Journal of Great Lakes Research 37 (2011) 1–8

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Heavy metals in sediments and uptake by burrowing mayflies in western Lake Erie basin

Sarah E. Opfer [a,1], John R. Farver [b,*], Jeffrey G. Miner [a], Kenneth Krieger [c]

[a] Department of Biological Sciences, Aquatic Ecology and Fisheries Laboratory, Bowling Green State University, Bowling Green, OH 43403, USA
[b] Department of Geology, School of Earth, Environment, and Society, Bowling Green State University, Bowling Green, OH 43403, USA
[c] Department of Biological and Environmental Sciences, and National Center for Water Quality Research, Heidelberg University, Tiffin, OH 44883, USA

ARTICLE INFO

Article history:
Received 17 August 2009
Accepted 7 September 2010
Available online 4 December 2010

Communicated by Christine Mayer

Index words:
Lake Erie
Heavy metals
Sediment
Hexagenia
Bioaccumulation

ABSTRACT

During the past two decades, burrowing *Hexagenia* mayflies have returned to the western basin of Lake Erie. Because of their importance as a prey resource for higher trophic levels and their extensive residence time in potentially contaminated sediment, *Hexagenia* may be a source of heavy metal transfer. To better understand the distribution and transfer of heavy metals in sediment and mayflies, sediment and mayfly nymphs were collected from 24 locations across the western basin of Lake Erie in May 2007. Following USEPA protocols, samples were analyzed for 16 elements using ICP-OES or ICP-MS. Metal concentrations in the sediments exceeded the Threshold Effect Level for at least one metal at all sample sites. Sediment heavy metal distribution profiles indicate metal concentrations are correlated with organic matter content, and the highest heavy metal concentrations were found in the central deeper region of the western basin where organic content in the sediments was greatest. *Hexagenia* were distributed throughout the western basin, with greatest density (1350/m^2) within the Detroit River plume. The Cd and Zn levels in mayflies were on average approximately 4 and 2 times greater, respectively, than sediment levels, and the Cd concentrations in the sediments exceeded the Threshold Effect Level at 27 of 28 sites and exceeded the Probable Effect Level at 9 of 28 sites. Spatial representation of heavy metal concentrations in mayflies exhibited a similar pattern to the spatial distribution of heavy metals and organic matter in the sediments with higher concentrations of metals found in mayflies residing in the central deeper region of the western basin.

Introduction

The mass emergences of mayflies (*Hexagenia* spp.) during the past decade in the western basin of Lake Erie are evidence to their strong recovery (Krieger, 1999; Krieger et al., 2007). In the late 1950s, prolonged periods of oxygen depletion in the hypolimnion caused the population of mayflies in Lake Erie to crash to virtual extinction (Brittain, 1982). The decline was attributed to increased nutrient enrichment which, when coupled with a late-summer thermocline, generated hypolimnetic hypoxia (Krieger et al., 1996). However, with binational efforts to enforce pollution abatement programs and increased water clarity caused by invasive dreissenid mussels (*Dreissena polymorpha* and *Dreissena bugensis*), mayfly populations have recovered since the 1990s to an overall western Lake Erie mean density of 195 nymphs/m^2 in 2004 (Krieger et al., 2007).

Mature mayfly nymphs are one of the largest macroinvertebrates in the Great Lakes and are an important food source for fish, as well as bioturbators of sediment (Krieger, 1999; Bachteram et al., 2005; Nordin, 2006). Mayfly nymphs spend their entire life (up to 2 years) burrowed 5 to 10 cm deep in soft-bottomed sediments at water depths of 20 m or less (Edsall et al., 2001) and are detritivores feeding in these sediments (Brittain, 1982; Goodyear and McNeill, 1999). A nymph's prolonged residency in the sediment makes it susceptible to uptake and accumulation of any pollutants present in the sediment, including heavy metals. For example, Bartsch et al. (1999) found significant accumulation of cadmium by mayflies exposed to Cd-spiked sediment in 21-day tests.

Emergence of mayflies from aquatic nymph to terrestrial adult is a critical survival period when their movement up into the water column makes them especially vulnerable to fish predators (Brittain, 1982). If mayfly nymphs accumulate metals from the sediments, there is a potential transfer up trophic levels to fish, and ultimately humans. In Lake Erie, *Hexagenia* spp. are important prey for several fish species. For example, diets of yellow perch (*Perca flavescens*), an important sport and commercial fish, consist of approximately 75% *Hexagenia* by weight during the late May to July emergence period (Bur et al., 2005), and the invasive round goby (*Neogobius melanostomus*) diet consists of

* Corresponding author.
E-mail addresses: Sarah.Opfer@noaa.gov (S.E. Opfer), jfarver@bgsu.edu (J.R. Farver), jminer@bgsu.edu (J.G. Miner), kkrieger@heidelberg.edu (K. Krieger).
[1] Present address: I.M. Systems Group, Inc., NOAA Marine Debris Program & Great Lakes Habitat Restoration Program, 240 W. Lake Street, Unit C, Oak Harbor, OH 43449, USA.

0380-1330/$ – see front matter © 2010 International Association for Great Lakes Research. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jglr.2010.10.005

approximately 70% *Hexagenia*, while northern madtom (*Noturus stigmosus*) diets are approximately 90% by volume during peak emergence (French and Jude, 2001).

Prior studies of mayflies in Lake Erie have demonstrated that they bioaccumulate organic compounds such as PCB congeners and polycyclic aromatic hydrocarbon (PAH) compounds to a much greater degree than other benthic invertebrates (Gewurtz et al., 2000). In addition, studies of heavy metal contents in burrowing mayflies (*Hexagenia bilineata* and *H. limbata*) from both spiked and non-spiked Mississippi River sediments have documented the accumulation of cadmium and mercury (Beauvais et al., 1995; Bartsch et al., 1999). These investigations have shown the accumulation of Cd and Hg in mayfly nymphs was correlated to the concentrations of Cd and Hg in the sediments, and accumulation was largely through gut assimilation (Goodyear and McNeill, 1999; Michaud et al., 2005). Heavy metal levels in mayflies from the western Lake Erie basin are not known, but these sediments have higher metal concentrations than the non-spiked Mississippi River sediments (Painter et al., 2001).

Before pollution abatement programs were initiated in the late 1970s, toxic metal contamination of sediments in the western basin of Lake Erie came mainly through input from the Detroit River, and also from smaller point sources such as the Maumee and Ottawa Rivers and the River Raisin (Corkum et al., 1997). Although measurable declines in sediment contamination have occurred recently, contaminant loading from these major discharges continues today (Painter et al., 2001; OLEC, 2006). These contaminants also have the potential for resuspension into the water column. Marvin et al. (2007) found that contaminated suspended sediments from the western basin of Lake Erie are heavily influenced by resuspended bottom sediments. Correspondingly, mayfly nymphs have the potential for facilitating resuspension of sediment-bound contaminants through bioturbation (Bartsch et al., 1999; Bachteram et al., 2005), particularly in spring during their emergence.

The major objectives of this study were (1) to identify locations of high heavy metal concentrations in sediments in the western Lake Erie basin, (2) to determine metal content in *Hexagenia* nymphs living in these sediments, and (3) to evaluate the correlation of metals concentrations in sediments and mayflies in the western Lake Erie basin.

Materials and methods

Study area

In Lake Erie, *Hexagenia* peak emergence, which is triggered by water temperature, is typically about the third week in June (Krieger et al., 1996). Therefore, at the end of May 2007, *Hexagenia* nymphs and sediments were sampled from sites along transects in the western Lake Erie basin. Sediment samples were collected in triplicate at sites in transects out from the Ottawa, Maumee, and Detroit Rivers and throughout the middle of the basin for a total of 24 sample sites (Table 1 and Fig. 1). Sample sites were selected such that most areas of the basin in Ohio and Michigan were sampled; it was expected that there would be a range of metal concentrations (Painter et al., 2001) and that *Hexagenia* would be found at these sites (Krieger, 1999). Eight of the 24 sites were previously sampled for mayfly nymphs as reported by Schloesser et al. (2000), permitting a historical comparison of mayfly densities/abundances at those sites. In addition, sites that were on open-lake transects were selected to be outside of the shipping channels routinely dredged by the U. S. Army Corps of Engineers.

Table 1
Sample site information and *Hexagenia* density estimates in western Lake Erie basin (May 2007). Site numbers in parentheses refer to sites sampled in 1998 as reported by Schloesser et al. (2000). Nearshore ≤ 5 km, Offshore > 5 km. Sampler used: E = Ekman, PP = Petite Ponar, P = Ponar.

Site	North Latitude	West Longitude	Nearshore (N)/Offshore (O)	Water Depth (m)	Sampler Used	1998 Density (nymphs/m^2)	May 2007 Density (nymphs/m^2)
Detroit River Region:							
6 (3D)	41°56.33'	83°12.17'	N	7.6	PP	298	550
20	41°55.5'	83°06.5'	O	8.5	E		1350
21	41°58.0'	83°07.5'	O	7.3	E		518
22(15D)	42°02.0'	83°09.17'	N	5.0	E	5	150
Maumee/Ottawa River Region:							
8 (8 M)	41°47.30'	83°21.27'	N	5.6	PP	394	83
11	41°41.5'	83°28.25'	N	1.1	E		0
12 (1 M)	41°42.83'	83°25.5'	N	2.3	P	494	7
13	41°44.21'	83°27.77'	N	1.4	E		0
14	41°44.55'	83°26.86'	N	1.8	PP		17
15	41°44.0'	83°26.0'	N	2.3	PP		150
16	41°42.0'	83°24.0'	N	2.2	P		0
17	41°45.5'	83°18.0'	O	6.4	PP		83
24 (7 M)	41°44.0'	83°17.8'	N	5.9	E	518	283
Open Lake Sites:							
1 (5B)	41°41.5'	82°46.0'	O	9.4	E	240	0
2 (1P)	41°32.92'	82°55.0'	N	5.9	PP	115	33
3	41°41.5'	82°55.0'	O	9.8	E		50
4	41°47.5'	82°56.0'	O	10.4	E		17
5	41°44.5'	82°59.0'	O	10.7	E		0
7 (7P)	41°41.25'	83°02.42'	O	8.8	E	173	267
9	41°48.0'	83°03.0'	O	9.8	E		83
10	41°44.0'	83°09.0'	O	8.2	E		383
18	41°49.5'	83°10.0'	O	8.5	E		100
19	41°52.0'	83°05.0'	O	9.8	E		33
23	41°52.11'	83°18.18'	N	6.1	P		0
25	41°40.5'	83°13.0'	N	5.8	PP		n/a
26	41°38.15'	83°08.2'	N	4.0	PP		n/a
27	41°36.3'	83°02.8'	N	3.7	PP		n/a
28	41°34.0'	82°58.0'	N	5.8	PP		n/a

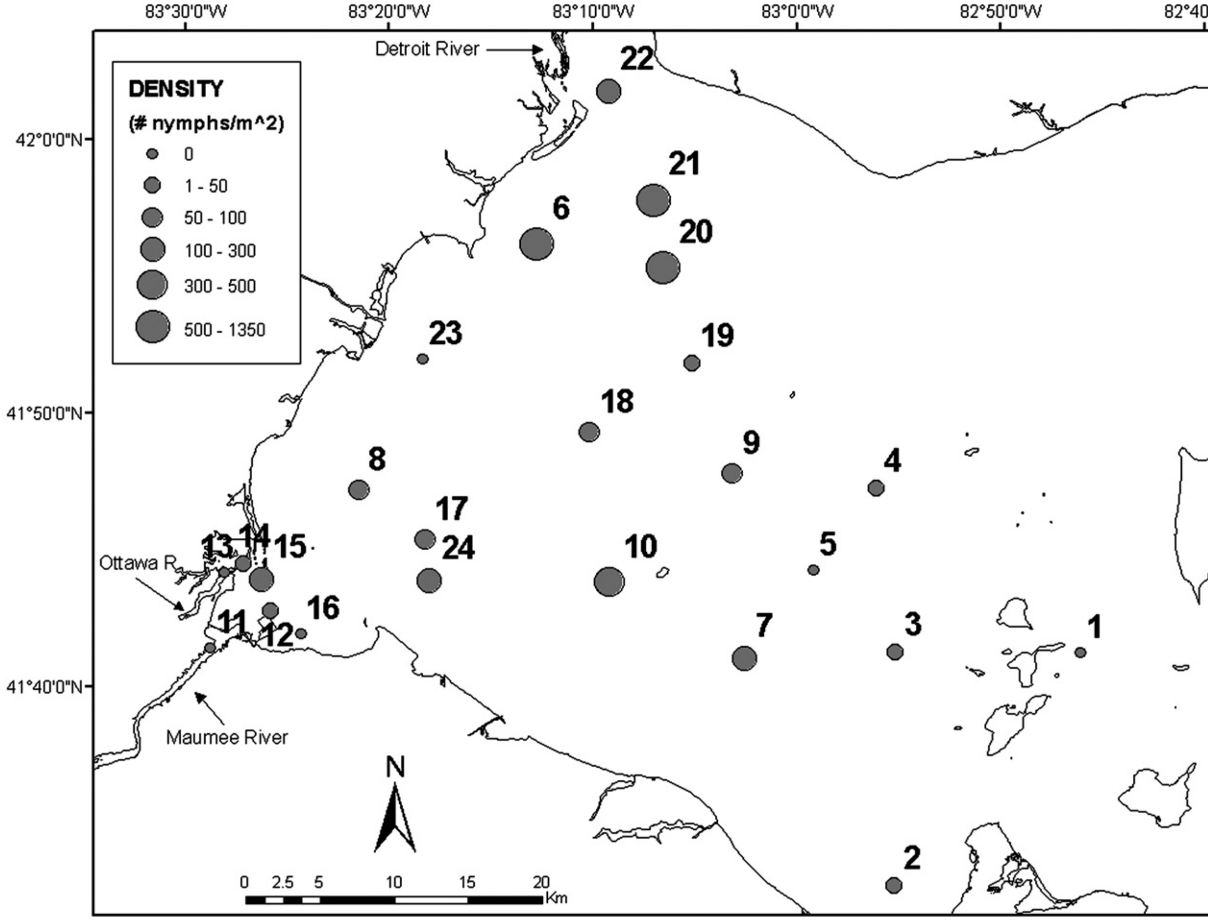

Fig. 1. Sample site locations and *Hexagenia* nymph density estimates in western Lake Erie basin (May 2007). Numeric labels indicate site numbers and dot sizes indicate nymph density estimates based on first three grabs/location (see Table 1).

Field methods

Mayfly nymphs and sediment were collected using acid-washed stainless steel Ekman and Petite Ponar grabs (approximately 0.02 m^2/grab). At three sites (sites 12, 16, and 23) a large Ponar (approximately 0.05 m^2/grab) was necessary because of hardpan and coarse sand sediment. Each grab was pulled up slowly and placed in a plastic tub to avoid washout of sediment. The center top 3 cm of sediment in the grab was collected using an acid-washed plastic spatula and placed in labeled double Ziploc® bags. Sediment samples were collected from three grabs at each site. Sediment samples were collected in June 2008 from four additional sites along the southern shore of the western basin (sites 25, 26, 27, and 28) to improve nearshore resolution in GIS interpolation maps.

Individual grab samples were then washed through an acid-washed plastic 800 μm mesh screen and collected mayfly nymphs were retrieved using a Teflon-coated forcep and transferred to Ziploc® bags. Before the first grab, equipment was acid-washed from the top down and then between grab samples, was rinsed thoroughly with lake water (USEPA, 1981). If there were no mayfly nymphs present after the third grab it was assumed that they were absent from the site (Krieger et al., 1996). Density estimates were based on the number of mayflies collected in the first three replicate grabs from each site (Krieger et al., 1996). When mayfly densities were low, additional grabs were taken in order to collect enough organisms for the metals analyses. All samples (sediments and nymphs) were placed on ice until return to the laboratory where they were frozen.

Laboratory sample processing

Preparation procedures for sediment samples followed the USEPA Method 3051A (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils) for spectrochemical determination of acid-leached elements. This leach method was used rather than a total digestion method because it is considered a better representation of the bioavailable metals content. Homogenized sediment samples were dried at 60 °C for 12 hours. Approximately 0.5 g samples were loaded into Teflon lined XP-1500 Plus™ vessels with 9 mL of trace-metals grade nitric acid (HNO_3) and 3 mL of hydrochloric acid (HCl). The microwave digestion was done using a CEM-MARS™ microwave digestion system following the USEPA Method 3051A protocol of 5.5-minute ramp to 175 ± 5 °C followed by 4.5-minute hold at temperature and air cooling back to room temperature. Digested extracts were then gravity filtered through qualitative filter paper and diluted to 50 mL with ultrapure (milli-Q) water.

The sediment solutions were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (ThermoElectron iCAP 6500). Sixteen elements were selected for analysis (Opfer, 2008); however, only the heavy metals arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) were investigated in this study. Elemental mercury (Hg) was not included in the final analyses because concentrations in all sediment samples were below instrument minimum detection limits (MDLs). The MDLs were calculated based on prepared standards and blanks. Method blanks and standard reference material (SRM 2709-San Joaquin Soil) were processed with each set of eight samples. The results were found to be within ±10% of reported leach data values (NIST, 2003). Analytical reproducibilities based on percent relative standard deviations (RSDs) were ≤1% for all metals analyzed. In addition to heavy metals content, the sediments were analyzed for total organic matter content (percent of dry weight) by ashing an aliquot of sediment in a muffle furnace at 500 °C for 3 hours (Evans et al., 1990).

In the lab, nymphs were identified to genus, enumerated, and measured for total length (tip of frontal processes to base of caudal filaments). Late instar nymphs (lengths greater than 20 mm) were separated from early instar individuals (less than 20 mm) as suggested by Beauvais et al. (1995). This allowed an assessment of the metals accumulation as a function of mayfly residence time in the sediment, provided the criterion of 20 mm length allows an accurate differentiation between instars. The two size classes of nymphs were analyzed separately per location where possible based on the amount of sample available.

Hexagenia nymphs were prepared for analysis using USEPA Method 3051 for microwave-assisted acid digestion. Whole nymphs were analyzed without the removal of ingested sediments because we were interested in the concentrations of metals in *Hexagenia* potentially available for food-chain transfer (Michaud et al., 2005). Nymphs from each location and size-class were dried in an oven at 60 °C for 12 hours (Mason et al., 2000), and were then homogenized using acid-washed glass vials and stirring rods. Approximately 40 mg dry weight of *Hexagenia* homogenate (based on amount available) was digested with 10 mL of trace-metals grade HNO_3. Microwave procedures were the same as outlined above for sediment analysis. Sample extracts were then gravity filtered through qualitative filter paper and diluted to 25 mL with ultrapure (milli-Q) water. Metal concentrations were determined using an ICP-MS (Varian v2.0) at the National Center for Water Quality Research at Heidelberg University. The minimum detection limits were 1 ppb (1 ng/g) for all metals.

Data analysis

The heavy metals data, along with mayfly abundance and sediment organic content, were entered into a Geographical Information System (GIS; ESRI®ArcMap 9.2) database to visualize trends of metal concentrations in the western Lake Erie basin. Data were interpolated using inverse distance weighting to determine gradients. All statistical analyses were performed using JMP 7 with $\alpha = 0.05$. Differences in nearshore (within 5 km) and offshore (>5 km) sites were analyzed using an ANOVA and t-test. Correlations were calculated using an ANOVA and linear regressions.

Results

Sediments

The results of multiple univariate correlation analyses indicated sediment heavy metal concentrations were always significantly correlated with each other (Table 2). Thus, locations in the western basin of Lake Erie that were high in any one metal were consistently high in all other metals investigated. When sediment metal concentrations were analyzed by site, several trends were evident. First, metal concentrations in sediments from sites around the Detroit River region and from open lake sites (see Table 1 for sites) were similar for all metals except Pb (Table 3). However, sediments from both locations had significantly greater metal concentrations when compared with sediments from the Maumee/Ottawa River region, except for Pb (Table 3, see also Opfer, 2008). Distributions of heavy metal concentrations in the sediments (e.g., GIS map of Cd, Fig. 2) exhibited a gradient of increasing concentrations toward the middle, deeper portion of the western basin. For comparison to previous studies that contrasted nearshore and offshore locations (Corkum et al., 1997; Schloesser et al., 2000; Marvin et al., 2002), our sites were designated as nearshore when ≤5 km from shore (n = 16) and offshore when >5 km from shore (n = 12). Using this designation, sediment metal concentrations obtained at offshore sites were greater than at nearshore sites for all metals (e.g., Fig. 3; Table 4).

Sediment quality guidelines have been developed to provide a measure of the potential impact of elevated chemical concentrations in sediments on organisms exposed to the sediments (Smith et al., 1996). Two of the commonly cited effect levels are the Threshold Effect Levels (TEL), which are the concentrations at which adverse effects rarely occur, and the Probable Effect Levels (PEL), which are the concentrations above which adverse effects are likely to occur (MacDonald, 1994; Buchman, 2008). Sediment metal concentrations at all sites sampled in this study exceeded the TEL for at least one of the metals analyzed (Table 3). In addition, at 12 of the 28 sites the PEL was exceeded for at least one of the metals (Table 3) and all of these sites were located in the middle deepest region of the basin (Table 1). Sediments from sites 18 and 19, located in the middle of the basin, exceeded the PEL for four of the seven heavy metals analyzed (As, Cd, Ni, and Pb), the most of any sites.

Table 2
Correlations of heavy metal concentrations in sediments from western Lake Erie basin. For all correlations $N = 28$ and $p < 0.0001$ (except As); As:Cd $p = 0.0006$, As:Cr $p = 0.0013$, As:Cu $p = 0.0003$, As:Ni $p = 0.0002$, As:Pb $p = 0.0011$, As:Zn $p = 0.001$.

	As	Cd	Cr	Cu	Ni	Pb	Zn
As	1	0.61	0.58	0.64	0.65	0.59	0.59
Cd		1	0.97	0.94	0.98	0.96	0.97
Cr			1	0.94	0.98	0.96	0.97
Cu				1	0.94	0.95	0.96
Ni					1	0.97	0.96
Pb						1	0.98

Table 3
Heavy metals concentrations in sediments from western Lake Erie basin. Threshold Effect Level (TEL) and Probable Effect Level (PEL) values are noted. Values that exceed TEL are in italics and values that exceed PEL are in bold. Percent organic matter (% OM) is also noted.

	As µg/g	Cd µg/g	Cr µg/g	Cu µg/g	Ni µg/g	Pb µg/g	Zn µg/g	% OM
TEL	5.9	0.596	37.3	35.7	18	35	123.1	
PEL	17	3.53	90	197	35.9	91.3	315	
Site 1	*10.79*	**3.97**	*76.15*	*36.39*	**44.12**	**104.13**	*173.03*	9.32
2	*7.27*	*1.76*	25.03	9.23	12.83	33.39	55.97	2.62
3	*12.64*	**4.00**	*75.06*	*39.52*	**41.81**	**108.90**	*171.93*	10.84
4	*10.24*	**3.67**	*68.34*	*36.62*	**38.05**	**97.69**	*162.03*	9.42
5	*12.89*	**4.50**	*85.09*	*45.89*	**50.18**	**124.50**	*204.57*	8.85
6	*13.87*	*2.80*	*49.96*	32.18	*22.29*	*72.94*	*130.50*	5.31
7	*16.15*	**4.00**	*71.83*	*38.61*	**45.00**	**112.20**	*177.90*	10.13
8	*10.81*	*3.39*	*56.20*	29.71	*34.72*	**91.82**	*133.33*	8.83
9	*13.44*	**3.76**	*68.52*	34.70	**42.14**	**110.44**	*175.43*	10.15
10	*15.90*	**4.16**	*73.95*	*37.85*	**47.80**	**120.57**	*190.83*	11.47
11	*9.49*	*2.78*	*42.75*	27.33	*27.22*	*77.98*	*126.30*	13.11
12	5.72	*1.54*	19.76	10.52	10.37	*46.57*	81.68	3.46
13	*12.39*	*2.91*	*45.95*	*36.59*	*30.72*	**103.72**	*149.20*	9.34
14	*7.24*	*1.81*	28.82	19.52	16.87	**60.68**	79.49	6.21
15	4.75	*1.12*	15.93	9.67	7.79	30.18	41.74	3.86
16	4.55	*1.11*	14.47	7.25	8.48	27.70	40.22	2.59
17	*13.90*	*3.43*	*40.84*	30.29	*31.77*	*78.21*	*127.63*	8.57
18	**19.35**	**4.30**	*69.37*	*43.23*	**48.80**	**118.20**	*206.10*	7.47
19	**20.83**	**4.43**	*87.08*	*50.00*	**53.14**	**133.90**	*216.80*	8.21
20	*14.56*	*3.31*	*55.05*	34.40	*32.55*	**95.56**	*151.67*	7.39
21	*12.13*	*3.16*	*47.83*	32.73	*29.10*	*80.24*	*137.13*	7.09
22	*8.06*	*2.60*	36.04	26.96	15.95	*55.50*	119.40	4.19
23	5.61	*0.99*	13.79	5.78	7.59	21.82	54.22	1.38
24	*11.15*	*2.78*	35.29	21.98	*24.25*	*69.06*	106.33	6.79
25	*13.40*	*2.44*	33.90	31.64	*24.28*	*49.68*	87.18	6.14
26	*16.70*	*1.09*	9.37	7.34	7.87	16.04	22.85	3.78
27	*13.60*	0.56	5.87	1.52	4.81	7.82	15.67	0.88
28	*10.50*	*3.17*	*46.20*	26.87	*31.51*	*63.29*	117.30	7.59

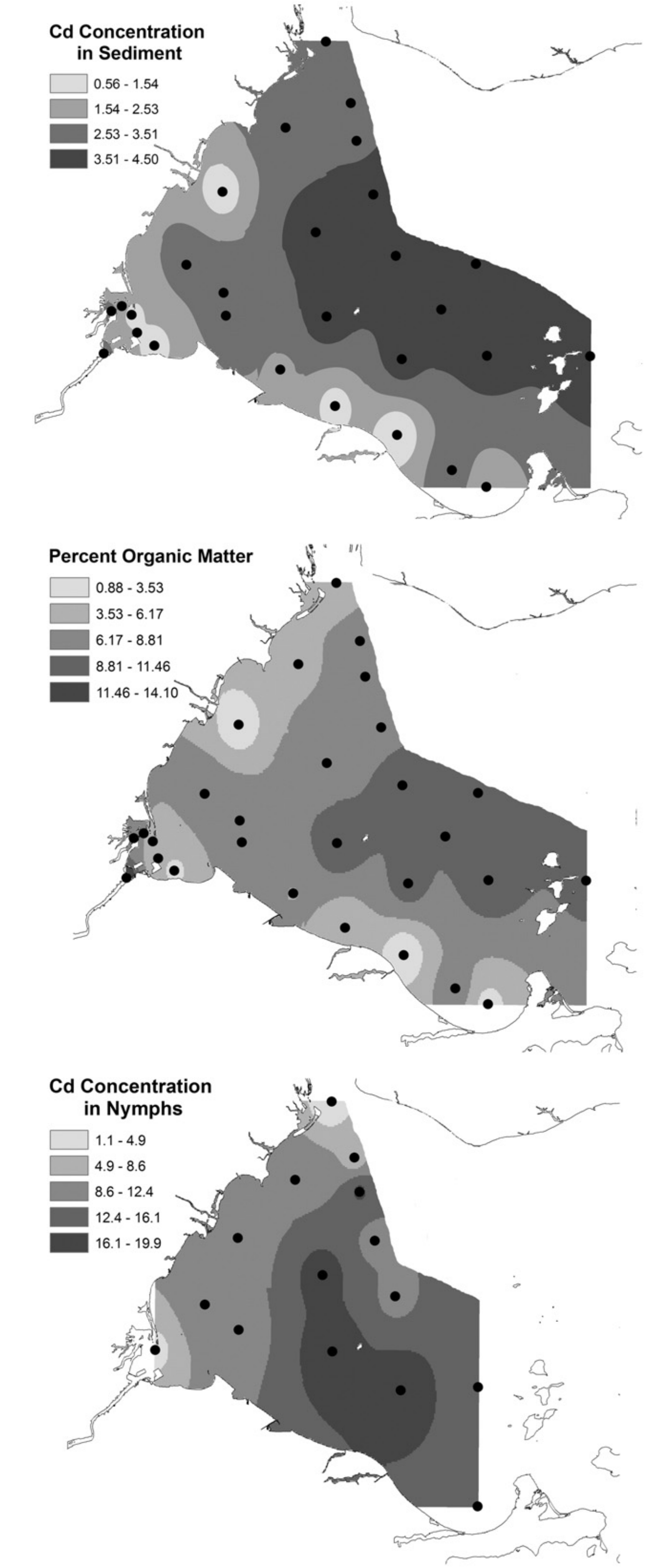

Fig. 2. Trends in Cd concentration and percent organic matter in sediments and Cd concentration in *Hexagenia* nymphs from western Lake Erie basin. Cd concentrations in μg/g dry wt. U.S. region interpolated using ArcGIS inverse distance weighting with dots indicating sample sites. For reference, sediment Cd Threshold Effect Level (TEL) is 0.596 μg/g and Probable Effect Level (PEL) is 3.53 μg/g. Note that there is limited accuracy in nymph interpolation along southern shore due to limited data points in that region.

The results of the sediment composition analysis indicate the sediment metal concentrations are correlated with the percent organic matter (Fig. 3). The results of this study also indicate that percent organic matter in the lake sediments differed by location. Specifically, offshore sites had a significantly higher percent organic matter than nearshore sites (Fig. 2) with highest organic contents occurring in the deepest region of the basin.

Hexagenia

Of the 24 sites sampled for mayflies, 18 (75%) had nymphs present (Fig. 1, Table 1) and the highest densities occurred near the mouth of the Detroit River. When compared to the 1998 density estimates reported by Schloesser et al. (2000) at eight sites where both groups sampled, our estimates were higher near the Detroit River (sites 6 and 22) and at site 7, but lower at the five other sites (sites 1, 2, 8, 12, and 24; Table 1).

Large (≥ 20 mm) and small (< 20 mm) nymphs were analyzed separately at locations where possible ($n = 3$; sites 6, 7, and 10) to determine if there was a difference in metal concentrations according to presumed nymph residency time in the sediment. These size classes also served as replicate subsamples to determine an estimate of within-site variability. The mass of dried composite samples of mayflies was too small for analysis of replicates at other sites. The results from these three sites indicate there was no significant difference (t-test, $p = 0.5343$) between the two size classes for mayfly metal concentrations and there was no significant within-site variability. In addition, the results do not indicate a bimodal length distribution of mayflies as expected based on Beauvais et al. (1995) and their 20 mm designation separating age 1 from age 2 mayfly nymphs. Therefore, nymphs from other sites were analyzed together without regard to their size.

Enough dried mayfly homogenate (40 mg) was obtained for analysis of metals in mayflies from fifteen sample sites (Table 5). The Cd and Zn concentrations in mayflies were approximately 4 and 2 times greater, respectively, than sediment levels. All other mayfly heavy metal concentrations were near to or below sediment metal concentrations. The As, Cd, Cr, and Ni concentrations in mayflies were significantly correlated to sediment heavy metal concentrations (regression analyses, Fig. 3; Table 6) and organic content. Lastly, spatial representation of metal concentrations in mayflies exhibited similar patterns to the spatial distribution of heavy metals and organic content in the sediments (Fig. 2), with higher concentrations of metals in mayflies residing in the deeper middle region of the western basin.

Discussion

Sediments

Metal concentrations in sediments exceeded effect levels at all of our sample sites across the western Lake Erie basin. The highest sediment metal concentrations were at sites located in the middle of the basin and are positively correlated to the organic matter content in the sediments, consistent with work done by Singh et al. (1999) who found organic matter and metal concentrations in river sediments were correlated. The higher organic content in sediments in the middle of the western Lake Erie basin is due to particulate organic matter transport and settlement in the deepest region of the basin.

The previously reported distribution of organic contaminants, most notably PCB, in sediments from the western Lake Erie basin shows a similar trend to the metals reported in this study. The PCB concentrations in sediments from the western Lake Erie basin are found to be highest in nearshore areas along the western shoreline reflecting point sources in that area, particularly associated with the River Raisin near Monroe, MI, but high PCB concentrations are also found in the middle of the basin (see Fig. 4 of Marvin et al., 2002). Similarly, empirically derived PCB contaminant contours of adult

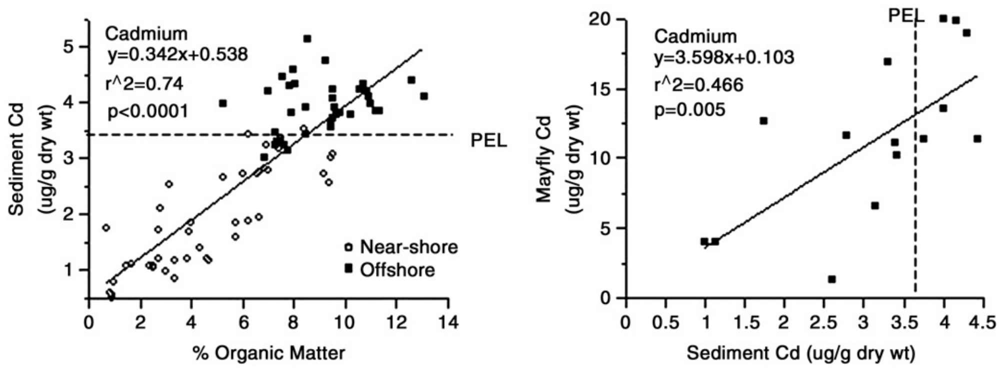

Fig. 3. Correlations of Cd concentrations in sediments to percent organic matter ($N = 84$) and to Cd concentrations in *Hexagenia* nymphs ($N = 15$) from western Lake Erie basin. Black squares indicate offshore samples (>5 km) and open circles indicate nearshore samples (≤5 km).

Hexagenia body burdens (see Fig. 3 of Corkum et al., 1997) reflect high contaminant concentrations near point sources along the western shoreline (e.g., River Raisin) and across the central portion of the basin. Corkum et al. (1997) suggested the elevated PCB concentrations found at Middle Sister and East Sister Islands may reflect the general west-to-east transport of sediment/contaminants from the western shoreline point sources across the basin, which is consistent with our metals results.

Both the Maumee and Detroit Rivers, which discharge into the western basin of Lake Erie, are listed as Areas of Concern through the USEPA (2001). The Maumee River is contaminated through agricultural nonpoint source pollution, contaminated industrial sites, combined sewer overflows, and disposal of dredged materials (Maumee RAP, 2006). The Detroit River impairments include runoff and discharges from urban and industrial development in the watershed, bacteria, PCBs, PAHs, metals, and oils and greases (USEPA, 2001). Results of prior research indicate sediments in the lower end of the Detroit River are heavily contaminated with metals, especially Cd (Nichols et al., 1991). In addition, Nichols et al. (1991) reported substantial contamination was found up to 60 km from any known point source of pollution. Also, Cd concentrations in sediments from the Detroit River reported by Szalinska et al. (2006) ranged from ~0.6 to ~8 μg/g dry weight, similar to the values obtained for the lake sediments analyzed in this study.

Hexagenia

As noted above, the density of mayfly nymphs collected in this study varied significantly from the densities at the same sites in the 1998 survey reported by Schloesser et al. (2000). This variation in mayfly density may simply reflect year-to-year variation in recruitment as suggested by Bridgeman et al. (2006). However, regardless of specific differences in density estimates, both studies show the same general trend of lower mayfly densities in the middle of the basin with higher densities in nearshore areas. Sample sites where Cd levels in the sediments exceeded PEL (middle of basin) had, in general, lower mayfly densities. As such, it is tempting to suggest the lower mayfly densities could be a result of the high sediment heavy metal contamination. However, other factors not investigated in this study such as mayfly life history characteristics (e.g., need to reach land to undergo last molt, mating in swarms usually at the land-water interface, limited flight capacity, physiological responses, etc) and hypoxic conditions at the water/sediment interface would also tend to result in higher mayfly densities in nearshore versus offshore locations. *Hexagenia* nymphs cannot survive more than 24 hours at dissolved oxygen (DO) concentrations below about 1 mg/L (Eriksen, 1963), and previous studies have shown that DO concentrations reach<2 mg/L at some locations in the western basin in late summer (Krieger et al., 1996).

The mayfly nymphs collected in this study showed a range of sizes rather than a bimodal distribution as suggested by Beauvais et al. (1995). This variation in sizes could be expected, based on analysis by Corkum and Hanes (1992), who suggested that a range in mayfly nymph lengths is attributable to a wide range of hatching times and nutrient availability, and hence larval size may not be a good indicator of larval age. Furthermore, Bartsch et al. (1999) and Michaud et al. (2005) demonstrated that nymphs accumulate a substantial amount of Cd within only a few weeks residence time in sediments. Therefore, the metal contents in the nymphs analyzed in this study are correlated to the metal contents available in the sediments and do not reflect residency time.

Cadmium levels in nymphs from this study were on average 4 times greater (1.18 to 19.89 μg/g dry weight) than sediment levels (0.56 to 4.50 μg/g dry weight) (see Tables 3 and 5, Fig. 2). Bartsch et al. (1999) showed burrowing *Heaxagenia* nymphs held in Cd-spiked (1 to 15 μg/g) Mississippi River sediments accumulated Cd to approximately

Table 4
Correlations of heavy metal concentrations to percent organic matter in sediments from western Lake Erie basin.

Element	Relationship	r^2	P
As	$y = 0.698x + 7.122$	0.22	<0.0001
Cd	$y = 0.342x + 0.538$	0.74	<0.0001
Cr	$y = 6.782x + 0.754$	0.67	<0.0001
Cu	$y = 3.781x + 1.793$	0.66	<0.0001
Ni	$y = 4.306x - 0.663$	0.72	<0.0001
Pb	$y = 10.443x + 4.750$	0.73	<0.0001
Zn	$y = 16.115x + 14.842$	0.68	<0.0001

Table 5
Heavy metal concentrations in *Hexagenia* nymphs from western Lake Erie basin. Concentrations in μg/g dry wt. Sites 6, 7, 10 had two replicates, all others had one. Minimum Detection Limits are 1 ppb (1 ng/g) and Relative Standard Deviation ≤ 1%.

Site	As, μg/g	Cd, μg/g	Cr, μg/g	Cu, μg/g	Ni, μg/g	Pb, μg/g	Zn, μg/g
2	2.23	12.47	14.86	19.73	12.76	12.53	194.33
3	2.82	13.47	11.71	28.93	8.95	8.97	269.70
6	2.19	11.49	19.93	26.87	13.42	21.14	303.60
7	2.06	19.89	22.70	26.27	17.33	24.44	299.37
8	1.85	10.94	17.99	23.48	16.73	9.01	185.29
9	1.99	11.21	10.35	15.89	8.38	9.87	201.86
10	2.57	19.68	26.03	28.59	20.56	29.27	340.56
15	1.95	3.87	9.53	13.74	7.92	7.44	136.00
17	1.95	10.03	14.48	20.93	12.61	11.59	151.21
18	2.18	18.89	24.45	26.50	17.43	27.88	215.58
19	2.46	11.23	23.01	25.50	15.69	22.91	194.33
20	2.11	16.75	24.32	32.86	16.94	27.02	276.79
21	2.07	6.41	20.92	25.07	15.65	23.88	199.54
22	2.04	1.18	12.34	23.17	10.51	10.51	228.64
23	1.13	10.58	9.79	33.69	8.01	20.98	316.01

Table 6
Correlations of heavy metal concentrations in *Hexagenia* nymphs and sediments from western Lake Erie basin. The four correlations that had significant slopes are presented. $N = 15$, Relative Standard Deviation ≤ 1%.

Element	Relationship	r^2	P
As	$y = 0.041x + 1.584$	0.27	0.0470
Cd	$y = 3.598x + 0.103$	0.47	0.005
Cr	$y = 0.158x + 9.211$	0.36	0.0179
Ni	$y = 0.158 + 8.555$	0.35	0.0198

half the concentration present in the sediments in 21 days, and the accumulation of Cd in the nymphs was linearly correlated to the Cd concentrations in the spiked sediments. In addition, Beauvais et al. (1995) reported nymphs living in non-spiked Mississippi River sediments had an increased accumulation factor (~0.8) with increased Cd concentrations in the sediments (maximum of 3.2 μg/g dry weight). The Cd accumulation factor reported by Beauvais et al. (1995) is lower than the accumulation factor reported in this study; however, after removing nymphs from the sediment, Beauvais et al. (1995) held the nymphs in river water until return to the laboratory, providing the possibility of some gut evacuation. Hence, trophic transfer of Cd in mayflies may increase with increased sediment concentration because the Cd is in the sediment in the gut of the mayfly as well as in the gut tissue (Hare et al., 1989; Cain et al., 2004). Michaud et al. (2005) concluded that Cd in the mayfly's gut was largely associated with heat-stable proteins such as the metal-binding protein metallothionein (in the cytosol), and these proteins, and thus associated metals, are readily available to consumers (i.e., fish) who assimilate metals from the cytosolic fraction of their food. Hence, the accumulation of Cd in the mayflies in the western basin of Lake Erie is of particular concern due to the high Cd levels found in the sediments, which exceeded the TEL at 27 of 28 sites and the PEL at 9 of 28 sites, and due to the potential for ready transfer to consumers.

As noted above, because we were concerned with the bioavailability and trophic transfer of metals through mayflies, we included their gut contents in the analysis. Therefore, the results of this study are more accurately described as measuring metals accumulation in mayfly nymphs rather than actual bioaccumulation of metals in the mayfly's tissues. Our data indicate mayflies accumulate both cadmium and zinc to a greater degree than the other metals analyzed, with Cu content in the mayflies about equal to the concentration in the sediments. These results are consistent with the results of Cain et al. (2004) who reported accumulations of Cd, Cu, and Zn in the mayflies from mining-impacted river sediments. The apparent greater accumulation of Cd in the mayflies in this study may be attributed to mayfly physiological response. Cain et al. (2004) suggested that the saturation of metal-binding proteins in mayflies in chronically contaminated sediments allows for "spillover," in which there is a higher rate of binding to non-metal-binding proteins. As such, the greater relative accumulation of Cd in the mayflies in our study reflects the relatively high Cd concentrations in the sediments.

The impact of mayflies on Cd transfer in the western basin of Lake Erie can be considered in two ways: by the potential total amount of Cd transferred by mayflies, and by the potential Cd uptake from mayfly consumption in fish. The potential total amount of Cd transferred by mayflies can be estimated from the number of mayflies that emerge each year. While mayfly densities vary substantially year to year, Krieger et al. (2007) reported a mean density for the western Lake Erie basin of 195 nymphs/m^2 in 2004. Given the area of the western basin is 3080 km^2 (Mortimer, 1987), we can estimate the number of mayflies in 2004 as approximately 6×10^{11} nymphs. Based on the average Cd concentration of 11.08 μg/g dry weight and average dry weight of 5.132 mg for the nymphs collected in this study, the total amount of Cd that could be transferred by mayflies is on the order of 34 kg per year. Clearly this value should be viewed with caution and makes no pretence as to where the Cd transferred by the mayflies ends up, as indeed much of the Cd is likely to be recycled back into the sediments.

A more meaningful consideration is how much Cd may be accumulated from mayfly consumption in a popular sport and commercial fish like the yellow perch. We can estimate this by using yellow perch diet information reported by Tyson and Knight (2001) who estimated the *annual* percentage of mayflies in yellow perch diets in 1997 was 20% (dry weight *Hexagenia* to dry weight of fish). They also reported the estimated average daily consumption for adult yellow perch from primary sites in the western Lake Erie basin for 1996 was 2.72% of body weight. Then the annual consumption of mayflies can be calculated as 20% of 2.72% per day for 365 days, or approximately 200% of the perch's body weight per year. Therefore, for an average Cd concentration of 11.08 μg/g dry weight of mayflies (from this study), the average annual uptake of Cd by adult yellow perch from mayfly consumption would be ~22 μg/g of the fish's body weight. Again, this calculation must be viewed with caution, as it involves basin-wide averages for mayfly densities that would vary year to year both in average value and in distribution with respect to different sediment Cd contents in the basin. Likewise, the estimates of mayfly consumption and average daily food consumption would vary year to year. In addition, the mayfly consumption will vary greatly seasonally with yellow perch diets consisting of ~75% mayflies during their peak emergence (Bur et al., 2005).

In their study of metals accumulation and metals-induced effects on indigenous yellow perch (*Perca flavescens*) collected from eight lakes in an active mining area, Campbell et al. (2003) showed food is the primary source for Cd accumulation in the yellow perch. Hence, Cd accumulation in yellow perch in the western basin of Lake Erie due to consumption of mayflies may lead to metal toxicity effects and should be investigated further.

Evaluating the impact of mayflies on heavy metals transfer in the western Lake Erie basin ecosystem must also include consideration of their role in bioturbation. In addition to accumulation of Cd in the mayflies, Bartsch et al. (1999) noted Cd concentrations in the overlying waters also increased significantly. They interpreted this increase in Cd to be due to mobilization of sediment-associated Cd through burrowing and respiration activities of the mayflies. Bioturbation is an important factor in physical and chemical processes at the water-sediment interface including the availability of sediment-associated metals. Bioturbation can increase both the amount of sediment-associated metal in the water and also its bioavailability. For example, Ankley et al. (1996) showed bioturbation can cause oxidation of acid volatile sulfide, thereby altering the partitioning of sediment-associated metals like Cd and enhancing their bioavailability. In addition, Marvin et al. (2007) noted that suspended sediments in the western Lake Erie basin were largely resuspended bottom sediments; hence, through bioturbation, mayfly nymphs may increase resuspended toxic contaminants (Bartsch et al., 1999; Bachteram et al., 2005), which increases Cd exposure for other aquatic organisms in the water column, including fish that may then take in Cd even without direct ingestion of mayflies. Based on the high Cd levels found in sediments in this study, the effect of mayflies on bioturbation is also of concern.

Conclusions

The Ohio Lake Erie Commission's most recent Lake Erie Quality Index assessment for contaminated sediments yielded a rating of "Poor" (OLEC, 2004). Remediation projects have focused on point source pollution of the major contributing rivers (OLEC, 2006). However, our results and those of Nichols et al. (1991) suggest heavy metals sediment contamination may be found far from a known pollution point source. Metal concentrations in sediments from the western Lake Erie basin exceeded TEL for at least one of the metals analyzed for all of the sampled sites and PEL for at least one of the metals at 9 of the 28 sampled sites. The highest sediment metal concentrations were at sites located in the deeper middle region of the basin, which also contained the greatest organic content.

Toxic metals in sediments are of great concern due to their potential to be transferred up the food chain. The results of this study suggest that mayflies may play an important role in the trophic-transfer of metals, especially cadmium and zinc, which had concentrations 4 and 2 times greater, respectively, in the mayflies than in the sediments. In addition, Marvin et al. (2007) noted that suspended sediments in the western Lake Erie basin were largely resuspended bottom sediments; hence, mayfly nymphs are potentially increasing resuspended toxic contaminants due to bioturbation (Bartsch et al., 1999; Bachteram et al., 2005), which may increase Cd exposure for other aquatic organisms in the water column, including fish, even without direct ingestion of mayfly nymphs.

Acknowledgments

This project was funded through a grant from the Ohio Lake Erie Protection Fund (LEPF 318-07) with additional funding provided from Ohio Sea Grant (R/LR-8) and the BGSU Summer Research Fund. This manuscript benefitted from reviews by Michael Gilek and an anonymous reviewer. We would like to thank the editor, Marlene Evans, and the associate editors, Christine Mayer and Ken Drouillard, for their insightful comments and help in processing this manuscript. Equipment was provided by BGSU, Ohio State Stone Laboratory, and the Ohio EPA. We especially thank Matt Thomas, Chris Winslow, and Betsy Hall for their help with sample collection.

References

Ankley, G.T., Leonard, E.N., Peterson, G.S., 1996. Effect of bioturbation on metal-sulfide oxidation in surficial freshwater sediments. Environ. Toxicol. Chem. 15, 2147.

Bachteram, A., Mazurek, K., Ciborowski, J.J.H., 2005. Sediment suspension by burrowing mayflies (*Hexagenia* spp., Ephemeroptera: Ephemeridae). J. Great Lakes Res. 31, 208–222.

Bartsch, M.R., Cope, W.G., Rada, R.G., 1999. Effects of cadmium-spiked sediment on cadmium accumulation and bioturbation by nymphs of the burrowing mayfly *Hexagenia bilineata*. Water Air Soil Pollut. 109, 277–292.

Beauvais, S.L., Wiener, J.G., Atchison, G.J., 1995. Cadmium and mercury in sediment and burrowing mayfly nymphs (*Hexagenia*) in the Upper Mississippi River, USA. Arch. Environ. Contam. Toxicol. 28, 178–183.

Bridgeman, T.B., Schloesser, D.W., Krause, A.E., 2006. Recruitment of *Hexagenia* mayfly nymphs in western Lake Erie linked to environmental variability. Ecol. Appl. 16, 601–611.

Brittain, J., 1982. Biology of mayflies. Annu. Rev. Entomol. 27, 119–147.

Buchman, M.F., 2008. NOAA Screening Quick Reference Tables, NOAA OR&R Report 08-1, Seattle, WA, Office of Response and Restoration Division, National Oceanic and Atmospheric Administration, 34pp.

Bur, M.T., Stapanian, M.A., Kocovsky, P.M., Galbreth, S.J., Cznarnecki, A.M., 2005. Surveillance and status of fish stocks in western Lake Erie, 2004. USGS Great Lakes Science Center, Lake Erie Biological Station, Sandusky, OH. 13pp.

Cain, D.J., Luoma, S.N., Wallace, W.G., 2004. Linking metal bioaccumulation of aquatic insects to their distribution patterns in a mining-impacted river. Environ. Toxicol. Chem. 23, 1463–1473.

Campbell, P.G.C., Hontela, A., Rasmussen, J.B., Giguere, A., Gravel, A., Kraemer, L., Kovesces, J., Lacroix, A., Levesque, H., Sherwood, G., 2003. Differentiating between direct (physiological) and food-chain mediated (bioenergetic) effects on fish in metal-impacted lakes. Hum. Ecol. Risk Assess. 9, 847–866.

Corkum, L., Hanes, E., 1992. Effects of temperature and photoperiod on larval size and survivorship of a burrowing mayfly (Ephemeroptera: Ephemeridae). Can. J. Zool. 70, 256–263.

Corkum, L., Ciborowski, J.H., Lazar, R., 1997. The distribution and contaminant burdens of adults of the burrowing mayfly, *Hexagenia*, in Lake Erie. J. Great Lakes Res. 23, 383–390.

Edsall, T.A., Haas, R.C., Adams, J.V., 2001. Annual production of burrowing mayfly nymphs (*Hexagenia* spp.) in U.S. waters of Lake St. Clair. J. Great Lakes Res. 27, 449–456.

Eriksen, C.H., 1963. Respiratory regulation in *Ephemera simulans* Walker and *Hexagenia limbata* (Serville) (Ephemeroptera). J. Exper. Biol. 40, 455–467.

Evans, K.M., Gill, R.A., Robotham, P.W.J., 1990. The PAH and organic content of sediment particle size fractions. Water Air Soil Pollut. 51, 13–31.

French, J.R.P., Jude, D.J., 2001. Diets and diet overlap of nonindigenous gobies and small benthic native fishes co-inhabiting the St. Clair River, Michigan. J. Great Lakes Res. 27, 300–311.

Gewurtz, S.B., Lazar, R., Haffner, G.D., 2000. Comparison of polycyclic aromatic hydrocarbon and polychlorinated biphenyl dynamics in benthic invertebrates of Lake Erie. USA. Environ. Toxicol. Chem. 19, 2943–2950.

Goodyear, K.L., McNeill, S., 1999. Bioaccumulation of heavy metals by aquatic macroinvertebrates of different feeding guilds: a review. Sci. Total Environ. 229, 1–19.

Hare, L., Campbell, P.G.C., Tessier, A., Belzile, N., 1989. Gut sediments in a burrowing mayfly (Ephemeroptera, *Hexagenia limbata*): Their contribution to animal trace element burdens, their removal, and efficacy of a correction for their presence. Can. J. Fish. Aquat. Sci. 46, 451–456.

Krieger, K., 1999. Final report, Lake Erie Protection Fund Project LEPF-08–94; Ecosystem change in western Lake Erie: cause and effect of burrowing mayfly recolonization. 13pp.

Krieger, K., Schloesser, D.W., Manny, B.A., Trisler, C.E., Heady, S.E., Ciborowski, J.H., Muth, K.M., 1996. Recovery of burrowing mayflies (Ephemeroptera: Ephemeridae: *Hexagenia*) in western Lake Erie. J. Great Lakes Res. 22, 254–263.

Krieger, K.A., Bur, M.T., Ciborowski, J.J.H., Barton, D.R., Schloesser, D.W., 2007. Distribution and abundance of burrowing mayflies (*Hexagenia* spp.) in Lake Erie, 1997-2005. J. Great Lakes Res. 33 (Supplement 1), 20–33.

MacDonald, D.D., 1994. Approach to the assessment of sediment quality of Florida coastal waters. Volume 1 – Development and evaluation of sediment quality assessment guidelines. Report prepared for the Florida Department of Environmental Protection, Tallahassee, FL. November 1994.

Marvin, C.H., Charlton, M.N., Reiner, E.J., Kolic, T., MacPherson, K., Stern, G., Braekevelt, E., Estenik, J.F., Thiessen, L., Painter, S., 2002. Surficial sediment contamination in Lakes Erie and Ontario: a comparative analysis. J. Great Lakes Res. 28, 437–450.

Marvin, C., Charlton, M., Milne, J., Thiessen, L., Schachtschneider, J., Sardella, G., Sverko, E., 2007. Metals associated with suspended sediments in Lakes Erie and Ontario, 2000-2002. Environ. Monit. Assess. 130, 149–161.

Mason, R.P., Laporte, J.M., Andres, S., 2000. Factors controlling the bioaccumulation of mercury, methylmercury, arsenic, selenium, and cadmium by freshwater invertebrates and fish. Arch. Environ. Contam. Toxicol. 38, 283–297.

Maumee RAP (Remedial Action Plan), 2006. Maumee area of concern stage 2 restoration plan. Toledo, OH. 232pp.

Michaud, A.L., Hare, L., Campbell, P.G.C., 2005. Exchange rates of cadmium between a burrowing mayfly and its surroundings in nature. Limnol. Oceanogr. 50, 1707–1717.

Mortimer, C.H., 1987. Fifty years of physical investigations and related limnological studies on Lake Erie, 1928-1977. J. Great Lakes Res. 13, 407–435.

Nichols, S.J., Manny, B.A., Schloesser, D.W., Edsall, T.A., 1991. Heavy metal contamination of sediments in the upper connecting channels of the Great Lakes. Hydrobiologia 219, 307–315.

NIST (National Institute of Standards and Technology), 2003. Addendum (leach data) to Certificate of Analysis for Soil Standard Reference Material 2709 San Joaquin Soil. 6 pp.

Nordin, D. 2006. Burrowing mayflies: a possible source of phosphorus loading. Twineline:16.

OLEC (Ohio Lake Erie Commission), 2004. State of Ohio 2004 state of the lake report: Lake Erie Quality Index. Ohio Lake Erie Office, Toledo, OH. 84pp.

OLEC (Ohio Lake Erie Commission), 2006. Lake Erie protection and restoration plan; third progress report. Ohio Lake Erie Office, Toledo, OH. 95pp.

Opfer, S.E., 2008. Heavy Metal Uptake by Burrowing Mayflies in Western Lake Erie. M. Sc. thesis, Bowling Green State University, Bowling Green, OH.

Painter, S., Marvin, C., Rosa, F., Reynoldson, T.B., Charlton, M.N., Fox, M., Thiessen, P.A.L., Estenik, J.F., 2001. Sediment contamination in Lake Erie: a 25-year retrospective analysis. J. Great Lakes Res. 27, 434–448.

Schloesser, D.W., Krieger, K.A., Ciborowski, J.J.H., Corkum, L.D., 2000. Recolonization and possible recovery of burrowing mayflies (Ephemeroptera: Ephemeridae: *Hexagenia* spp.) in Lake Erie of the Laurentian Great Lakes. J. Aquat. Ecosyst. Stress Recovery 8, 125–141.

Singh, A.K., Hasnain, S.I., Banerjee, D.K., 1999. Grain size and geochemical partitioning of heavy metals in sediments of the Damodar River—a tributary of the lower Ganga, India. Environ. Geol. 39, 90–98.

Smith, S.L., MacDonald, D.D., Keenleyside, K.A., Ingersoll, C.G., Field, L.J., 1996. A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. J. Great Lakes Res. 22, 624–638.

Szalinska, E., Drouillard, K.G., Fryer, B., Haffner, G.D., 2006. Distribution of heavy metals in sediments of the Detroit River. J. Great Lakes Res. 32, 442–454.

Tyson, J.T., Knight, R.L., 2001. Response of yellow perch to changes in the benthic invertebrate community of western Lake Erie. Trans. Am. Fish. Soc. 130, 766–782.

USEPA (United States Environmental Protection Agency), 1981. Procedures for handling and chemical analysis of sediment and water samples. Environmental Laboratory, US. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi. 118pp.

USEPA (United States Environmental Protection Agency), 2001. Detroit River remedial action plan update report. Water Division, SE Michigan Field Office, Grosse Ile, MI. 157pp.