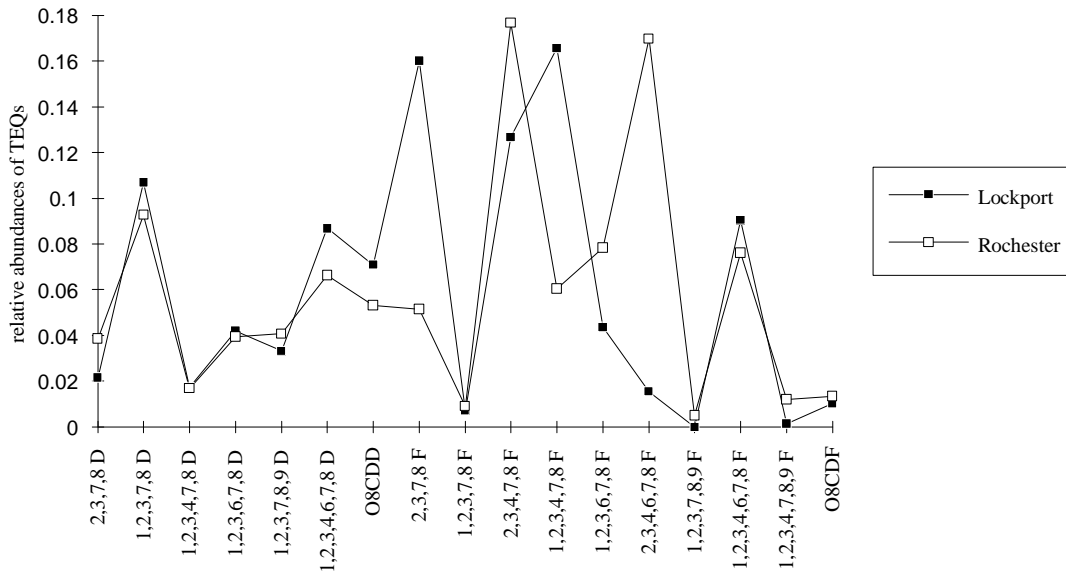


Figure 7. Relative abundances of dioxin and furan congeners denominated as TEQs, means from Lockport (sampled 6/5; 8/1; 10/4) and Rochester (sampled 7/2; 7/18; 10/31).

Figure 8 shows a similar comparison between whole water mean relative abundances of dioxin/furan congeners from Alden and Carthage. The similarity in PCDD/PCDF congener patterns between the Carthage plant (80% paper making waste) and Alden (residential) suggests the possibility that both patterns are derived from paper rather than from combustion sources.

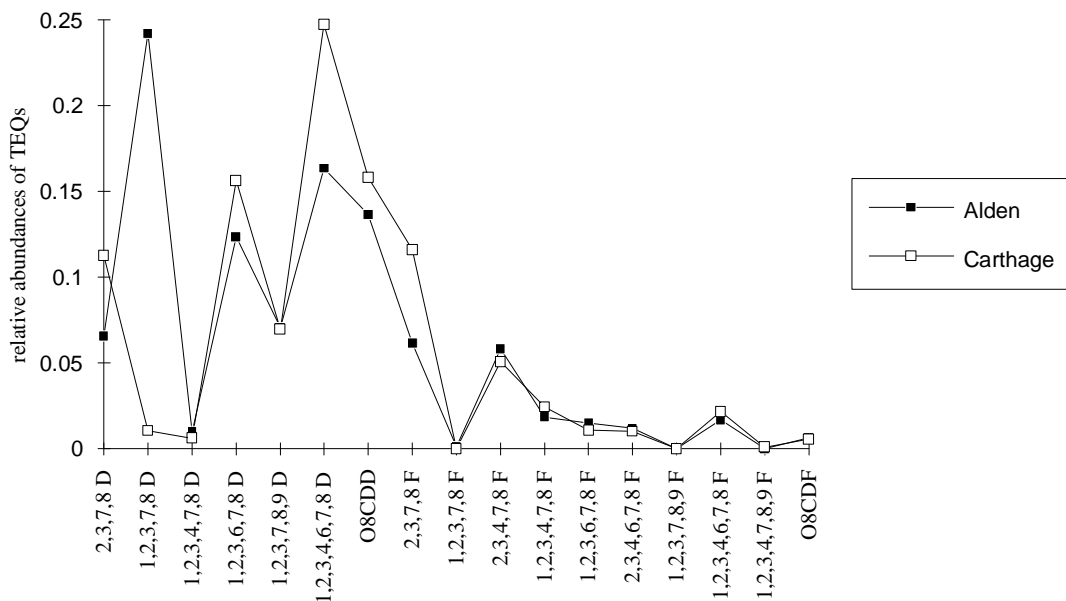


Figure 8. Relative abundances of dioxin and furan congeners denominated as TEQs, means from Alden (sampled 6/12; 9/17; 10/24) and Carthage (sampled 7/12; 9/30; 10/17).

Similarly, **Figure 9** plots the whole water mean TEQ weighted relative congener distributions from Tonawanda.

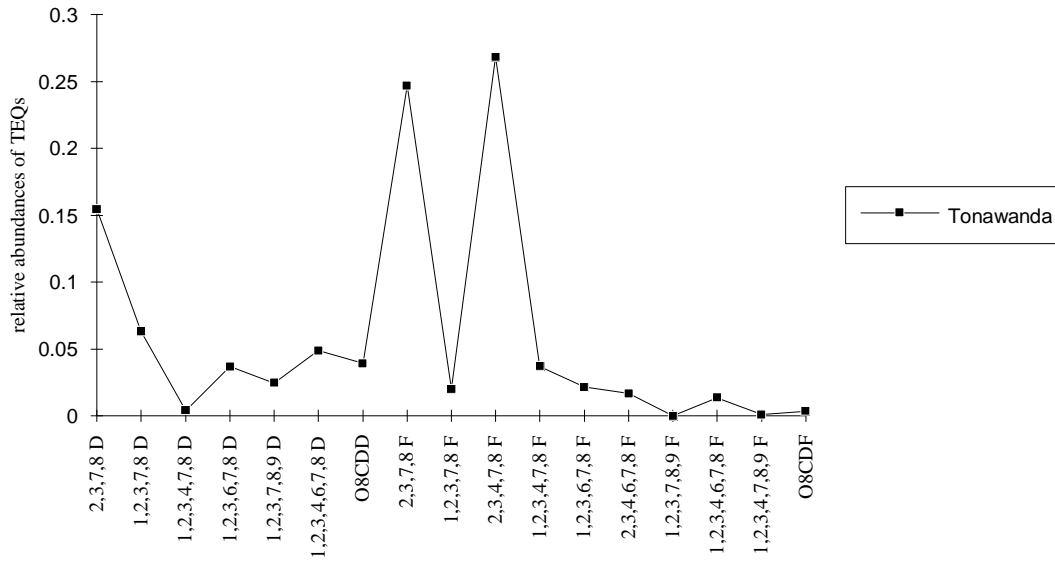


Figure 9. Relative abundances of dioxin and furan congeners denominated as TEQs, means from Tonawanda (sampled 6/20; 8/15; 10/11).

Two pairs of surface whole water samples, from Eighteenmile Creek above and below the Burt Dam in Burt and from the Hudson River at Lock 3 in Mechanicville, are displayed in **Figure 10**.

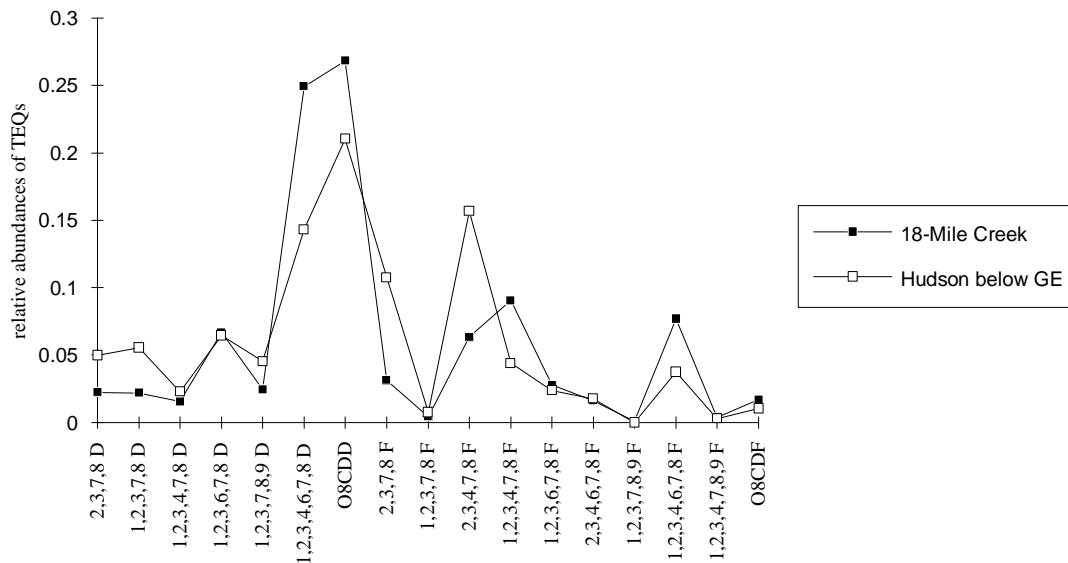


Figure 10. Relative abundances of dioxin and furan congeners denominated as TEQs, means from 18-Mile Creek and Hudson River at Ft. Edward and Mechanicville.

Figure 11 ranks the dioxin samples according to the percentage of whole water TEQs from dioxins.

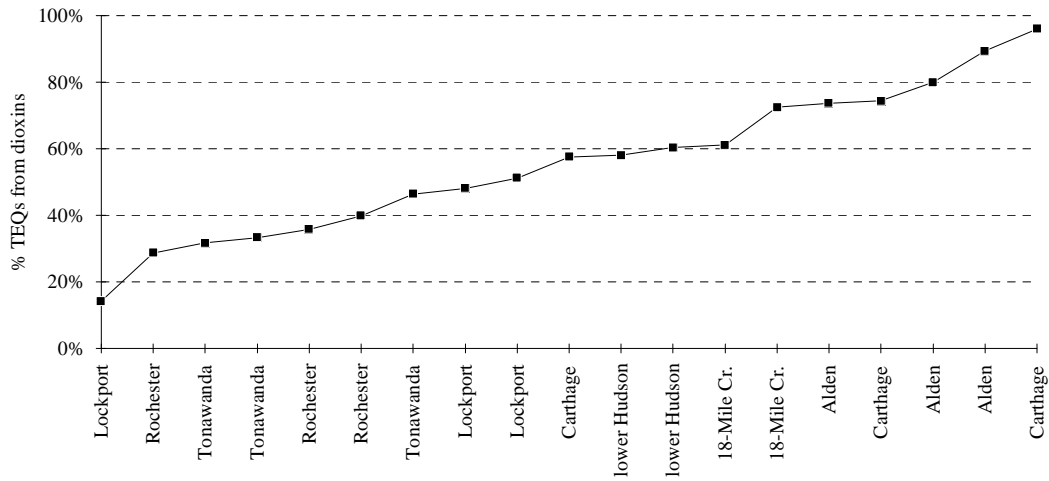


Figure 11. Percent TEQ from dioxins.

Here we see the similarity of Carthage and Alden on the dioxin dominant side and the similarity of Lockport, Rochester, and Tonawanda on the furan dominated end. Literature values show a dominance of dioxin TEQs in some municipal sewage sludges (**Figure 12**) and a dominance of furans from combustion sources (**Figure 13**).¹²

Municipal Sewage Sludge. Darskus and Schlesing, 1989.

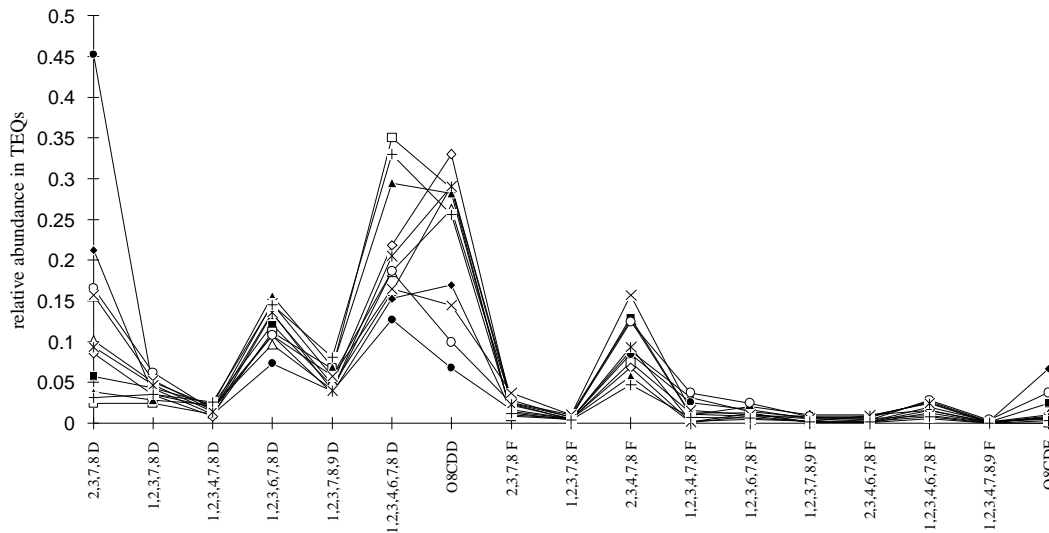


Figure 12. Dioxin/furan congeners in relative TEQs from municipal sewage sludge.

¹² Wenning, R.J., D.J. Paustenbach, M.A. Harris, and H. Bedbury. 1993. Principal components analysis of potential sources of polychlorinated dibenzo-p-dioxin and dibenzofuran residues in surficial sediments from Newark Bay New Jersey. *Arch. Environ. Contam. Toxicol.* 24 (3) 271-289.

Chimney Soot from Central Oil Heating, Thoma, 1988.

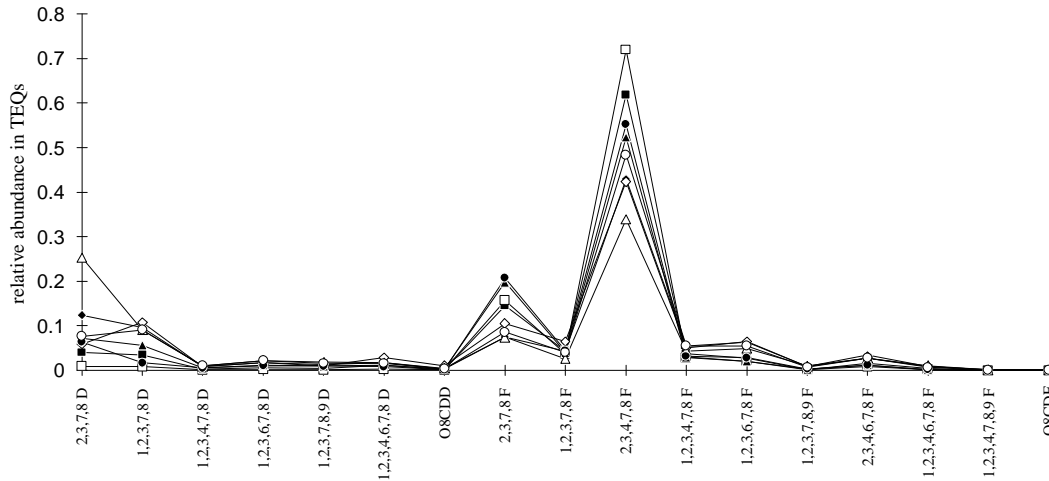


Figure 13. Dioxin/furan congeners in relative TEQs from soot from home heating oil.

PAHs

PAH analyses were scaled back during the course of the project for budgetary reasons so that fewer observations are available. **Table 6** shows the total PAH concentrations from the sites and the proportion due to the solid phase.

Table 6 Summary of total PAHs.

site	date	total conc in ng/L	% of total on solids
North Creek	9/25/96	1.57	84%
Polaris	8/5/96	3.39	2%
Carthage	10/17/96	4.22	NC
Hudson R at Lock #3	11/4/96	6.26	23%
Polaris	7/26/96	7.20	1%
Hudson R. at Ft. Edward	11/15/96	8.92	59%
Tonawanda	10/11/96	11.28	NC
18-Mile Cr. at Burt Dam	11/26/96	15.76	NC
Alden	6/12/96	21.78	25%
18-Mile Cr. below Burt Dam	11/25/96	34.38	64%
Lockport	10/4/96	39.45	83%
Lockport	6/5/96	82.55	69%
Carthage	7/12/96	103.20	23%
Rochester	7/18/96	203.21	67%
Tonawanda	6/20/96	234.72	45%
Rochester	10/31/96	304.18	79%
Tonawanda	8/15/96	701.67	64%
Lockport	8/1/96	729.14	87%
Rochester	7/2/96	1367.40	NC

Despite the large range in concentrations, the source pattern among the PAHs tested remained fairly stable. **Figure 14** shows the mean and +/- one standard deviation for relative abundances of the 16 target PAHs from Lockport, Tonawanda, and Rochester suspended solids.

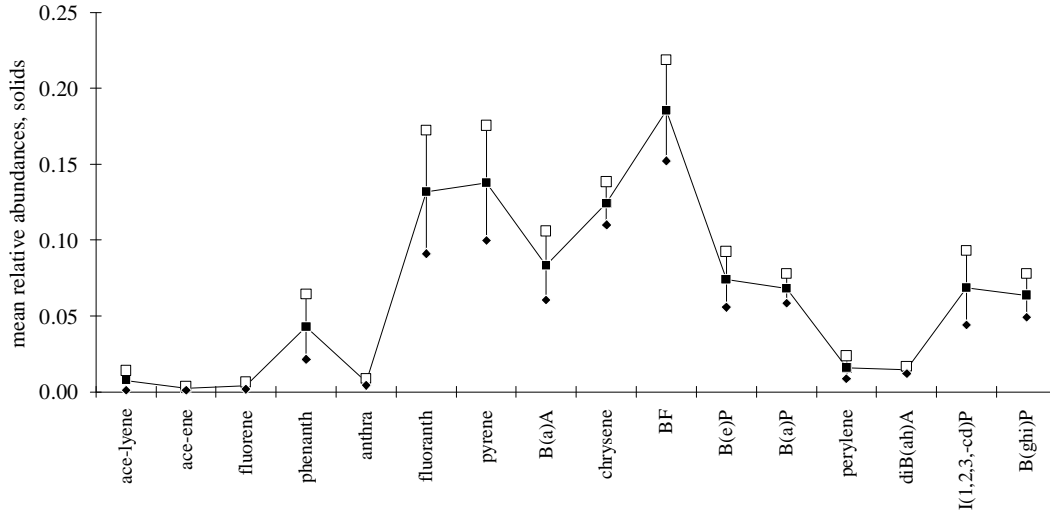


Figure 14. Means of relative abundances of targeted PAHs from three replicates each of suspended solids samples taken at Lockport, Tonawanda, and Rochester. Also shown is the one standard deviation range about the mean.

Figure 15 shows the relative abundances of PAHs found in surface water suspended solids at Eighteenmile Creek above and below the Burt Dam and the Hudson River at Fort Edward and Lock 3 at Mechanicville.

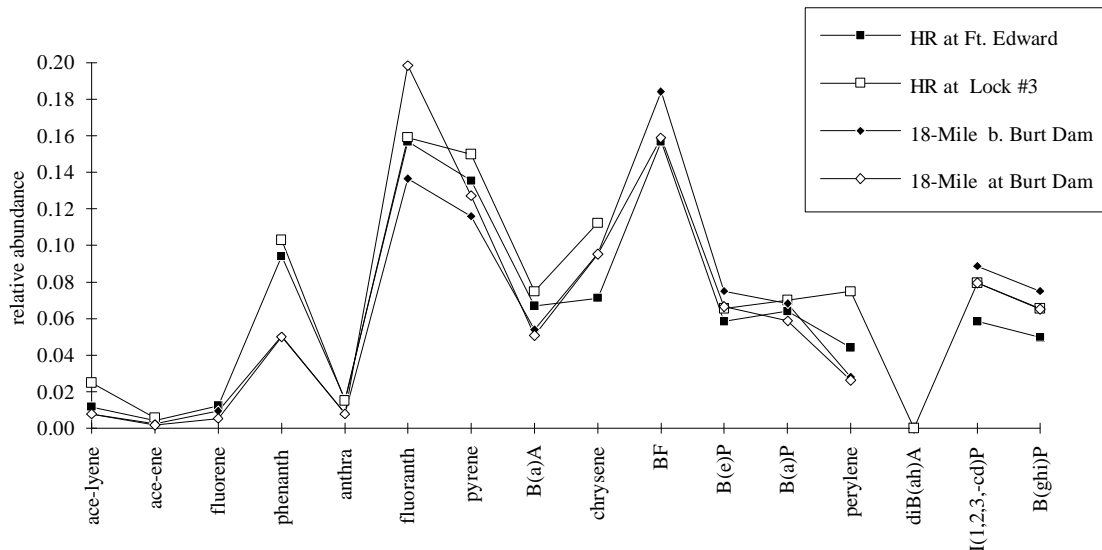


Figure 15. Relative abundances of PAHs from two sites on the Hudson River and two sites on Eighteenmile Creek (below Burt Dam and above Burt Dam), suspended solids.

All the suspended solids samples from Lockport, Tonawanda, and Rochester, and from the surface waters in Eighteenmile Creek and the Hudson at Ft. Edward and Lock 3, had detectable levels of benzo(a)pyrene (B(a)P). Only one suspended solids sample taken at Carthage was analyzed for PAHs (no B(a)P detected) and two were analyzed from Carthage where one had B(a)P detected and the other did not. B(a)P was not detected from the Hudson River at North Creek.

The TOPS system was less successful in dealing with dissolved phase PAHs. For example, B(a)P was detected from the dissolved phase only in Tonawanda. Most of the PAHs lighter than benzo(a)pyrene were detected in wastewater samples but the sample to sample variabilities were greater than those from the suspended solids phase where much larger sample sizes were taken. **Figure 16** displays two sets of relative abundances from Lockport, **Figure 17** shows two each from Rochester and Tonawanda, and **Figure 18** gives the results from three sets of surface water observations. Of the three surface waters, those from the Hudson were clearly insufficient.

Two break-through experiments were performed for PAHs. The Lockport experience (10/4/96) had 6.6 ng/L total PAH on the first column and only 0.18 ng/L on the second. A similar experiment from Rochester (10/31/96) saw more break-through, 60 ng/L on the first column and 5.2 ng/L on the second.

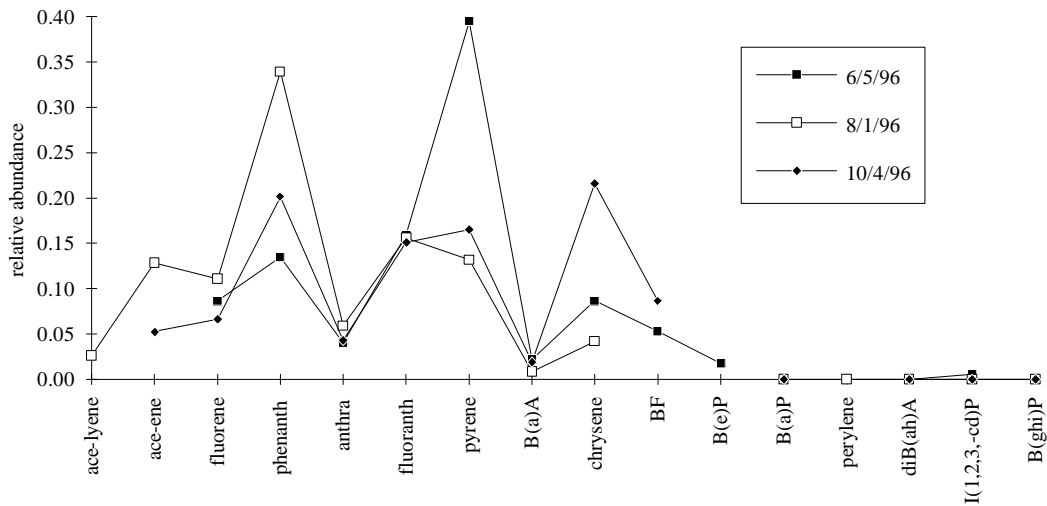


Figure 16. Relative abundances of PAHs in Lockport dissolved phase.

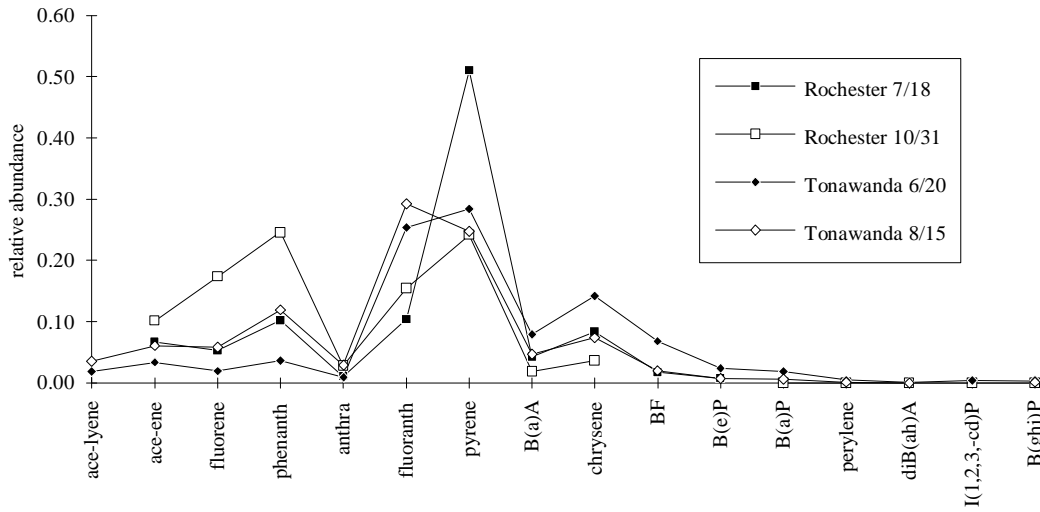


Figure 17. Relative abundances of PAHs in Rochester and Tonawanda dissolved phase.

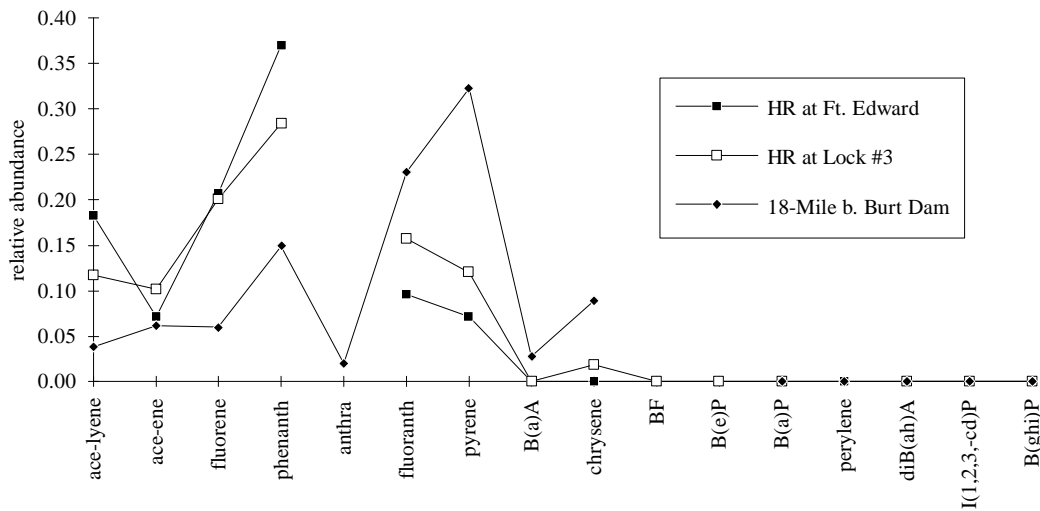


Figure 18. Relative abundances of PAHs in the dissolved phase from surface water samples in Eighteenmile Creek and two sites on the Hudson River.

PCBs

PCB data are given in **Table 7**. No significant contamination seemed to occur among the field blanks. The phase distribution of PCBs was uneven. Some large volume samples showed most of the PCB on XAD (Tonawanda 8/15, and Alden 9/17) but on other occasions the majority of PCB appeared on the filters (Lockport 8/1). The two surface water samples from the lower Hudson River had significantly different relative suspended solids contributions. On two sampling events (Carthage 9/30 and Rochester 7/2) total PCB concentrations were large but filter plugging occurred before the XAD column was exposed to a sufficient flow to ensure adequate flushing of residual methanol. In the case

Table 7. Total PCB in ng/L and percent on solids from all sampling events.

		PCB. Total ng/L	% on solids
Polaris	7/26/96	0.00	NC
Polaris	8/5/96	0.00	NC
Orenda	9/4/96	0.00	NC
Hudson R. at North Creek	9/25/96	0.01	100%
Sauquoit	5/23/96	0.02	66%
Cayuga Cr. at Como Park	9/18/96	0.02	no XAD
Orenda	3/14/96	0.05	30%
Cayuga Cr. at Clinton	9/17/96	0.86	no XAD
Lockport	10/4/96	1.2	74%
Tonawanda	10/11/96	1.3	16%
Alden	6/12/96	2.6	36%
Alden	10/24/96	2.8	29%
Lockport	6/5/96	3.0	47%
Tonawanda	8/15/96	3.3	5%
Carthage	7/12/96	4.8	67%
Lockport	8/1/96	5.3	90%
Alden	9/17/96	6.3	21%
Tonawanda	6/20/96	6.7	46%
Rochester	10/31/96	7.0	97%
Carthage	10/17/96	7.3	100%
Rochester	7/18/96	7.7	58%
18-Mile Cr. at Burt Dam	11/26/96	9.4	no XAD
Rochester	7/2/96	17	no XAD
Hudson R. at Ft. Edward	11/15/96	23	64%
Hudson R. at Lock #3	11/4/96	23	11%
18-Mile Cr. below Burt Dam	11/25/96	44	19%
Carthage	9/30/96	78	99%

of the Carthage sample, the XAD column was analyzed but it contained very little PCB. The XAD column from the quickly plugged Rochester sample was not analyzed. There were also a possible failures in the XAD PCB process on one occasion, Rochester 10/31. At this event there should have been an adequate volume of water sampled, 35 L, but the total amount of recovered PCB was extremely low, only 6.6 ng from two XAD columns in series. Mechanical failure of the TOPS seems unlikely because PAHs were recovered from the columns but there was poor dioxin recovery as well as poor PCB and pesticide recovery. The dissolved phase does appear to be an important one for PCB transport.

Figure 19 shows the distributions of relative homolog abundances from means of the three suspended solids samples from each facility. Noteworthy here is the pattern from Carthage which also had the greatest PCB concentration of all (78 ng/L, 9/30). In 1989 passive sampler investigations had suggested a PCB source to the Black River in the vicinity of Carthage¹³. The homologs from suspended solids at the Carthage plant show a

¹³ Litten, S., B. Mead, and J. Hassett. 1993. Application of passive samplers (PISCES) to locating a source of PCBs on the Black River, NY. *Environ. Toxicol. and Contam.* 12 639-647.

left shift where trichlorobiphenyls are proportionally greater than from the other plants. Trichlorobiphenyl domination at Carthage is also shown by XAD samples (**Figure 20**). The passive sampler investigation showed that the PCB homolog pattern in the Black River changed from an upstream one dominated by tetra-, penta-, and hexachlorobiphenyls to a downstream one dominated by trichlorobiphenyls.

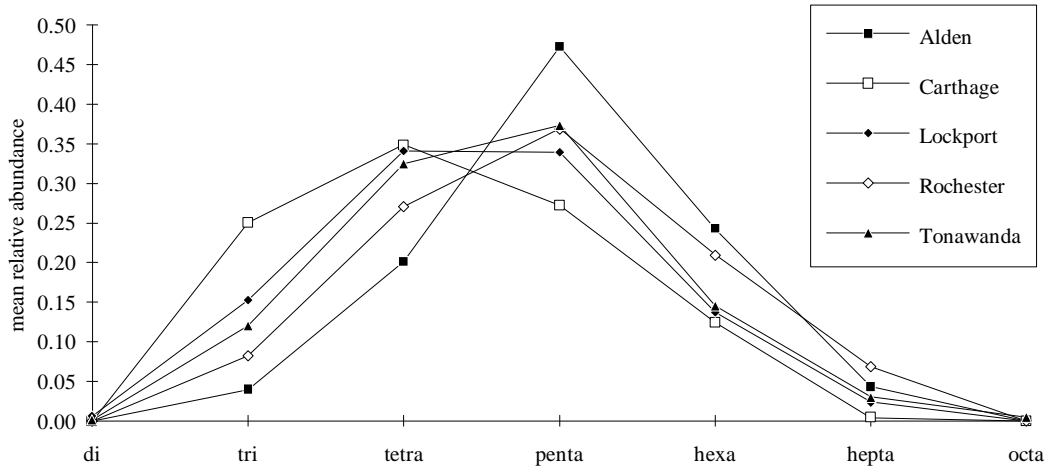


Figure 19. Mean relative abundances of PCB homologs from suspended solids.

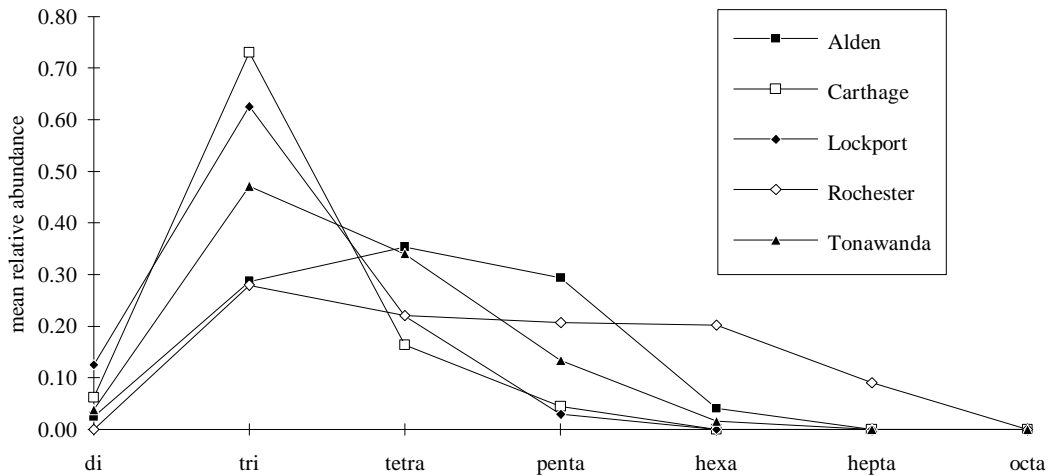


Figure 20. Mean PCB homolog relative abundances, XAD means.

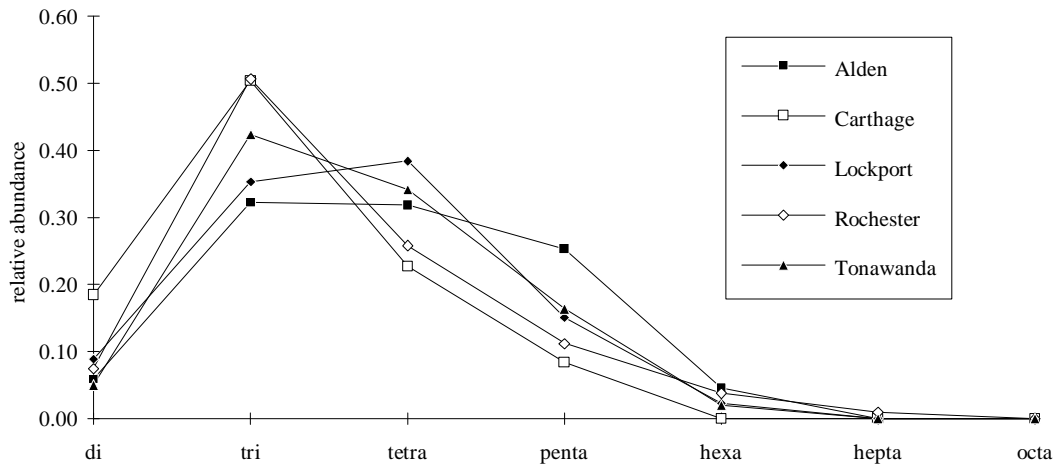


Figure 21. Mean PCB homolog relative abundances from PISCES.

Pesticides

Table 8 shows for total DDT, total chlordane, hexachlorobenzene, dieldrin, and heptachlor epoxide, the total concentrations (dissolved plus suspended solids) in ng/L and the percent on the filters. Concentrations exceeding the GLI guidelines are indicated in boldface. "Total DDT" is the sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,o'-DDT, and p,p'-DDT. "Total chlordane" is the sum of trans-chlordane, cis-chlordane and oxychlordane.

Table 9 shows the sum of XAD and filter concentrations (whole water) concentrations for a-hexachlorocyclohexane, b-hexachlorocyclohexane, g-hexachlorocyclohexane (or lindane), total nonachlor (trans-nonachlor plus cis-nonachlor), a-endosulfan, and methoxychlor in ng/L. Pesticides observed fewer than 7 times are shown in **Table 10**, again as whole water values and in ng/L.

Table 9. TOPS pesticide data, ng recovered.

site	date	a-HCH	b-HCH	g-HCH	total nonachlor	a-endosulphan	methoxychlor
Orenda	3/14/96	ND	ND	ND	ND	ND	ND
Orenda	4/25/96	ND	ND	ND	ND	ND	ND
Sauquoit	5/23/96	ND	ND	0.07	ND	ND	ND
Lockport	6/5/96	ND	ND	2.75	0.02	0.10	0.43
Alden	6/12/96	0.03	0.04	0.46	0.03	ND	0.12
Tonawanda	6/20/96	0.18	0.09	1.48	0.24	0.04	0.58
Rochester	7/2/96	ND	ND	ND	0.40	0.09	0.72
Carthage	7/12/96	0.43	ND	4.85	ND	0.07	ND
Rochester	7/18/96	ND	ND	5.68	0.42	0.07	2.36
Polaris	7/26/96	ND	ND	ND	ND	ND	ND
Lockport	8/1/96	0.36	ND	5.55	0.05	ND	0.23
Polaris	8/5/96	ND	ND	ND	ND	ND	ND
Tonawanda	8/15/96	0.17	0.14	1.97	ND	0.07	35.51
Orenda	9/4/96	ND	ND	ND	ND	0.03	ND
Alden	9/17/96	0.13	0.15	1.46	0.04	ND	1.54
Hudson R. at North Creek	9/25/96	0.16	ND	ND	ND	ND	ND
Carthage	9/30/96	ND	ND	6.68	ND	1.07	ND
Lockport	10/4/96	0.13	0.04	3.94	0.01	ND	0.09
Tonawanda	10/11/96	0.13	0.10	5.77	0.02	ND	ND
Carthage	10/17/96	0.13	0.12	29.94	0.11	0.14	ND
Alden	10/24/96	0.04	0.04	0.38	0.02	ND	0.23
Rochester	10/31/96	0.01	0.01	12.31	0.25	0.64	1.50
Hudson R. at Lock #3	11/4/96	0.12	ND	0.25	ND	ND	ND
Hudson R. at Ft. Edward	11/15/96	0.12	ND	ND	ND	ND	0.06
18-Mile Cr. b. Burt Dam	11/25/96	0.14	ND	1.49	0.04	0.03	0.02
18-Mile Cr. at Burt Dam	11/26/96	ND	ND	ND	0.03	ND	0.06

Table 10. Rarely observed pesticides, in ng/L, whole water.

		Heptachlor	aldrin	mirex	endrin
Tonawanda	6/20/96	0.041	0.002		0.029
Rochester	7/18/96			0.135	
Tonawanda	10/11/96	0.008			
Alden	10/24/96	0.003			
Rochester	10/31/96	0.015			0.375
18-Mile Cr. below Burt Dam	11/25/96			0.08	
18-Mile Cr. at Burt Dam	11/26/96				0.024

Metals

Grab sample whole water (not filtered) results for metals are shown in **Table 11**.

Table 11. Whole water grab metal samples and GLI guidance values for mercury, in ng/L.

site	Hg ng/L	As ug/L	Pb ug/L	mercury field blank, ng/L
Lockport				
6/5/96	3.07	ND	1.54	
8/1/96	2.87	0.904	0.368	
10/3/96	2.53	0.742	0.2	
Rochester				
7/3/96	38.6	0.88	1.34	
7/18/96	18.1	0.774	0.709	
11/13/96	15.2	0.679	0.81	<0.1
Carthage				
9/11/96	2.19	0.33	0.12	0.29
9/30/96	25.2	0.782	1.1	
10/17/96	10.2	0.397	0.47	0.41
Alden				
6/12/96	3.52	0.33	0.26	
8/8/96	11.6	0.342	0.041	
9/17/96	2.81	0.435	0.16	
10/24/96	2.59	0.498	0.17	0.07
Tonawanda				
6/20/96	16.1	1.11	0.49	
8/15/96	2.53	1.05	0.29	
10/11/96	1.8	0.503	2.45	0.19
NYS Guidance	200	50000	5000	
GLI Guidance	1.8	na	na	
max	38.6	1.11	2.45	0.41
average	9.93	0.65	0.66	0.24
min	1.80	0.33	0.04	0.07
count	16	15	16	5

Accessory parameters

Total suspended solids (TSS), total organic carbon (TOC), and dissolved organic carbon (DOC) were sampled as grabs taken during TOPS set-up. On some occasions, the DOC sample was taken too soon after the TOPS had been started and traces of the cleaning solvent methanol were still being flushed. This has resulted in unusable DOC data.

Table 12. Total suspended solids (TSS) in mg/L, dissolved organic carbon (DOC) in mg/L, and total organic carbon (TOC) in mg/L.

	TSS	DOC	TOC
Lockport			
6/4/96	8	NA	NA
7/31/96	5	suspect	8.7
7/31/96-duplicate	5	suspect	8.5
10/3/96	3	suspect	7.9
10/3/96 duplicate	3	suspect	8
Alden			
6/12/96	1	5.5	7.8
8/7/96	1	24	12
9/16/96	6		21
Tonawanda			
6/19/96	4	26	28
6/19/96-duplicate	4	27	29
8/14/96	<1	97	29
8/14/96 - duplicate	<1	98	28
10/10/96	2	suspect	9.7
10/23/96	2		91
10/23/96	1	11	91
Rochester			
7/2/96	48	21	21
7/2/96 - duplicate	60	21	22
7/17/96	11	24	11
7/17/96- duplicate	11		12
10/30/96	28	suspect	19
10/30/96-duplicate	32	suspect	18
Carthage			
7/12/96	31	32	33
7/12/96 -duplicate	na	32	34
10/1/96	6		140
10/17/96	100	suspect	53
Hudson River			
North Creek - 9/25/1996	<1		4
North Creek - 9/25/1996	1		4.1
Ft. Edward	3	6.7	6.9
Cayuga Cr			
Clinton - 9/17/96	29	7.4	11
Como Pk 9/18/96	46		12
18-Mile Cr.			
at Burt Dam - 11/26/96	5		8.9

PISCES

Passive samplers were deployed at the sampling sites where the TOPS was installed but remained in the waste stream for a longer time (two or more weeks). Due to mishaps, fewer PISCES samples than TOPS samples were achieved. Altogether, 13 PISCES were successfully recovered. **Table 13** shows the PISCES derived PCB and pesticide data

expressed in ng/L where the formula for uptake rate developed for PCBs was applied to the pesticides.

Table 13. PISCES derived PCB and pesticide concentrations, in "ng/L".

	start	end	PCB	HCB	lindane	T DDT	hept epox.	dieldrin	methoxy.	T. nona.	T chlord.
Alden	12-Jun	2-Jul	1.9	0.07	0.89	0.02	ND	0.39	0.66	ND	0.08
Alden	7-Aug	27-Aug	2.3	0.09	0.94	0.07	0.04	0.36	0.08	ND	0.09
Alden	7-Aug	27-Aug	2.4	0.09	0.82	0.07	ND	0.39	0.70	ND	0.12
Carthage	12-Jul	1-Aug	2.8	ND	5.6	0.10	ND	0.10	ND	ND	ND
Lockport	31-Jul	14-Aug	1.3	0.06	3.9	0.04	0.03	0.16	ND	ND	ND
Lockport	31-Jul	14-Aug	0.78	0.09	3.5	ND	ND	0.22	ND	ND	0.03
Rochester	2-Jul	17-Jul	1.9	0.22	10	ND	0.20	0.76	1.3	ND	ND
Rochester	30-Oct	13-Nov	2.9	1.3	20	ND	0.37	1.0	2.1	0.08	0.39
Rochester	30-Oct	13-Nov	2.4	1.4	22	0.17	0.34	1.2	3.3	0.10	0.24
Tonawanda	14-Aug	27-Aug	17	1.4	31	0.36	1.5	2.8	120	0.22	1.43
Tonawanda	14-Aug	27-Aug	12	0.92	14	0.38	ND	2.2	43	0.16	1.4
Tonawanda	11-Oct	24-Oct	21	2.6	270	1.7	14	7.0	7.6	0.82	6.1
Tonawanda	11-Oct	24-Oct	29	2.9	300	2.2	14	8.3	2.6	1.0	8.1

Comparison between PISCES results and those from TOPS did not show a high degree of correlation. It is possible that the lack of correspondence was due to the differences in exposure timing. For example, PISCES from two weeks exposure at Tonawanda in August and October collected large amounts of PCBs and lindane. TOPS from single day exposures at Tonawanda in August and October failed to see elevated levels of either substance. In Alden, the mean TOPS PCB concentration was 3.90 ng/L and 2.1 ng/L from PISCES. In Lockport, the TOPS mean was 3.18 and the PISCES mean only 1.04, and from the Rochester samples where XAD was used, TOPS saw 7.33 ng/L and PISCES 2.65 ng/L. The significance of these differences should not be overstated. However, it seems likely that TOPS would recover more analyte than PISCES because it samples both phases with assuming equivalent efficiency. PISCES may sample the suspended solids phase with some degree of success, as is suggested by **Figure 21** which shows a PCB homolog pattern that seems more like a combination of the patterns from XAD and from the filters.

Conclusions

While the primary mission of this project was successfully accomplished, certain defects in the design and operation of TOPS were revealed. The device has been re-configured to make modifications easier to perform in the field. The version used here could not be opened conveniently in the field so that filters might be replaced. A second flow totalizer will be placed below the XAD column to ensure proper water volume measurement. A more versatile timer is now being used. More significantly, experiments should be performed to document the potential of contaminant wash-out from the XAD and to observe the effects high dissolved organics concentrations or greases may have on XAD capacity.

The target analytes, PCBs, dioxins, chlorinated pesticides, mercury, lead, and arsenic are quantifiable in virtually all samples. With the exception of one surface water sample and four “blank” samples, all dioxin/furan samples exceeded the proposed GLI guidance value. All mercury samples from treated waste waters exceeded the GLI guidance value. With the exception of three “blanks”, all samples exceeded the New York State proposed ambient water quality standard for health (fish consumption) for PCBs (0.001 ng/L). New York State has proposed ambient water quality standards for health (fish consumption) for p,p'-DDE (0.007 ng/L), p,p'-DDD (0.08 ng/L), and p,p'-DDT (0.01 ng/L). None of these were exceeded for the blanks, they were exceeded by three of the five surface water samples and by all but two of the waste water samples.

The Trace Organics Platform Sampler (TOPS) filtration/XAD system is capable of concentrating chemicals from a sufficient sample volume so that, in cooperation with a competent laboratory, target chemicals are consistently quantified in all waste waters and all surface waters.