US Army Corps
of Engineers®
Buffalo District

Eighteenmile Creek
Great Lakes Area of Concern (AOC)
Niagara County, New York

Concentrations, Bioaccumulation and Bioavailability of Contaminants in Surface Sediments

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TABLE OF CONTENTS

EXECUTIVE SUMMARY 3
INTRODUCTION 5
MATERIALS AND METHODS 8
RESULTS AND DISCUSSION 12
Particle Size Distribution and TOC Content of Sediments 12
Assessment of Sediment-Associated Contaminants 12
Metals 12
Concentrations and Toxicity 12
Bioaccumulation and Bioavailability 15
Summary of Heavy Metals Assessment 16
Chlorinated Pesticides 18
Concentrations and Toxicity 18
Bioaccumulation and Bioavailability 18
Equilibrium Partitioning (EqP)-Based Criteria 18
Empirical Data 19
PCBs 22
Concentrations and Toxicity 22
Bioaccumulation and Bioavailability 23
EqP-Based Criteria 23
Empirical Data 23
PCDD/Fs 25
Concentrations and Toxicity 25
Bioaccumulation and Bioavailability 27
EqP-Based Criteria 27
Empirical Data 27
Summary of Organic Contaminant Assessment 27
CONCLUSION 31
REFERENCES 32

EXECUTIVE SUMMARY

The Eighteenmile Creek Great Lakes Area of Concern (AOC) has three identified use impairments, all of which are linked to sediment contamination: (1) restrictions on fish and wildlife consumption; (2) degradation of benthos; and (3) restrictions on dredging activities. The main contaminants of concern (COCs) associated with these impairments include the organic compounds chlorinated pesticides, polychlorinated biphenyls (PCBs) and dioxins/dibenzofurans (PCDD/Fs), and metals such as chromium, copper, lead, manganese, mercury, nickel, zinc and cyanide.

To assess the overall toxicological risk of surficial sediment contamination within the AOC that is currently exposed to the aquatic community, the U.S. Army Corps of Engineers (USACE), Buffalo District collected sediment samples from 15 locations within the lower reach of Eighteenmile Creek in August 2003. These discrete samples were composited to represent five separate reaches within the AOC: moving upstream from approximately upper Olcott Harbor to Burt Dam, these were Reaches EBU1, EBU2, EBU3, EBU4 and EBU5. The sediment samples were subjected to laboratory physical, chemical and bioaccumulation testing. Chemical testing included various heavy metals, and organic contaminants including chlorinated pesticides, PCBs and PCDD/Fs. The bioaccumulation experiments entailed a standard 28-day freshwater laboratory test using the surficial sediment deposit feeding aquatic oligochaete *Lumbriculus variegatus*, and focused on metals, chlorinated pesticides and PCBs. The specific objectives of this investigation were to:

- Ascertain the concentrations of all of the contaminants tested in surface sediments within the AOC. Evaluate these levels relative to selected freshwater toxicity threshold values, mainly relevant sediment quality criteria, and;
- Assess the bioaccumulation of metals, chlorinated pesticides and PCBs to determine their potential to bioaccumulate in aquatic organisms. Further, quantify and assess the bioavailability of pesticides and PCBs through the calculation and evaluation of biota-sediment accumulation factors (BSAFs).

Heavy metals data indicated that concentrations of various metals in surficial sediments, particularly copper, chromium, lead, nickel and zinc, may exert chronic toxicity throughout the AOC. Metal contamination in sediments within reaches EBU3 and EBU5 appear to have the most potential to pose chronic toxicity. Potential for sediment-associated lead and zinc toxicity was consistent throughout the AOC. The bioaccumulation data suggest little bioavailability or bioaccumulation risk associated with heavy metal contamination.

Organic contaminant data indicated that levels of the pesticide dichlorodiphenyldichloroethylene (DDE) in surficial sediments within Reaches EBU1 through EBU4 may be chronically toxic. Bioaccumulation data indicated that DDE was bioavailable throughout AOC surface sediments (mean BSAF range = 1.21 to 5.41). The high bioavailability of DDE in surficial sediment in Reaches EBU3 (BSAF = 4.60) and

EBU5 (BSAF = 5.41) indicate that it is bioaccumulating in benthic invertebrates, and is likely to bioaccumulate in predator fish and higher trophic levels. Both sediment and bioaccumulation data suggest that PCBs in surficial sediments throughout most or all of the AOC are being bioaccumulated to levels that pose a risk to aquatic organisms. PCB concentrations are bioavailable in surface sediments throughout the AOC (mean BSAF range = 1.55 to 4.36). The high bioavailability of PCBs in the surficial sediments in Reaches EBU3 (BSAF = 2.95) and EBU5 (BSAF = 4.36) indicate that they are bioaccumulating in benthic invertebrates, and are likely to bioaccumulate in predator fish and higher trophic levels. The site-specific BSAFs determined in this investigation can be used in a model to conservatively predict the bioaccumulation of DDE and PCBs by indigenous benthic organisms from AOC sediments. PCDD/F contamination in surficial sediments throughout the AOC indicate a bioaccumulation risk to wildlife.

The results of this investigation indicate that surficial sediments throughout the AOC contain levels of contaminants that should be of toxicological concern. When considering both metal and organic compound contamination, surficial sediments within AOC Reaches EBU3 and EBU5 are the most contaminated and appear to present the highest toxicological risk.

This investigation was performed under the authority of Section 401 of the Water Resources Development Act (WRDA) of 1990, as Amended, with the Niagara County Department of Planning, Development and Tourism as a non-Federal cost-share partner. This report was prepared by Scott W. Pickard of the U.S. Army Corps of Engineers (USACE), Buffalo District[1] and reviewed by the U.S. Army Engineer Research and Development Center (USAERDC).

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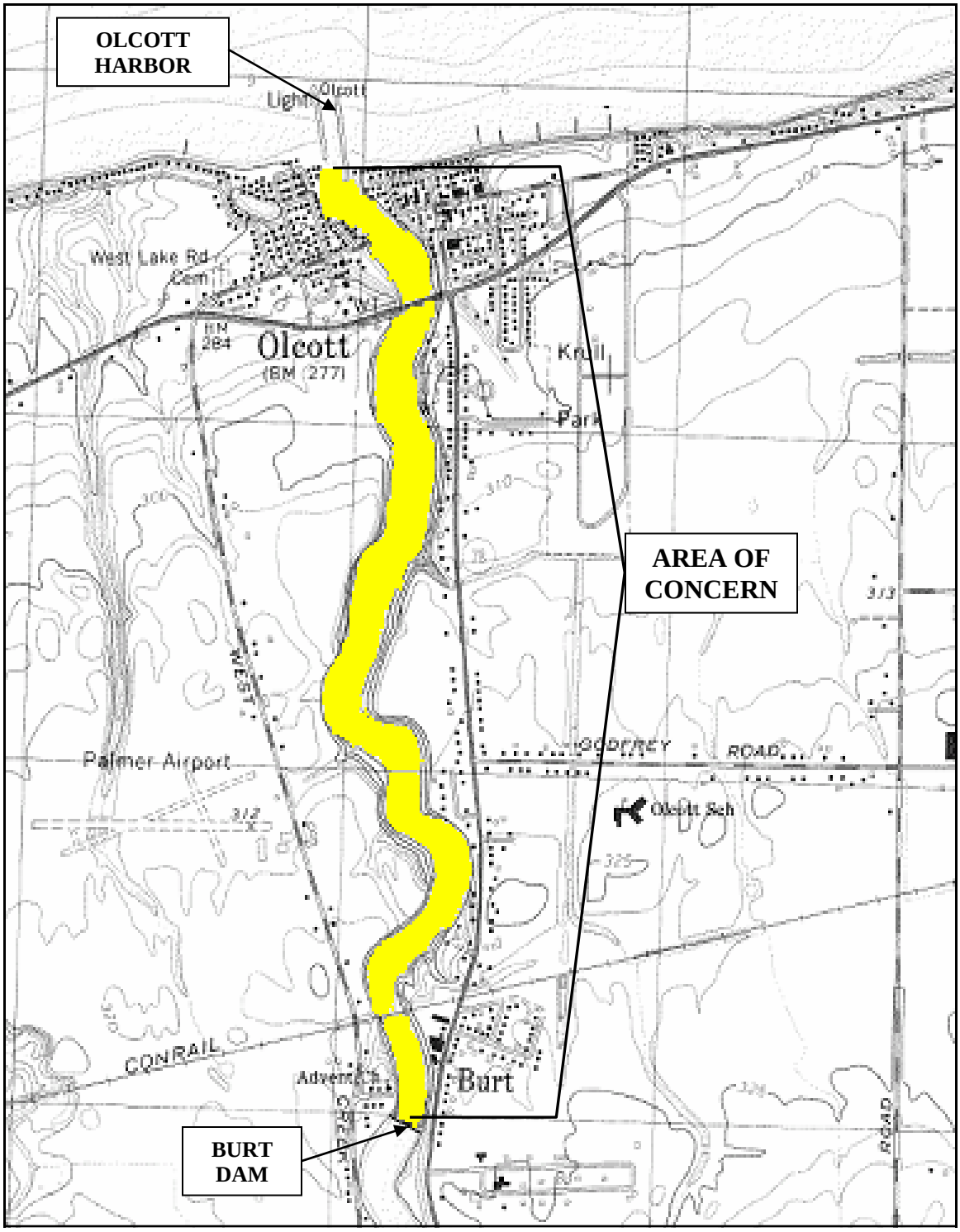
INTRODUCTION

The Eighteenmile Creek AOC is located in the lower reach of Eighteenmile Creek near its mouth on Lake Ontario, in the hamlet of Olcott, Niagara County, New York (Figure 1). The creek flows from the south into the lake through Olcott Harbor, about 18 miles east of the Niagara River mouth at Lake Ontario. The AOC includes that portion of the creek between Olcott Harbor, upstream to the farthest point at which backwater conditions exist during Lake Ontario's highest monthly average lake level (generally, just downstream of Burt Dam) (U.S. Environmental Protection Agency [USEPA] 2001). Three use impairments have been identified in a combined Stage 1/2 Remedial Action Plan (RAP) report (New York State Department of Environmental Conservation [NYSDEC] 1997). All of these use impairments are linked to bottom sediment contamination. The primary COCs within the AOC include the organic compounds including chlorinated pesticides, PCBs and PCDD/Fs, and metals such as chromium, copper, lead, manganese, mercury, nickel, zinc and cyanide. Sources of contamination include upstream industrial discharges, inactive hazardous waste sites, contaminated sediments, air deposition and Lake Ontario. These COCs are present at the sediment-water interface and, consequently, may be available to impart toxicological effects on the existing aquatic community. Specific use impairments include:

- *Restrictions on fish and wildlife consumption due to PCB and PCDD/F contamination*
- *Degradation of benthos due to sediment contamination*
- *Restrictions on dredging activities due to sediment contamination*

Sediment-associated contaminants in the aquatic environment behave differently, which depend largely, either directly or indirectly, on their chemical structure. All have a tendency to adsorb to fine particles (such as silts and clays) and total organic carbon (TOC) in bottom sediments. Metals typically bioaccumulate (accumulate in the tissues of organisms) at lower concentrations relative to hydrophobic organic compounds. However, they can be toxic at certain concentrations. In contrast, organic contaminants such as PCBs, pesticides and PCDD/Fs, are bioaccumulative and can also biomagnify (increase in concentration in the organism's predator). They are hydrophobic (do not mix with water and partition to TOC) and accumulate in organism lipid (fat) because they are lipophylic. They are neutral and do not tend to interact with other organic chemicals at environmentally-relevant concentrations. At certain concentrations, organic contaminants can also be either acutely or chronically toxic. The potential of a sediment-associated contaminant concentration to induce toxicity is considerably influenced by its concentration in the tissues (bioaccumulation), which in turn is influenced by the compound's bioavailability (portion of chemical available for biological uptake). A variety of physiochemical and biological factors can affect bioavailability, both independently and interactively. Therefore, information on bioavailability is integral to the assessment of a sediment contaminant's risk to the exposed aquatic community.

FIGURE 1. Eighteenmile Creek Great Lakes AOC.



The overall objectives of this investigation on the Eighteenmile Creek AOC were to (1) ascertain the levels of contaminants in surface sediments within the AOC; and (2) determine and evaluate the levels of the contaminants in these surface sediments relative to selected toxicity threshold values or potential to bioaccumulate in aquatic organisms. These objectives are consistent with a RAP remedial strategy focusing on "contaminated bottom sediment assessment and action determination" (NYSDEC 1997).

To accomplish the goals of this investigation, surficial sediment samples were collected from the AOC and analyzed for a variety of inorganic and organic contaminants. In addition, sediment samples were subjected to bioaccumulation testing for metals, chlorinated pesticides and PCBs. The data generated from these testing procedures were used to assess the potential toxicity, bioaccumulation and bioavailability of AOC surface sediments to the aquatic community.

MATERIALS AND METHODS

In August 2003, discrete surficial sediment samples were collected from the bottom of Eighteenmile Creek at a total of 15 locations within the AOC (Figure 2). The sediment samples were obtained using a Peterson Grab sampler and a total volume of at least six liters were collected per site. The samples were gathered in a stainless steel pan and homogenized. For the discrete samples, equal amounts of sediment were placed in 0.95-liter glass jars and labeled EMC-1 through EMC-15. They were chemically analyzed in the laboratory for the following parameters:

- Heavy metals – Aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, selenium, silver, sodium, thallium, vanadium and zinc
- TOC
- Organic contaminants – Chlorinated pesticides, PCBs and PCDD/Fs

Another sample for each site was contained in labeled 0.95-liter glass jars for particle size analysis.

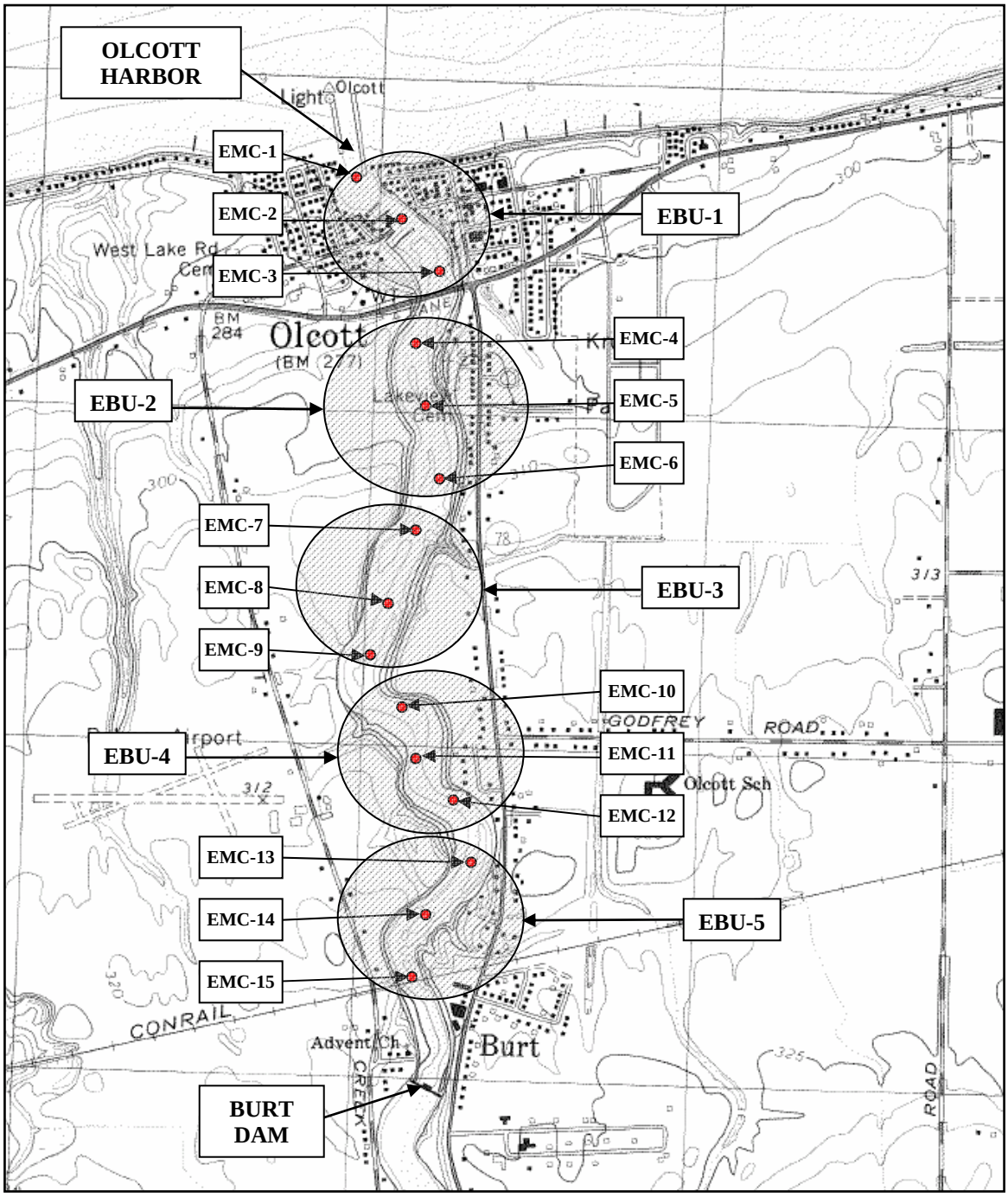
For the bioaccumulation testing, equal volumes of sediment from every three, successive discrete sample locations were combined and thoroughly mixed into a single 7.6-liter sample, resulting in a total of five composite samples. These samples were used to represent five separate reaches within the AOC, from downstream to upstream, as follows (Figure 2):

Reach Composite Sample	Composited Discrete Samples	Description
EBU1	EMC-1, EMC-2 and EMC-3	Just upstream of Olcott Harbor
EBU2	EMC-4, EMC-5 and EMC-6	Just South of State Route 104
EBU3	EMC-7, EMC-8 and EMC-9	Just upstream of unnamed tributary on east side of creek under Route 78
EBU4	EMC-10, EMC-11 and EMC-12	Foot of Godfrey Road
EBU5	EMC-13, EMC-14 and EMC-15	Just downstream of Burt Dam

These reach sediment samples were tested for:

- Concentrations of all the above listed heavy metals, pesticides, PCBs and TOC
- The bioaccumulation of heavy metals, chlorinated pesticides and PCBs

FIGURE 2. Eighteenmile Creek AOC sediment sampling sites and reaches.



USAERDC conducted the bioaccumulation tests using standard procedures. The freshwater aquatic, surficial deposit feeding oligochaete (worm) *Lumbriculus variegatus* was exposed to the sediment samples over a 28-day period in the laboratory according to guidelines provided in the USEPA/USACE Great Lakes Dredged Material Testing and Evaluation Manual (USEPA/USACE 1998). This procedure and test species was used because the bioaccumulation of PCBs by *L. variegatus* in the laboratory provides a

reasonable quantitative estimate of the bioaccumulation of PCBs by oligochates in field sediment (i.e., Ankley *et al.* 1992). The worms were exposed to test and control (Browns Lake, Vicksburg, MS) sediments in 6-L box aquaria (31.5 x 18 x 10.5 cm) using five replicates per treatment. Adequate exposure conditions were maintained using an intermittent flow system for overlying water renewal. At exposure termination, worms were recovered from the test/control sediments, placed in water for gut purging (12-hour), blotted dry and frozen at –20ºC. The worm tissues were subsequently analyzed for metals, chlorinated pesticides and PCBs, as well as for lipid content.

All chemical analyses on the sediment and worm tissues followed standard USEPA SW846 methodologies:

Matrix	Parameter	Method	Laboratory Reporting Limit (LRL) (unless otherwise noted)
Sediment	Metals (TAL)	6010B	0.050
	Mercury	7471	0.025
	TOC	9060 Modified	500
	PCB (congeners)	8082	0.010
	Pesticides	8081A	0.010
	PCDD/Fs	8290	0.000002
Tissue	Metals (TAL)	6020/6010B	0.025
	Mercury	7470A	0.0040
	PCBs (congener summations)	8082	0.025
	Pesticides	8081A	0.025
	Lipid	Van Handel (1995)	1 µg

Particle size analyses followed ASTM Procedure D422.

Using the metals bioaccumulation data, bioaccumulation factors (BAFs) were calculated for heavy metals to screen for overall bioavailability (Harrahy and Clements 1997):

$$BAF = \frac{C_t}{C_s}$$

Where:

C_t = Concentration of heavy metal in tissue (mg/kg wet weight)
C_s = Concentration of heavy metal in sediment (mg/kg dry weight)

Mean heavy metal BAFs were calculated for each reach of the AOC using the five replicate BAFs. For any non-detectable concentrations, the specified laboratory reporting limit (LRL) was used as a substitute to produce a maximum and most conservative BAF. Mean BAFs were also determined for the entire AOC.

For selected chlorinated pesticides and PCBs, biota-sediment accumulation factors (BSAFs) were calculated from the bioaccumulation data to express the bioavailability of the sediment-associated compounds (Ferraro *et al.* 1990):

$$BSAF = \frac{C_t / L}{C_s / TOC}$$

Where:

C_t = Concentration of neutral organic contaminant in tissue (µg/kg wet weight)
L = Concentration of lipid in *L. variegatus* tissue (percent of wet weight)
C_s = Concentration of neutral organic contaminant in sediment (µg/kg dry weight)
TOC = Total organic carbon concentration in sediment (percent of dry weight)

Mean BSAFs for chlorinated pesticides and PCBs were calculated for each AOC reach based on the five replicate BSAFs. For non-detectable concentrations, the specified LRL was used as a substitute to produce a maximum and most conservative BSAF. Mean BSAFs were also determined for the entire AOC.

RESULTS AND DISCUSSION

Raw data generated in this investigation are contained in USAERDC (2004). Therefore, the reader is refered to this report for further, more detailed information.

Particle Size Distribution and TOC Content of Sediments

A summary of the grain size distribution and TOC level data on the composited samples is presented in Table 1 (discrete data are available in USAERDC 2004). Grain size analyses showed that the AOC sediments were composed of between 19.5% (Reach EBU5) to 68.8% (Reach EBU2) silts and clays, and 31.3% (Reach EBU2) to 80.5% (Reach EBU5) sands and gravels. The sediments at Reaches EBU1 through EBU4 were composed of at least around one-half fine-grain particles, and sediments from Reaches EBU5 were very coarse-grain. TOC levels in the sediments across the AOC reach samples were fairly consistent, ranging from 2.9 to 3.9% at Reaches EBU5 and EBU2, respectively.

TABLE 1. Particle size distribution and TOC level data on surficial composite sediment samples collected within the AOC (from USAERDC 2004).

AOC Reach	Particle Size Distribution (%)		TOC (%)
	Fines (silts/clays)	Coarse (sands/gravels)	
EBU1	48.7	50.9/0.4	3.3
EBU2	68.8	31.3/0	3.9
EBU3	67.5	31.3/1.2	3.6
EBU4	48.6	50.0/1.5	3.1
EBU5	19.5	40.9/39.6	2.9

Assessment of Sediment-Associated Contaminants

Metals

Concentrations and Toxicity

The concentrations of metals in the composited reach samples, and the corresponding mean bioaccumulated tissue residues, are summarized in Table 2 (for metals data on discrete samples, see USAERDC 2004). All of the heavy metals were detected in the majority of the sediment and tissue samples. The heavy metals data on the sediment samples were compared to four separate sets of non-site specific criteria:

- Sediment Quality Guideline (SQG) freshwater probable effect levels (PELs) (Environment Canada 2003)
- Severe effect levels (SELs) (NYSDEC 1999)
- Consensus-based freshwater sediment probable effect concentrations (PECs) (MacDonald *et al.* 2000)

- Lake Ontario reference area (background levels) (Engineering and Environment 1997)

TABLE 2. Concentrations of heavy metals in AOC reach surficial composite sediment samples, and in corresponding oligochaete tissues. All units are in mg/kg (from USAERDC 2004).

Heavy Metal	AOC Reach									
	EBU1		EBU2		EBU3		EBU4		EBU5	
	Sediment	Mean Tissue	Sediment	Mean Tissue	Sediment	Mean Tissue	Sediment	Mean Tissue	Sediment	Mean Tissue
Aluminum	10,800	292	12,800	422	11,600	409	12,800	585	10,700	632
Antimony	0.35	0.03	0.45	0.07	0.56	0.07	2.97	0.05	0.33	0.06
Arsenic	3.4	0.89	4.13	1.24	3.75	1.25	3.38	1.07	2.78	0.88
Barium	113	45.3	137	57.9	122	68.7	122	69.7	65.8	63.0
Beryllium	0.52	0.04	0.68	0.04	0.60	0.05	0.63	0.05	0.60	0.04
Cadmium	0.75	0.15	1.25	0.35	1.52	0.32	0.90	0.16	0.36	0.14
Calcium	20,000	1,781	14,300	1,079	10,400	1,164	19,200	1,791	12,900	1,358
Chromium	41	5.2	74.1	7.8	109	15.7	52.5	11.6	102	11.1
Cobalt	8.77	0.95	12.1	1.20	13.9	1.76	12.3	1.29	11.8	0.62
Copper	64.7	9.8	123	15.6	157	25.4	73.5	15.7	31.7	7.3
Iron	21,200	1,023	25,900	1,728	25,400	1,914	27,600	2,160	23,400	1,362
Lead	102	7.1	146	16.4	203	29.9	153	21.4	69.9	11.6
Magnesium	6,270	337	6,820	356	6,380	403	6,410	387	6,770	342
Manganese	535	41.5	409	24.4	475	40.0	517	42.6	440	34.7
Mercury	0.17	2.37	0.33	0.11	0.37	0.17	0.17	0.07	0.04	0.03
Nickel	31.2	4.7	56.9	8.5	20.5	20.3	47.9	5.3	39.9	2.9
Selenium	0.50	0.46	0.45	0.48	3.53	0.34	0.32	0.42	0.10	0.30
Silver	0.47	0.01	0.62	0.02	0.62	0.04	0.34	0.03	0.18	0.09
Sodium	187	628	180	661	158	589	186	670	463	547
Thallium	0.20	0.06	0.29	0.03	0.29	0.04	0.24	0.02	0.13	0.02
Vanadium	20.8	1.39	25.3	1.72	24.5	2.32	23.5	2.13	20.5	1.53
Zinc	328	70.0	536	102	800	173	444	93.1	238	93.1

Table 3 summarizes the numeric criteria to which the sediment concentration data were compared.

With respect to the metals data on the reach sediments, chromium exceeded the PEL at Reaches EBU3 and EBU5. The SEL and/or PEC for copper was exceeded at Reaches EBU2 and EBU3. Lead exceeded the PEL at Reaches EBU1 through EBU4, and the SEL and/or PEC at Reaches EBU2 through EBU4. The SEL for nickel was exceeded at Reach EBU2. In addition, the PEL, and SEL and/or PEC for zinc were exceeded at Reaches EBU1 through EBU4.

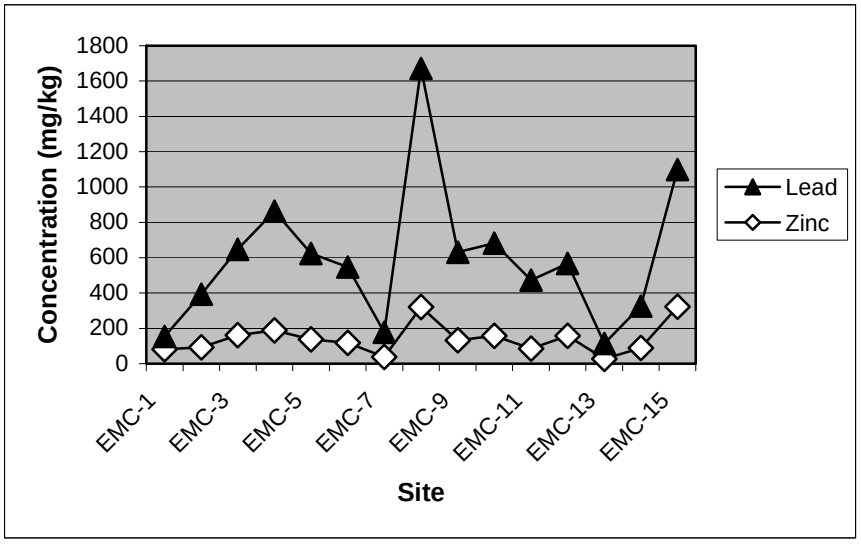
In general, the discrete sediment data were consistent with the data on the AOC Reach samples. However, some of the discrete samples showed significantly higher heavy metal concentrations or levels that did exceed a PEL, SEL and/or PEC. For example, at Site EMC-15, the chromium concentration of 867 mg/kg, about nine to eight times the PEL, and SEL and PEC, respectively. Chromium concentrations also exceeded the PEL at Site EMC-4, and PEL, SEL and PEC at Site EMC-8. The copper level of 245 mg/kg at Site EMC-8 exceeded the PEL, SEL and PEC. Lead and zinc concentrations exceeded the PELs, SELs and PECs at many of the sites. In the case of zinc, the levels were several-fold the PEL and SEL at Sites EMC-4, EMC-8 and EMC-15. The lead concentration of 322 mg/kg at Site EMC-15 exceeded the PEL, SEL and PEC. The nickel concentration of 172 mg/kg at Site EMC-8 exceeded the SEL and PEC. Figure 3

plots the lead and zinc levels in surficial sediments at discrete sites within the AOC. Both metals show peak concentrations at Sites EMC-4, 8 and 15, with the maximum levels at Site EMC-8.

TABLE 3. Summary of metal freshwater sediment quality criteria applied in this report. An asterisk denotes that the criterion was not determined.

Heavy Metal	Sediment Threshold Value (mg/kg, dry weight)			Lake Reference Level Range (mg/kg, dry weight)
	PEL	SEL	PEC	
Aluminum	-*	-	-	9,350-15,800
Antimony	-	25	-	0.81-1.37
Arsenic	17	33	33	5.24-8.8
Barium	-	-	-	62.8-101
Beryllium	-	-	-	0.49-0.90
Cadmium	3.5	9.0	4.98	0.87-1.20
Calcium	-	-	-	23,800-40,700
Chromium	90	110	111	26.2-33.6
Cobalt	-	-	-	7.29-11.4
Copper	197	110	149	25.6-41.3
Iron	-	40,000	-	18,200-28,800
Lead	91.3	110	128	24.5-32.2
Magnesium	-	-	-	9,440-16,200
Manganese	-	1100	-	499-767
Mercury	0.49	1.3	1.06	0.10-0.19
Nickel	-	50	48.6	23.1-35.0
Selenium	-	-	-	1.34-2.27
Silver	-	2.2	-	0.42-0.62
Sodium	-	-	-	229-265
Thallium	-	-	-	<0.51-<0.71
Vanadium	-	-	-	21.8-32.3
Zinc	315	270	459	109-152

FIGURE 3. Levels of lead and zinc in discrete surficial sediment samples collected from the AOC (based on data from USAERDC 2004).



Bioaccumulation and Bioavailability

With respect to the mean bioaccumulated heavy metal data contained in Table 2, sediments from AOC Reach EBU3 generally showed higher tissue residues (particularly for cadmium, cobalt, copper, lead, nickel and zinc). Table 4 summarizes the heavy metal BAFs. In general, the BAFs for most metals (except for cobalt, mercury, nickel and sodium) at Reach EBU5 were either comparable or higher when compared to the other reaches. This higher bioavailability was likely associated, to some extent, with the relatively higher coarse-grain content of the surficial sediment in this AOC reach (Table 1). The mean BAF of 13.9 for mercury at Reach EBU1 was greatly influenced by Replicate EBU1-2 (BAF=67.6). Reach EBU3 showed a BAF of 0.99 for nickel, which was higher than the other reaches. Reach EBU5 showed a BAF of 2.96 for selenium, which was higher than the other reaches.

TABLE 4. BAFs for heavy metals in surficial composite sediment samples collected from the AOC (based on data from USAERDC 2004).

Heavy Metal	AOC Reach					Mean BAF
	EBU1	EBU2	EBU3	EBU4	EBU5	
Aluminum	0.03	0.03	0.04	0.05	0.06	0.04
Antimony	0.10	0.16	0.12	0.02	0.18	0.11
Arsenic	0.26	0.30	0.33	0.32	0.32	0.31
Barium	0.40	0.42	0.56	0.57	0.96	0.58
Beryllium	0.07	0.07	0.09	0.08	0.07	0.08
Cadmium	0.19	0.28	0.21	0.17	0.38	0.25
Calcium	0.40	0.42	0.56	0.57	0.96	0.58
Chromium	0.13	0.11	0.14	0.22	0.11	0.14
Cobalt	0.11	0.08	0.13	0.11	0.05	0.09
Copper	0.15	0.13	0.16	0.21	0.23	0.18
Iron	0.05	0.07	0.08	0.08	0.06	0.07
Lead	0.07	0.11	0.15	0.14	0.17	0.13
Magnesium	0.06	0.05	0.06	0.06	0.05	0.06
Manganese	0.08	0.06	0.08	0.08	0.08	0.08
Mercury	13.9	0.34	0.46	0.42	0.66	3.17
Nickel	0.15	0.15	0.99	0.11	0.07	0.30
Selenium	0.91	1.08	0.10	1.32	2.96	1.27
Sodium	3.36	3.67	3.72	3.6	1.18	3.11
Silver	0.05	0.05	0.07	0.11	0.53	0.16
Thallium	0.32	0.12	0.14	0.14	0.26	0.20
Vanadium	0.07	0.07	0.09	0.09	0.08	0.08
Zinc	0.21	0.19	0.22	0.21	0.39	0.24

Luomo and Rainbow (2005) outline the difficulties involved in using metal bioaccumulation data to evaluate ecological risks. While the bioaccumulation of metals and metalloids is of particular value in polluted ecosystems as an exposure indicator to organisms (mainly because metals are not metabolized), the process can be quite complex. It is influenced by multiple routes of exposure (diet and solution) and geochemical effects on bioavailability. Variable patterns of accumulation occur among species, including the regulation of body concentrations of some metals by some species, and vastly different concentrations among species and environments. The links between

bioaccumulation and toxicity are intricate. Toxicity is determined by the uptake of metal internally, and the species-specific partitioning of accumulated metal between metabolically active and detoxified forms. For these reasons, the potential adverse effects metals in sediments are best evaluated using comparison to SQG and direct measurement of toxicity using laboratory sediment testing.

Summary of Heavy Metals Assessment

Table 5 identifies AOC reaches where the sediment-associated heavy metals in either composite or discrete sample-related data exceeded the selected toxicity criteria and/or were determined to preliminarily be a bioaccumulation/bioavailability risk based on the empirical uptake and/or BAF data. The intent of this table is to summarize the heavy metals data on AOC surficial sediments within a general toxicological risk framework. Based on this table, deductions with respect to the AOC reaches are as follows:

- **Reach EBU1**—All listed metal concentrations in these sediments, except for mercury, significantly exceeded lake reference levels. Copper, lead, nickel and zinc concentrations often appear to be chronically toxic. Mercury may be very bioavailable and bioaccumulative. Note that this heightened bioavailability is attributable to a single replicate sample.
- **Reach EBU2**—All listed metal concentrations in these sediments, except for selenium, notably exceeded lake reference levels. Copper, lead, nickel and zinc concentrations often appear to be chronically toxic. Some of the zinc concentrations were over twice the SEL and/or PEC.
- **Reach EBU3**—All listed metal concentrations in these sediments, except for cobalt and mercury, notably exceeded lake reference levels. Chromium, copper, lead, nickel and zinc concentrations often appear to be chronically toxic. Mercury may be chronically toxic in some instances. Some of the copper, lead and zinc concentrations were over twice the SEL and/or PEC.
- **Reach EBU4**—All listed metal concentrations in these sediments, except for silver, significantly exceeded lake reference levels. Lead and zinc concentrations often appear to be chronically toxic. Silver may be chronically toxic in some instances.
- **Reach EBU5**—All listed metal concentrations in these sediments, except for selenium, significantly exceeded lake reference levels. Chromium, copper, iron, lead and zinc often appear to be chronically toxic. Some of the chromium, iron, lead and zinc concentrations were over twice the SEL and/or PEC. Bioaccumulation data on the sediments in this reach suggested higher bioavailability of metals in comparison to the other reaches.

TABLE 5. AOC reaches where heavy metal concentrations appear to be a concern with respect to selected sediment criteria. If the metal concentration exceeded only the lake reference level, it was not included in the reach listing. KEY TO SHADED AREAS IN TABLE:

● = Reach sample level exceeded the specified criterion for this metal; discrete sample level also exceeded the specified criterion
○ = Discrete sample level for this metal exceeded the specified criterion, and possibly other criteria
◙ or ◘ = At least a discrete sample level within this reach was twice the SEL and/or PEC

AOC Reach	Heavy Metal	Criteria					
		PEL	SEL	PEC	Lake Reference	Bioaccumulation	High BAF
EBU1	Chromium				●		
	Copper		○		●		
	Lead	●	○		●		
	Mercury					●	●
	Nickel		○	○	○		
	Zinc	●	●		●		
EBU2	Cadmium				●		
	Chromium				●		
	Copper		●	○	●		
	Barium				●		
	Lead	●	●	●	●		
	Nickel		●	●	●		
	Selenium						
	Zinc	●	◙	◙	●		
EBU3	Cadmium				●	●	
	Chromium	●	○	○	●		
	Cobalt					●	
	Copper	○	◙	●	●	●	
	Lead	●	◙	◙	●	●	
	Mercury	○					
	Nickel		○	◘	○	●	●
	Zinc	●	◙	◙	●	●	
EBU4	Barium				●		
	Chromium				●		
	Copper				●		
	Lead	●	●	●	●		
	Silver		○				
	Zinc	●	●	●	●		
EBU5	Barium				○		
	Cadmium				○		
	Chromium	●	○	◘	●		
	Copper		○	○	○		
	Iron		◘		○		
	Lead	○	◘	◘	●		
	Selenium						●
	Zinc	○	◘	○	●		

In summary, the majority of heavy metal concentrations in the AOC surficial sediments exceeded lake reference levels. Data in all of the reaches indicated that lead and zinc levels were chronically toxic. Surficial sediments in Reaches EBU3 and EBU5 showed the overall highest toxicity risk. Heavy metals bioaccumulation data on the reaches did not yield any definitive data to evidence inordinate sediment bioavailability.

Chlorinated Pesticides

Concentrations and Toxicity

Most of the chlorinated pesticides in the 15 discrete sediment surficial samples were non-detectable (for the data on the discrete samples, see USAERDC 2004). Endosulfan sulfate was measured at concentrations ranging from 2.46 µg/kg at Site EMC-11 to 4.12 µg/kg at Site EMC-9. Most notably, 4,4'-dichlorodiphenyldichloroethylene (DDE), a common breakdown product/metabolite of 4,4'-dichlorodiphenyltrichloroethane (DDT), was detected at all of the sites (except for EMC-1), ranging in concentration from 3.24 µg/kg at Site EMC-13 to 37.3 µg/kg at Site EMC-12. The other DDT breakdown product/metabolite 4,4'-dichlorodiphenyldichloroethane (DDD) was also detected at four of the sites, ranging in concentration from 3.22 to 13.7 µg/kg at Sites EMC-1 and EMC-12, respectively. In the reach samples, DDE concentrations ranged from 4.07 to 22.7 µg/kg at Reaches EBU5 and EBU4, respectively (Table 6). In addition, DDD was measured in the Reach EBU4 sediments at 10.7 µg/kg. Mean lipid levels in *L. variegatus* exposure replicates ranged from 1.15 to 1.69%, and averaged 1.21%. Such values are typical for this species and field oligochaetes (i.e., Ankley *et al.* 1992; Pickard *et al.* 2001 and 2006).

DDE levels in sediments in Reaches EBU1 through EBU4 all exceeded the PEL of 6.75 µg/kg (Environment Canada 2003). Most of the DDE concentrations in the discrete samples also exceeded the PEL. None of the DDE levels in sediments in any of the reach samples exceeded the PEC of 31.3 µg/kg (MacDonald *et al.* 2000). However, discrete samples from Sites EMC-3 and EMC-12 exceeded this guideline.

Bioaccumulation and Bioavailability

Equilibrium Partitioning (EqP)-Based Criteria

None of the DDE concentrations in reach surficial sediments exceeded their respective EqP-based criterion for wildlife bioaccumulation (based on 1.0 µg/g TOC criterion for DDE [NYSDEC 1999]) (Table 6). However, the DDD/DDE/DDT sum (referred to as ∑DDT) of 33.4 µg/kg at Reach EBU4 (and ∑DDT of 55 µg/kg at Site EMC-12 within this reach) exceeded the respective criteria.

TABLE 6. DDD, DDE, DDT and ∑DDT concentrations in AOC reach surface sediments. Shaded areas indicate values that exceed the respective EqP-based sediment criterion for wildlife bioaccumulation.

AOC Reach	Concentration (µg/kg)			∑DDT Concentration (µg/kg)	EqP-derived Sediment Criterion (µg DDE/kg sediment)
	DDD	DDE	DDT		
EMC-1	3.22	<2.22	<2.22	7.67	11
EMC-2	<3.36	17.4	<3.36	24.1	32
EMC-3	<4.87	33.3	<4.87	27.1	47
EBU1	<3.61	16.2	<3.67	23.5	33
EMC-4	<4.40	27.9	<4.40	36.7	45
EMC-5	<3.97	25.8	<3.97	33.7	44
EMC-6	<3.18	16.3	<3.18	22.3	30
EBU2	<3.83	22.5	<3.83	30.2	39
EMC-7	<3.71	6.75	<3.71	14.2	35
EMC-8	<3.36	29.2	<3.36	35.9	36
EMC-9	<3.39	20.0	<3.39	26.8	30
EBU3	<3.64	14.1	<3.64	21.4	36
EMC-10	<3.03	11	<3.03	17.1	24
EMC-11	<2.76	9.75	<2.76	15.3	32
EMC-12	13.7	37.3	<4.88	55.9	48
EBU4	10.7	22.7	<3.52	40.0	31
EMC-13	<3.24	3.24	<3.24	9.72	32
EMC-14	<2.42	6.65	<2.42	11.5	18
EMC-15	10.4	16.2	<3.50	30.1	45
EBU5	<2.63	4.07	<2.63	9.33	29

Empirical Data

The bioaccumulation data on the AOC sediments for chlorinated pesticides are contained in USAERDC (2004). Most of the chlorinated pesticides were non-detectable in the *L. variegatus* issues. Intermittent detections of B-BHC, endosulfan sulphate, endrin and gamma chlordane were noted in some of the tissue replicates, most of which appeared to be clustered around the EBU3 and EBU4 AOC reaches. Due to the sporadic nature of the data and mostly non-detectable sediment concentrations, BSAFs were not determined for these particular pesticides.

DDE was detected in all of the *L. variegatus* tissue replicates and was the dominant DDT metabolite in both sediments and tissues. Therefore, it is being bioaccumulated in benthic invertebrates within the AOC. Mean tissue residues of DDE ranged from 10.5 to 19.3 µg/kg in Reaches EBU2 and EBU1, respectively (see Table 9). DDT and DDD were also measured above the LRL in about 24% of the tissue replicates. Mean lipid levels in the worms ranged from 0.95 to 1.7% in Reaches EBU4 and EBU2, respectively. Collectively, these data showed no definitive evidence that the worms were metabolizing (i.e., internally breaking down) DDE from the sediments.

BSAFs were calculated from the bioaccumulation data to quantify the bioavailability of DDE at the sediment surface within the AOC. In order to account for the detected DDT and DDD concentrations, ∑DDT BSAFs were also calculated to quantify the bioavailability of the three related compounds as a group. This is important because DDT is known to be biodegraded (broken down by microorganisms) and biotransformed (metabolized by organisms) in aquatic ecosystems. Table 7 summarizes the DDT-related BSAFs. The coefficients of variation were very high for the DDE (129%) and ∑DDT (110%) BSAFs (USARDC 2004), which reflected high variability. DDE tissue residue data from Replicate 2 in EBU-1 and Replicate 5 in EBU-5 were the major contributors to this variability. Therefore, these BSAF values were regarded as statistical outliers and were not included in the mean BSAF calculations (USAERDC 2006). Among the AOC reaches, the mean DDE BSAFs ranged from 1.21 to 5.41 at Reaches EBU2 and EBU5, respectively. The mean ∑DDT BSAFs were consistent with the DDE BSAFs, ranging from 1.58 to 5.44 at Reaches EBU2 and EBU5, respectively. Ingersoll *et al.* (2003) calculated DDT/DDD/DDE BSAFs based on *L. variegatus* exposures to freshwater sediments from Huntsville, Alabama. For 4,4'-DDE, a BSAF of about 1.0 was yielded on day 28, which did not appreciably increase through day 56. Further, for five DDT-related compounds (2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD and 4,4'-DDT), the BSAFs ranged from about 0.9 to 4.0, for an average of about 2.5 (Ingersoll *et al.* 2003). Therefore, the BSAFs at Reaches EBU1, EBU2 and EBU4, and mean of 1.67, were what would be generally expected.

TABLE 7. Bioavailability of DDE and ∑DDT in AOC surface sediments.

AOC Reach	Mean BSAF	
	DDE	∑DDT
EMU1	1.91	2.15
EMU2	1.21	1.58
EMU3	4.60	4.94
EMU4	1.89	1.90
EMU5	5.41	5.44
Mean AOC BSAF	3.00	3.20

The DDE BSAFs were inordinately high in Reaches EBU3 and EBU5, ranging from 4.60 to 5.41, with an average of 5.01. In addition to the results of Ingersoll *et al.* (2003) using *L. variegatus*, DDT BSAFs for a variety of other aquatic invertebrates, ranging from 0.05 to 2.13, are summarized in Table 8. The mean DDE BSAF of 3.00 for surface sediments across the AOC is outside the range and higher in comparison to these other DDT BSAFs, indicating a high bioavailability. The higher bioavailability of DDE at Reach EBU5 was likely associated, to some extent, with the relatively higher coarse-grain content of the surficial sediment in this AOC reach (Table 1). The high bioavailability of DDE in surficial sediment in Reaches EBU3 and EBU5 indicate that it is bioaccumulating in benthic invertebrates, and is likely to bioaccumulate in predator fish and higher trophic levels.

TABLE 8. DDT BSAFs for various aquatic invertebrates based on field-collected sediments.

Species (taxonomic group)	BSAF	Reference
Hyalella azteca (amphipod)	0.44-2.08	Lotufo *et al.* 2001
Diporeia spp. (amphipod)	0.07-0.56	Lotufo *et al.* 2001
Rephoxinius abronius (amphipod)	0.09	Meador *et al.* 1997
Macoma nasuta (bivalve)	0.05	Boese *et al.* 1997
Hetermastus filiformis (polychaete)	0.4-0.8	Mulsow and Landrum 1995
Armandia brevis (polychaete)	0.2	Meador *et al.* 1997

BSAFs are an integral component of the theoretical bioaccumulation potential (TBP) model, an equilibrium theory-based algorithm used to predict the potential bioaccumulation of neutral, organic compounds in sediments (McFarland 1984). The empirical DDE (or ∑DDT) BSAFs determined can be used to predict the uptake of total PCBs from the AOC sediments by indigenous benthic organisms, particularly invertebrates that reside in the sediments. For pelagic fish (i.e., a fish that is normally not in direct contact with bottom sediments), TBP should only be used as a worst-case estimate of bioaccumulation potential.

The TBP model is expressed as:

$$TBP = BSAF\ (L)\ (C_s/TOC)$$

Where:

TBP = Whole body tissue concentration of organic contaminant (µg/kg wet weight)
L = Concentration of lipid in target animals (percent of wet weight)
C_s = Concentration of organic contaminant in sediment (µg/kg dry weight)
TOC = TOC concentration in sediment (percent of dry weight)

For example, when applying the mean AOC BSAF of 3.0 at site EMC-14 sediments with a surface DDE concentration of 6.65 µg/kg and TOC level of 1.8% (USAEDRC 2004), the whole body concentration of DDE in oligochaetes (lipid level = 1.0%) is predicted as:

$$TBP = 3.0\ (1.0\%)\ (6.65\mu g/kg\ /\ 1.8\%) = 11.1\ \mu g/kg$$

For a bullhead (lipid level = 2.6% [USEPA/USACE 1998]) at the same site, the whole body concentration of DDE is conservatively estimated as:

$$TBP = 3.0\ (2.6\%)\ (6.65\mu g/kg\ /\ 1.8\%) = 28.8\ \mu g/kg$$

Table 9 summarizes the mean *L. variegatus* DDE bioaccumulation data and TBP estimates for field oligochaetes at each AOC sampling site, using site-specific BSAFs. The TBP predictions based on the individual reach BSAFs were either close to or overestimated average actual bioaccumulation within a factor of two. Application of the AOC mean DDE BSAF of 3.0 always overpredicted average actual bioaccumulation

within a factor of two. These results support the validity of the TBP model and demonstrate the utility of these empirical BSAFs in predicting the bioaccumulation of DDE from AOC surface sediments.

TABLE 9. TBP estimates for DDE in field oligochaetes in AOC surficial sediments based on site-specific BSAFs and an assumed 1% lipid content, in comparison to actual bioaccumulation. Discrete sediment DDE and TOC data obtained from USAERDC (2004).

Site	AOC Reach	Mean Bioaccumulated DDE (µg/kg)	Reach BSAF	TBP (µg/kg)	Mean TBP (µg/kg)	
					Reach BSAF	AOC BSAF (3.0)
EMC-1	EBU1	10.0	1.91	3.9	9.3	14.5
EMC-2				10.4		
EMC-3				13.5		
EMC-4	EBU2	10.5	1.21	7.5	7.1	17.5
EMC-5				7.1		
EMC-6				6.6		
EMC-7	EBU3	13.4	4.60	8.9	25.6	16.7
EMC-8				37.3		
EMC-9				30.7		
EMC-10	EBU4	12.4	1.89	8.7	9.7	15.4
EMC-11				5.8		
EMC-12				14.7		
EMC-13	EBU5	6.8	5.41	5.5	15.0	8.3
EMC-14				20		
EMC-15				10.5		

In addition to TBP and other models used to estimate nonpolar compound residues in aquatic organisms, BSAFs can serve several other useful applications. For example, they can be principal components in the assessment of ecological risks of contaminated sediments (i.e., USEPA/USACE 1998), the development of water quality standards for human health (USEPA 2000) and the development of bioaccumulation factors and water/sediment criteria for aquatic ecosystems (Burkhard 1995). Site-specific BSAFs are particularly desirable for prediction purposes because the BSAF incorporates all processes and conditions influencing bioaccumulation at that site (Burkhard *et al.* 2005).

PCBs

Concentrations and Toxicity

Total PCB concentrations (congener summation) in the reach sediments ranged from 77.9 to 279 µg/kg at Reaches EBU5 and EBU4, respectively (Table 9), and were quite consistent throughout the AOC (Note: The summations did not include below reporting limit [BRL] levels or concentrations that were not reported due to co-elution

and/or interferences [NR]). Across the AOC, PCB-31, 44, 49 and 52 were always the four most dominant congeners in the reach samples, comprising between about 34 to 58% of the total concentration. The PCB data on the reach sediments were generally consistent with those on the discrete samples (for discrete sample data, see USAERDC 2004). The congener composition of the PCBs generally denoted the Aroclor 1248 mixture, which was the identified mixture in the quality assurance (QA) sample (EMC-4 QA). Reaches EBU3 and EBU4 marginally exceeded the PEL of 277 µg/kg (Environment Canada 2003). None of the reach sediments exceeded the PEC of 676 µg/kg (MacDonald *et al.* 2000).

Bioaccumulation and Bioavailability

EqP-Based Criteria

Total PCB concentrations in surficial sediments in all of the reaches exceeded their respective EqP-based PCB sediment criterion for wildlife bioaccumulation (based on 1.4 µg/g TOC criterion for PCBs [NYSDEC 1999]) (Table 9). Consequently, the surficial sediments may present an appreciable risk to piscivorous wildlife from consuming fish or other aquatic organisms. The congener makeup of the PCBs in these sediments indicates that they are quite bioaccumulative and have the potential to biomagnify (e.g., Koslowski *et al.* 1994).

TABLE 10. Total PCB concentrations in AOC reach surface sediments and their associated bioavailability. Shaded areas indicate values that exceed the respective EqP-based sediment criterion for wildlife bioaccumulation.

AOC reach	Total concentration (µg/kg)	EqP-derived Sediment Criterion (µg PCB/kg sediment)	Mean BSAF
EBU1	236	46.2	1.76
EBU2	229	54.6	1.55
EBU3	279	50.4	2.95
EBU4	278	43.4	1.91
EBU5	77.9	40.6	4.36
		MEAN AOC BSAF	2.51

Empirical Data

The PCB bioaccumulation data on the AOC sediments are contained in USAERDC (2004). Most PCB congeners were detected in all of the *L. variegatus* tissue replicates. Therefore, they are bioaccumulating in benthic invertebrates within the AOC. Mean bioaccumulated PCBs ranged from 93.4 µg/kg in Reach EBU5 to 169 µg/kg in Reach EBU3 (see Table 11). With one minor exception, the top five most bioaccumulated congeners throughout between Reaches EBU1 and EBU4 were PCBs 31, 44, 49, 52 and 101. With one exception, the top five bioaccumulated congeners in Reach EBU5 were PCBs 44, 49, 52, 101 and 138. Thus, PCBs 44, 49 and 52 were always

among the top five bioaccumulated congeners from surficial sediments throughout the AOC.

The total PCB BSAFs are contained in Table 9 (these BSAFs included only those congeners that were quantified for both sediments and tissues for a given replicate). Among the AOC reaches, the mean PCB BSAFs ranged from 1.55 to 4.36 at Reaches EBU2 and EBU5, respectively. The BSAFs at Reaches EBU1, EBU2 and EBU4 ranged from 1.55 to 1.91, and averaged 1.74. This mean is comparable to the results of Pickard *et al.* (2001), who calculated a mean total PCB BSAF of 1.69 for upper Ashtabula River sediments based on 28-day *L. variegatus* bioaccumulation experiments. The BSAF of 1.74 is also consistent with total PCB BSAFs of 0.66 to 2.24 (Call *et al.* 1993) and 0.84 (Ankley *et al.* 1992) using 28-day bioaccumulation data on *L. variegatus.* It is also comparable to the PCB BSAF grand means of 1.3 and 2.2 for all benthic species based on laboratory exposures and field data, respectively, contained in a BSAF database (USAERDC 2005). Therefore, the BSAFs at Reaches EBU1, EBU2 and EBU4 were what would be generally expected.

The PCB BSAFs were higher at Reaches EBU3 and EBU5. When treated as a separate group, they averaged 3.7 and were notably higher than the PCB BSAF grand means of 1.3 and 2.2 (USAERDC 2005). The higher bioavailability at Reach EBU5 was likely associated, to some extent, with the relatively higher coarse-grain content of the surficial sediment in this AOC reach (Table 1). These data indicate that PCBs in surface sediments at Reaches EBU3 and EBU5 are highly bioavailable, and indicate that they are bioaccumulating in benthic invertebrates and likely to bioaccumulate in predator fish and higher trophic levels. The mean AOC BSAF of 2.51 is comparatively high and indicates that PCBs are quite bioavailable in surficial sediments throughout the AOC.

With regard to using the empirical BSAFs to estimate bioaccumulation, Table 11 summarizes the mean *L. variegatus* PCB bioaccumulation data and TBP predictions for field oligochaetes at each AOC sampling site based on site-specific BSAFs. Similar to the DDE BSAFs calculated in this investigation, TBP predictions using the individual reach BSAFs were close to or overestimated actual average total PCB bioaccumulation within a factor of two. Application of the AOC mean total PCB BSAF of 2.51 consistently overpredicted bioaccumulation, but well within a factor of two of average actual bioaccumulation, and closely estimated it across Reaches EBU1, EBU3 and EBU5. This indicates that these empirical BSAFs can serve as a useful predictive tool for the bioaccumulation of DDE from AOC surface sediments.

TABLE 11. TBP estimates for total PCBs in field oligochaetes in AOC surficial sediments based on site-specific BSAFs and an assumed 1% lipid content, in comparison to actual bioaccumulation. Discrete sediment PCB and TOC data obtained from USAERDC (2004).

Site	AOC Reach	Mean Bioaccumulated Total PCBs (µg/kg)	Reach BSAF	TBP (µg/kg)	Mean TBP (µg/kg)	
					Reach BSAF	AOC BSAF (2.51)
EMC-1	EBU1	126	1.76	84.7	87.9	125
EMC-2				44.4		
EMC-3				135		
EMC-4	EBU2	127	1.55	101	97.9	159
EMC-5				92.7		
EMC-6				99.6		
EMC-7	EBU3	170	2.95	88.4	217	185
EMC-8				361		
EMC-9				203		
EMC-10	EBU4	156	1.91	172	151	199
EMC-11				85.5		
EMC-12				196		
EMC-13	EBU5	93.4	4.36	104	169	97.6
EMC-14				219		
EMC-15				185		

PCDD/Fs

Concentrations and Toxicity

The concentrations of 2378-tetrachlorodibenzo-*p*-dioxin (TCDD), viewed as the most toxic PCDD/F congener, and PCDD/F toxic equivalents (TEQs) for each discrete sediment sample from the AOC are summarized in Table 12 (congener-specific PCDD/F data on the discrete samples can be obtained from USAERDC [2004]). Toxic equivalency factors (TEFs) are applied to PCDD/F congeners in order to normalize their concentration relative to TCDD. The values for each congener can then be summed to determine a PCDD/F TEQ for the sediment sample. All 15 of the discrete sediment samples showed detectable concentrations of many of the 17 PCDD/F congeners, ranging from 0.35 pg/g of 123478-HxCDD at Site EMC-6 to 2,800 pg/g of OCDD at Site EMC-15. Site EMC-15 showed the highest concentration of total PCDD/Fs. With respect to TCDD, concentrations ranged from non-detectable at most of the sites, to two detected concentrations of 0.6 and 0.72 pg/g at Sites EMC-8 and EMC-10, respectively. PCDD/F TEQs ranged from 0.21 to 16.2 pg/g at Sites EMC-13 and EMC-16, respectively.

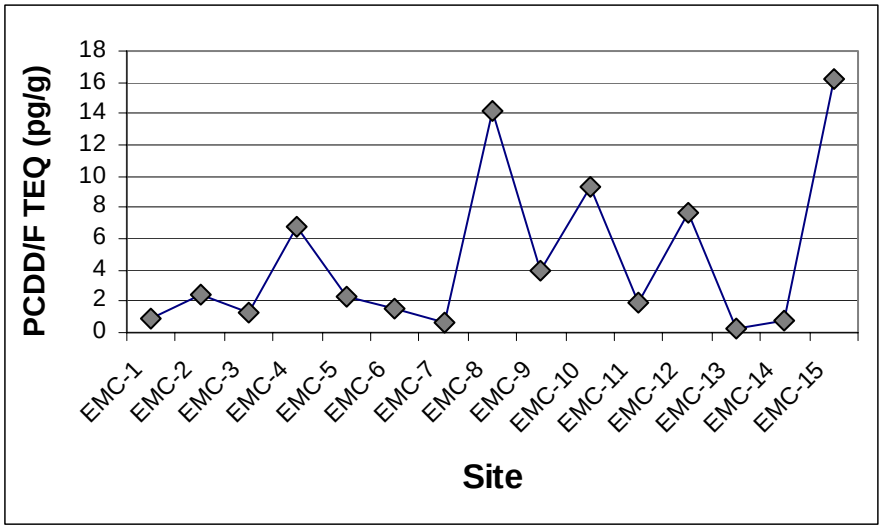
TABLE 12. TCDD concentrations and PCDD/F TEQs for discrete samples collected from the AOC. Shaded and outlined areas indicate TEQ values that exceed the proposed and existing EqP-based sediment criteria for wildlife bioaccumulation, respectively.

Site	TCDD Concentration (pg/g)	PCDD/F TEQ (pg/g)	EqP-derived Sediment Criteria, PCDD/F TEQ (pg/g)	
			Existing (0.0002 µg/g TOC)	Proposed (0.000032 µg/g TOC)
EMC-1	<0.50	0.88	2.2	0.35
EMC-2	<0.87	2.41	6.4	1.0
EMC-3	<0.75	1.27	9.4	0.94
EMC-4	<0.55	6.76	9.0	1.4
EMC-5	<0.65	2.28	8.8	1.4
EMC-6	<0.36	1.54	6.0	0.96
EMC-7	<0.63	0.63	7.0	1.1
EMC-8	0.6	14.2	7.2	1.2
EMC-9	<0.42	3.96	6.0	0.96
EMC-10	0.72	9.28	4.8	0.76
EMC-11	<0.55	1.97	9.6	1.0
EMC-12	<0.73	7.64	6.4	1.5
EMC-13	<0.56	0.21	3.6	1.0
EMC-14	<0.54	0.79	9.0	0.58
EMC-15	<1.7	16.2	5.8	1.4

Figure 4 presents the TEQ values for discrete samples within the AOC, based on TEFs from Van den Berg *et al.* (1998) (the TEQs did not include non-detectable concentrations). TEQs ranged from 0.21 pg/g at Site EMC-13 to 16.2 pg/g at Site EMC-15, none of which exceeded the PCDD/F PEL of 21.5 pg/g TEQ (Environment Canada 2003). Therefore, PCDD/F contamination in surface sediments within the AOC does not appear to be remarkable from the standpoint of this guideline. The relatively higher congener concentrations and maximum TEQ at Site EMC-15 indicate an upstream source of PCDD/Fs above Burt Dam. In addition, there is a general downward trend in the TEQs, downstream of Burt Dam to just upstream of the harbor. Smaller peaks are noted at Sites EMC-12, 10, 8 and 4.

It is important to note that the use of TEFs is only intended as an interim approach to enumerate PCDD/F toxicity. TEFs are of low confidence because they are imprecise and have high uncertainties. Summing the TEF-modified concentrations to obtain TEQs adds another layer of uncertainty. Safe *et al.* (1998) showed that the interaction of dioxin-related compounds (i.e., PCDD/Fs and PCBs) with the intracellular aryl hydrocarbon (Ah) receptor varied substantially, evidencing highly variable toxicity. Such potentially contributing factors are not considered in TEFs.

FIGURE 4. TEQs for PCDD/F congeners in discrete surficial sediment samples collected from the AOC (based on data from USAERDC 2004).



Bioaccumulation and Bioavailability

EqP-Based Criteria

EqP-derived sediment criteria using the existing 0.0002 µg/g TOC criterion for 2378-TCDD (NYSDEC 1999) and discrete TOC data yielded criteria ranging from 2.2 to 9.6 µg/kg sediment (Table 12). Four of the PCDD/F TEQs exceeded their respective wildlife bioaccumulation criterion. NYSDEC is in the process of revising the NYSDEC (1999) criteria for a number of contaminants, and the newly proposed PCDD/F TEQ criterion is 3.2×10^{-5} µg/g TOC (NYSDEC-Albany, personal communication). All sites in the AOC, except for EMC-7 and EMC-13, exceeded these criteria, suggesting that the surficial sediments may present an appreciable risk to piscivorous wildlife from consuming fish or other aquatic organisms.

Empirical Data

The sediment samples were not tested for PCDD/F bioaccumulation. Therefore, empirical BSAFs were not calculated to quantify PCDD/F bioavailability in surface sediments within the AOC.

Summary of Organic Contaminant Assessment

Table 13 identifies AOC reaches where the analyzed sediment-associated organic contaminants exceeded the selected toxicity criteria and/or were determined to preliminarily be a bioaccumulation/bioavailability risk based on the EqP-based, empirical uptake and/or BAF data. The intent of this table is to summarize the organic contaminant data within a general toxicological risk framework. Based on this table, deductions with respect to the AOC reaches are as follows:

- **Reach EBU1**—DDE concentrations in these sediments significantly exceeded lake reference levels, and may be chronically toxic. However, EqP-based estimates did not indicate a bioaccumulation risk to wildlife. Total PCB concentrations significantly exceeded lake reference levels and appear to be a bioaccumulation risk to wildlife. PCDD/F TEQs appear to indicate a bioaccumulation risk to wildlife.
- **Reach EBU2**—DDE concentrations in these sediments significantly exceeded lake reference levels, and may be chronically toxic. Total PCB concentrations significantly exceeded lake reference levels and appear to be a bioaccumulation risk to wildlife. PCDD/F TEQs appear to indicate a bioaccumulation risk to wildlife.
- **Reach EBU3**—DDE concentrations in these sediments significantly exceeded lake reference levels, and may be chronically toxic. DDE is highly bioavailable. However, EqP-based estimates did not indicate a bioaccumulation risk to wildlife. Total PCB concentrations significantly exceeded lake reference levels, may be chronically toxic and appear to be a bioaccumulation risk to wildlife. PCBs are highly bioavailable. The PCDD/F TEQ for a site within this reach significantly exceeded the lake reference TEQ. PCDD/F TEQs appear to indicate a bioaccumulation risk to wildlife.
- **Reach EBU4**—DDE concentrations in these sediments significantly exceeded lake reference levels, and may be chronically toxic. Sum DDD/ DDE/DDT levels evidenced a bioaccumulation risk to wildlife. Total PCB concentrations significantly exceeded lake reference levels, may be chronically toxic and appear to be a bioaccumulation risk to wildlife. The PCDD/F TEQ for a site within this reach significantly exceeded the lake reference TEQ. PCDD/F TEQs appear to indicate a bioaccumulation risk to wildlife.
- **Reach EBU5**—DDE concentrations in these sediments significantly exceeded lake reference levels, and they are highly bioavailable. However, EqP-based estimates did not indicate a bioaccumulation risk to wildlife. Total PCB concentrations significantly exceeded lake reference levels and appear to be a bioaccumulation risk to wildlife. PCBs are highly bioavailable. The PCDD/F TEQ for a site within this reach significantly exceeded the lake reference TEQ. PCDD/F TEQs appear to indicate a bioaccumulation risk to wildlife.

TABLE 13. AOC reaches where DDT/DDD/DDE , PCBs and PCDD/Fs appear to be a concern with respect to selected sediment criteria.

KEY TO SHADED AREAS IN TABLE:

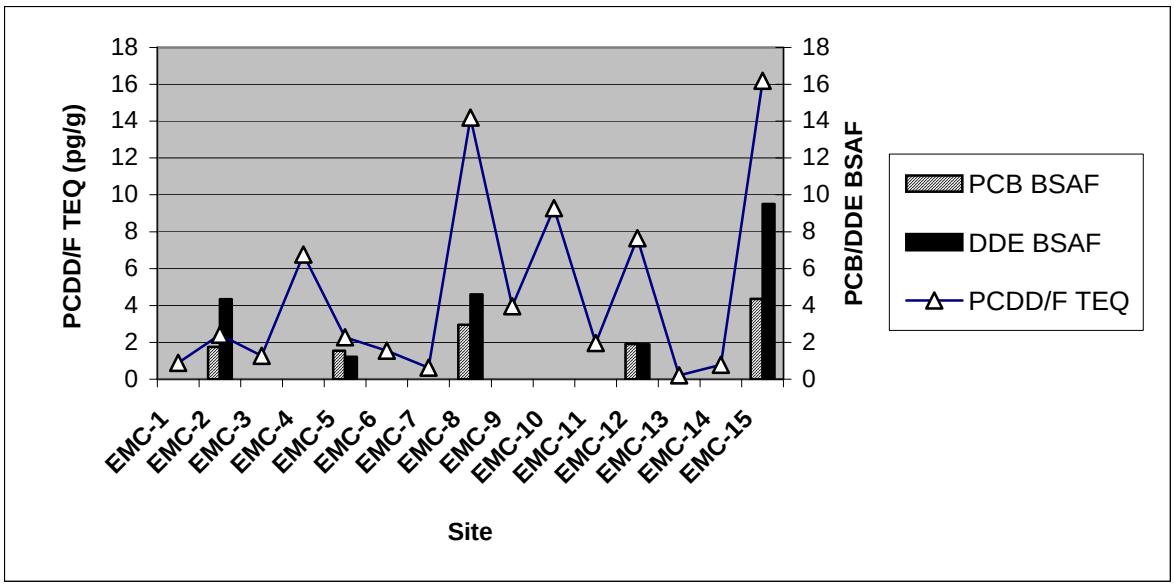
● = Reach sample level exceeded the specified criterion; for this organic; discrete sample level also exceeded the specified criterion
○ = Discrete sample level for this organic exceeded the specified criterion, and possibly other criteria

AOC Reach	Organic Compound	Criteria					
		PEL	SEL	PEC	Lake Reference	Bioaccumulation*	High BSAF
EBU1	DDE	●		○			
	Total PCBs					●	
	PCDD/Fs					○	
EBU2	DDE	●					
	Total PCBs					●	
	PCDD/Fs					○	
EBU3	DDE	●					●
	Total PCBs	●				●	●
	PCDD/Fs					○	
EBU4	DDE	●		○			
	∑DDT					●	
	Total PCBs	●				●	
	PCDD/Fs					○	
EBU5	DDE						●
	Total PCBs					●	●
	PCDD/Fs					○	

*For the bioaccumulation criterion, only the EqP-based estimate for wildlife bioaccumulation (NYSDEC 1999) was used.

Figure 5 is a graph of DDE and PCB BSAFs overlaid by PCDD/F TEQs (note that the BSAFs are relative to reach sediments while the TEQs pertain to discrete samples). Except for Reach EBU1, this suggests a general correspondence between the DDE and PCB bioavailability in all of the reaches. It also illustrates that sediments in Reaches EBU3 and EBU5 may present a relatively higher bioaccumulation risk of PCDD/Fs, and higher bioavailability of DDE and PCBs. Therefore, the bioaccumulation of PCDD/Fs, PCBs and DDE from surficial sediments in these two reaches should be emphasized.

FIGURE 5. DDE and PCB BSAFs, and PCDD/F TEQs in surficial composite and discrete sediment samples collected from the AOC.



In summary, every reach of the AOC shows an organic contaminant in surficial sediments that should be of toxicological concern. All concentrations exceeded lake reference levels. In general terms with respect to organic contamiants, surficial sediments in Reaches EBU1, EBU3, EBU4 and EBU5 showed the highest toxicity risk, while sediments in Reach EBU2 appeared to be of least toxicity risk. With the exception of Reach EBU5, DDE appeared to be chronically toxic throughout the AOC. PCBs and PCDD/Fs appear to present a bioaccumulation risk to wildlife throughout the AOC.

Some of the bioaccumulation and bioavailability information summarized in Table 11 may seem inconsistent. However, the two variables are not the same, and bioaccumulation depends, among other factors, on bioavailability. In addition, the bioaccumulation information in the table is based solely on EqP-based estimates, which are generic and do not consider various site-specific influences, including bioavailability. Therefore, if the estimated EqP-based bioaccumulation risk of an organic compound is acceptable but the bioavailability is very high (in terms of a higher BSAF), the empirical bioavailability data represent a stronger line of evidence, and thence should be assigned more weight. This suggests that the bioaccumulation of DDE from Reaches EBU3 and EBU5 should be regarded as a risk.

CONCLUSION

This investigation examined the overall quality of surficial sediments within the Eighteenmile Creek AOC, in order to quantify and assess the levels of specific COCs that are exposed to aquatic organisms within the ecosystem. The AOC was subdivided into five separate reaches in an attempt to determine notable spatial variations in sediment contamination. The results indicate that surficial sediments throughout the AOC contain concentrations of some COCs that should be of toxicological concern.

Metal contamination in surficial sediments may exert chronic toxicity throughout the AOC. Among the reaches, sediments in Reaches EBU3 and EBU5 appear to have the most potential to be chronically toxic with respect to metals. Evidence for sediment-associated lead and zinc toxicity was consistent throughout the AOC. Based on the discrete data, lead and zinc concentrations peaked at Site EMC-8 within Reach EBU3. Other evidenced metal toxicity in the AOC sediments involved copper, chromium and nickel. This investigation generated little data that evidenced a significant bioavailability or bioaccumulation risk associated with heavy metal contamination.

With respect to organic compounds, DDE concentrations in surficial sediments in Reaches EBU1 through EBU4 may be chronically toxic. DDE was highly bioavailable in Reach EBU3 and EBU5 sediments (mean BSAFs = 4.60 and 5.41, respectively). This indicates that DDE is accumulating in benthic organisms, and is likely to bioaccumulate in predator fish and higher trophic levels. Sediment data indicate that PCB levels in surficial sediments throughout most of the AOC present a bioaccumulation risk. PCBs are highly bioavailable in the surficial sediments in Reaches EBU3 and EBU5 (mean BSAFs = 2.95 and 4.36, respectively). This indicates that PCBs are accumulating in benthic organisms, and likely to bioaccumulate in predator fish and high trophic levels. The BSAFs developed in this investigation are site-specific and can be used to estimate the bioaccumulation of DDE and PCBs by indigenous benthic organisms from AOC sediments. PCDD/F contamination in surficial sediments throughout the AOC suggests a bioaccumulation risk to wildlife.

Overall, surficial sediments in Reaches EBU3 and EBU5 are the most contaminated and appear to present the greatest toxicological risk within the AOC.

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