

Polychlorinated Biphenyls and Hexachlorobenzene in the Water Column of the Ashtabula River and Harbor

Prepared for

The Ashtabula River and Harbor Natural Resource Damage Assessment

by

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Introduction

The Ashtabula River is located in northeast Ohio, flowing into Lake Erie at Ashtabula Ohio. Tributaries include Fields Brook, Hubbard Run, Strong Brook, and Ashtabula Creek. The bottom sediments, bank soils and biota of Fields Brook have been severely contaminated by unregulated discharges of hazardous substances. Hazardous substances have migrated downstream from Fields Brook to the Ashtabula River and Harbor, contaminating sediments, fish and wildlife. Hazardous substances include polychlorinated biphenyls (PCBs), chlorinated benzenes, chlorinated ethenes, hexachlorobutadiene, polycyclic aromatic hydrocarbons (PAHs), other organic chemicals, heavy metals and low level radionuclides.

Fields Brook was placed on the National Priorities List (Superfund) of uncontrolled hazardous waste sites in 1983, pursuant to the Comprehensive Environmental Response, Compensation and Liability Act, 42 USC §9601 et seq. (CERCLA) and is being remediated under that authority. In 1994 the Ashtabula River Partnership (Partnership) was formed to facilitate a voluntary cleanup of the Ashtabula River. If the Partnership is successful, the cleanup will be funded by the U. S. Army Corps of Engineers and the State of Ohio, as well as the Ashtabula River Cooperating Group (ARCG), which consists of Cabot Corp., Detrex Corp., Elkem Metals Co., First Energy Corp., GenCorp, Inc., Mallinckrodt Inc., Millennium Inorganic Chemicals, Millennium Petrochemicals Inc., Ohio Power Co., Olin Corporation, Occidental Chemical Corporation, Pennsylvania Lines LLC, RMI Titanium Co., The Sherwin Williams Company, Union Carbide Corporation, and Viacom International Inc. If implemented, the Partnership project will result in the removal of much of the contaminated sediment in the Ashtabula River. However, the Partnership project does not fully address injuries to natural resources. Therefore, the U.S. Department of the Interior (DOI) represented by the U.S. Fish and Wildlife Service (Service), the Ohio Environmental Protection Agency (Ohio EPA) and the U.S. Department of Commerce represented by the National Oceanic and Atmospheric Administration (NOAA), collectively the Trustees, are conducting a Natural Resource Damage Assessment (NRDA) in the Ashtabula River and Harbor. The NRDA will assess injuries to natural resources that have occurred due to the release of hazardous substances and determine whether compensation is due the public. Compensation will be used to restore, rehabilitate, replace or acquire the equivalent of the injured natural resources and the services they provide.

The United States Department of the Interior has established regulations for conducting Natural Resource Damage Assessments (United States Department of the Interior 1996). The regulations authorize the Trustees to, among other things, establish the source of the hazardous substance(s), establish the pathway by which the hazardous substance(s) reached the injured natural resource(s) and determine the extent of injury to those natural resources.

The first phase in the NRDA process is the completion of a Preassessment Screen (PAS), which reviews existing data and determines whether injuries are likely to have occurred.

The PAS was completed and released on May 18, 2001 (USFWS and Ohio EPA 2001). The PAS determined that:

- 1. Releases of hazardous substances have occurred***
- 2. Natural resources for which the trustees may assert trusteeship under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Federal Water Pollution Control Act (FWPCA) have been adversely affected by the discharge or release of hazardous substances;***
- 3. The quantity and concentration of the released hazardous substances are sufficient to potentially cause injury to natural resources;***
- 4. Data sufficient to pursue an assessment are readily available or likely to be obtained at a reasonable cost; and***
- 5. Response actions planned will not sufficiently remedy the injury to natural resources without further action.***

The second phase in the NRDA process is the completion of the Assessment Plan, which describes the work and studies the Trustees will undertake as part of the assessment. The Assessment Plan for the Ashtabula River and Harbor was finalized on March 21, 2003, following completion of this study (U. S. Fish and Wildlife Service 2003). Typically, assessment studies are not conducted until release of the final Assessment Plan. However, the impending remediation of Fields Brook in 2002 required that water column sampling in the Ashtabula River be conducted in 2001. This was necessary because water column concentrations of hazardous substances would likely be reduced following completion of the remedy, and would therefore not reflect pre-remedy conditions. Collection of such ephemeral data, prior to completion of the Assessment Plan, is allowed under the NRDA regulations (43 CFR 11.22(b)(2)).

In June and August, 2001 the Service and the Ohio EPA conducted water column sampling in the Ashtabula River. The purpose of this sampling was to begin collecting data to support evaluation of pathways and injury to surface waters and biological resources. PCBs and hexachlorobenzene (HCB) were selected because they are present in Ashtabula River sediments at concentrations greatly exceeding sediment benchmarks (OME 1993, MacDonald et al. 2000) and appropriate water column data were not available. This report summarizes the results of that sampling. The results of this, and other studies described in the Assessment Plan, will be included in the Administrative Record and considered by the Trustees in the pathway and injury determinations.

Methods

Sampling was conducted June 4 through 6, 2001 and August 6 through 8, 2001 at the locations identified in Figure 1 and Table 1. Sampling sites were selected to allow comparison of PCB and HCB concentrations upstream of Fields Brook with those immediately downstream, as well as to provide current water column data for PCBs and HCB. A linear distance of at least 100 feet separates these locations.

Figure 1. Approximate sampling locations for water column samples collected the Ashtabula River and Harbor in June and August 2001.

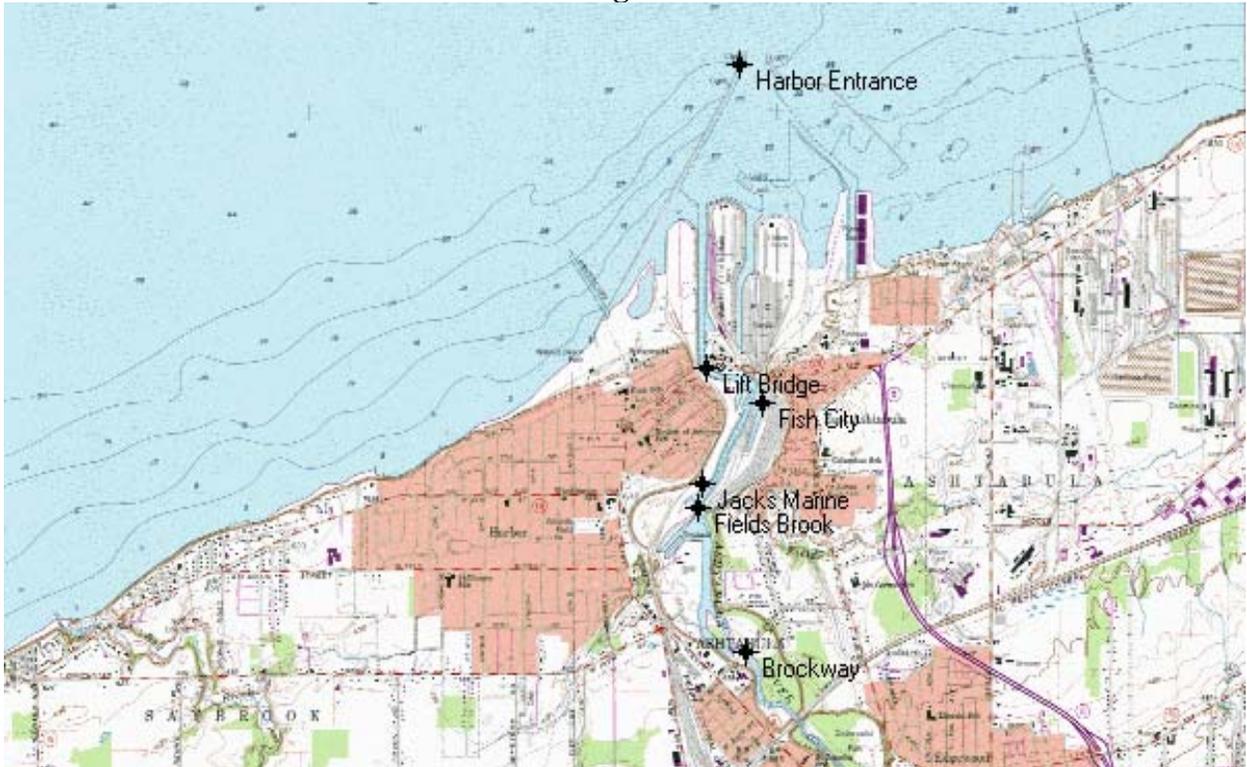


Table 1. Sample collection data for water column samples collected in June and August 2001.

Location	Approximate Latitude & Longitude	Approximate River Mile	Date	Volume Sampled (liters)
Brockway	41 52 56N 80 47 40W	2.4	06/04/01	120
Brockway	41 52 56N 80 47 40W	2.4	06/06/01	95
Brockway	41 52 56N 80 47 40W	2.4	08/07/01	74
Brockway	41 52 56N 80 47 40W	2.4	08/06/01	120
Fields Brook	41 53 29N 80 47 55W	1.6	06/05/01	117
Fields Brook	41 53 29N 80 47 55W	1.6	06/06/01	43
Fields Brook	41 53 29N 80 47 55W	1.6	08/07/01	111
Fields Brook	41 53 29N 80 47 55W	1.6	08/07/01	110
Jacks Marine	41 53 33N 80 47 55W	1.5	06/05/01	120
Fish City	41 53 53N 80 47 34W	1.2	06/06/01	50
Fish City	41 53 53N 80 47 34W	1.2	08/06/01	120
Lift Bridge	41 54 01N 80 47 52W	0.7	08/07/01	112
Lift Bridge	41 54 01N 80 47 52W	0.7	08/07/01	116
Harbor Entrance	41 55 10N 80 47 41W	West Breakwall	08/07/01	116

Samples for PCB and HCB analysis were collected using Infiltrax samplers mounted on bulkheads and other existing structures in the Ashtabula River and Harbor. Multiple samples were collected from some locations (Table 1) to allow statistical comparisons. Samples were collected at approximately mid depth in the water column.

The internal pump of the Infiltrax pulls water into the multiplate filter head, distributing it among the eight 142 mm GF/F glass fiber filters, which collect the particulate phase of the water column sample. The filtrate is then pulled through the in-line Teflon column containing XAD-2 resin that adsorbs the organic contaminants from the dissolved phase of the water. The filters and XAD-2 resin are then extracted and analyzed for the contaminants of interest. Filtration through glass fiber filters, followed by extraction of the dissolved phase on XAD-2 resin is a common and widely accepted method for water

column PCBs (Swackhamer and Armstrong 1987, Marti and Armstrong 1990, Jeremiason et al. 1994, Trowbridge and Swackhamer 2002).

The Infiltrax samplers were each loaded with 8 ashed (500° C for 4 hours) 142 mm GF/F glass fiber filters using acetone rinsed forceps and with a column containing pre-cleaned XAD-2 resin at a shore facility immediately prior to deployment. The samplers were programmed to sample up to 120 liters at a flow rate of 200 mL/minute. The samplers were programmed to begin sampling 45 minutes after deployment to allow any bottom sediments suspended during sampler deployment to settle prior to sampling.

Upon completion of the sampling, the Infiltrax was retrieved and taken to a shore facility where the volume sampled, and sampling start and stop times were recorded. Acetone rinsed forceps were used to fold each GF/F filter into quarters and place them in ashed (500° C for 4 hours) aluminum foil. The foil wrapped filters were labeled with sample identification information, placed in plastic Ziplock bags and stored on ice until they could be frozen. The filters were frozen within two hours of sampler retrieval. The XAD-2 resin columns were removed, labeled with sample identification information, capped and stored on ice or otherwise refrigerated. The filters and columns were shipped, on ice, to Axys Analytical Laboratory in British Columbia.

In the analytical laboratory, the XAD resin was removed from the columns and dried by filtration through a Millipore filtration apparatus. The resin was then placed in a Soxhlet thimble, spiked with surrogate standards, and extracted with dichloromethane. The extract was concentrated by rotary evaporation. The GF/F glass fiber filters were air-dried, placed in a Soxhlet thimble and spiked with surrogate standards and extracted as above.

The extract was loaded onto a Florisil column (2.1% deactivated) and eluted with hexane followed by a 15:85 dichloromethane:hexane solution. Elution fractions were collected together and contained PCB congeners and HCB. The fraction was concentrated, an aliquot of recovery standard added and the extract transferred to an autosampler vial in preparation for instrumental analysis. For the analysis of non-ortho-substituted congeners, the fraction was first split, and one half subjected to additional cleanup on carbon/Celite to isolate the non-ortho-substituted PCBs.

Analysis was carried out using a Finnigan INCOS 50 mass spectrometer (MS) equipped with a Varian 3400 GC, a CTC A200S autosampler and a DG10 data system running Incos 50 (Rev 11) software. The MS was operated at unit mass resolution in the Multiple Ion detection mode. Chromatographic separation was achieved with a DB-5 capillary column (60m, 0.25 mm i.d., 0.10 µm film thickness). A splitless/split injection sequence was used. A calibration solution was run every 12 hours and response factors determined. Analytes were quantified using the internal standard method, comparing the area of analyte peak to that of the corresponding surrogate standard and correcting for response factors. The samples were analyzed for 119 individual and co-eluting PCB congeners, as well as HCB.

As described above, the Infiltrax samplers were programmed to begin sampling 45 minutes after deployment to avoid contaminating samples with particulates resuspended during sampler deployment. To preclude this potential source of sample contamination entirely, only the dissolved phase data are reported.

Total PCBs were estimated by summing the concentrations of individual and co-eluting congeners. Those congeners that were present at concentrations below quantitation limits are assumed to be zero. This, along with the exclusion of particulate phase data for both PCBs and HCB, results in underestimates of the water column concentrations of PCBs and HCB.

Results and Discussion

Dissolved phase PCB concentrations ranged from 0.25 ng/L at the Ashtabula Harbor entrance in August to 89.3 ng/L just downstream of the confluence of Fields Brook (river mile 1.6) in June 2001. PCB concentrations on both surveys were higher downstream of Fields Brook than upstream. HCB followed the same pattern with the lowest concentration at the Ashtabula Harbor entrance in August and the highest downstream of Fields Brook in June 2001. HCB concentrations on both surveys were higher downstream of Fields Brook than upstream (Table 2).

Table 2. Dissolved phase PCB and HCB concentrations (ng/L) in the Ashtabula River and Harbor in June and August 2001.

Location	Approximate River Mile	Date	Total PCB	Hexachlorobenzene
Brockway	2.4	06/04/01	0.65	0.16
Brockway	2.4	06/06/01	0.36	0.08
Brockway	2.4	08/07/01	1.40	0.24
Brockway	2.4	08/06/01	0.97	0.12
Fields Brook	1.6	06/05/01	89.3	18.6
Fields Brook	1.6	06/06/01	76.9	18.0
Fields Brook	1.6	08/07/01	16.0	3.95
Fields Brook	1.6	08/07/01	20.9	3.82
Jacks Marine	1.5	06/05/01	23.2	6.61
Fish City	1.2	06/06/01	27.7	8.16
Fish City	1.2	08/06/01	9.91	3.24
Lift Bridge	0.7	08/07/01	8.14	1.95
Lift Bridge	0.7	08/07/01	7.17	1.70
Harbor Entrance	West Breakwall	08/07/01	0.25	0.07

The “pathway” describes the process(es) and route(s) by which the hazardous substance(s) moves from its source(s) to natural resources. Specifically, pathway is defined as “the route or medium through which oil or a hazardous substance is or was transported from the source of the discharge or release to the injured resource” (43 CFR 11.14 (dd)). The water column samples collected in June and August, 2001 will contribute to the definition of the surface water pathway for PCBs and HCB.

In June 2001, mean dissolved PCB concentrations at river mile 2.4, upstream of Fields Brook were 0.50 ng/L. The mean concentration increased to 83.1 ng/L at river mile 1.6, just downstream of Fields Brook, and remained at elevated concentrations through the farthest downstream sampling point at river mile 1.2. In August, dissolved PCBs averaged 1.18 ng/L at river mile 2.4, increased to 18.4 ng/L at river mile 1.6, and remained at elevated concentrations through river mile 0.7 (Table 3).

HCB followed a pattern similar to PCBs. In June, the mean HCB concentration at river mile 2.4 was 0.12 ng/L. The mean concentration increased to 18.3 ng/L at river mile 1.6 and remained elevated through the farthest downstream sampling point at river mile 1.2. In August, the mean HCB concentration was 0.18 ng/L at river mile 2.4, increased to 3.88 ng/L at river mile 1.6 and remained elevated through river mile 0.7 at the Lift Bridge (Table 3).

Table 3. Mean dissolved water column PCB and HCB concentrations in June and August, 2001 ± standard deviation (ng/L).

	Approximate River Mile	PCB	HCB	number of samples
June	2.4	0.50 ± 0.20	0.12 ± 0.06	2
	1.6	83.1 ± 8.77	18.3 ± 0.42	2
	1.5	23.2	6.61	1
	1.2	27.7	8.16	1
August	2.4	1.18 ± 0.30	0.18 ± 0.09	2
	1.6	18.4 ± 3.46	3.88 ± 0.09	2
	1.2	9.71	3.24	1
	0.7	7.66 ± 0.69	1.82 ± 0.18	2
	Harbor	0.24	0.07	1

Figures 2 and 3 illustrate the spatial distribution of dissolved PCBs and HCB on the June and August 2001 surveys. It is clear from the data in Table 3 and Figures 2 and 3 that both PCBs and HCB increase downstream of Fields Brook and remain elevated well downstream.

Figure 2. Dissolved water column PCB concentrations in the Ashtabula River and Harbor in June and August, 2001 (means and standard deviations)

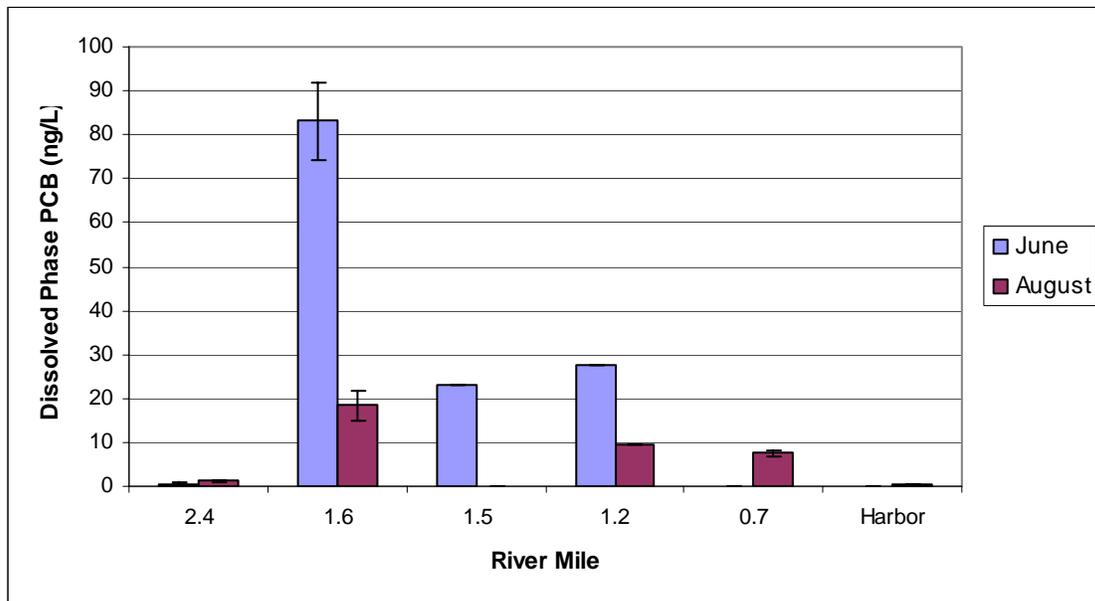
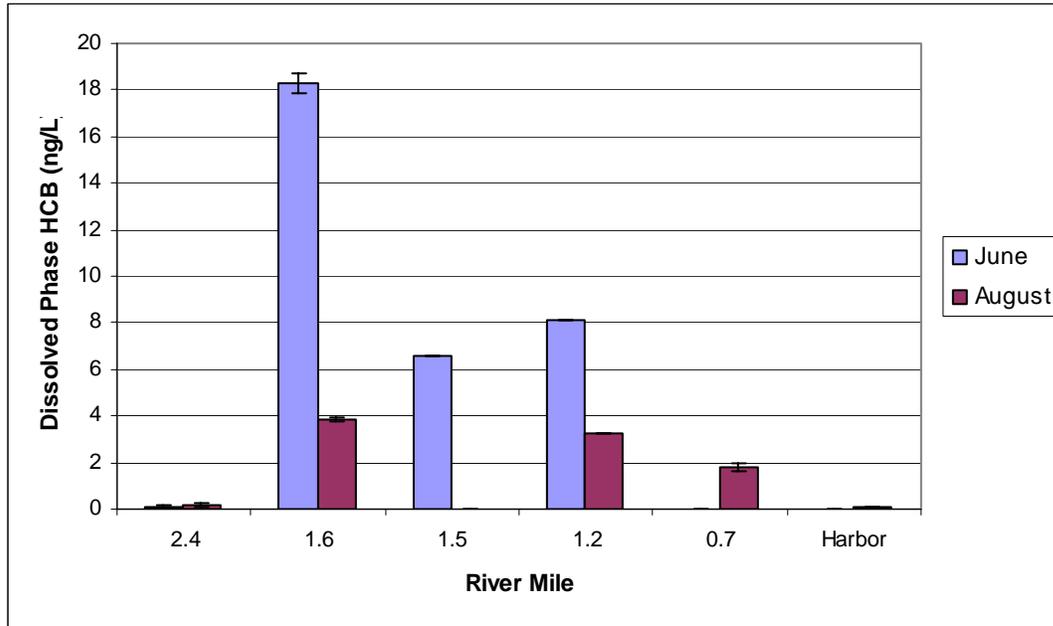


Figure 3. Dissolved water column HCB concentrations in the Ashtabula River and Harbor in June and August, 2001 (means and standard deviations)



There are numerous standards and bench marks to which water column concentrations of PCBs and HCB may be compared. For the purposes of this report we will limit comparisons to water quality criteria established by the State of Ohio and the US Environmental Protection Agency's Great Lakes Water Quality Objectives.

HCB:

The State of Ohio has established a water quality criterion for HCB in both drinking and non-drinking water in the Lake Erie Basin of 0.45 ng/L for the protection of human health (Ohio Environmental Protection Agency 2002).

HCB concentrations (Table 2) in two samples from river mile 2.4, upstream of Fields Brook, in June 2001 were 0.16 ng/L and 0.08 ng/L. HCB concentrations in two samples from the same location in August 2001 were 0.24 ng/L and 0.12 ng/L. All samples taken upstream of Fields Brook, in both June and August, were well below the Ohio water quality criterion of 0.45 ng/L. HCB concentrations in two samples from river mile 1.6, downstream of Fields Brook, in June 2001 were 18.6 ng/L and 18.0 ng/L. In August, concentrations at this location were 3.95 ng/L and 3.82 ng/L. On both surveys, mean HCB concentrations were significantly (t-test, $p < 0.05$) different downstream of Fields Brook than those upstream. Analysis of pooled data from the June and August surveys also indicate a statistically significant difference (t-test, $p < 0.05$) between concentrations upstream of Fields Brook (river mile 2.4) and those downstream of Fields Brook at river mile 1.6.

In June, the water quality criterion was exceeded downstream of Fields Brook and was not achieved through the farthest downstream sampling point at river mile 1.2. In August the water quality criterion was again exceeded immediately downstream of Fields Brook and was not achieved until the Harbor entrance (Table 3). Dissolved phase HCB concentrations downstream of Fields Brook exceeded the HCB criterion of 0.45 ng/L by more than 40 times in June, 2001 and by more than 8 times in August, 2001.

PCBs:

The State of Ohio has established a water quality criterion of PCBs at 0.026 ng/L for the protection of human health and a criterion of 0.12 ng/L for the protection of wildlife (Ohio Environmental Protection Agency 2002).

In June 2001, total dissolved phase PCB concentrations in samples upstream of Fields Brook at river mile 2.4 were 0.65 ng/L and 0.36 ng/L (Table 2). In August 2001, total dissolved phase PCB concentrations at this location were 1.40 ng/L and 0.97 ng/L. Total dissolved phase PCB concentrations downstream of Fields Brook (river mile 1.6) were 89.3 ng/L and 76.9 ng/L in June 2001, and 16.0 ng/L and 20.9 ng/L in August 2001. In June, upstream and downstream dissolved phase PCB concentrations were significantly different at $p < 0.05$ (t-test). In August, the upstream and downstream dissolved phase PCB concentrations were significantly different at $p < 0.1$ (t-test). When the June and August data were pooled, a statistically significant difference at $p < 0.1$ (t-test) was observed.

PCB concentrations exceed the water quality criteria for both the protection of human health (0.026 ng/L) and the protection of wildlife (0.12 ng/L) throughout the study area. The U.S. Environmental Protection Agency has established a Water Quality Objective of 0.07 ng/l for PCBs in the Great Lakes for the protection of fish and wildlife species (USEPA 1995). PCB concentrations in the Ashtabula River downstream of Fields Brook are 100 to 1,200 times the Great Lakes Water Quality Objective and 150 to 680 times the State of Ohio criterion for the protection of wildlife.

The Trustees are conducting additional studies in the Ashtabula River and Harbor as described in the Assessment Plan (U. S. Fish and Wildlife Service 2003).

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