Toxics Chemicals in NYS Tributaries to Lake Ontario: A Report on Sampling Undertaken in 2007 and 2008 with Special Emphasis on the Polychlorinated Dibenzodioxins and Furans

Report to the U.S. Environmental Protection Agency,
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This project could not have been done without the assistance of Loraine Gregory, Dan Hayes, and John Donlon. Thanks to Jim Swart and his staff, we have access to an enormous amount of sediment data through the NYSDEC DOW National Sediment Inventory. I also want to thank the New York State residents at all the sites who stopped to ask us questions. The highest proportion of interested onlookers was in Pulaski. They seemed to understand, more so than others, the importance of clean water to their economy and well being.

Summary

This project was undertaken to provide estimates of loading of synthetic chemicals into Lake Ontario from several New York tributaries.

We estimate that 18-Mile Creek, Genesee River, Oswego River, Salmon River, and Black River together contribute 97 g/day total mercury, 38 g/day dissolved mercury, 66 g/day PCB, and 2.5 mg/day 2,3,7,8-TCDD equivalents to Lake Ontario.

The highest mercury loading rates (g/day, g/capita, and g/sq km) were seen in the Black River. PCB loading rates were particularly high on 18-Mile Creek. 18-Mile Creek also showed high concentrations of pesticides, particularly DDT and its metabolites. 18-Mile Creek showed very high dioxin dioxin loads on an area basis but less so on a per capita basis. Population density in a drainage basin may turn out to be an important predictor of dioxin concentrations.

The PCDD/F congener patterns in Lake Ontario sediments appear to be more like those of the Niagara River sites at Cayuga Island and Love Canal than of the principal tributaries.

The Erie Canal may move PCDD/Fs from the Tonawanda/Lockport area to the Genesee River. Overall, congeners 2,3,4,7,8-PeCDF (congener 10), 1,2,3,4,6,7,8-HpCDD (congener 6), and 1,2,3,7,8-PeCDD (congener 2) are most often the greatest contributors to TEQ in the water samples. Congeners 10 and 2 are often associated with combustion. We have not been able to identify industrial processes that generate congener 6.

Raw concentrations of congener 6 are in most samples about a tenth that of octachlorodioxin (congener 7). Mono-dechlorination of congener 7 can produce only 1,2,3,4,6,7,9-HpCDD (which is not reported in regulatory work) or congener 6. Congener 6 has a TEF 100 times that of congener 7 and its bioaccumulation factor is 5 times greater than that of congener 7. Microbial dechlorination of congener 7 does occur in laboratory experiments. [1] Dechlorination of the very large reservoir of octachlorodioxin could be a long term source of dioxin toxicity in NYS sediments.

Introduction

The New York State Department of Health recommends that women of childbearing age and children under the age of 15 eat no freshwater fish. Levels of PCBs, Mirex, and dioxins are problematic in many fish species (causing consumption recommendations) throughout Lake Ontario, from the Niagara River, and from 18- Mile Creek in Niagara County.[2] The sources of Lake Ontario contaminants are from historic sediment deposition, mass transfer from upstream water (assessed by the Upstream/Downstream Niagara River Monitoring Program), the Lake Ontario Air Deposition Study, point sources (assessed in NYS through the State Pollution Discharge Elimination System - SPDES), and tributary inputs. Tributary inputs have been assessed in the past (from 2002- 2008) in the NYS tributaries by Richard Coleates of USEPA Region 2 and, for the Black River, by Richard and Eckhardt.[3].

Table 1. Tributary data from USEPA Region 2.

site	date	Total DDT ng/L	Dieldrin ng/L	Total Mercury ng/L	PCBs ng/L	Dioxins TEQ pg/L
18-Mile Creek	4/16/02	U	U	12.4	35.7	U
18-Mile Creek	9/17/02	U	U	0.863	32.5	13.9
18-Mile Creek	5/6/03	U	U	4.53	29.6	0.016
18-Mile Creek	7/9/03	U	U	1.43	38.7	U
18-Mile Creek	10/7/03	U	U	1.3	21.5	U
18-Mile Creek	5/11/04	U	U	4.6	51.3	NA
18-Mile Creek	9/28/04	U	U	1.35	39.5	NA
18-Mile Creek	5/3/05	0.943	0.276	3.28	35.5	NA
18-Mile Creek	8/30/05	0.807	0.375	2.07	47.3	NA
18-Mile Creek	7/26/06	NA	NA	1.42	50.4	NA
18-Mile Creek	9/19/06	NA	NA	5.73	52.2	NA
18-Mile Creek	6/26/07	NA	NA	1.03		NA
18-Mile Creek	10/16/08	NA	NA	1.22		NA
	median	0.875	0.3255	1.43	38.7	6.958
Black River	4/18/02	U	U	4.99	1.85	U
Black River	9/18/02	U	U	1.67	0.76	U
Black River	5/7/03	U	U	3.55	0.425	NA
Black River	7/10/03	U	U	2.5	1.17	NA
Black River	10/8/03	U	U	4.65	0.417	NA
Black River	5/12/04	U	U	2.74	1.31	NA
Black River	9/29/04	U	U	2.46	19.5	NA
Black River	5/5/05	QB	U	2.82	12.2	NA
Black River	7/25/05	NA	NA	2.84	1.52	NA
Black River	9/1/05	U	U	5.55	10.3	NA
Black River	9/20/06	NA	NA	2.19	0.385	NA
Black River	6/27/07	NA	NA	2.15		NA
Black River	10/17/08	NA	NA	2.57		NA
	median			2.74	1.31	
Genesee R.	4/16/02	U	U	10.9	0.157	0.041
Genesee R.	9/17/02	U	U	1.13	0.414	U
Genesee R.	5/6/03	U	U	2.26	U	U
Genesee R.	7/9/03	U	U	1.83	0.015	U
Genesee R.	10/7/03	U	U	1.97	0.256	U
Genesee R.	5/11/04	U	U	2.53	0.022	NA
Genesee R.	9/28/04	U	U	4.23	0.149	NA
Genesee R.	5/4/05	QB	U	2.63	0.313	NA

Table 1. Continued.

site	date	Total DDT ng/L	Dieldrin ng/L	Total Mercury ng/L	PCBs ng/L	Dioxins TEQ pg/L
Genesee R.	8/30/05	U	U	1.14	0.338	NA
Genesee R.	7/26/06	NA	NA	3.16	0.358	NA
Genesee R.	9/20/06	NA	NA	2.81	0.596	NA
Genesee R.	6/26/07	NA	NA	1.18		NA
Genesee R.	10/16/08	NA	NA	2.15		NA
	median			2.26	0.2845	
Oswego R.	4/17/02	U	U	3.31	0.166	U
Oswego R.	9/18/02	U	U	1.24	0.366	U
Oswego R.	5/7/03	U	U	1.59	U	NA
Oswego R.	7/10/03	U	U	1.25	0.017	NA
Oswego R.	10/8/03	U	U	U	0.203	NA
Oswego R.	5/12/04	U	U	2.2	0.193	NA
Oswego R.	9/29/04	U	U	1.3	0.54	NA
Oswego R.	5/4/05	QB	U	1.71	4.76	NA
Oswego R.	7/25/05	NA	NA	1.69	0.335	NA
Oswego R.	8/30/05	U	U	U	0.107	NA
Oswego R.	9/20/06	NA	NA	1.22	0.026	NA
Oswego R.	6/27/07	NA	NA	0.869		NA
Oswego R.	10/17/08	NA	NA	0.78		NA
	median			1.3	0.198	
Salmon R.	4/17/02	U	U	2.85	0.3	U
Salmon R.	9/18/02	U	U	0.915	0.257	U
Salmon R.	5/7/03	U	U	2.18	U	NA
Salmon R.	7/10/03	U	U	1.68	0.013	NA
Salmon R.	10/8/03	U	U	1.92	0.149	NA
Salmon R.	5/12/04	U	U	2.22	U	NA
Salmon R.	9/29/04	U	U	1.74	0.473	NA
Salmon R.	5/5/05	QB	U	1.68	7.4	NA
Salmon R.	7/25/05	NA	NA	1.95	U	NA
Salmon R.	9/1/05	U	U	1.178	0.848	NA
Salmon R.	9/20/06	NA	NA	1.83	0.39	NA
Salmon R.	6/27/07	NA	NA	1.29		NA
Salmon R.	10/17/08	NA	NA	0.868		NA
	median			1.74	0.345	

Each project has its own methods, sampling sites, and approaches to data handling.

Here we will look at some recent data on mercury (total and dissolved), polychlorinated biphenyls (PCBs), chlorinated pesticides, and, most intensely, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurams (PCDD/Fs) from five New York State Tributaries – 18- Mile Creek, Genesee River, Oswego River, Salmon River, and the Black River.

The Watersheds

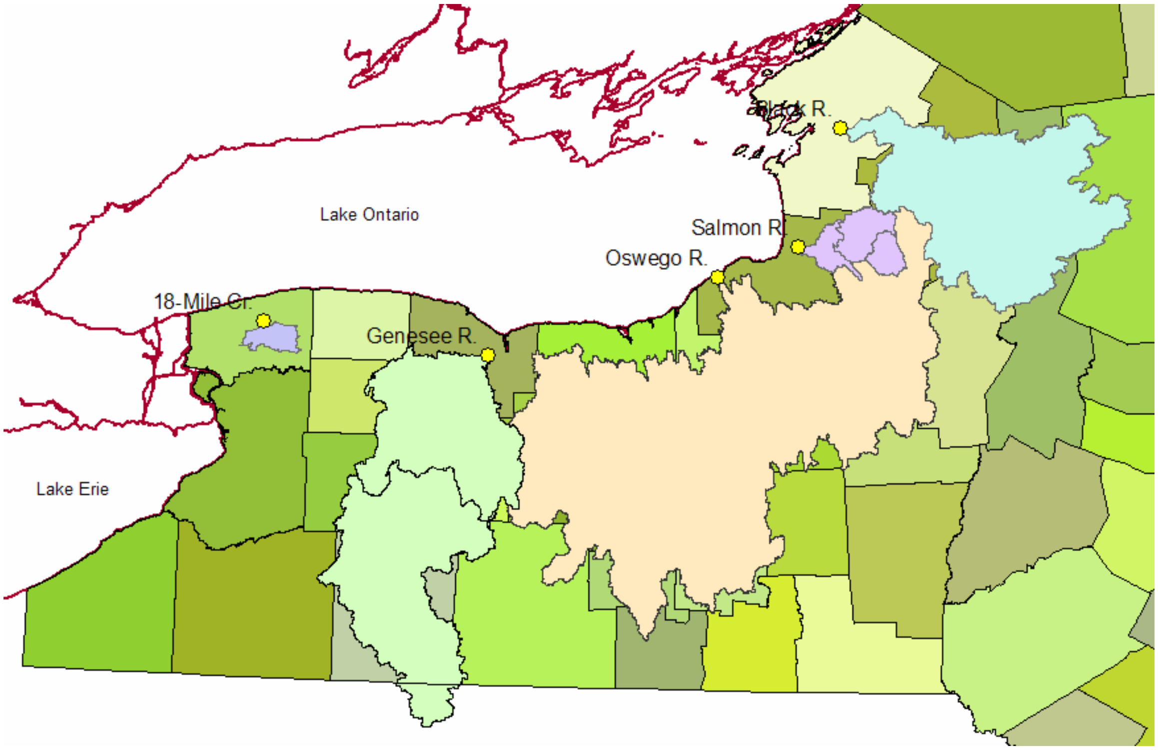

Figure 1. Sampling sites visited and watersheds.

The sampling locations were selected to be as near Lake Ontario as possible while being upstream of lake influence, safe, and practical. With the exception of Lock 8 at Oswego, all the samples were taken from bridges. We were unable to perform equal area or equal discharge-type sampling due to the requirement of obtaining very large volume samples for PCDD/F analysis.

TABLE 2. Sampling Sites

site name	lat	long	sq km area sampled	2000 pop sampled
18- Mile Cr. at Jacques Rd, Corwin, NY	43.2523	-78.6979	185	30,458
Black R. at VanDuzee St. Watertown	43.9856	-75.925	4,827	65,341
Genesee R. Andrews St., Rochester, NY	43.159	-77.6123	6,414	333,977*
Oswego R. at Lock 8	43.4553	-76.5108	13,201	995,937
Salmon R. at Rt 11, Pulaski, NY	43.5659	-76.1275	713	6,576

*Population is only from the NY portion of the watershed.

Discharges from the Genesee, Oswego, Black Rivers were taken from U.S. Geological Survey (USGS) gages that were either at the sampling location or very near. The Salmon River is gauged at Pineville and 18-Mile Creek is not gauged. To obtain discharges for Salmon River at Pulaski the USGS discharge data from Pineville were multiplied by the ratio:

[watershed area above Pulaski]/[watershed area above Pineville] = 1.157

18- Mile Creek, as noted, is not gauged. Discharge from near-by Tonawanda Creek at Rapids, NY was multiplied by the ratio:

[watershed area of 18-Mile Cr. above Jacques Rd.]/[watershed area of Tonawanda Cr. above Rapids, NY] = 0.205.

18-Mile Creek receives 50 cfs in overflow from the Erie Canal at Lockport and 15 cfs from overflow of the Erie Canal at Gasport during canal season (May 1 to November 15). It also receives discharge from the Lockport POTW. Daily average POTW discharges were added.

The study period was 5/1/2007 to 10/1/2008. Table 3 shows discharge statistics from the sampled streams during the study period and statistics of discharges during sampling events.

TABLE 3. Discharge (cubic feet per second) statistics for period of record and for sampling events.

5/1/2007-10/1/2008	Black	Oswego	Genesee	Salmon	18 Mile Cr.
mean	4,578	6,497	2,434	836	132
median	3,240	3,580	1,520	577	97
50% disch.[1]	20.60%	20.00%	18.30%	22.10%	26.92%
Sampling events					
mean	6,188	12,276	3,214	2,363	176
percentile[2]	77	80	78	95	85
median	5,065	11,900	1,691	2,400	158

1. Half of the total flow in the Black R. occurred over 20.6% of the time
2. The mean discharge in the Black R. during sampling events was at the 77th percentile of daily discharges in the Black over the study period.

Analysis

Table 4 summarizes the projects parameters, procedures, preservatives, holding times, detection limits, precision, accuracy, and methods for organic analytes.

TABLE 4. Analytical methods.

	PCDD/F	PCB	Pesticides	POC	Hg
Procedure	filter	grab	Grab	filtration	grab/filtration
Preservative	<= 4ºC	<= 4ºC	<= 4ºC	freezing	<= 4ºC
Holding time	1 year	7 days	7 days	6 months	7 days
Detection Limit	0.091 pg/L	0.098 pg/L	42 pg/L (Total DDT)	0.01 mg/L	0.2 ng/L
Accuracy (RSD)	25-164%	50-150%	76-116%		77-123%
Precision	27%	40%	21%	5%	8.30%
Field/Lab Method	1613B	1668A	NYSDECHRMS2	wet oxidation	1631

Sampling

Sampling was conducted using a modification of the Trace Organics Platform Sampler (TOPS) procedure. TOPS is specifically designed to field-concentrate highly dilute hydrophobic chemicals but the procedure facilitates other kinds of sampling. Pressurized water can be pushed through a filter to obtain dissolved mercury samples, water is readily available for filtering particulate carbon, and water is available for collecting whole-water PCB/pesticide samples. Figures 2 and 3 schematically illustrate the TOPS set-up.

Sampling for PCDD/Fs (Dioxins)

Dioxins were sampled by pumping water through pre-cleaned glass fiber cartridge filters having a nominal porosity of 1 µm. The system is run for a minimum of 10 minutes (timed with a stop watch) before the cartridge filter is mounted in the stainless steel housing. Filtered water is wasted. The filters were previously ashed 4 hours at 450°C, wrapped in aluminum foil, double bagged, and stored prior to use in a laboratory freezer. One (or two, depending on the distance from the water to the bridge deck) 5C-MD March magnetic impeller pump brings water from a stainless steel intake mounted on an epoxy painted sampling fish suspended 2 feet below the water's surface. The shaped "fish" orients into the current. Water comes to the deck of the bridge where it enters a tee. Some of the water is wasted (used for other aspects of sampling) and some is drawn by a peristaltic pump into a TOPS. Inside the TOPS, the water passes a pressure sensor and then goes through a cartridge filter held in a stainless steel housing. Sampled water is not exposed to the air and is completely self-contained.

The pump rate is usually held constant and is measured by noting the time required to fill a 20 L plastic carboy. The carboy is weighed on a certified scale full and empty. The flow rate is calculated. During each deployment carboys are filled and weighed at least three times. If field conditions are unfavorable, the carboys can be capped and brought back to the lab for weighing. If the flow rate is changed, the flows are re-calibrated. Careful note is taken of start and stop times for the pump. To obtain the volume of water filtered the average pump rate (L/min) is multiplied by the minutes of pumping.

When the pressure sensor detects a back-pressure of 15 psi the TOPS shuts off. Ideally, TOPS is run to automatic shut-off but in practice, this is not always achievable. The stainless steel housing is opened and the loaded glass fiber cartridge (and any residual water) is quickly dumped into a certified wide-mouth bottle which had been previously rinsed 3X with site water. The bottle is capped, labeled, and brought back to a refrigerator at the NYSDEC laboratory in Albany prior to being shipped out for analysis at a contract analytical lab. Between field deployments the TOPS is cleaned by recirculating hot soapy water for 10 minutes. As much soapy water as possible is drained before rinsing the unit with fresh hot water for 10 minutes. Two blanks were created by loading clean glass fiber cartridges into the TOPS after cleaning and pumping through 4 L of nanograde laboratory water. A field duplicate was created by running two TOPS units simultaneously off a single intake.

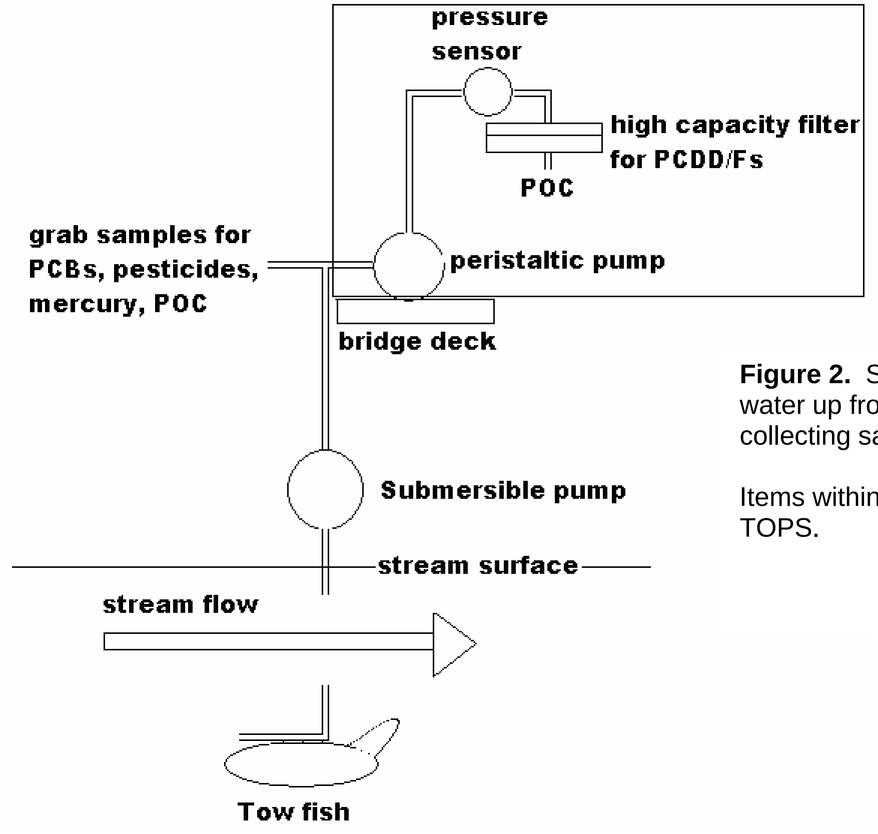

Figure 2. Set-up for bringing water up from a stream channel, collecting samples, and filtration.

Items within the box are called TOPS.

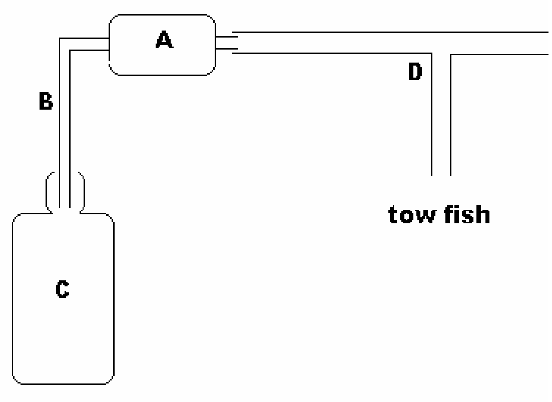

Figure 3. Set up for collecting filtered water for dissolved mercury.

Sampling for Mercury.

Water coming up from the tow fish passes through a tee (part D). Tubing to the right of part A is polyethylene. Some water goes to the right and some is wasted (going to the left in the illustration). Mercury sampling was done with a modified clean hands procedure after the system has been flushed with site water for about one hour. Filters and bottles are supplied by the lab double bagged in Ziplocs. The person playing the role of “Dirty Hands”, while wearing Class 100 gloves, assists Clean Hands in putting on his Class 100 gloves. During the entire process Clean Hands touches nothing other than the inner surfaces of the outer Ziploc, the inner Ziploc, and the bottles and filters. Dirty Hands opens the outer Ziploc bag holding part A –a Gelman Sciences 0.45 µm high capacity groundwater sampling capsule. Clean Hands opens the inner Ziploc and extracts the capsule. Dirty Hands steadies the ½ inch ID polyethylene tube (to the left of the tee) while Clean Hands inserts the intake end of the sampling capsule into the polyethylene. Filtered water now exits through tube B which has been pre-cleaned and was attached to the sampling capsule by the mercury analytical lab prior to double bagging. Clean Hands makes sure to not let the tube B contact foreign surfaces. After a few minutes of flushing, Dirty and Clean Hands have un-bagged a sample container (part C). Clean Hands shields the opening of the sample bottle while it is being filled to prevent dust from entering. After filling the sample bottle is quickly capped and re-inserted into the double bags. The process is repeated without the filter for the whole water sample. Clean Hands takes care not to contact the sample bottle with the polyethylene tubing. Sample labels are attached to the inner surface of the outer Ziploc.

Sampling for Particulate Organic Carbon

Particulate organic carbon (POC) was measured in raw and filtered (post TOPS) water. The glass fiber cartridge filters used in TOPS have a high capacity for suspended particles but they are fairly coarse (nominal porosity of 1 µm) and are thus inefficient. Trapping efficiency is a function of particle size and particle loading. As filters load, porosity decreases making the filter more efficient. We measure TOPS trapping efficiency by using 0.7 µm flat glass fiber GFF filters. The GFF filters were partially wrapped in aluminum foil and ashed at 450ºC for 4 hours; resealed while warm; and stored doubled bagged in Ziplocks in a laboratory freezer prior to deployment.

Broad-headed stainless steel forceps are used to place the filters into a magnetic filter holder set into a 2 L side arm Erlenmeyer flask. Vacuum is supplied by an electric bench-top pump. The magnetic filter holder has a 200 mL reservoir. Prior to loading the filter, the assembly is rinsed with site water. Water that had passed through the TOPS glass fiber cartridge filter is processed first. Water is filtered until plugging reduces flow to a drip. The reservoir is fully filtered and the vacuum is broken. The broad-head forceps are used to transfer the filter into a clean close fitting plastic Petri dish. The resealed Petri is labeled and kept cold in the field and frozen in the lab prior to analysis. The filtering process is repeated on for raw water.

Sampling for PCBs and Pesticides

Whole water samples for PCBs and pesticides were obtained by filling 1 L pre-clean certified amber bottles (Boston Rounds) with water from the same ½ inch polyethylene line as was used for the mercury samples. Three bottles were filled for each sample. The bottles were rinsed 3x with site water prior to final filling.

Mercury Results

Table 5 gives mercury concentrations and loads. Highlighted values were less than 5 x the maximum (of 3) field blanks. There were no field blanks for filtered water.

Mercury loads were estimated for the entire period of record by calculating a log concentration – log discharge linear relationship. The slope and intercept coefficients were applied to the known or (in the case of Salmon and 18-Mile Creek) calculated discharges so that a mercury concentration was estimated for each day. In cases where there were missing records, the mean between the days preceding and following the censored observations was applied.

TABLE 5. Mercury samples, results, and instantaneous loads.

site	date	discharge cf/sec	g/hour filtered	g/hour whole	ng/L filtered	ng/L whole
18-Mile Cr.	5/1/2007	210	0.02	0.06	1.11	3.35
	3/3/2008	101	0.01	0.14	2.49	29.8[#]
	3/24/2008	273	0.07	0.19	2.86	7.42
	4/7/2008	301	0.12	0.15	4.28	5.16
	4/29/2008	70	0.02	0.03	1.39	2.33
	5/27/2008	107	0.01	0.05	0.56	5.41
	6/9/2008	96	0.01	0.07	1.73	8.42
18-Mile Cr. average		165	0.037	0.099	2.06	5.35
Black R.	5/3/2007	8730	1.59	2.5	1.79	2.81
	1/9/2008	14000	3.64	14.56	2.55	10.2*
	3/13/2008	12200	2.13	3.62	1.71	2.91
	5/28/2008	2660	0.28	0.48	1.04	1.78
	6/10/2008	3580	0.53	1.42	1.45	3.88
Black R. average		8234	1.63	4.52	1.71	2.85
Genesee R.	5/2/2007	4250	0.29	1.15	0.66	2.65
	3/4/2008	4680	0.52	1.97	1.09	4.13
	4/8/2008	8030	0.76	3.5	0.93	4.27
	5/28/2008	1680	0.1	0.31	0.56	1.79
	6/10/2008	1417	0.04	0.18	0.28	1.24
	6/19/2008	827	0.05	0.16	0.65	1.9
	9/30/2008	1451		0.15	<0.15	1.01
Genesee R. average		3191	0.293	1.06	0.695	2.43
Oswego R.	5/2/2007	19700	1.53	4.9	0.76	2.44
	10/25/2007	9570	0.33	2.38	0.34	2.44
	1/10/2008	15200	1.32	2.96	0.85	1.91
	3/4/2008	11900	0.76	1.33	0.63	1.1
	3/25/2008	16600	2.47	4.48	1.46	2.65
	4/30/2008	11800	1.72	3.06	1.43	2.54
	9/30/2008	1160	0.03	0.08	0.28	0.64
Oswego R. average		12276	1.17	2.74	0.821	1.96
Salmon R.	5/3/2007	1533	0.23	0.34	1.48	2.19
	1/10/2008	2581	0.47	0.69	1.8	2.63
	4/8/2008	2998	0.45	0.88	1.47	2.89
	5/1/2008	2096	0.4	0.52	1.85	2.43
Salmon R. average		2302	0.390	0.610	1.65	2.54

[#] value not used in load calculations.

1/9/2008 was the occasion of a significant weather anomaly. Temperatures in much of the eastern US were 30°F above normal. Wind gusts at Watertown reaching 60 mph on the day of sampling made operations extremely difficult. The high mercury concentration may have been the result of wind blown dust.

Correlations between concentration and discharge were poor for total and dissolved mercury in 18-Mile Creek and poor for dissolved mercury at Salmon River. These data suggest that the Black River is an important mercury source to Lake Ontario. Salmon R. shows a higher mercury loading rate per sq km and per capita than do the Genesee or the Oswego Rivers (Table 6).

TABLE 6. Mercury loads derived from log/log regressions.

	slope	intercept	r2	total load (g)	g/sq km	g/capita	g/day
total mercury							
18-Mile Cr.	0.242	0.161	9%	847	4.58	0.03	1.63
Black R.	0.531	-1.483	45%	23,532	4.88	0.36	45.25
Genesee R.	0.559	-1.562	67%	8,890	1.39	0.03	17.10
Oswego R.	0.467	-1.614	67%	15,244	1.15	0.02	29.31
Salmon R.	0.401	-0.942	98%	1,745	2.45	0.27	3.36
dissolved mercury							
18-Mile Cr.	0.595	-1.046	26%	344	1.86	0.01	0.66
Black R.	0.393	-1.291	80%	9,760	2.02	0.15	18.77
Genesee R.	0.346	-1.378	40%	2,262	0.35	0.01	4.35
Oswego R.	0.468	-2.022	50%	6,023	0.46	0.01	11.58
Salmon R.	0.048	0.053	1%	1,452	2.04	0.22	2.79

Broken mercury thermometers have been seen in the Black River immediately downstream from the sampling point. An elevated sediment mercury sediment concentration (2.4 mg/kg) was seen 5.2 km upstream from the sampling point on the Black River.

Concentrations of mercury in water may be contextualized through examining the distribution of mercury in sediments.

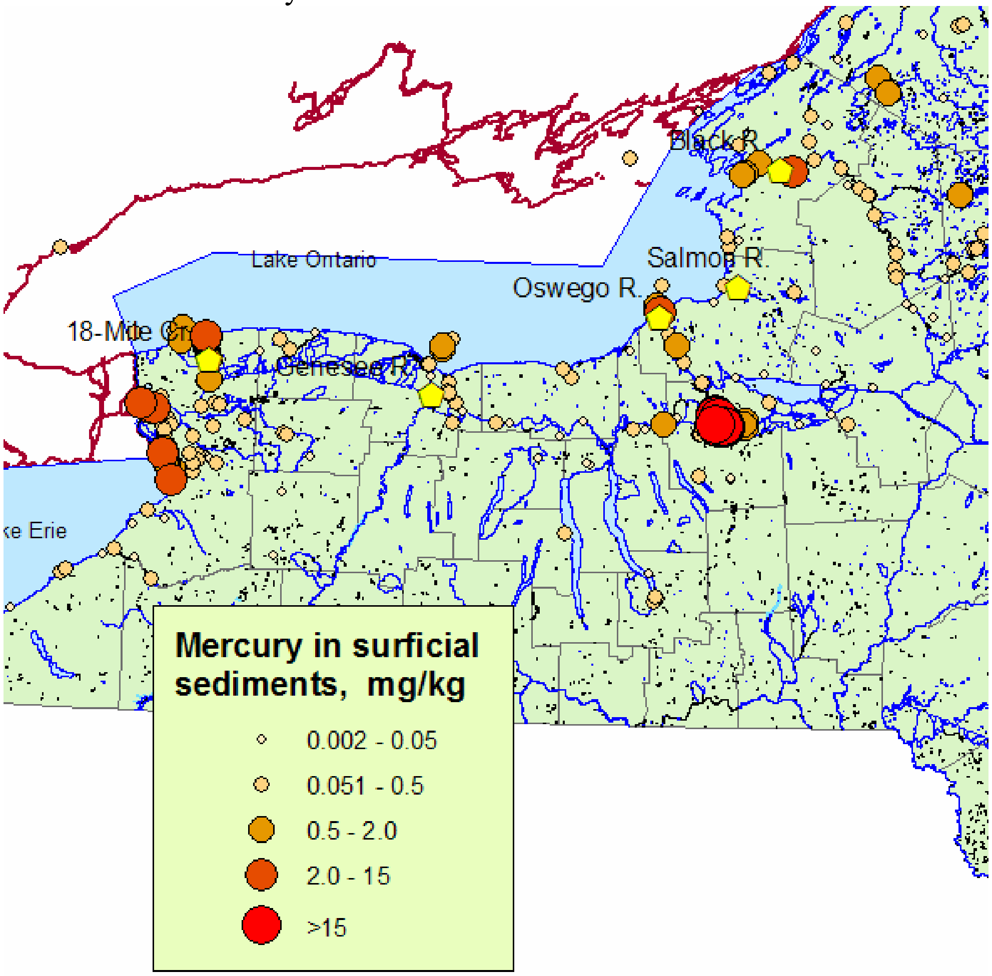

Figure 4. Mercury in Great Lakes Basin surficial sediments taken from the NYSDEC National Sediment Inventory.

PCB Results

Measurement of PCBs was hampered by detection limits that were in most places high relative to the native concentrations. Table 7 shows all measured total PCB concentrations. Highlighted records have PCB concentrations that were less than 5 times the highest blank. Individual congener concentrations and detection levels are shown in the Appendix. Sample specific detection limits averaged by sites and homologs are also shown in the Appendix.

Concentration/discharge relations were calculated as log/log linear equations and the slopes and intercepts were applied to the actual discharges that occurred over the period of record. Summary statistics were calculated and shown in Table 8. Yellow-shaded records are of low confidence due to inadequate detection limits and, for the Oswego and Black Rivers, poor correlations. It is likely that PCB concentrations in the Black, Genesee, Oswego, and Salmon Rivers are overestimates.

TABLE 7. PCB samples, results, and instantaneous loads.

site	date	total, ng/L	disch., CFS	g/hr
18-Mile Cr.	5/1/07	103	210	1.92
18-Mile Cr.	3/3/08	109	101	0.52
18-Mile Cr.	3/24/08	33	273	0.83
18-Mile Cr.	4/7/08	56	301	1.59
18-Mile Cr.	4/29/08	93	70	1.03
18-Mile Cr.	5/27/08	145	107	1.32
18-Mile Cr.	6/9/08	383	96	3.15
Black R.	5/3/07	1.8	8730	1.60
Black R.	10/24/07	1.8	6980	1.30
Black R.	3/13/08	0.77	12200	0.96
Black R.	5/28/08	2.2	2660	0.61
Black R.	10/1/08	1.8	1900	0.36
Genesee R.	5/2/07	0.65	4250	0.28
Genesee R.	3/4/08	0.37	4680	0.17
Genesee R.	4/8/08	0.85	8030	0.69
Genesee R.	5/28/08	2.3	1680	0.39
Genesee R.	6/10/08	1.8	1417	0.26
Genesee R.	6/19/08	1.5	827	0.13
Genesee R.	9/30/08	0.84	1451	0.12
Oswego R.	5/2/07	0.76	19700	1.53
Oswego R.	10/25/07	0.57	9570	0.56
Oswego R.	1/10/08	0.49	15200	0.76
Oswego R.	3/4/08	0.15	11900	0.19
Oswego R.	3/25/08	0.13	16600	0.22
Oswego R.	4/30/08	1.9	11800	2.31
Oswego R.	9/30/08	0.56	1160	0.07
Salmon R.	5/3/07	0.30	1533	0.05
Salmon R.	1/10/08	0.77	2581	0.20
Salmon R.	4/8/08	0.45	2998	0.14
Salmon R.	5/1/08	0.47	2096	0.10
duplicate				
Oswego R.	4/30/08	0.89	11800	1.07
field blanks				
Genesee R.	9/30/08	0.41	1451	
Oswego R.	9/30/08	0.38	1160	

TABLE 8. PCB loads derived from log/log regressions.

	slope	intercept	r2	total load (g)	g/sq km	g/capita	g/day
18-Mile Cr.	-0.75	3.58	53%	15,720	85	0.52	30
Black R.	-0.35	1.62	15%	11,741	2.4	0.18	23
Genesee R.	-0.70	2.35	66%	2,631	0.41	0.008	5.1
Oswego R.	-0.12	0.15	2%	3,850	0.29	0.004	7.4
Salmon R.	0.92	-3.40	69%	333	0.47	0.051	0.64

Figure 5 shows PCBs in surficial sediments.

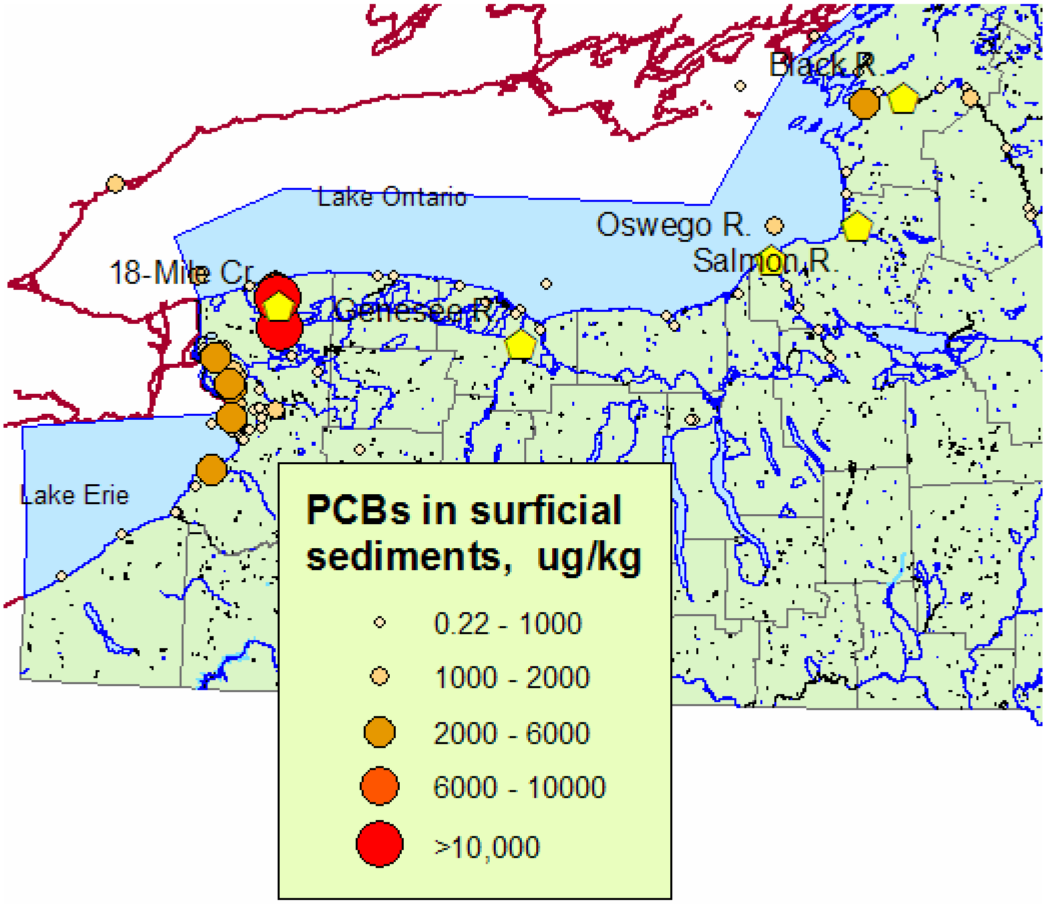

Figure 5. Total PCBs in Great Lakes Basin surficial sediments taken from the NYSDEC National Sediment Inventory.

Pesticides Results

Table 9 shows the pesticides (and metabolites) that were measured here, pesticide groupings, and NYS water quality standards. Pesticide observations were spotty. Table 10 shows the strongest pesticide data – all observations at least five times greater than field blanks, and five times larger than method blanks. The most frequently observed pesticides were dieldrin, endosulfan, and the metabolite, heptachlor epoxide.

Table 9. Pesticides, groupings, NYS Water Quality Standards

pesticide	grouping	WQS. ng/L	pesticide	grouping	WQS. ng/L
BHC, alpha	BHC	2	4,4'-DDE	DDT	0.007
BHC, beta	BHC	7	4,4'-DDT	DDT	0.01
BHC, delta	BHC	8	Aldrin	Dieldrin	1
BHC, gamma	BHC	8	Dieldrin	Dieldrin	0.0006
Chlordane, cis	Chlordane	0.02	Endosulfan sulfate	Endosulfan	NA
Chlordane, trans	Chlordane	0.02	Endosulfan, alpha	Endosulfan	NA
Chlordane,oxy-	Chlordane	0.02	Endosulfan, beta	Endosulfan	NA
Nonachlor, cis-	Chlordane	0.02	Endrin	Endrin	2
Nonachlor, trans-	Chlordane	0.02	Endrin aldehyde	Endrin	NA
Hexachlorobenzene	Chlorobenzene	0.03	Endrin ketone	Endrin	NA
2,4'-DDD	DDT	NA	Heptachlor	Heptachlor	0.2
2,4'-DDE	DDT	NA	Heptachlor epoxide	Heptachlor	0.3
2,4'-DDT	DDT	NA	Methoxychlor	Methoxychlor	30
4,4'-DDD	DDT	0.08	Mirex	Mirex	0.001

Pesticide concentrations were highest in 18-Mile Creek, particularly on the 3/3/2008 sampling event. Most noteworthy was the high concentration of parent (4,4'-) DDT. DDT was banned in NYS in 1970, two years before being banned nationally by EPA.

TABLE 10. Pesticides concentrations (ng/L)

Site	date	2,4'-DDD	2,4'-DDE	2,4'-DDT	4,4' DDD	4,4' DDE	4,4' DDT	Aldrin	alpha BHC	beta BHC	delta BHC	gamma BHC
18-Mile Cr.	5/1/07	0.076			0.156	0.342		0.008				
	3/3/08	4.19	0.500	10.800	6.22	39.2	71.8				0.009	0.075
	3/24/08	0.086		0.068	0.163	1.21	0.435					0.076
	4/7/08				0.223	0.550	0.189		0.138	0.185	0.026	0.142
	4/29/08				0.179	0.234				0.059	0.014	0.094
	5/27/08				0.232	0.233			0.041	0.053		0.078
	6/9/08				0.406	0.456	0.524	0.246				
18-Mile Cr. Avg		1.45	0.500	5.43	1.08	6.03	18.2	0.127	0.090	0.099	0.016	0.093
Black R	10/24/07					0.040						
	1/9/08					0.102						
	5/28/08											0.029
	10/1/08							0.020				
Black R. Avg						0.071		0.020				0.029
Genesee R.	5/2/07	0.024				0.154						
	3/4/08			0.025	0.036	0.234	0.119					
	4/8/08					0.203	0.115		0.038			0.030
	6/10/08					0.055						
	6/19/08					0.097						
Genesee R. Avg		0.024		0.025	0.036	0.149	0.117		0.038			0.030
Oswego R.	5/2/07	0.027			0.074	0.134			13.0	1.61		0.169
	10/25/07					0.107						
	1/10/08					0.127	0.086					
	3/4/08				0.018	0.044						
	3/25/08			0.051	0.050	0.222	0.204					
	4/30/08								0.030			0.037
Oswego R. Avg		0.027		0.051	0.047	0.127	0.145		4.353	1.610		0.081
Salmon R.	1/10/08					0.041						
Salmon R. Avg						0.041						

Table 10. Continued.

site	date	cis Chlordane	trans-Chlordane	oxy-Chlordane	Dieldrin	sulfate Endosulfan	alpha, Endosulfan	beta, Endosulfan
18-Mile Cr.	5/1/07				0.299	0.250		
	3/3/08	0.220	0.207	0.026	2.30	22.5	1.85	7.08
	3/24/08	0.029		0.018	0.192	0.670	0.121	
	4/7/08	0.130	0.140		0.298	0.617		
	4/29/08	0.043	0.046	0.061	0.351	0.438		
	5/27/08	0.128	0.071		0.326	0.213		
	6/9/08	0.186			0.480	0.384		
18-Mile Cr. Avg		0.123	0.116	0.035	0.607	3.58	0.986	7.08
Black R.	10/24/07				0.028	0.187		
	1/9/08		0.052		0.031	0.115		
	5/28/08				0.023	0.079		
Black R. Avg			0.052		0.027	0.127		
Genesee R.	3/4/08	0.034			0.133	0.088	0.042	
	4/8/08	0.020	0.014		0.046			
	5/28/08	0.040	0.031		0.088	0.124		
	6/10/08				0.105	0.174		
	6/19/08				0.126	0.392		
	9/30/08			0.057	0.094			
Genesee R. Avg		0.031	0.023	0.057	0.099	0.195	0.042	
Oswego R.	5/2/07				0.092			
	10/25/07		0.016		0.051	0.173		
	1/10/08		0.016		0.070	0.195		
	3/4/08	0.015			0.059	0.125	0.051	
	3/25/08				0.075	0.180	0.078	
	4/30/08	0.015	0.014		0.093	0.148		
Oswego R. Avg		0.015	0.015		0.076	0.161	0.065	
Salmon R.	1/10/08				0.021	0.061		
	4/8/08		0.014		0.017			
	5/1/08				0.029	0.075		
Salmon R. Avg			0.014		0.022	0.068		

Table 10. Continued.

site	date	Endrin	ketone, Endrin	Heptachlor	epoxide Heptachlor	Hexachloro-benzene	Methoxychlor	Mirex	cis+trans Nonachlor
18-Mile Cr.	5/1/07				0.029				
	3/3/08	0.333	0.282	0.042	0.052	0.189	0.045	0.036	0.243
	3/24/08		0.028	0.011	0.033				
	4/7/08		0.031	0.043	0.034				0.051
	4/29/08		0.019		0.046				0.041
	5/27/08				0.042			0.018	0.091
	6/9/08			0.095	0.056			0.072	
18-Mile Cr. Avg		0.333	0.090	0.048	0.042	0.189	0.045	0.042	0.117
Black R.	5/3/07				0.013				
	10/24/07								
	1/9/08								0.027
	5/28/08			0.011					0.016
	10/1/08			0.027					
Black R. Avg				0.019	0.013				0.022
Genesee R.	5/2/07				0.024	0.786			

	3/4/08				0.042				

site	date	Endrin	ketone, Endrin	Heptachlor	epoxide Heptachlor	Hexachloro-benzene	Methoxychlor	Mirex	cis+trans Nonachlor
	4/8/08			0.020	0.017				0.049
	5/28/08				0.028				0.069
	6/10/08				0.032				
	6/19/08				0.032				
Genesee R. Avg				0.020	0.029	0.786			0.059
Oswego R.	5/2/07			0.005	0.020				0.014
	10/25/07							0.264	0.016
	1/10/08	0.018			0.023			0.012	0.011
	3/4/08				0.013				
	3/25/08		0.020		0.010				
	4/30/08		0.015		0.016				0.013
Oswego R. Avg		0.018	0.018	0.005	0.016			0.138	0.027
Salmon R.	4/8/08								0.039
	5/1/08								0.013
Salmon R. Avg									0.035

Table 11 shows the average ratio by which pesticides exceed the Water Quality Standard. Non-detections are censored. Cases where there were no observed instances of an exceedence are not shown. The 18-Mile Creek sampling site was directly adjacent to a busy and prosperous-looking farm.

Table 11. Exceedence ratio.

pesticide	18-Mile Cr.	Black R.	Genesee R.	Oswego R.	Salmon R.
BHC, alpha				2.18	
Chlordane + Nonachlor	14.4	2.38	3.93	1.33	1.65
Hexachlorobenzene	6.3		26.2		
4,4'-DDE	13.5				
4,4'-DDD	862	10.1	21.2	18.1	5.86
4,4'-DDT	1824		11.7	14.5	
Dieldrin	1011	45.6	164	127	37.2
Mirex	42			138	

Table 12. Instantaneous loads for pesticides with Water Quality Standards (g/day). Sites with maximum average loads are highlighted.

site	date	4,4' DDD	4,4' DDE	4,4' DDT	Aldrin	alpha BHC	beta BHC	D+G BHC	Chlordane	Dieldrin	Endrin
18-Mile Cr.	5/1/07	0.070	0.153		0.003					0.134	
	3/3/08	0.709	4.47	8.18				0.010	0.052	0.262	0.038
	3/24/08	0.099	0.737	0.265				0.046	0.029	0.117	
	4/7/08	0.152	0.376	0.129		0.094	0.126	0.115	0.185	0.204	
	4/29/08	0.047	0.062				0.016	0.029	0.040	0.093	
	5/27/08	0.051	0.051			0.009	0.012	0.017	0.043	0.071	
	6/9/08	0.080	0.090	0.104	0.049				0.037	0.095	
18-Mile Cr. Avg		0.173	0.848	2.17	0.026	0.052	0.051	0.046	0.064	0.139	0.038
Black R.	10/24/07		0.683							0.478	
	1/9/08		3.49						1.78	1.06	
	5/28/08							0.189		0.150	
	10/1/08				0.093						
Black R. Avg			2.089		0.093			0.189	1.78	0.563	
Genesee R.	5/2/07		1.60								

site	date	4,4' DDD	4,4' DDE	4,4' DDT	Aldrin	alpha BHC	beta BHC	D+G BHC	Chlordane	Dieldrin	Endrin
	3/4/08	0.412	2.68	1.36					0.389	1.52	
	4/8/08		3.99	2.26		0.747		0.589	0.668	0.904	
	5/28/08								0.292	0.362	
	6/10/08		0.191							0.364	
	6/19/08		0.196							0.255	
	9/30/08								0.202	0.334	
Genesee R. Avg		0.412	1.73	1.81		0.747		0.589	0.388	0.624	
Oswego R.	5/2/07	3.57	6.46			627	77.6	8.146		4.43	
	10/25/07		2.51						0.375	1.19	
	1/10/08		4.72	3.20					0.595	2.60	0.669
	3/4/08	0.524	1.28						0.437	1.72	
	3/25/08	2.03	9.02	8.29						3.05	
	4/30/08					1.73		2.108	1.67	5.34	
Oswego R. Avg		2.04	4.80	5.74		314	77.6	5.127	0.770	3.06	0.669
Salmon R.	1/10/08		0.259							0.133	
	4/8/08								0.103	0.125	
	5/1/08									0.149	
Salmon R. Avg			0.259						0.103	0.135	

Table 12. Continued.

site	date	Heptachlor	epoxide Heptachlor	Hexachloro-benzene	Methoxy-chlor	Mirex	cis+trans Nonachlor
18-Mile Cr.	5/1/07		0.013				
	3/3/08	0.005	0.006	0.022	0.005	0.004	0.028
	3/24/08	0.007	0.020				
	4/7/08	0.029	0.023				0.035
	4/29/08		0.012				0.011
	5/27/08		0.009			0.004	0.020
	6/9/08	0.019	0.011			0.014	
18-Mile Cr. Avg		0.015	0.013	0.022	0.005	0.007	0.023
Black R.	5/3/07		0.278				
	1/9/08						0.925
	5/28/08	0.072					0.104
	10/1/08	0.126					
Black R. Avg		0.099	0.278				0.515
Genesee R.	5/2/07		0.249	8.17			
	3/4/08		0.481				
	4/8/08	0.393	0.334				0.963
	5/28/08		0.115				0.284
	6/10/08		0.111				
	6/19/08		0.065				
Genesee R. Avg		0.393	0.226	8.17			0.623
Oswego R.	5/2/07	0.251	0.945				0.675
	10/25/07					6.18	0.375
	1/10/08		0.855			0.446	0.409
	3/4/08		0.379				
	3/25/08		0.406				
	4/30/08		0.924				0.375
Oswego R. Avg		0.251	0.702			3.31	0.458
Salmon R.	4/8/08						0.286
	5/1/08						0.067

Salmon R. Avg	0.176

Sediment data (taken from the NYSDEC National Sediment Inventory) are shown for 4,4'-DDT, dieldrin, and total chlordanes in Figures 6, 7, and 8.

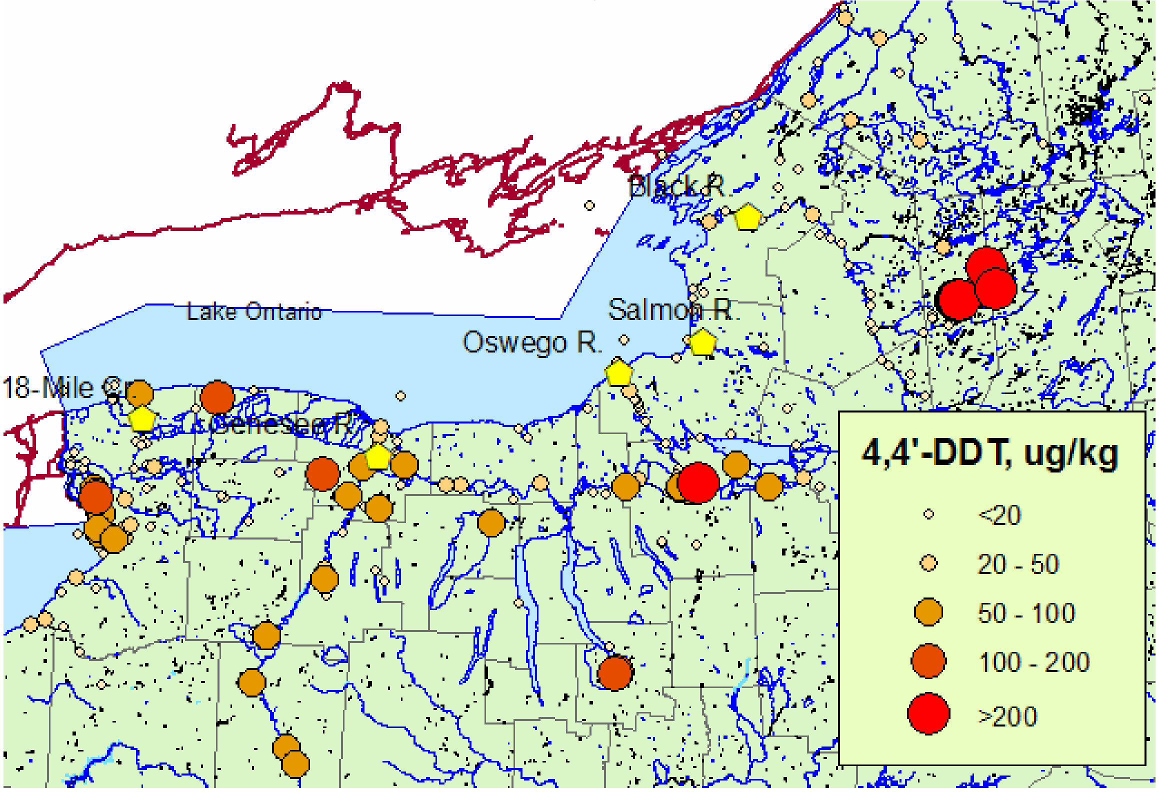

Figure 6. 4,4'-DDT in Great Lakes Basin surficial sediments.

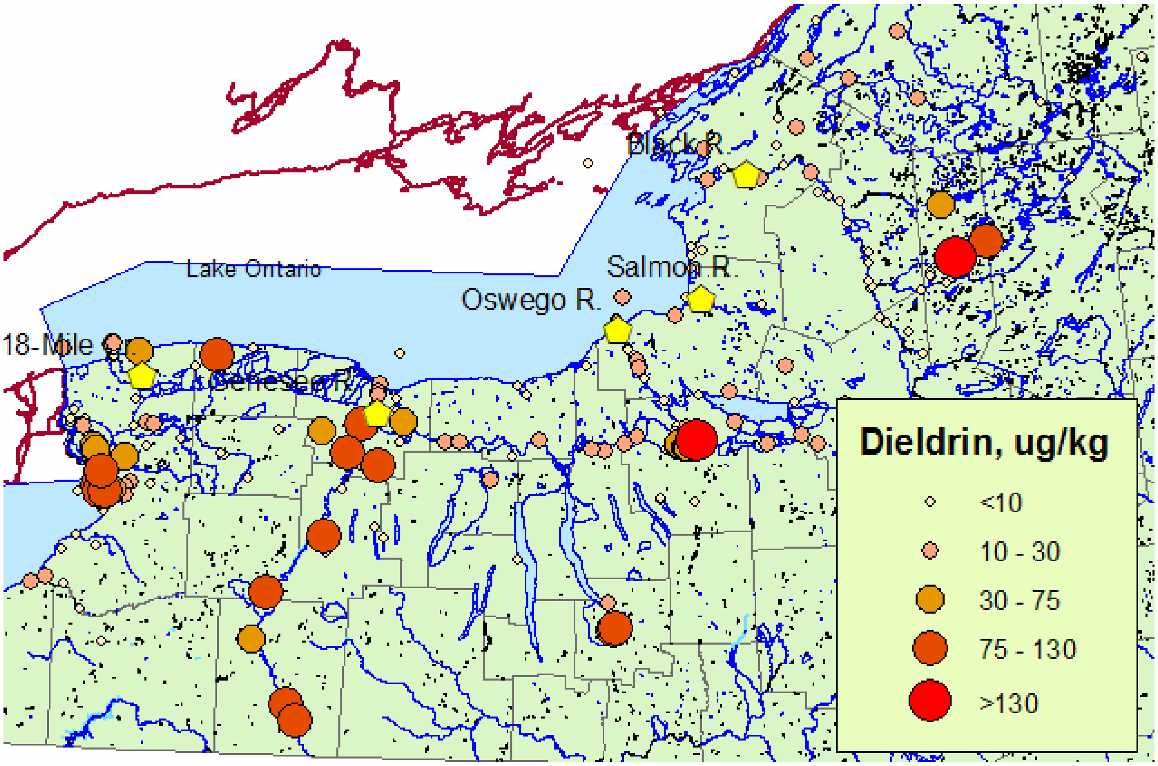

Figure 7. Dieldin in Great Lakes Basin surficial sediments.

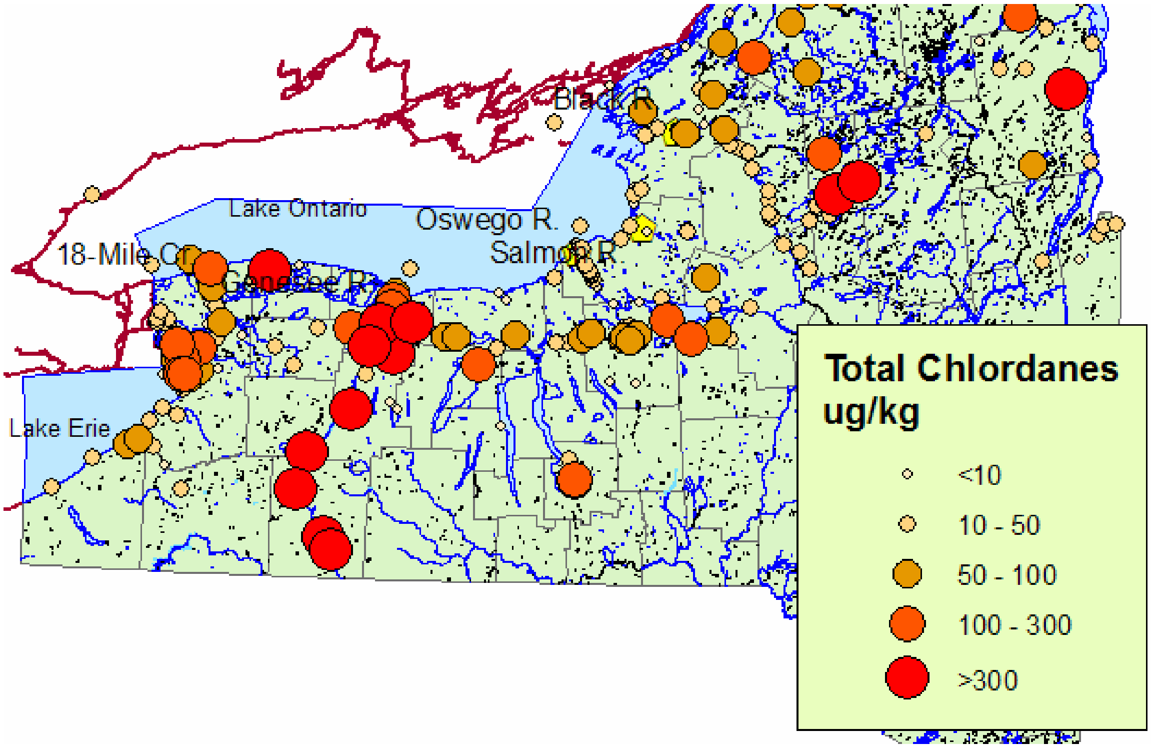

Figure 8. Total chlordanes in Great Lakes Basin surficial sediments.

PCDD/F Results

"Dioxins" is shorthand for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). There are theoretically 75 distinct PCDDs (called congeners) and 135 PCDF congeners. There are an equal number of polybrominated analogs. Potentially, there are 337 mixed chlorinated and brominated dioxins (PXDDs) and 647 furans (PXDFs). In the regulatory world, however, only 7 PCDDs and 10 PCDFs are routinely measured. These regulatory target PCDD/Fs have chlorine atoms attached to 2, 3, 7, and 8 positions on the dibenzo-p-dioxin or dibenzofuran skeleton. Up to four more chlorine atoms can be attached to other positions.

It is not the intention of this report to discuss dioxin health effects but we will point out that some of the congeners are extraordinarily toxic.[4-11] New York State's Water Quality Standard for the sum[a] of all 17 PCDD/Fs is 0.6 femtograms/L.[b] Table 13 lists the 17 regulatory PCDD/Fs along with their toxic equivalency factors (TEFs) from the World Health Organization [12] and the bioaccumulation equivalency factors (BEFs) used by NYS. From time to time an expert panel considers new informations and amends the TEFs as appropriate. The effects of these changes vary with the composition of the sample but on average they have reduced the overall calculated toxicity by about 19%.

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[a] The WQS multiplies the concentration of each congener by a toxic equivalency factor or TEF taken from the World Health Organization (1994) consensus document and by a bioaccumulation equivalency factor (BEF). The products are summed to yield a toxic equivalency (TEQ).

[b] Femtogram/L or part per quintillion – 1 x 10E-15 g/L

Almost all the change was between WHO94 and 1998 revision. The mean relative percent difference between all of this project's total TEQs caluculated with WHO98 and WHO05 is 4.45%. Table 13 also gives a Congener Order for each congener that will be used subsequently in place of the longer congener name.

Individual congener concentrations and detection limits are shown in the Appendix.

Table 13. Dioxins, names, congener orders, evolving TEF, and BEFs.

congener order	congener	WHO94	WHO98	WHO05	BEF
1	2,3,7,8-TCDD	1	1	1	1
2	1,2,3,7,8-PeCDD	0.5	1	1	0.9
3	1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	0.3
4	1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	0.1
5	1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	0.1
6	1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01	0.05
7	OCDD	0.001	0.0001	0.0003	0.01
8	2,3,7,8-TCDF	0.1	0.1	0.1	0.8
9	1,2,3,7,8-PeCDF	0.05	0.05	0.03	0.2
10	2,3,4,7,8-PeCDF	0.5	0.5	0.3	1.6
11	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1	0.08
12	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1	0.2
13	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1	0.7
14	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1	0.6
15	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.4
17	OCDF	0.001	0.0001	0.0003	0.02

Table 14. Sites, dates, times, and L processed for dioxin samples.

site	date	start	end	L filtered
18-Mile Cr.	5/1/07	12:47	14:16	336
18-Mile Cr.	3/3/08	14:36	15:29	284
18-Mile Cr.	3/24/08	13:19	16:59	923
18-Mile Cr.	4/7/08	14:02	17:30	1,169
18-Mile Cr.	4/29/08	13:21	17:00	1,244
18-Mile Cr.	5/27/08	13:58	15:48	543
18-Mile Cr. DU	5/27/08	13:58	15:57	591
18-Mile Cr.	6/9/08	14:06	15:32	430
Black R.	5/3/07	13:55	16:30	647
Black R.	10/24/07	11:45	14:30	305
Black R.	1/9/08	14:06	15:27	157
Black R.	3/13/08	11:08	13:38	594
Black R.	5/28/08	14:33	18:51	1,279
Black R.	6/10/08	15:10	17:20	759
Equip. Blank	2/27/08	10:27		1
Equip. Blank	6/11/08	11:07		1
Genesee R.	5/2/07	7:49	9:20	309
Genesee R.	3/4/08	8:44	10:49	518
Genesee R.	4/8/08	8:20	8:49	151
Genesee R.	5/28/08	7:59	10:10	759
Genesee R.	6/10/08	8:40	10:20	604
Genesee R.	6/19/08	14:33	16:09	580
Genesee R.	9/30/08	11:40	12:38	395

Oswego R.	5/2/07	14:06	16:35	599
site	date	start	end	L filtered
Oswego R.	10/25/07	10:18	14:53	830
Oswego R.	1/10/08	8:18	11:00	630
Oswego R.	3/4/08	14:29	16:41	562
Oswego R.	3/25/08	14:25	18:03	921
Oswego R.	4/30/08	12:09	16:51	1,411
Oswego R.	9/30/08	16:36	18:22	679
Salmon R.	5/3/07	7:58	10:43	652
Salmon R.	1/10/08	13:30	16:36	654
Salmon R.	4/8/08	13:32	15:07	515
Salmon R.	5/1/08	8:43	14:25	1,726

Table 15 shows for sample the total PCDD/F concentration calculated with each of the three TEFs and the bioaccumulation equivalency factor that is used in the NYSDEC Water Quality Standard. The later WHO TEFs reflect evolving science but the WHO 94 value is in regulation.

Table 15. Total TEQs in fg/L calculated with three different TEFs.

site	date	WHO 94, BEF	WHO 98, BEF	WHO 05, BEF
18-Mile Cr.	5/1/07	84.7	91.2	68.6
18-Mile Cr.	3/3/08	527	576	436
18-Mile Cr.	3/24/08	64.3	69.2	50.9
18-Mile Cr.	4/7/08	22.3	26.9	27.0
18-Mile Cr.	4/29/08	65.0	68.2	48.6
18-Mile Cr.	5/27/08	326	341	246
18-Mile Cr.	6/9/08	510	535	382
Black R.	5/3/07	7.21	8.44	6.86
Black R.	10/24/07	31.4	37.5	29.7
Black R.	1/9/08	63.7	63.4	46.6
Black R.	3/13/08	2.29	3.41	3.41
Black R.	5/28/08	7.57	8.68	6.49
Black R.	6/10/08	9.24	9.20	6.14
Genesee R.	5/2/07	36.1	41.7	34.6
Genesee R.	3/4/08	29.3	35.2	30.6
Genesee R.	4/8/08	40.3	46.8	35.6
Genesee R.	5/28/08	89.5	99.9	75.5
Genesee R.	6/10/08	65.1	72.3	56.4
Genesee R.	6/19/08	68.2	76.8	58.7
Genesee R.	9/30/08	67.9	73.7	55.4
Oswego R.	5/2/07	27.1	31.4	24.8
Oswego R.	10/25/07	37.3	43.8	34.7
Oswego R.	1/10/08	15.9	19.0	15.0
Oswego R.	3/4/08	0.81	0.79	0.78
Oswego R.	3/25/08	13.2	16.2	13.3
Oswego R.	4/30/08	23.3	27.1	22.0
Oswego R.	9/30/08	13.7	15.6	12.3
Salmon R.	5/3/07	9.30	11.2	8.63
Salmon R.	1/10/08	12.4	12.4	8.35
Salmon R.	4/8/08	18.1	21.3	16.3
Salmon R.	5/1/08	7.91	9.29	7.04

Table 16 shows TEQs for PCDD/F samples. The table gives:

TEQ, pg recov.	Sum of the products of PCDD/F congeners and the WHO98 TEF.
ratio	Ratio of the ΣTEQs calculated where non-detections are assigned values of 0 or the sample specific detection limit. As the ratio gets lower, the possible error from the non-detections increases.
POC, mg/L	Concentration of particulate organic carbon in unfiltered water.
TEQ, fg/L	TEQ concentration in fg/L.
trapping efficiency	The efficiency of the cartridge filter in trapping particles is assessed by 1-(F/R) where F = the POC concentration in water that has passed through the cartridge filter and R is the raw unfiltered water.
corrected TEQ, fg/L	TEQ concentration divided by trapping efficiency. This value is used in load calculations.

Appendix A shows concentrations for each PCDD/F congener and PCDD/F homolog.

Table 16. Dioxins in NYS Tributaries to Lake Ontario, total TEQ (WHO98). Highlighted records have TEQ pg recoveries less than 5 x the maximum field blank.

site	date	TEQ pg recov.	ratio	POC mg/L	TEQ, fg/L	trapping efficiency	corrected TEQ, fg/L
18-Mile Cr.	5/1/07	74	97%	0.20	220	52%	424
18-Mile Cr.	3/3/08	353	90%	1.70	1,246	49%	2,556
18-Mile Cr.	3/24/08	137	85%	0.21	149	49%	305
18-Mile Cr.	4/7/08	181	66%	0.33	155	65%	238
18-Mile Cr.	4/29/08	155	84%	0.22	125	41%	304
18-Mile Cr.	5/27/08	433	82%	0.44	760	37%	2,066
18-Mile Cr.	6/9/08	497	87%	0.60	1,156	73%	1,588
Black R.	5/3/07	9	83%	0.37	14	79%	18
Black R.	10/24/07	24	94%		80	65%	123
Black R.	1/9/08	20	75%	1.13	126	81%	155
Black R.	3/13/08	4	45%	0.16	7	52%	13
Black R.	5/28/08	16	74%	0.19	13	56%	23
Black R.	6/10/08	12	56%	0.30	16	57%	28
Genesee R.	5/2/07	21	93%	0.32	69	62%	110
Genesee R.	3/4/08	32	88%	0.23	61	62%	98
Genesee R.	4/8/08	11	69%	0.80	73	50%	146
Genesee R.	5/28/08	147	85%	0.4	193	69%	280
Genesee R.	6/10/08	81	92%	0.40	134	69%	194
Genesee R.	6/19/08	85	87%	0.50	147	68%	214
Genesee R.	9/30/08	43	91%	0.59	108	62%	174
Oswego R.	5/2/07	32	88%	0.19	53	63%	83
Oswego R.	10/25/07	81	98%	0.43	98	73%	133
Oswego R.	1/10/08	20	89%	0.25	33	67%	49
Oswego R.	3/4/08	3	33%	0.12	6	51%	12
Oswego R.	3/25/08	23	81%	0.25	25	41%	61
Oswego R.	4/30/08	78	83%	0.27	55	64%	86
Oswego R.	9/30/08	20	86%		29	60%	49
Salmon R.	5/3/07	10	85%	0.12	15	75%	20
Salmon R.	1/10/08	13	69%	0.25	20	81%	25
Salmon R.	4/8/08	15	65%	0.29	29	82%	36
Salmon R.	5/1/08	21	69%	0.12	12	63%	19

Table 17 shows POC corrected regressions for total TEQ. Yellow highlights signify low confidence due to poor correlations in the concentration/discharge relationship.

Table 17. Dioxin loads derived from log/log regressions.

Total TEQ	slope	intercept	R2	total load (ug)	ug/sq km	ug/capita	ug/day TEQ
18-Mile Cr.	-1.02	5.03	33	127,480	689	4.19	246
Black R.	0.42	-0.04	7.3	225,798	47	3.46	436
Genesee R.	-0.32	3.31	52	469,277	73	1.41	906
Oswego R.	0.06	1.52	0.5	460,851	35	0.46	890
Salmon R.	0.78	-1.23	68	17,949	25	2.73	34.7

The loading rate (µg/sq km of watershed) was very much greater in 18-Mile Cr. than elsewhere but the total loadings were greatest in the larger rivers. Other than as laboratory standards or for research purposes, dioxins were never intentionally manufactured. There are, however, a large variety of natural [13], industrial [14, 15], and inadvertent or accidental [16-18] events that have been shown to generate dioxins.

Figure 9 shows an overview of PCDD/F concentrations (as WHO 98 TEQs) from the NYSDEC National Sediment Inventory database of surficial sediment samples taken in the Lake Erie/Lake Ontario/St. Lawrence drainage where at least six of the 17 congeners were quantified. The size of the circles indicates concentration. Relatively high concentrations occur in the Niagara River, 18-Mile Creek, Onondaga Lake, and across Lake Ontario.

Congener patterns may provide insights into PCDD/F sources. Congener concentrations (normalized by WHO 98 TEFs) were ranked. Each sample was labeled with the congener order (see Table 13) contributing the highest and second highest TEQ. Table 18 shows the number of instances where various congeners were the largest contributor to total TEQ. Congeners 1 and 2 both have TEFs of 1 giving them both the highest toxicities. However, congener 6, while only having a TEF of 0.01, is much more abundant and is most often the largest single contributor of total TEQ.

Processes differ in the patterns of congeners formed. For example, the manufacture of trichlorophenoxy acetic acid used as a component in the Vietnam War era defoliant Agent Orange was particularly effective at producing 2,3,7,8-TCDD (Congener 1).[9, 16] Uncontrolled fires are often rich sources congener 10.[15, 19] Bleaching kraft process paper pulp with elemental chlorine resulted in formation of congeners 1 and 8.[20] While the PCDD/Fs are lumped together under the TEQ rubric, they are actually chemically distinct substances with different sources.

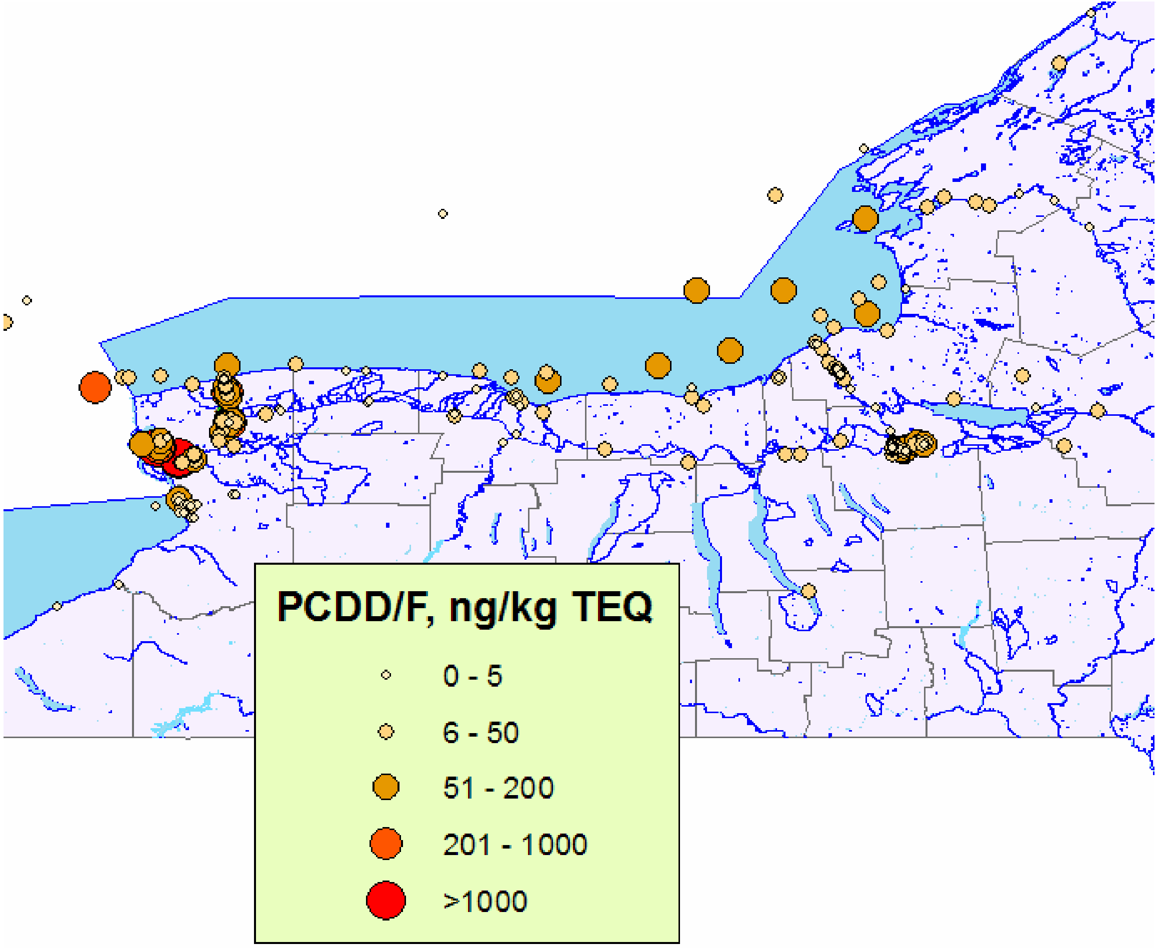

Figure 9. Total PCDD/Fs in Great Lakes Basin surficial sediments. NYSDEC National Sediment Inventory.

Table 18. Instances where particular PCDD/F congeners are the greatest contributor to total TEQ (WHO 98) in the NY portion of the Great Lakes Basin.

Congener Order	instances
6	138
1	97
10	90
8	85
11	64
2	52
15	3
4	1
12	1
13	1

Forty-two patterns of first/second congener dominance were found. Of the 532 sediment samples, 87% had one of 18 couplet patterns (Table 19). The first entry in Table 19 (couplet 8-10) shows that congener 8 was the largest and congener 10 was the second largest contributor to total TEQ.

Congener couplets	instances
8-10	73
10-8	48
1-2	41
6-4	39
1-11	32
2-1	25
6-10	25
6-2	22
11-10	21
10-2	20
6-11	20
6-15	20
1-10	18
11-15	14
11-6	12
2-6	12
2-10	11
10-6	10

Table 19. Instances where particular PCDD/F congener couplets are the greatest contributor to total TEQ (WHO 98) in the NY portion of the Great Lakes Basin.

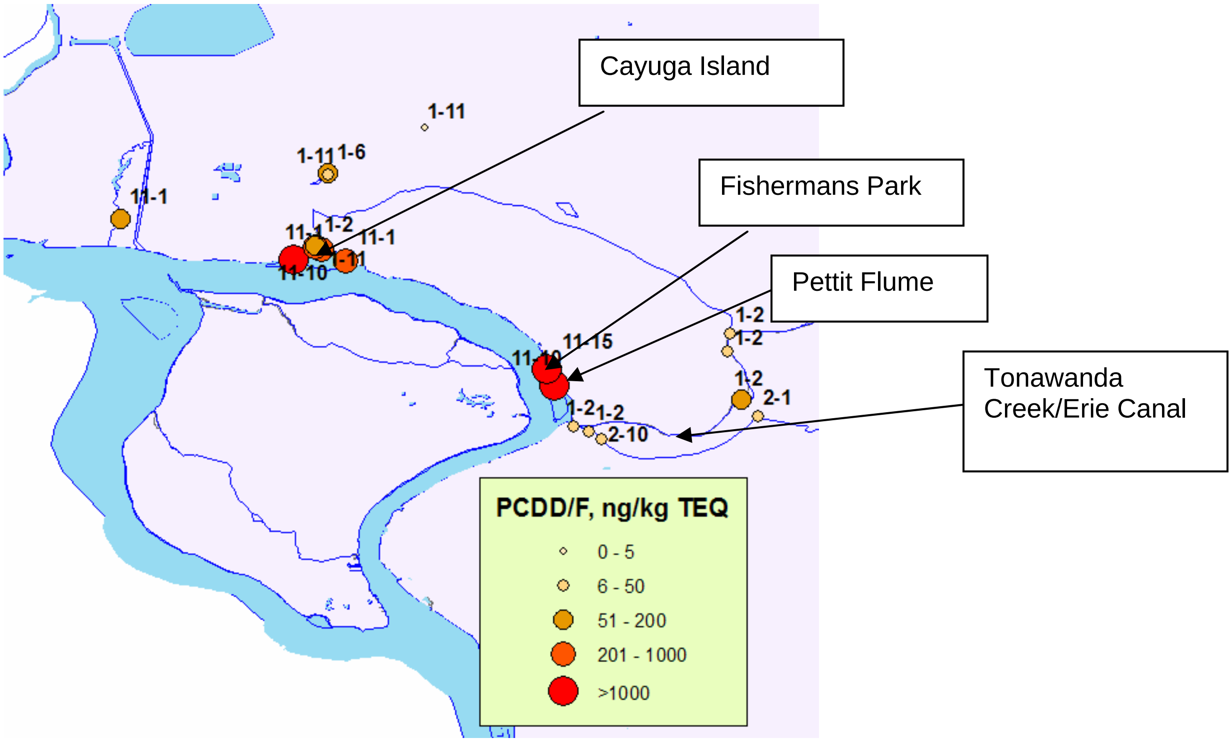

Figure 10. PCDD/F sediment concentrations and congener patterns (in TEQ) from the Niagara River and vicinity. NYSDEC National Sediment Inventory.

The Occidental Durez site in North Tonawanda manufactured phenolic resins using the Raschig-Hooker Process. Benzene is chlorinated by exposing it to a hot air-HCl mix. The resulting chlorobenzenes were then exposed to NaOH to form phenol, NaCl and water.[21] Side reactions occurred whereby PCDD/Fs and octachlorostyrene were also formed. Durez discharged liquid waste to sewers which emptied into the Niagara River at the Pettit Flume, in North Tonawanda. A sediment core taken from 740 m downstream at Fisherman's Park in 1999 shows the highest sediment PCDD/F levels measured in NYS. The Pettit Flume was remediated between 1989 and 1995.

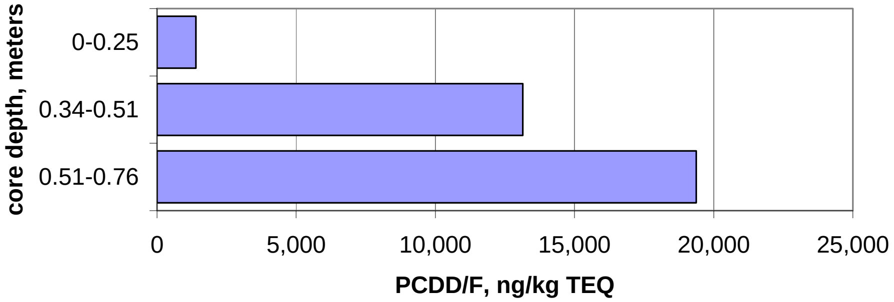

Figure 11. PCDD/F concentrations from a sediment core at Fisherman's Park. Surficial concentrations are much lower than deeper ones. NYSDEC National Sediment Inventory.

When the relative abundances of the congeners are plotted, however, the three samples appear virtually identical. Dominant congeners here were 11 and 15. A number of samples dominated by congeners 1 and 11 clusters around Cayuga Island and the Love Canal area. Sediments from throughout Lake Ontario show the 1-11 pattern. Sediments downstream from Pettit Flume in the Caygua Little River (Niagara Falls) also show congener 11 dominance. Congener 1 is dominant in Caygua Creek proper.

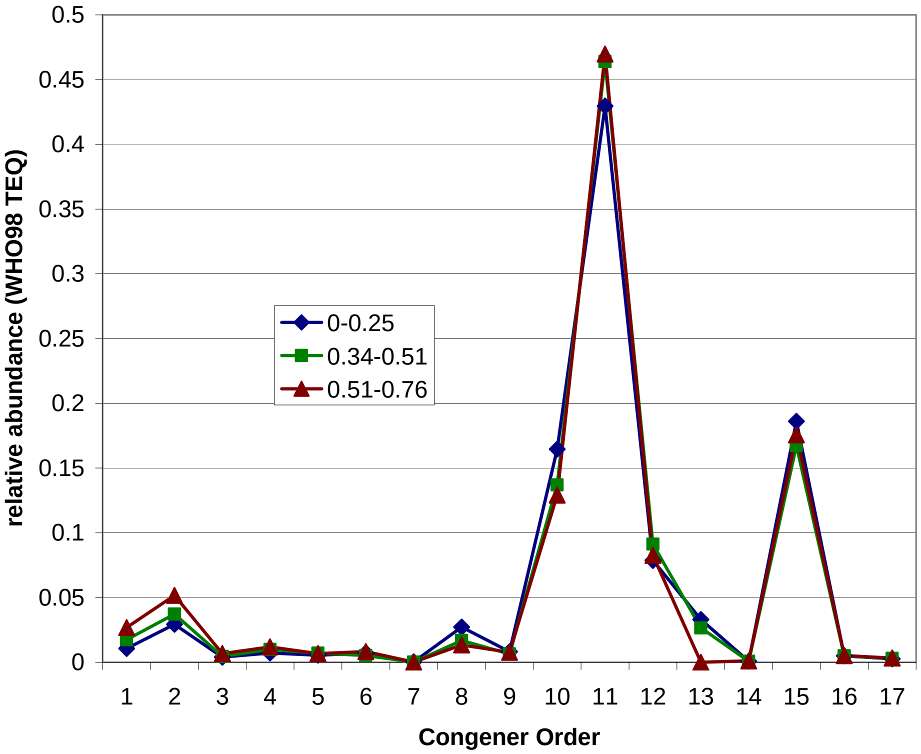

Figure 12. PCDD/F fingerprints from the Fisherman's Park sediment core. NYSDEC National Sediment Inventory. Legend indicates core depth in m. See Figure 11.

Tonawanda Creek naturally ran into the Niagara River but the lower portion of the creek has been converted into the Western end of the Erie Canal. During navigation season water flows from the Niagara into the lower Tonawanda Creek and through the canal. At Lockport (and Gasport) three gates let a total of 65 cfs from the Erie Canal into 18-Mile Creek (and the East Branch of 18-Mile Creek).

18-Mile Creek – Sediment

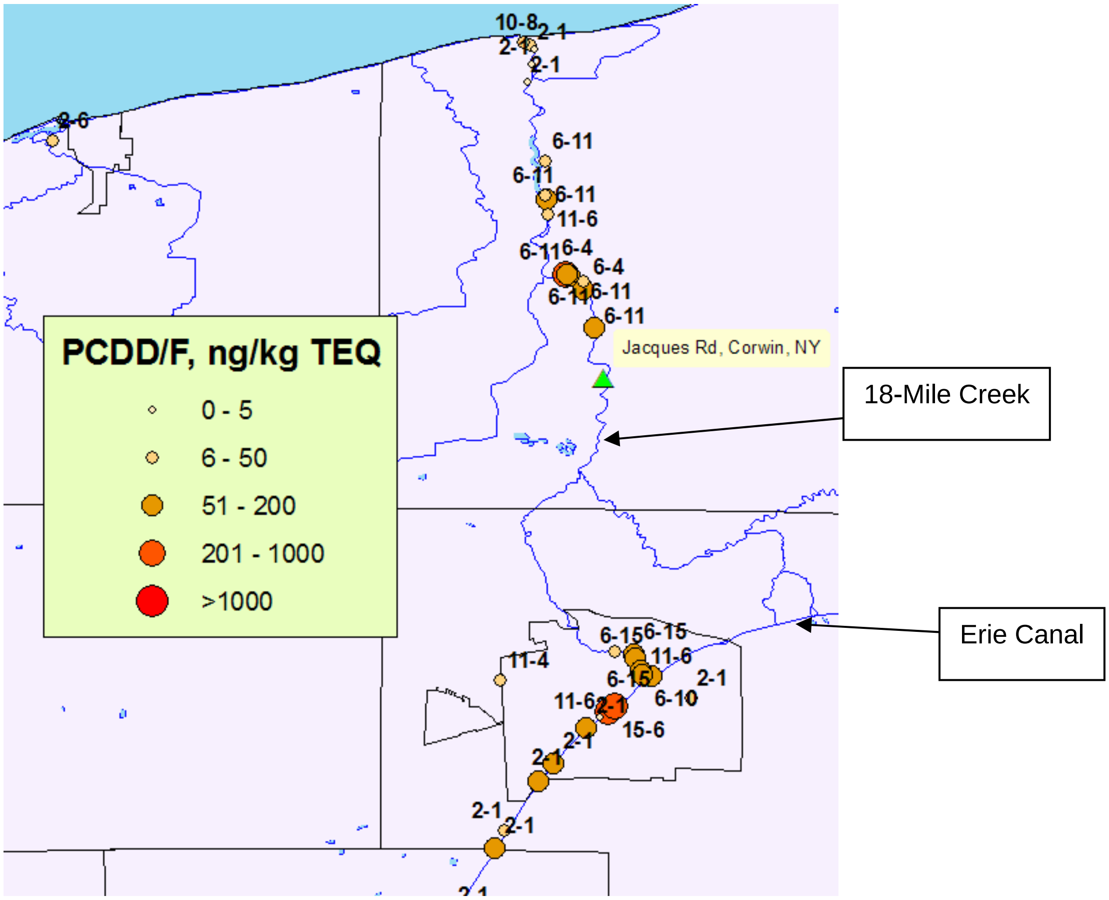

Figure 13. Surficial PCDD/F sediment concentrations and dominant congener couplets in the Erie Canal and in 18-Mile Creek. NYSDEC National Sediment Inventory.

PCDD/F concentrations in surficial Tonawanda Creek sediments are dominated by congeners 2 and 1. Samples taken within the City of Lockport show several new congeners, particularly 6 and 11. PCDD/F patterns change in Lockport suggesting sources with unusually high relative amounts of congeners 11 and 15. Congener 6 was also very abundant, particularly in the lower strata of a sediment core.

18-Mile Creek - Water

Table 20 shows the rank orders of the top five PCDD/F congeners from the 18-Mile Creek water (suspended sediment) samples.

Table 20. Ranks of congener contributions to total TEQ, 18-Mile Creek. The highest rank is 1.

Congener order	1	2	4	5	6	10	11	12	15
18-Mile Cr.-3/24/2008-SA			5		1	2	3		4
18-Mile Cr.-5/1/2007-SA			5		1	2	3		4
18-Mile Cr.-6/9/2008-SA			5		1	2	3		4
18-Mile Cr.-3/3/2008-SA					1	2	4	3	5
18-Mile Cr.-5/27/2008-DU			5		1	2	4		3
18-Mile Cr.-4/7/2008-SA		5	4		1		2		3
18-Mile Cr.-4/29/2008-SA			5		2	1	3		4
18-Mile Cr.-5/27/2008-SA			5		2	1	4		3

Genesee River - Sediment

Comparatively few sediment samples were taken upstream from the sampling site on the Genesee River. These are shown in Figure 14.

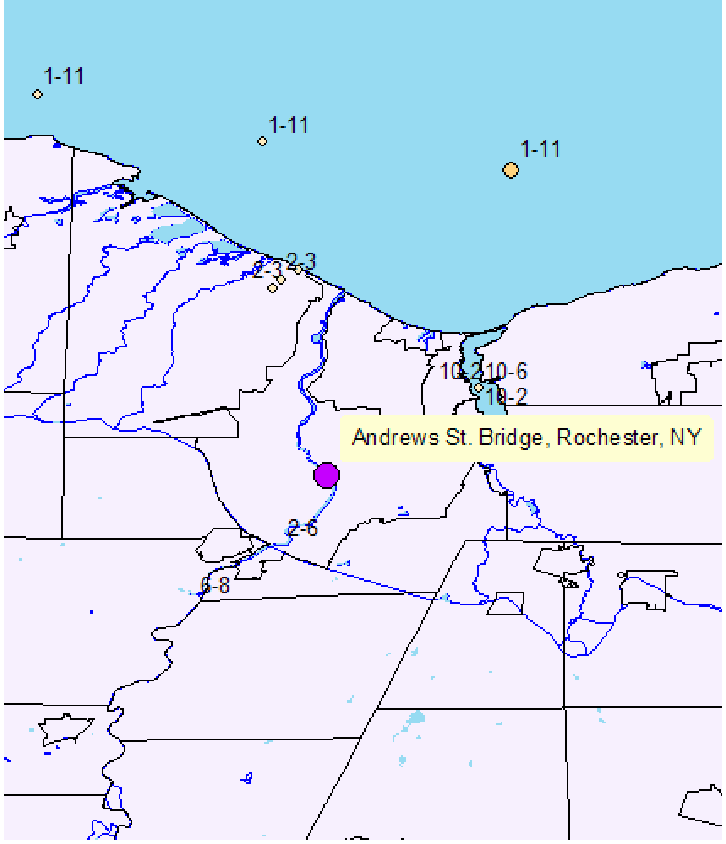

Figure 14. Sediment samples and dominant congener couplets in the vicinity of the Genesee River sampling site off the Andrews St. Bridge. NYSDEC National Sediment Inventory.

Genesee River – Water

Samples taken during canal navigation season had higher PCDD/F concentrations than those taken in the winter (158 vs 68 fg/L TEQ). Congener abundances were also different. Congeners 11 and 15 were more abundant during navigation season. Congener 2 was more prevalent in non-navigation season.

Table 21. Ranks of congener contributions to total TEQ, Genesee River. The highest rank is 1.

	1	2	4	5	6	10	11	12	15
Genesee R.-5/28/2008-SA		4			2	1	3		5
Genesee R.-6/10/2008-SA		4			2	1	3		5
Genesee R.-6/19/2008-SA		4			2	1	3		5
Genesee R.-9/30/2008-SA		4	5		2	1	3		
Genesee R.-4/8/2008-SA		2	5		3	1	4		
Genesee R.-5/2/2007-SA	4	1			2	3	5		
Genesee R.-3/4/2008-SA	4	1		5	2	3			

Oswego River – Sediment

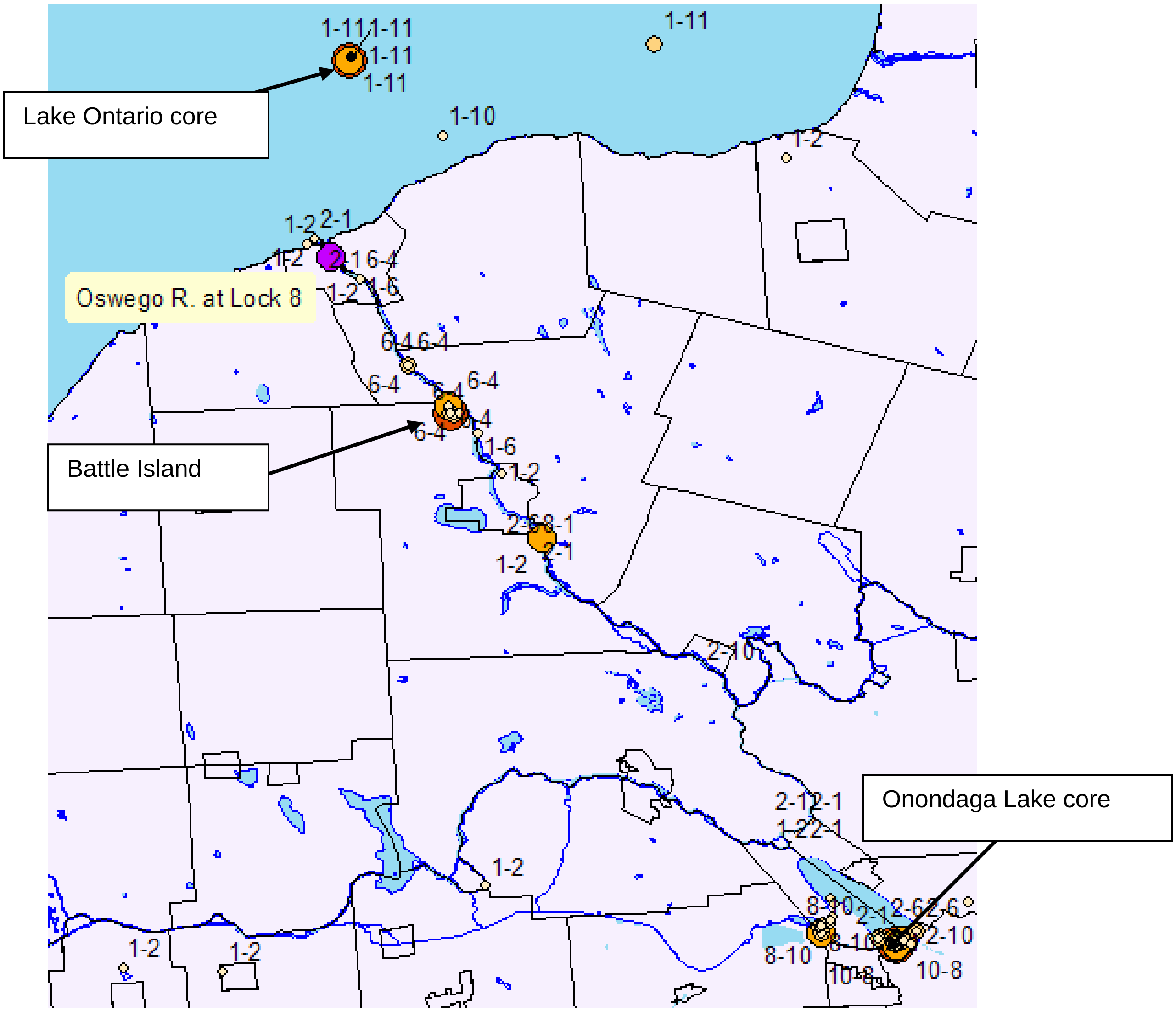

Figure 15. Surficial and core sediment data from the Oswego River and vicinity. NYSDEC National Sediment Inventory.

Sediment cores from this area demonstrate the range of congener patters stemming from different sources. Figure 16 shows a core in Lake Ontario. This is the same pattern that appeared in the Cayuga Island/Love Canal samples indicated in Figure 10.

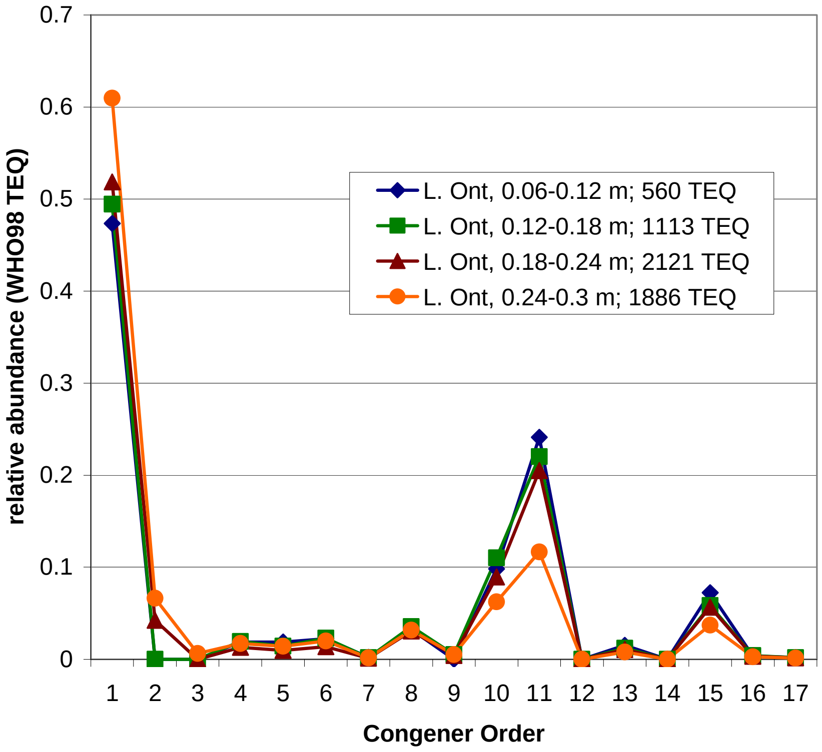

Figure 16. Sediment core in Lake Ontario off from Oswego River. NYSDEC National Sediment Inventory.

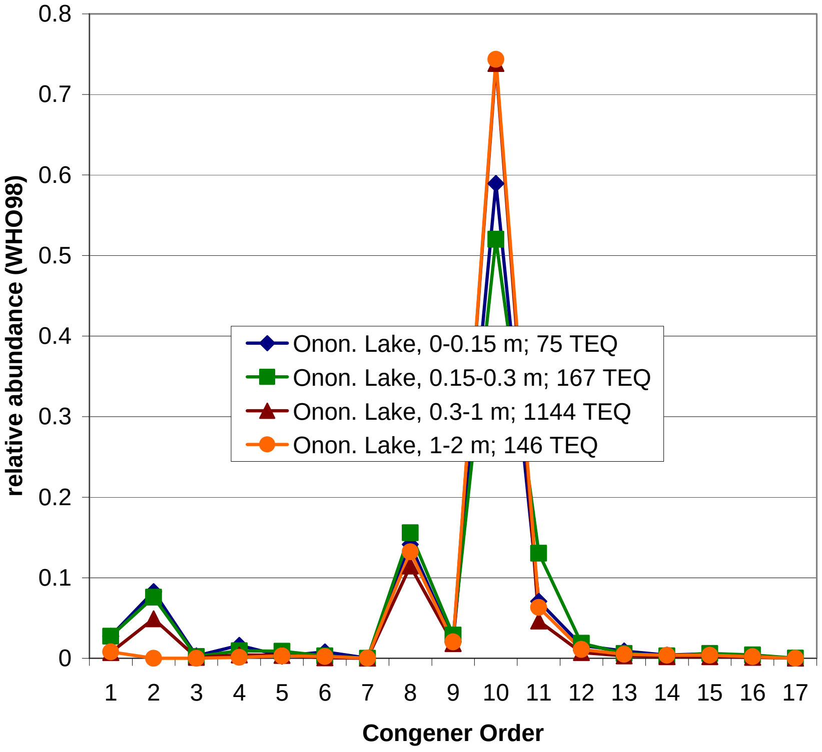

Figure 17. Sediment core in Onondaga Lake near waste water treatment plant. NYSDEC National Sediment Inventory.

Dominance of congener 10 is associated with combustion and incineration activities.

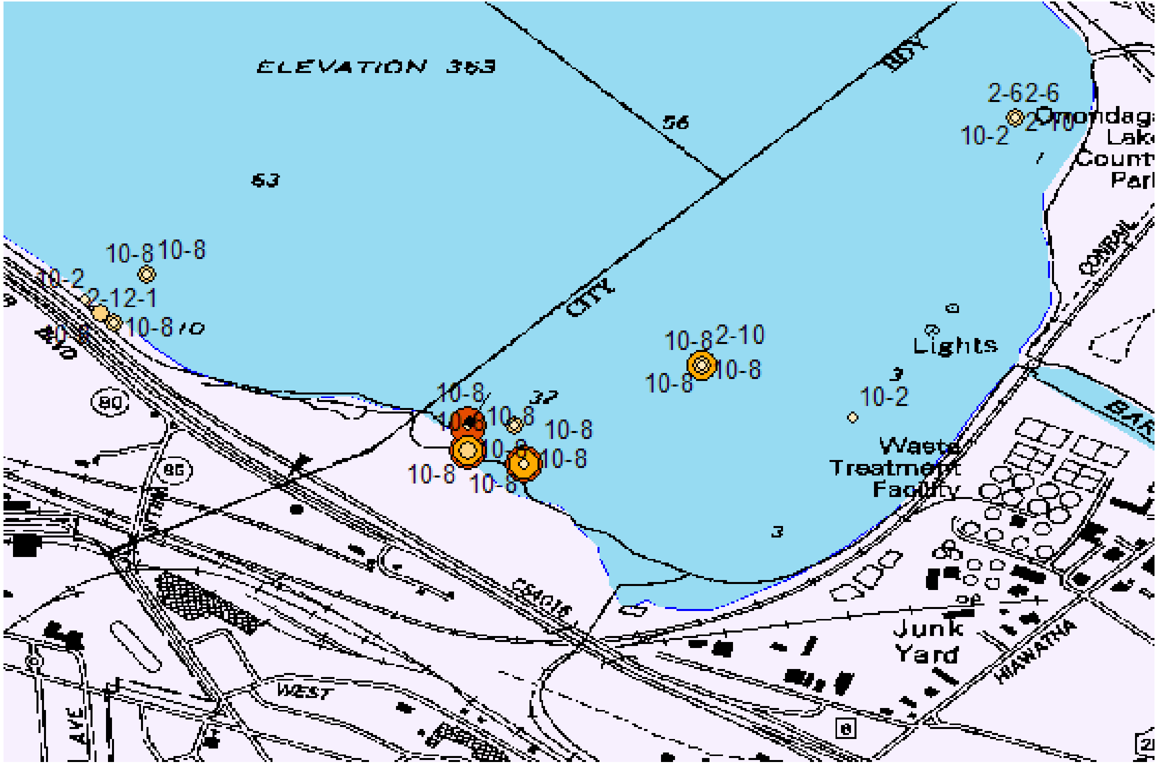

Figure 18. Site of sediment core in Onondaga Lake near wastewater treatment plant. NYSDEC National Sediment Inventory.

Most of the sediment samples from the southern portion of Onondaga Lake were rich in congeners 10 and 8. This pattern could have been generated by incineration.

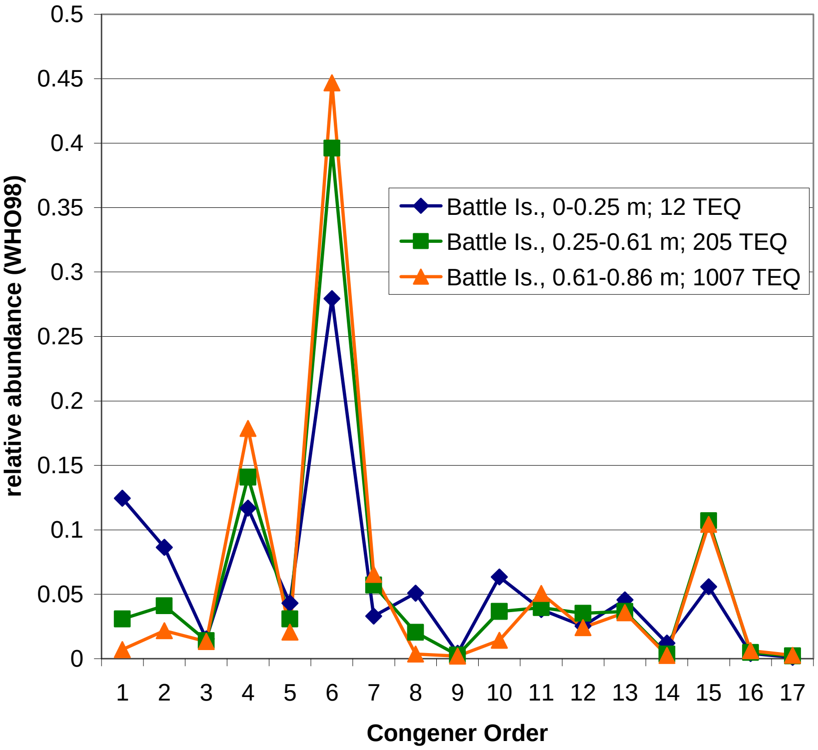

Figure 19. Sediment core off Battle Island in the Oswego River upstream of water sampling site at Lock 8. ng/kg. NYSDEC National Sediment Inventory.

Oswego River - Water

The dioxin abundances observed at Lock 8 from suspended sediment (water) samples included congeners 6 and 10 seen in upstream sediments. Congener 2 was relatively more abundant in the suspended sediment samples than it had been in upstream bottom sediments..

Table 22. Ranks of congener contributions to total TEQ, Oswego River. The highest rank is 1.

	1	2	4	5	6	10	11	12	15
Oswego R.-10/25/2007-SA		2	4	5	1	3			
Oswego R.-4/30/2008-SA		2	4		1	3			5
Oswego R.-5/2/2007-SA		3	4	5	1	2			
Oswego R.-9/30/2008-SA		3	4	5	1	2			
Oswego R.-1/10/2008-SA		1	5	4	3	2			
Oswego R.-3/25/2008-SA		1	5	4	3	2			

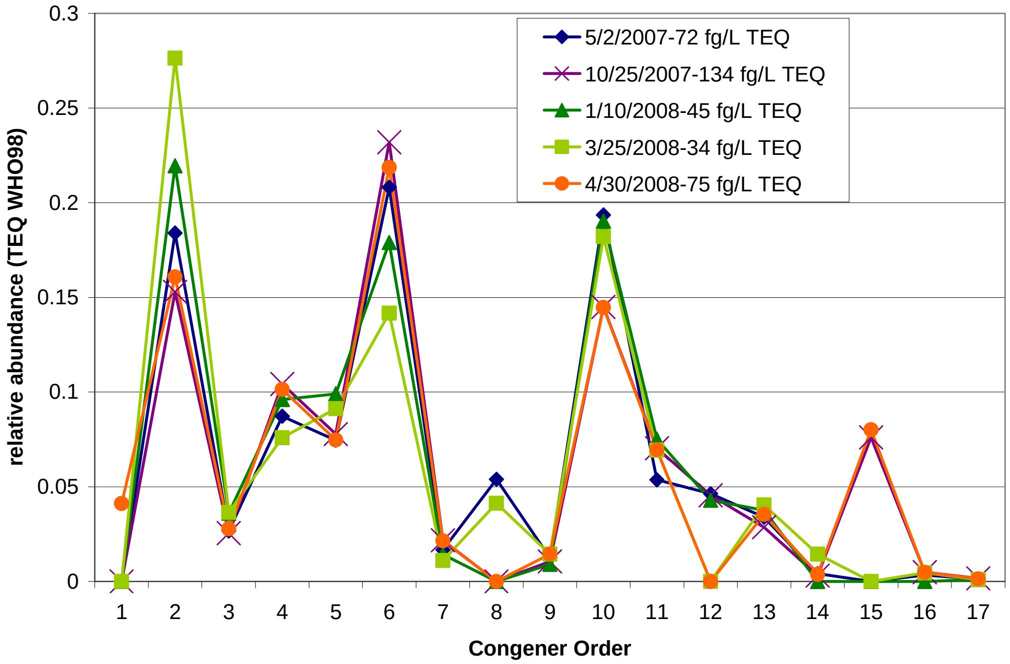

Figure 20. PCDD/F relative abundances, Oswego River at Oswego

Salmon River - Water

There are no sediment data for dioxins from the Salmon River. This project put significant effort into sampling the Salmon R. but the quality of the results was generally poor.

Table 23. Comparisons of level of effort and success in PCDD/F sampling in the five tributaries.

Site	Avg L sampled	Avg ratio, ND=0/ND=DL
18 Mile Cr., Corwin	690	0.84
Black R., Watertown	624	0.71
Genesee R., Rochester	487	0.86
Oswego R., Oswego	826	0.79
Salmon River, Pulaski	887	0.72

Table 24. Ranks of congener contributions to total TEQ, Salmon River. The highest rank is 1.

	1	2	4	5	6	10	11	12	15
Salmon R.-4/8/2008-SA		2		5	3	1	4		
Salmon R.-5/1/2008-SA		2		5	3	1	4		
Salmon R.-1/10/2008-SA			5	4	3	1	2		
Salmon R.-5/3/2007-SA		1	5	4	3	2			

Congener 10 often appears abundant from combustion or incineration activities. For example, it was the most abundant congener in the ash and dust from 9/11/01 World Trade Center disaster. These samples were taken from a relatively pristine area where much of the local economy revolves around sport fishing. It is conceivable that wood boilers, wood stoves, and back-yard burn barrels may be contributing to this PCDD/F signal.[15]

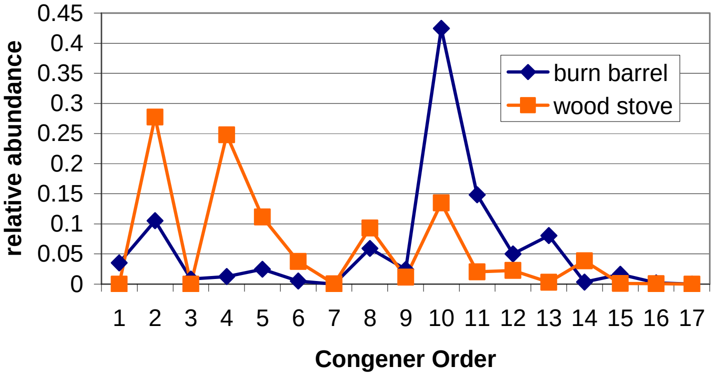

Figure 21. Characteristic patterns of PCDD/F congener abundances from backyard burn barrels and from wood stoves.

Black River - Sediment

Figure 22 shows the locations of the Black River (and the Salmon River) sampling sites. Dioxin concentrations are low in Black River sediments and sediment patterns are dominated by congeners 6, 15, and 2.

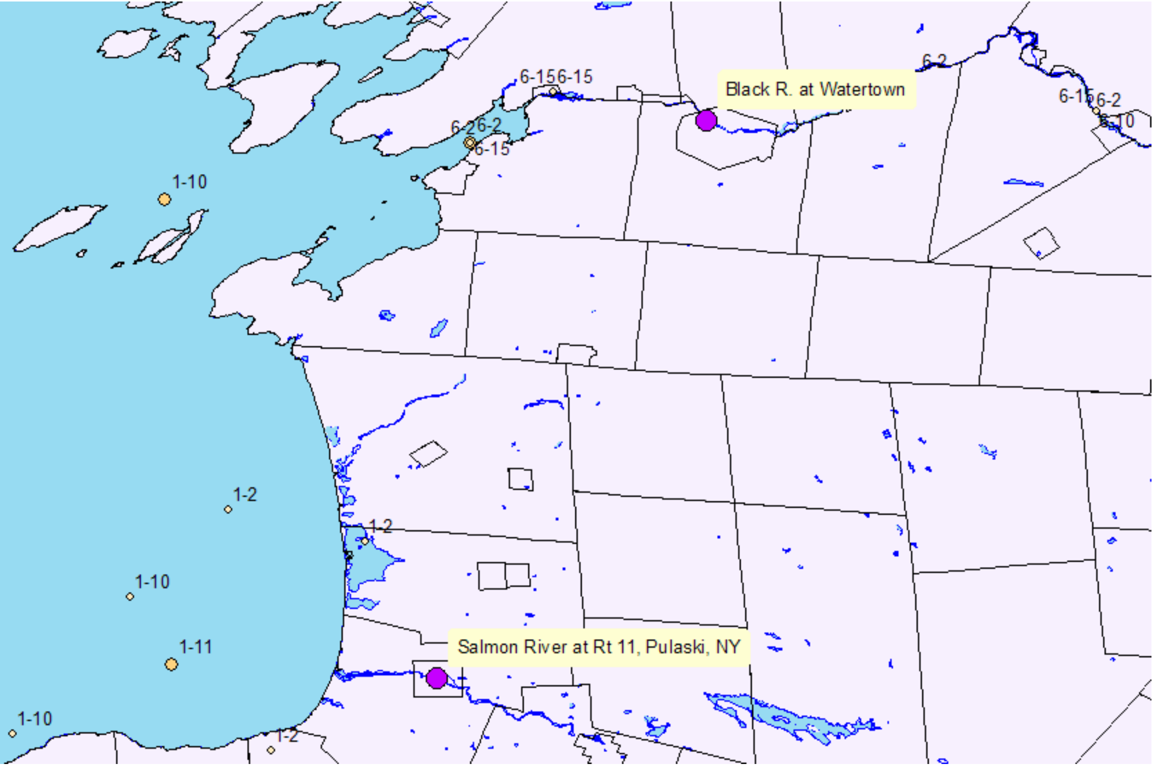

Figure 22. Sediment and water sampling sites on the Salmon and Black Rivers. NYSDEC National Sediment Inventory.

Black River - Water

Table 25 shows the ranks of congeners found in Black River water samples. While congener 15 was important in some of the sediment samples, it was a minor component of the suspended sediment PCDD/Fs.

Table 25. Ranks of congener contributions to total TEQ, Black River. The highest rank is 1.

	1	2	4	5	6	10	11	12	15
Black R.-1/9/2008-SA			3	4	1	2	5		
Black R.-10/24/2007-SA		2	4	5	1	3			
Black R.-5/3/2007-SA		1	4	5	2	3			
Black R.-5/28/2008-SA		2	4	5	3	1			

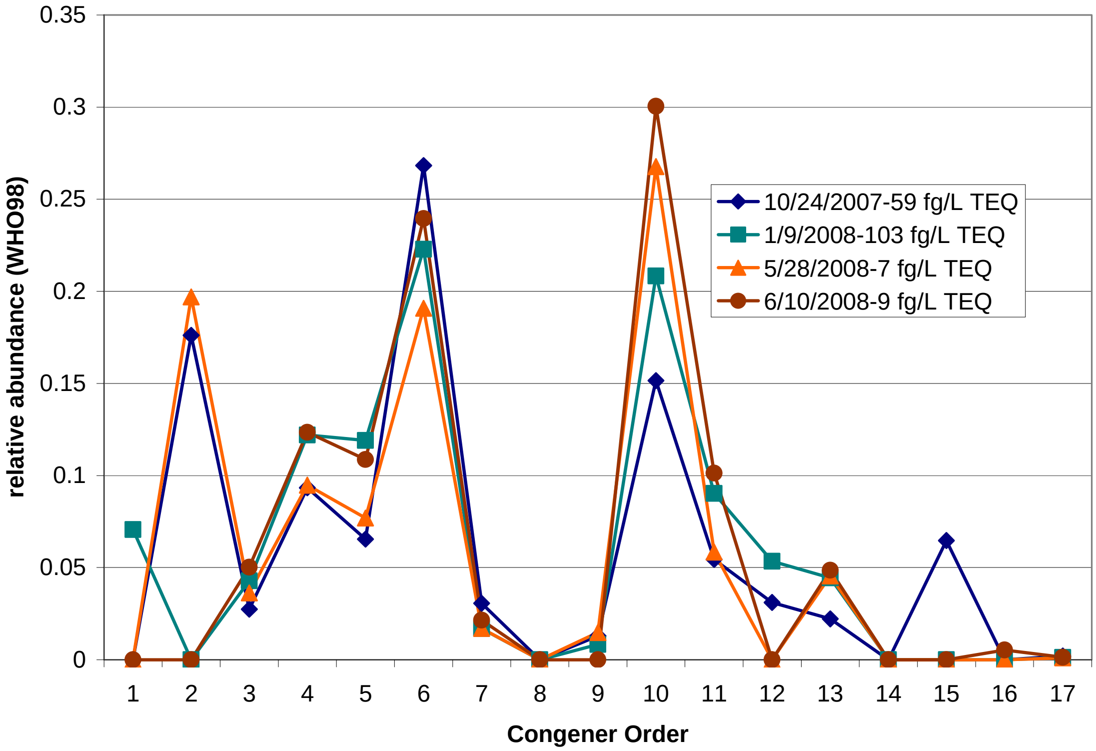

Figure 23. PCDD/F relative abundances, Black River at Watertown.

Does Congener 6 Come From Dechlorination of Octachlorodioxin?

We have seen frequent examples of the importance of heptachlorodioxin (congener 6) to total TEQ. What are the sources of congener 6? EPA surveyed the literature and published characteristic PCDD/F congener patterns from a variety of industrial activities ranging from crematoria to municipal solid waste (MSW) incinerators to copper smelters [14, 15]. Of 53 different source patterns, only one (diesel trucks) showed congener 6 making a significant contribution to total TEQ. Another pattern ("Baltimore tunnel") also represents diesel trucks but here congener 6 was not even the 5th most important congener.

Table 26. Congener couplets identified in EPA's survey of PCDD/F sources.

Source	Congener couplets
Kraft pulp sludge	1-8
Kraft pulp	1-8
auto exhaust, unleaded	1-10
Pb smelter, after scrubber	1-10
tire combustion	1-10
chlor-alkaki, DOW	1-11
ferrous foundries	2-1
residential wood stove chimney soot, Canadian	2-4
cars, leaded	2-10
MSW bottom ash	2-10
utility, oil	2-10
bleached-kraft mill sludge in wood residue boilers	8-10
landfill flare	8-10
Baltimore tunnel	10-1

Source	Congener couplets
auto exhause, diesel	10-1
Pb smelter, before scrubber	10-1
Al smelter, 2	10-2
Al smelter, 5	10-2
Al smelter, 6	10-2
cement kiln	10-2
cement kiln, haz waste, high temp	10-2
crematorium	10-2
forest fires	10-2
indust. wood burner	10-2
indust. wood burner, ash	10-2
large municipal waste combustors	10-2
MSW fly ash	10-2
oil fired industrial boilers	10-2
residential coal combustors	10-2
Al smelter, 1	10-8
cement kiln, 2000	10-8
cement kiln, haz waste, low temp	10-8
cement kiln, non haz waste	10-8
lightweight aggregate kiln	10-8
sewage sludge incineration	10-8
utility, coal	10-8
Al smelter, 3	10-11
Al smelter, 4	10-11
burn barrel	10-11
chlor-alkaki, PPG	10-11
Cu smelter, Chemetco	10-11
halogen acid furnace, 2000	10-11
Haz waste incinerators, 1993-6	10-11
Hot Sided ESP boilers, 1993-6	10-11
Hot Sided ESP boilers, 2000	10-11
burn barrel, avid recycler	10-13
burn barrel, avid recycler, non recycler	10-13
industrial wood combustors	10-14
Cu smelter, Franklin	11-10
hazardous waste incinerators, 2000	11-10
metal recovery facility ash/soil, open burn sites	14-10
metal recovery facility fly ash	14-10
diesel truck	14-6

If octachlorodioxin loses a single chlorine, the two possibilities are 1,2,3,4,6,7,9-HpCDD or 1,2,3,4,6,7,8-HpCDD (congener 6). 1,2,3,4,6,7,9-HpCDD is not normally reported under regulatory sampling because it lacks the 2,3,7,8- required chlorination positions. Monodechlorination of the most abundant congener would produce congener 6. Sediment data (see Figure 19) suggests that the proportion of congener 6 is greater in deeper and older sediments. It is possible that a former technology produced significantly more congener 6 that those EPA surveyed or it may be that monodechlorination of octachlorodioxin is occurring. Bacterial dechlorination of refractory organics, like octachlorodioxin, usually does not occur until the target substance is very abundant and constitutes an important energy source. But what are the alternative explanations?

Appendix – PCB and PCDD/F Data

Results are shown for PCB (ng/L) and PCDD/F (fg/L) congeners where there were detections. PCB congeners are identified by the standard Ball-Schmitter Zell (BZ) numbers. Samples for PCBs are designated by code to save space.

Appendix Table 1. PCB sample code

sample	code	sample	code
18-Mile Cr.-3/24/2008-SA	A-1	Oswego R.-1/10/2008-SA	D-1
18-Mile Cr.-3/3/2008-SA	A-2	Oswego R.-10/25/2007-SA	D-2
18-Mile Cr.-4/29/2008-SA	A-3	Oswego R.-3/25/2008-SA	D-3
18-Mile Cr.-4/7/2008-SA	A-4	Oswego R.-3/4/2008-SA	D-4
18-Mile Cr.-5/1/2007-SA	A-5	Oswego R.-4/30/2008-DU	D-5
18-Mile Cr.-5/27/2008-SA	A-6	Oswego R.-4/30/2008-SA	D-6
Black R.-10/1/2008-SA	B-1	Oswego R.-5/2/2007-SA	D-7
Black R.-10/24/2007-SA	B-2	Oswego R.-9/30/2008-FB	D-8
Black R.-3/13/2008-SA	B-3	Oswego R.-9/30/2008-SA	D-9
Black R.-5/28/2008-SA	B-4	Salmon R.-1/10/2008-SA	E-1
Black R.-5/3/2007-SA	B-5	Salmon R.-4/8/2008-SA	E-2
Genesee R.-3/4/2008-SA	C-1	Salmon R.-5/1/2008-SA	E-3
Genesee R.-4/8/2008-SA	C-2	Salmon R.-5/3/2007-SA	E-4
Genesee R.-5/2/2007-SA	C-3		
Genesee R.-5/28/2008-SA	C-4		
Genesee R.-6/10/2008-SA	C-5		
Genesee R.-9/30/2008-FB	C-6		
Genesee R.-9/30/2008-SA	C-7		

Appendix Table 2. PCB detection limits, site and homolog averages, pg/L

homolog	18-Mile Cr.	Black R.	Genesee R.	Oswego R.	Salmon R.
1	30.7	11.2	4.14	9.29	3.32
2	22.9	34	26.2	33.7	26.7
3	7.7	10.3	7.12	12.1	6.34
4	7.66	10.2	5.69	8.89	5.96
5	6.82	7.26	4.7	7.46	5.16
6	7.36	12.2	6.01	10.6	9.09
7	4.79	8.08	6.41	10	7.73
8	7.59	11.6	6.25	11.2	5.91
9	6.67	11.2	7.55	12.4	6.26
10	6.38	14.2	8.94	20.2	6.26

Appendix Table 3. PCBs, ng/L

BZ	A-1	A-2	A-3	A-4	A-5	A-6	B-1	B-2	B-3	B-4	B-5	C-1
1	0.102	0.179		0.089		0.621	0.0513	0.142	0.0564	0.839	0.412	
2							0.0023	0.00244		0.0088		
3	0.0103					0.0583		0.0179	0.0071	0.119		
4	0.409	2.84		3.8	0.118	9.69	0.32	5.66	0.268	11.2	10.2	
5				0.371								
6		0.257		0.227		1.12		0.349	0.023	1.44	0.952	
7						0.097		0.043		0.105	0.092	
8		0.277				1.08	0.087	0.34	0.065	1.61	0.933	
9						0.147		0.054		0.16	0.124	
10				0.064		0.277		0.141	0.018	0.196	0.302	
11				0.06		0.124	0.035			0.128	0.142	
12						0.595		0.281		0.713	0.819	
15		0.444		1.39		1.77	0.03	0.935		2.1	2.48	
16		0.089		0.287		0.599	0.0211	0.309		0.591	0.79	
17		0.953		2.66	0.026	4.8	0.0775	2.58	0.0399	5.54	6.71	
18	0.076	0.691	0.048	2.04	0.038	3.88	0.0948	2.04	0.0503	4.26	5.14	
19	0.099	0.796	0.059	1.66	0.043	3.43	0.0986	1.93	0.0576	3.74	4.05	
20	0.0721	0.538	0.095	2.6	0.0318	3.2	0.0896	1.75	0.0552	3.49	4.85	0.0145
21	0.0165	0.04		0.115		0.201	0.0249	0.102	0.0142	0.181	0.279	0.0056
22	0.0175	0.095	0.015	0.328		0.524	0.0256	0.238	0.0155	0.545	0.719	
24												
25	0.0147	0.308	0.015	1.54		2.1	0.0187	1.28	0.0105	2.75	3.15	
26	0.0415	0.528	0.037	2.54	0.0098	4.15	0.0445	2.24	0.0254	4.66	5.97	
27	0.051	0.335	0.037	1.02		2.19	0.0471	1.11	0.0246	2.16	2.86	
31	0.0828	0.721	0.084	3.15	0.0246	4.47	0.0944	2.44	0.0632	5.33	6.52	0.0104
32	0.033	0.418		1.28		2.43	0.0307	1.32	0.0236	2.95	3.51	
34				0.039		0.0705		0.0387		0.0681	0.102	
35				0.017						0.0115	0.0179	
37		0.061		0.338	0.011	0.216		0.129	0.0102	0.235	0.39	
39				0.028				0.0131			0.0374	
40		0.791		3.34		2.39	0.0382	1.46	0.0257	2.53	4	
42		0.429		1.93		1.35		0.804	0.0125	1.38	2.41	
43		0.055		0.243		0.235	0.0029	0.144		0.19	0.383	
44	0.0742	1.63	0.153	7.18	0.053	5.43	0.0891	3.22	0.0511	5.65	9.39	0.028
45		0.282		1.29		1.5	0.0267	0.871	0.0127	1.56	2.37	
46		0.079		0.372		0.464	0.0055	0.266		0.444	0.715	
48		0.141		0.561		0.453	0.0117	0.265		0.398	0.741	
49	0.0503	1.31	0.057	5.68	0.034	4.25	0.0607	2.58	0.0405	4.46	7.31	
50	0.0366	0.25	0.032	1.17		1.88	0.0351	1.03	0.0202	1.95	2.61	
52	0.114	1.92	0.127	7.92	0.057	6.29	0.108	3.82	0.0773	6.82	10.1	
54		0.025		0.082				0.0526		0.0938	0.128	
56	0.0139	0.304	0.03	1.36		0.558	0.0175	0.452	0.0152	0.731	1.19	
57				0.078		0.0421				0.042		
59		0.118		0.513		0.422		0.233		0.352	0.711	
60	0.0083		0.02	0.597		0.294	0.0117	0.2	0.0079	0.277	0.557	
61		1.38	0.157	5.7	0.058	2.86	0.0822	1.98	0.0702	3.24	5.42	0.022
63		0.059		0.246		0.133		0.082		0.128	0.248	
64	0.0325	0.618	0.051	2.71	0.022	1.86	0.0381	1.12	0.0266	1.9	2.89	
66		0.76	0.073	3.31	0.029	1.5	0.0402	1.03	0.0333	1.71	2.97	0.0135
67				0.113		0.0547				0.052	0.11	
68				0.1		0.0539	0.0034	0.0358		0.051	0.101	

Appendix Table 3. Continued

BZ	A-1	A-2	A-3	A-4	A-5	A-6	B-1	B-2	B-3	B-4	B-5	C-1
72		0.029		0.125		0.0709		0.0449		0.067	0.129	
77		0.07		0.293		0.096		0.0792		0.105	0.22	
79						0.0168						
81						0.0021		0.00215				
82		0.168		0.532		0.148		0.159	0.0043	0.186	0.378	
83	0.0193	0.729	0.054	2.45		0.955	0.0255	0.733	0.0198	0.907	2.08	
84		0.315	0.02	1.31		0.695	0.0136	0.452		0.667	1.36	
85		0.239	0.126	0.769		0.257		0.207	0.0083	0.287	0.637	
86	0.0315	0.715	0.063	2.38		0.934	0.0293	0.712	0.0294	0.926	2.02	
88		0.22		0.904		0.424	0.0091	0.285	0.0064	0.416	0.874	
89		0.025		0.097		0.0505		0.0318		0.0429	0.0933	
90	0.0455	0.861	0.083	2.99	0.025	1.26	0.0436	0.917	0.0526	1.31	2.62	0.021
92		0.205		0.744		0.34	0.0089	0.232		0.325	0.711	
93		0.114		0.421		0.23		0.149		0.205	0.443	
94				0.087				0.0284		0.0419	0.0851	
95	0.0475	0.672	0.058	2.74	0.02	1.55	0.0388	0.969	0.0387	1.55	2.92	0.015
96		0.019				0.0476		0.0269		0.0379	0.0907	
103				0.059		0.0316		0.0206		0.0273	0.0598	
104								0.00283		0.0041		
105	0.0128	0.502	0.029	1.37		0.351	0.0135	0.347	0.0133	0.412	0.917	
107		0.074		0.22		0.0645	0.00174	0.057		0.0647	0.155	
108		0.033		0.097		0.0298		0.0259		0.0301	0.068	
110	0.0501	1.38		4.78	0.027	1.95	0.0502	1.6	0.0482	2.05	4.1	0.0222
114		0.039		0.086				0.0236		0.024	0.0623	
118	0.0332	0.995	0.065	2.84	0.023	0.804	0.0277	0.772	0.0344	0.971	1.99	0.016
120											0.00549	
122		0.021		0.056		0.0166		0.0158		0.012		
123		0.021		0.06		0.0186	0.00118	0.0193		0.0176	0.0439	
126								0.00136			0.00422	
128		0.119		0.288		0.0693		0.0675		0.0779	0.19	
129	0.0665	0.874	0.083	1.92	0.034	0.446	0.0397	0.461	0.0534	0.489	1.18	0.049
130		0.048		0.113				0.0285		0.03	0.073	
131						0.0072		0.0072				
132		0.294		0.693		0.184		0.182	0.0196	0.21	0.47	
133				0.036		0.0103		0.0088		0.0104		
134		0.042		0.114		0.0317		0.0303		0.0337	0.0714	
135	0.0271	0.256		0.522		0.172	0.0136	0.135	0.0209	0.186	0.395	
136		0.082		0.186		0.0706	0.0043	0.0549		0.0685	0.158	
137		0.044		0.106				0.025		0.0215	0.0556	
139				0.038				0.0097				
141		0.156		0.26		0.0665	0.0061	0.0627		0.0716	0.159	
144				0.057		0.0175	0.0014	0.0145		0.0184	0.0391	
146		0.098		0.215		0.0575	0.0052	0.0544	0.0084	0.0617	0.149	
147	0.0487	0.603	0.051	1.37	0.025	0.387	0.0276	0.336	0.0446	0.426	0.933	0.038
148						0.00272		0.00207		0.0026		
150										0.0018		
152								0.00127		0.0019		
153	0.0528	0.639	0.056	1.28	0.033	0.316	0.0301	0.302	0.0508	0.325	0.765	0.045
154				0.033		0.0103		0.00855			0.0243	
156		0.093		0.241		0.0427		0.0477		0.0461	0.122	

Appendix Table 3. Continued

BZ	A-1	A-2	A-3	A-4	A-5	A-6	B-1	B-2	B-3	B-4	B-5	C-1
158		0.082		0.165		0.0407	0.0029	0.0407		0.0419	0.104	
159						0.00223		0.00211				
164		0.044		0.098		0.0261		0.0247		0.0268	0.066	
167		0.028		0.0656		0.0136		0.0143		0.0154	0.0335	
170		0.171		0.45		0.0565	0.011	0.0511	0.0138	0.0665	0.143	
171		0.052		0.115			0.00286	0.0155		0.0191	0.0446	
172		0.028		0.075			0.00176	0.0096		0.0123	0.0284	
174		0.2		0.398		0.0584	0.01	0.0587	0.0163	0.0669	0.149	
175								0.00224			0.00629	
176		0.028		0.053		0.00849		0.00721			0.0211	
177		0.104		0.237		0.0386	0.00557	0.0363	0.0082	0.0417	0.0969	
178		0.043		0.093		0.0188		0.0176	0.0035	0.019	0.0456	
179		0.083		0.161		0.0329		0.0294	0.0073	0.0352	0.0812	
180	0.0287	0.371	0.03	1.06	0.026	0.135	0.0267	0.131	0.0346	0.143	0.357	0.04
183		0.106		0.244		0.0376	0.00597	0.0292	0.0093	0.0418	0.0968	
187	0.0154	0.273	0.019	0.642		0.103	0.0152	0.0954	0.023	0.119	0.264	0.025
189				0.0196				0.00206		0.0033	0.00484	
190		0.032		0.085		0.0113		0.00982		0.0112	0.0267	
191				0.019				0.00185			0.00535	
194		0.068		0.387		0.0302	0.00461	0.0333	0.0049	0.0372	0.0895	
195		0.028		0.128		0.0107		0.0122		0.0135	0.0318	
196		0.046		0.195				0.017		0.0195	0.0445	
198		0.1		0.434		0.0465		0.0453		0.054	0.128	
200				0.051						0.0071		
201				0.05		0.00472				0.0069	0.0136	
202				0.081		0.0102		0.0103		0.0112	0.0287	
203		0.069		0.307		0.0257	0.00368	0.0281		0.0323	0.0795	
205				0.018				0.00146			0.00358	
206		0.036		0.272		0.0222		0.0274		0.039	0.0845	
207				0.025		0.00301		0.003			0.00977	
208				0.094						0.0158	0.0335	
209		0.03		0.262		0.0247		0.0321		0.0468	0.119	
Total	1.83	32.5	1.83	109	0.768	92.9	2.25	55.7	1.79	103	145	0.365

Appendix Table 3. Continued

BZ	C-2	C-3	C-4	C-5	C-6	C-7	D-1	D-2	D-3	D-4	D-5
1	0.0029	0.0052	0.0085							0.011	0.00317
2			0.0042								
3	0.0032	0.0032									
4			0.111	0.163		0.163					0.0316
8	0.022		0.03	0.021							
11	0.026		0.055	0.0261							
15			0.045	0.048							
16											0.0146
17	0.0138	0.0113	0.0585	0.0638							0.0191
18	0.0245	0.0154	0.0664	0.0792							0.0317
19		0.0062	0.0404	0.0552							0.0077
20	0.0388	0.0227	0.0844	0.069	0.0141	0.077	0.0228	0.0219	0.0165	0.0081	0.0456
21	0.0109	0.0084	0.0226	0.0139							0.0178
22	0.00506	0.0072	0.021	0.0135							0.0134
24				0.0141							
25	0.00185		0.0174	0.0232							0.0085
26	0.00685	0.0071	0.0344	0.0399							0.015
27				0.0247							
31	0.0283	0.0197	0.068	0.0643	0.0107	0.068	0.019	0.0159	0.0139	0.0071	0.0369
32		0.007	0.0323								
37	0.00361	0.0068	0.0225	0.0139							0.0124
40	0.01088	0.0114	0.0543	0.0477							
42		0.0095									0.0111
44	0.037		0.116	0.104		0.0947	0.061	0.079	0.025	0.021	0.0466
45	0.005		0.0263	0.0266							
46			0.0085	0.0078							0.0023
48			0.0104	0.0109							0.0053
49	0.01523	0.0156	0.0751	0.0769		0.0467					0.0263
50	0.00163	0.0047	0.025								0.0065
52	0.0131	0.0321	0.124	0.12	0.0145		0.034	0.033		0.017	0.0454
56	0.00248	0.0073	0.028	0.0176							0.0103
59	0.00063			0.0079							
60	0.00152		0.016	0.0073							0.0055
61	0.0319	0.0281	0.095	0.0619			0.0294	0.0294	0.021		0.0413
64	0.01096	0.0106	0.042	0.041							0.0144
66	0.00564	0.0155	0.065	0.0397			0.0135	0.0152			0.0198
68	0.00199										0.003
77				0.0048							0.0033
82				0.0081							0.0035
83	0.00661	0.0151	0.0495	0.0378							0.0183
84	0.0031										
85		0.0051	0.0159	0.011				0.048			0.0041
86	0.02291	0.0196	0.0541	0.0485							0.0218
88	0.00143	0.0046	0.0135	0.0121							0.0046
90	0.0345	0.0351	0.0763	0.0594	0.0345	0.107	0.037	0.04		0.015	0.0338
92	0.0035		0.0156	0.0122	0.0052						
93				0.0065							
95	0.02317	0.0223	0.0595	0.0529	0.0311	0.087	0.025	0.03			0.0273
105	0.01167	0.009	0.0257	0.0181			0.0084	0.0096			0.0104
107			0.00419								
110	0.0398	0.0334	0.0942	0.0762	0.0233		0.027		0.019	0.018	0.0342
114			0.00195								
118	0.0115	0.022	0.0544		0.0182	0.065	0.0211	0.0259	0.0136	0.0113	0.0247
128	0.00275	0.0054	0.0113								

Appendix Table 3. Continued

BZ	C-2	C-3	C-4	C-5	C-6	C-7	D-1	D-2	D-3	D-4	D-5
129	0.0685	0.0438	0.0748	0.0485	0.0661	0.122	0.053	0.06		0.023	0.0461
132	0.0079	0.014	0.0209		0.026						
135		0.0175	0.0252	0.0141			0.02				
136			0.0086			0.012					
141	0.0096		0.0131	0.0067							0.0063
144	0.00095	0.0021									0.0026
146		0.0073	0.0089	0.0059							
147	0.0471	0.0388	0.0534		0.0587		0.04	0.042			0.0339
153	0.0257	0.0402	0.0596	0.0369	0.06		0.046	0.05		0.021	
156	0.0059		0.0074		0.0095						0.0043
158	0.00212										0.0034
164	0.00152										
167	0.0018										0.0018
170	0.02155										0.0105
171	0.00219		0.0056								0.0038
172			0.0033								
174	0.01627		0.0168								0.0108
175			0.001								
176											0.00208
177	0.01119	0.0076			0.0111						
178	0.00432										
179	0.00744		0.00672	0.0042	0.0092						0.00503
180	0.0502	0.0251	0.0437				0.032	0.031	0.02		0.0282
183	0.00754	0.0067	0.0099								
187	0.0276		0.0252	0.0155							0.0172
190	0.00272										
194	0.0102		0.00975								
195	0.00147										
196			0.0042								
198	0.0122	0.0066									0.0085
203	0.0082	0.0044									
206	0.0056		0.0144	0.0065							
208			0.0049								0.00596
209		0.0048		0.0076	0.0131			0.039			0.0178
Total	0.846	0.646	2.30	1.80	0.405	0.842	0.489	0.570	0.129	0.153	0.890

Appendix Table 3. Continued.

BZ	D-6	D-7	D-8	D-9	E-1	E-2	E-3	E-4
1							0.00772	0.0059
2	0.0024					0.0022		
3	0.003						0.00271	0.004
8					0.057		0.037	
11						0.026		
17	0.012							
18	0.0261	0.02				0.014	0.0208	0.013
19							0.0077	
20	0.041	0.0303	0.0103	0.0304	0.103	0.02	0.0271	0.0167
21	0.0167	0.0097			0.054	0.0101	0.0144	0.0081
22	0.0117				0.035	0.00719	0.00924	0.0055
25	0.00557	0.0059						
26	0.0112	0.0096			0.0144		0.00585	0.0025
31	0.0316	0.0231	0.0072	0.0231	0.0776	0.0136	0.021	0.0131
32	0.0089							
35	0.00154							
37	0.015	0.0086			0.014	0.0049	0.00825	0.0042
40		0.0117					0.0078	
44	0.0655	0.0271		0.0276	0.088	0.0208	0.0217	0.0095
45	0.0122					0.00406	0.0056	
46	0.0028							
48	0.0098					0.0018		
49	0.0396	0.0172		0.0179		0.00559	0.00807	0.0047
50							0.00317	
52	0.0659	0.0315		0.0431	0.034	0.011	0.0146	
56	0.0289	0.0092				0.00315	0.0057	
60	0.0217	0.0057					0.0044	
61	0.141	0.0337			0.045	0.016	0.0225	0.0143
63	0.004							
64		0.0103				0.00405	0.00634	
66	0.0668	0.0182		0.0135	0.02	0.00748	0.0108	0.0067
67	0.0025							
68	0.0026							
77	0.0113	0.0029				0.00195		
82	0.0112							
83	0.0624	0.0134				0.00911		0.0067
84	0.0194	0.0056		0.0071		0.0021		
85				0.0023				
86	0.0648					0.00935	0.0103	0.0089
88	0.0147						0.00143	
90	0.0929	0.0325	0.0232	0.0344	0.035	0.0169	0.0162	0.0218
92	0.0163					0.00284		
95	0.0527	0.0232	0.0213	0.0336	0.022	0.0102	0.011	
105	0.0404			0.0088		0.0057		0.0051
107	0.00626					0.00126		
110	0.0996	0.0357	0.0185	0.0323	0.026			0.0149
118	0.0993	0.0267	0.0145	0.0246	0.0173	0.0135		0.014
123	0.00207							
128	0.0115					0.0029		
129	0.109	0.0496	0.0586	0.0656	0.049	0.038	0.0302	0.0365
132	0.0268	0.0142	0.0245			0.0077	0.0059	
135	0.0313	0.0171	0.0213	0.0206		0.0111	0.00999	
136	0.0092			0.0071		0.00282		
137	0.0038							

Appendix Table 3. Continued.

BZ	D-6	D-7	D-8	D-9	E-1	E-2	E-3	E-4
141		0.0102		0.0161		0.0062	0.0042	0.0074
144	0.0047					0.00152		
146	0.0125		0.0098			0.0043	0.0034	
147	0.0596	0.0367	0.0448	0.0512	0.036	0.0218		0.0248
153	0.0917	0.0433	0.0517	0.0567	0.044	0.0308	0.0285	0.0302
156	0.0134					0.00405	0.003	0.003
158	0.0105					0.0032	0.0019	
164	0.0052						0.0017	
167	0.00522							
170	0.0274		0.0198			0.0109	0.00993	0.0094
171	0.0072							
174	0.0223	0.0114				0.0078	0.0073	0.0081
176						0.0017		
177	0.0127	0.0066						
179	0.00821							
180	0.0607	0.0265	0.0344	0.0315		0.0262	0.0236	
183	0.0161					0.0059		
187	0.0327	0.0164	0.0169			0.0144	0.0133	
189							0.00083	
190						0.0022		
194	0.0103	0.0064				0.00432		
195	0.0043							
196	0.00534					0.0019		
198	0.0135	0.0089						
201	0.00121							
203	0.0083							
206	0.0108	0.0332		0.0171				
208	0.005	0.0135						
209	0.0245	0.054					0.00639	
Total	1.92	0.760	0.377	0.565	0.771	0.455	0.466	0.299

A separate set of samples codes are used for the PCDD/Fs:

Appendix Table 4. PCDD/F sample code.

sample	code		sample	code
18-Mile Cr.-3/24/2008-SA	A-1		Genesee R.-3/4/2008-SA	C-1
18-Mile Cr.-3/3/2008-SA	A-2		Genesee R.-4/8/2008-SA	C-2
18-Mile Cr.-4/29/2008-SA	A-3		Genesee R.-5/2/2007-SA	C-3
18-Mile Cr.-4/7/2008-SA	A-4		Genesee R.-6/10/2008-SA	C-4
18-Mile Cr.-5/1/2007-SA	A-5		Genesee R.-6/19/2008-SA	C-5
18-Mile Cr.-5/27/2008-DU	A-6		Genesee R.-9/30/2008-SA	C-6
18-Mile Cr.-5/27/2008-SA	A-7		Oswego R.-1/10/2008-SA	D-1
18-Mile Cr.-6/9/2008-SA	A-8		Oswego R.-10/25/2007-SA	D-2
Black R.-1/9/2008-SA	B-1		Oswego R.-3/25/2008-SA	D-3
Black R.-10/24/2007-SA	B-2		Oswego R.-3/4/2008-SA	D-4
Black R.-3/13/2008-SA	B-3		Oswego R.-4/30/2008-SA	D-5
Black R.-5/28/2008-SA	B-4		Oswego R.-5/2/2007-SA	D-6
Black R.-5/3/2007-SA	B-5		Oswego R.-9/30/2008-SA	D-7
Black R.-6/10/2008-SA	B-6		Salmon R.-1/10/2008-SA	E-1
Equip. Blank-2/27/2008-FB	EB-1		Salmon R.-4/8/2008-SA	E-2
Equip. Blank-6/11/2008-FB	EB-2		Salmon R.-5/1/2008-SA	E-3
			Salmon R.-5/3/2007-SA	E-4

Appendix Table 5. Site mean PCDD/F detection limits in fg/L

Order	18-Mile Cr.	Black R.	Genesee R.	Oswego R.	Salmon R.
1	15.1	3.5	5.16	2.46	2.23
2	9.29	8.03	5	2.05	2.86
3	6.02	3.26	4.59	2.02	1.91
4	126	4.14	4.88	1.88	2.01
5	6.32	3.11	4.47	1.85	1.87
6	20.8	3.37	6.17	1.99	2.04
7	23.1	7.58	7.11	3.64	3.12
8	40.7	6.18	20.7	9.83	18.1
9	69.6	3.79	5.52	1.95	8.42
10	16.5	3.37	5.21	2.19	1.99
11	6.26	3.58	4.81	1.82	1.8
12	626	9.13	66.7	16.9	20.2
13	6.56	3.1	5.16	1.94	1.99
14	6.82	3.17	5.65	2.05	2.12
15	13.9	209	363	136	85.3
16	16.6	9.38	7.11	4.43	5.47
17	8.86	6.21	7.27	3.63	3.56

PCDD/F congeners are designated as stated above in Table 10. Raw masses, reported by the lab as pg/sample, have been divided by the number of L filtered to yield concentration units (fg/L).

Appendix Table 6. PCDD/F results, fg/L.

Code	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	B-1	B-2	B-3	B-4
1									8.91			
2	11.8	116	7.88	11.5	15.8	42.3	33.9	61.7		14.1	2.53	2.5
3	18.6	141	14.1	20.9	24.1	90.4	69.5	118	54.1	22	4.38	4.61
4	128		105	171	186	726	584	1060	154	74.9		12
5	54.7	405	36.2	51.5	66.4	223	188	319	150	52.5	8.42	9.77
6	3370	25200	2420	4210	4820	19000	13500	24200	2810	2150	194	242
7	36700	300000	31700	56500	53000	247000	165000	277000	21300	24600	1390	2150
8	41.8	303	60.3	62.5	78	269	223	403			6.73	
9	34.2	254			38.7			279	21	20.7		3.75
10	57.1	437	61.6		70.6	325	275	477	52.6	24.3		6.8
11	215	1720	174	305	322	1230	1150	1890	114	43.7		7.43
12		1800			115				67.5	25		
13	38.1	283	28.7	44.7	38.1	227	203	179	56	17.7	4.04	5.79
14	4.01		2.33	3.68		15.7	12.5	23				
15	1820	14300	1600	2850	2900	12800	11900	16400		519		
16	78.4	599	54.2	99.2	88.8	416	402	500				
17	2880	25400	2220	4690	4500	15600	14800	29800	1510	1630	88.6	130

Appendix Table 6. Continued.

Code	B-5	B-6	EB-1	EB-2	C-1	C-2	C-3	C-4	C-5	C-6	D-1	D-2
1					6.75		7.76	5.96		4.81		
2	2.78				13.5	15.2	12.9	16.5	19.8	13.4	7.15	14.9
3	4.48	8.03			20.6	21.2	16.5	31.8	37.4	24.1	11.8	24.9
4	12.5	19.8			50	58.2	44.6	93.7	109	71.1	31.3	102
5	11.3	17.4		1400	59.6	54.9	49.8	77.8	94	49.6	32.2	76
6	264	383	3500	8300	1170	1310	1240	2170	2380	1700	583	2270
7	2160	3440	22300	82700	20400	32700	26000	29100	30500	23100	4640	21200
8	10.4				10.4			49.6	58.1	46.1		
9			2600		11.2	21.2	12.9	27	31.1	29.4	5.88	20.7
10	4.95	9.61	2400		14.3	35.1	22.3	49.3	56.6	57.2	12.4	28.3
11	8.19	16.2	2800	2100	36.8	68.8	59.5	182	214	137	24.5	68.7
12	6.18		3400	1900			26.5			41	14	44.5
13	4.79	7.77	1600	1400	17.6	26.5	16.2	30.9	32.9	31.9	12.2	28
14	2.01											3.01
15								1350	1510			743
16		8.43			20.8		18.1	44	50.2	37.2		48.2
17	158	216	3700	8100	658	900	705	1740	1550	1050	353	1590

Appendix Table 6. Continued.

Code	D-3	D-4	D-5	D-6	D-7	E-1	E-2	E-3	E-4
1			2.27						
2	6.84		8.86	9.68	4.42		7.18	3.07	4.14
3	9.01		15.3	14	7.95	9.48	10.7	4.06	4.89
4	18.8	11.6	55.9	45.9	32.5	17.7	21.2	8.52	10.1
5	22.6	15.7	41.2	39.2	17.5	27.1	26.4	11.8	14
6	351	199	1200	1090	798	274	342	131	193
7	2730	1510	11800	8780	7360	1930	2290	869	1260
8	10.2			28.4	15.9				
9	7.16	2.85	15.9	13.2	7.07				5.21
10	9.01		15.9	20.4	10.2	12.5	15.7	7.01	7.82
11	17.1	6.58	38.3	28.2	13	28.7	32.2	13	7.51
12				24.4	9.72	14.7			6.9
13	9.98	4.8	19.5	17.9	9.57	13.3	14.9	5.97	5.98
14	3.58		2.06	2.17					
15			442						
16	11.3		26.4	17.5					4.45
17	234	108	737	656	530	136	178	56.3	95.8

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