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Case Study

Assessment of the Ecological Effects of Arsenic on a Southern Ohio, USA Stream

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ABSTRACT

Davis Creek is a southern Ohio, USA stream that receives a permitted discharge from the Belpre Elastomers Plant (BEP). A sediment quality triad investigation of Davis Creek was conducted over a 2-y period that included sediment and surface water chemistry measurements, toxicity tests of whole sediment, interstitial and surface water, and benthic and artificial substrate community assessments. The concentration of arsenic in surface and interstitial water was below United States Environmental Protection Agency ambient water quality criteria and was not toxic in laboratory tests (*Ceriodaphnia dubia*, *Pimephales promelas*). Similarly, sediments did not significantly affect survival and growth of *Hyalella azteca* and *Chironomus tentans* at most sampling locations despite sediments exceeding arsenic sediment screening values in nearly all samples collected. Differences in benthic community structure, determined by rapid bioassessment and Hester–Dendy sampling methods, were related primarily by variations in sediment moisture, particle size, and ammonia and not to arsenic concentrations. The Invertebrate Community Index (ICI) for Davis Creek was lower than values established for other warm-water ecoregional reference streams in Ohio. However, this ICI comparison may have been invalid because, unlike the reference streams, the Davis Creek watershed is small with intermittent headwater flow that limits macroinvertebrate recruitment and energy input. The sediment quality triad investigation indicated that Davis Creek was not significantly affected by arsenic associated with the BEP discharge despite having measured arsenic concentrations that exceeded sediment screening values.

Keywords: Arsenic Sediment Toxicity Benthic community

INTRODUCTION

Arsenic is a metalloid that naturally occurs in rocks, soils, water, sediments, and biological tissues in concentrations ranging from parts per billion to parts per million (API 1998; Eisler 2000). Although arsenic is considered ubiquitous in nature, anthropogenic activities such as copper smelting and coal combustion can result in associated increased concentrations in surface water, soil, and sediment, often exceeding acute and chronic ambient water quality criteria (USEPA 1985) or sediment and soil benchmarks (Smith et al. 1996). Exceeding these criteria or benchmarks can lead to a conclusion that organisms are affected, either directly through toxicity or on the basis of changes in community structure characteristics. Ecological effects are not always associated with exceedances of criteria, particularly if factors influencing bioavailability (e.g., water hardness, sediment particle size, organic matter content, oxidation reduction potential, and so on) are not taken into consideration. Therefore, a finding that the concentration of arsenic exceeds a medium-specific criterion or benchmark value should be used only as an initial screen to indicate a potential for biological effects. Direct measurements of toxicity and community structure characteristics should be made to assess whether biological effects are manifested.

This investigation assessed the biological effects of arsenic in surface water and sediments in Davis Creek, a small stream receiving a National Pollution Discharge Elimination System (NPDES) permitted discharge from the Belpre Elastomers Plant (BEP) near Belpre, Ohio, USA. The BEP is a thermoplastic elastomer manufacturing facility that had released arsenic in their effluent in excess of NPDES limits, thus prompting this investigation. Davis Creek is a tributary of the Ohio River, consisting of small channels, beaver pond remnants, riparian vegetation, and wetland habitats. The lower 1.29 km of Davis Creek is bordered on the east by the BEP and receives the permitted discharge from the facility. Under low-rainfall periods, the BEP discharge makes up the entire flow of Davis Creek. As a consequence of the controlled discharge, permitted concentrations of arsenic have been released into Davis Creek.

Previous investigations of Davis Creek indicated that concentrations of arsenic ranged from approximately 12 to 150 µg/L in surface water and 5 to 38 mg/kg in sediments. Surface water concentrations were below the acute and chronic ambient water quality criteria of 360 and 190 µg/L, respectively (USEPA 1985). Most measurements of total arsenic concentrations in sediments exceeded the threshold effects level (TEL) of 5.9 mg/kg and probable effects level (PEL) of 17 mg/kg (Smith et al. 1996; Buchman 1999). These values are based primarily on *Hyalella azteca* and *Chironomus* sp. effects data from arsenic-contaminated sediments. Hence, based on a comparison to the TEL, arsenic in Davis Creek sediments could be affecting sediment-dwelling organisms and stream ecology (Long and McDonald 1998).

The objective of this investigation was to determine if arsenic in surface water and sediments was adversely affecting Davis Creek biota. Potential effects on Davis Creek biota were assessed using a weight-of-evidence approach as applied

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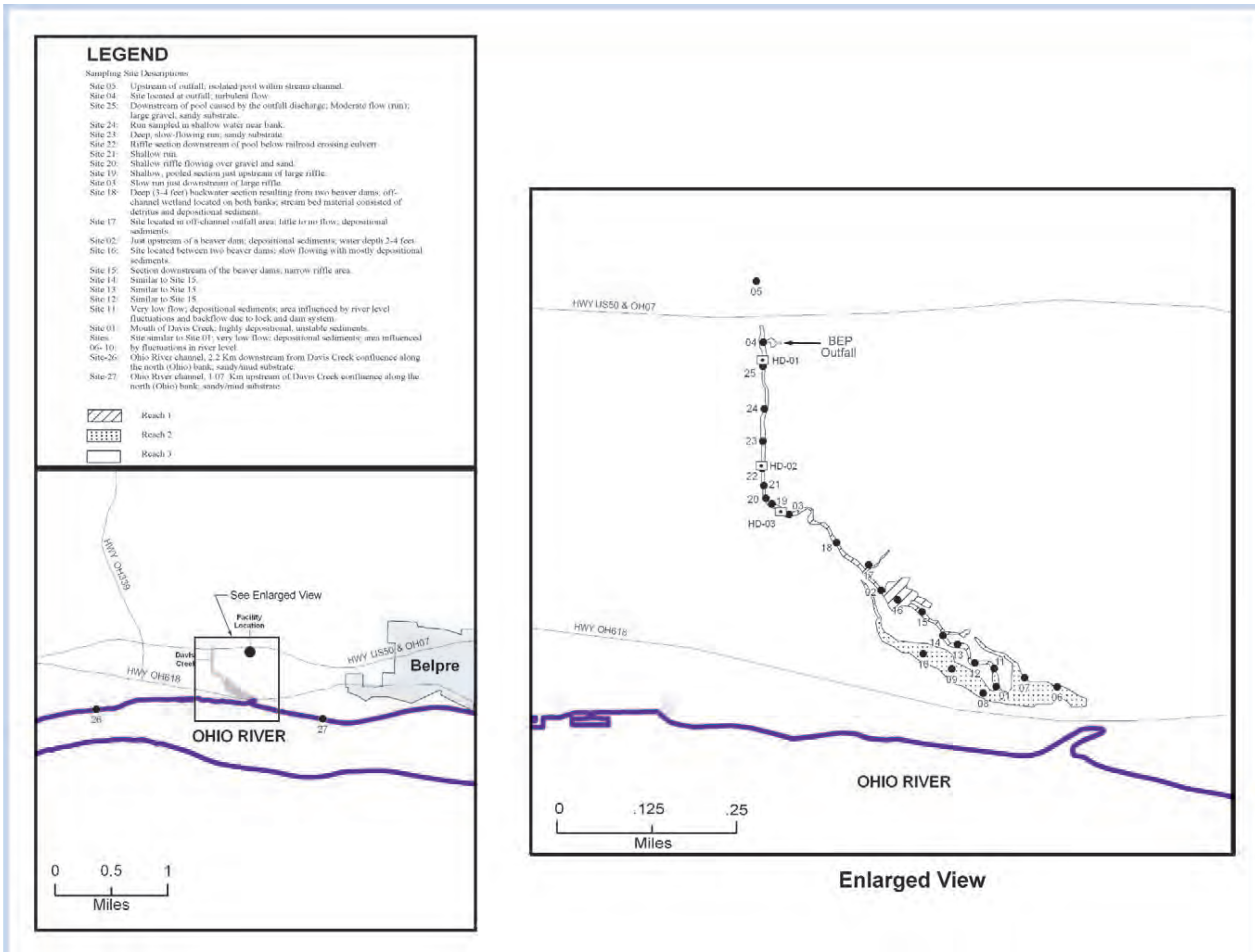

Figure 1. Davis Creek in southern Ohio, USA.

in sediment quality triad studies (Chapman 1990; Chapman et al. 1992), consisting of physical/chemical measurements, laboratory toxicity testing, and benthic community structure analysis. The triad provides a weight-of-evidence approach to determine whether ecological effects can be attributed to properties (e.g., chemical contaminants) associated with sediments (Chapman 1990; Chapman et al. 1992; USEPA 1999). The outcome of the assessment was used to make decisions regarding remediation, if any, of Davis Creek.

MATERIALS AND METHODS

Study area

The BEP and Davis Creek are located in southern Ohio, along the Ohio River between river miles 188 and 189 (Figure 1). This investigation focused on the lower 1.29 km of Davis Creek from the BEP discharge to its confluence with the Ohio River. Twenty-five sampling sites were designated within Davis Creek (Figure 1). Two additional sampling sites were established on the Ohio River, 1 site upstream and 1 site downstream of the Davis Creek confluence. This work was performed in 2000 (phase 1) and 2002 (phase 2).

Field investigations

On 21 and 22 August 2000, a preliminary, a field investigation was conducted involving reconnaissance of Davis Creek and collection of surface water, sediment, and benthic macroinvertebrates from 5 locations in the creek (sites 01–05; Figure 1). A second field investigation was conducted on 11 September 2000 to collect surface water, sediments, and benthic macroinvertebrates at 20 additional sites in Davis Creek (sites 06–25) and 2 sites on the Ohio River (sites 26 and 27; Figure 1). On 29 July 2002, surface water, sediments, and pore water were collected from sites 04, 06, 11, 12, 15, and 22, and fixed-substrate macroinvertebrate samplers were deployed.

Surface water

Prior to sample collection, direct-read field meters (YSI Model 63 and Model 95, Yellow Springs Instruments, Yellow Springs, OH, USA) were used to measure pH, temperature, dissolved oxygen, conductivity, and salinity at each sampling site. Collection of water samples began at the most downstream location in Davis Creek and proceeded upstream. Water samples were collected 7 to 10 cm below the surface using a 4-L Kemmerer bottle in phase 1 and a clean 19-L container in phase 2. Samples were transferred to clean cubitainers, placed on ice, and shipped to laboratories for analysis of total arsenic (USEPA Method 1638, 6020A); inorganic arsenic, As(III), and As(V) (USEPA Method 1638); alkalinity (USEPA Method 310.2); hardness (USEPA Method 130.2); ammonia nitrogen (USEPA Method 350.1); total dissolved solids (USEPA Method 160.1); total suspended solids (USEPA Method 415.1); and total organic carbon (USEPA Method 160.2).

The freshwater cladoceran *Ceriodaphnia dubia* and fathead minnow *Pimephales promelas* were used to assess the toxicity of Davis Creek surface water collected during phase 1 sampling. *Ceriodaphnia dubia* assays were 3-brood, 7-d duration, measuring survival and reproduction endpoints. *Pimephales promelas* tests were 7-d duration, measuring survival and growth. All toxicity tests were static renewal and followed standard USEPA protocol (USEPA 1994). Two control waters were used in the toxicity evaluations: A deionized mineral water (DMW) (USEPA 1994) and a field-collected secondary control water obtained from a man-made wetland on the campus of Ohio State University, Columbus, Ohio, USA.

Sediment

The top 15 cm of sediment were collected using a Petite Ponar (15 × 15 cm) in phase 1 and a precleaned flat shovel in phase 2, taking care to maintain the integrity and consistency of sediments. Samples were transferred to clean 8.4-L plastic containers, placed on ice, and delivered to laboratories for analysis of total arsenic (USEPA Method 1638, 200.8), As(III), and As(IV) (USEPA Method 1639); carbonate and bicarbonate (Black Method 62–3.4.2); calcium, aluminum, magnesium, sodium, and potassium (USEPA Method 200.7); chloride (USEPA Method 325.3); sulfate (USEPA Method 375.4); ammonia (USEPA Method 350.2); nitrate (USEPA Method 353.2); pH (USEPA Method 150.1); particle size (USEPA Method 3.4.3.5); and total organic carbon (USEPA Method 3.2.6).

Toxicity analysis—The epibenthic amphipod *H. azteca* and larval insect *Chironomus tentans* were used to assess whole-sediment toxicity in 10-d laboratory assays (ASTM 2000; USEPA 2000). Surface water collected from site 04 (at the BEP outfall) was used as overlying water in the phase 2 assays. Control sediments were obtained from a wetland at the headwaters of the Broadman River near Traverse City, Michigan, USA, for phase 1 testing and from the Wye River, Maryland, USA, for phase 2. Toxicity endpoints were survival and growth. Total arsenic, As(III), and As(V) in surface water and sediments were analyzed at the initiation of each test.

Sediment pore water

Pore water was extracted from homogenized sediment samples (as described previously) by centrifugation at high speed (10000 *g*) for 30 min. Pore-water supernatant was decanted, and an aliquot was preserved for total arsenic, As(III), and As(V) analysis.

Pore-water toxicity bioassays using *H. azteca* were conducted for the 6 locations sampled during phase 2. The static, 10-d bioassays followed standard USEPA protocol (USEPA 2000). Moderately hard, synthetic freshwater was used as a control, and survival and growth endpoints were recorded at test termination. Ammonia was measured in pore water at test initiation and termination, and 3 aliquots from each sample were collected for analysis of total arsenic, As(III), and As(V) at test initiation.

Benthic macroinvertbrates

Sample collection—In phase 1, benthic macroinvertebrates were collected at all sediment sampling locations using a 15 × 15-cm Eckman dredge (1 sample per site). Macroinvertebrate samples were rinsed in a 500-µm sieve using Davis Creek water, preserved in 70% ethanol in 1-L Nalgene® containers, and delivered to the laboratory for identification to the lowest practical taxonomic level. Ten benthic metrics were calculated for each sampling site: taxa richness; family richness; number of individuals; number of Ephemeroptera, Plecoptera, and Trichoptera (EPT) taxa; ratio of EPT to Chironomidae abundance; percent dominant taxa; percent nondipterans; Shannon's Diversity Index; percent tolerant organisms; and family biotic index (Ohio EPA 1988a, 1988b; Resh and Jackson 1993; USEPA 1999).

In phase 2, macroinvertebrates were collected from 3 sites (Figure 1) using fixed substrate Hester-Dendy sampling techniques according to Ohio Environmental Protection Agency (Ohio EPA) protocols (Ohio EPA 1988b). At each sampling location, 5 samplers were deployed, with flow velocity of approximately 0.3 ft/s. Samplers were placed in the stream on 29 July 2002 and removed on 9 September 2002. During retrieval of samples, plates were detached and carefully placed into a dip net positioned downstream to ensure capture of organisms. A composite sample was prepared using the 5 samplers and was placed into an 8-L plastic bucket. The composite sample was preserved with a solution of 10% formalin and transported to the laboratory for identification of macroinvertebrate organisms.

Qualitative samples of benthic macroinvertebrates inhabiting the natural substrates were also collected at the time of sampler retrieval. A kick net (46 × 23-cm opening; 900-µm mesh) was used to collect samples from all available habitats in the vicinity where the Hester-Dendy samplers were placed. Sampled habitats included pools, riffles, runs, and stream banks. Samples were collected from cobble substrates, snags, undercut banks, root wads, root mats, and leaf packs. Organisms were handpicked from the dip net, placed in labeled plastic 1-L jars, and preserved in 10% formalin for identification to the lowest practical taxonomic level. Direct-read field meters (YSI Model 63 and Model 95) were used to measure pH, temperature, dissolved oxygen, and conductivity at each benthic sampling site.

Data analysis

Statistical analysis of laboratory toxicity data was performed to determine if differences existed between treatments and controls in terms of organism survival and growth or reproduction. Tests for normality employed Shapiro–Wilks's test, and the *F* test was used to test for homogeneity of variances. Both an analysis of variance (ANOVA) and *t* tests were conducted to determine whether control and test samples were equal. For the ANOVAs, Dunnett's test was used to detect differences between test samples and the control. Wilcoxon 2-sample tests were used when data were nonnormally distributed. All significance testing was conducted using a test size of $\alpha = 0.05$.

Analysis of the phase 2 benthic data followed Ohio EPA (1989) guidance and generated the Invertebrate Community Index (ICI). The ICI consists of 10 structural community metrics with scoring categories of 6, 4, 2, and 0 points. The point scores evaluate a sample against a database of relatively undisturbed reference sites throughout Ohio. The summation of the individual metric scores results in the ICI value. The ICI is determined by the relevant attributes of a sample with some consideration given to stream drainage area. Metrics 1

Table 1. Arsenic concentrations in sediments and surface water collected from Davis Creek and the Ohio River

	Water				Sediment		
Sampling site	Average total As (μg/L)[a]	Total inorganic As (μg/L)	As(III) (μg/L)	As(V) (μg/L)	Average total As (mg/kg)[a]	As(III) (mg/kg)	As(V) (mg/kg)
01	*28.4*	NS[b]	NS	NS	*70.1*	NA[c]	NA
02	*32.7*	NS	NS	NS	*31.6*	NA	NA
03	*46.5*	NS	NS	NS	*44.0*	NA	NA
04	*41.1*	NS	NS	NS	*339.3*	NA	NA
05	*ND*[d]	NS	NS	NS	*6.0*	NA	NA
06	21.6 ± 0.9	20.8	5.0	15.8	29.8 ± 0.4	1.0	15.8
07	65.9 ± 2.7	58.9	17.9	41.0	23.6 ± 6.6	1.0	15.9
08	35.8 ± 2.3	32.0	8.1	23.9	22.4 ± 9.9	1.4	18.5
09	34.2 ± 2.1	31.3	7.2	24.1	31.9 ± 9.1	5.8	28.9
10	35.9 ± 1.2	33.9	7.3	26.7	32.3 ± 6.4	5.4	20.8
11	45.2 ± 2.6	49.1	9.1	40.1	29.3 ± 11.8	0.7	17.5
12	46.8 ± 1.7	48.0	8.6	39.4	17.8 ± 5.7	3.0	8.5
13	85.7 ± 5.2	80.5	13.0	67.5	19.3 ± 6.2	1.0	ND
14	50.0 ± 1.7	50.0	9.3	40.7	26.9 ± 16.8	1.0	13.5
15	47.7 ± 3.0	48.8	7.9	40.9	28.7 ± 3.5	ND	21.5
16	51.50 ± 0.3	52.3	6.0	46.3	21.9 ± 5.1	ND	16.4
17	49.5 ± 1.1	50.3	5.0	45.3	11.6 ± 5.4	1.1	ND
18	53.5 ± 2.1	53.8	5.1	48.8	18.5 ± 5.5	ND	19.7
19	54.2 ± 3.3	55.1	5.4	49.8	11.1 ± 4.1	0.5	ND
20	53.4 ± 2.8	57.1	5.9	51.2	14.1 ± 6.5	2.0	ND
21	54.5 ± 2.5	55.5	5.9	49.6	11.8 ± 5.7	1.0	ND
22	53.8 ± 4.4	57.3	5.9	51.4	10.7 ± 2.1	1.6	ND
23	61.8 ± 8.1	58.8	5.9	52.9	9.6 ± 3.1	0.9	ND
24	55.8 ± 2.8	59.6	6.4	53.2	12.8 ± 5.8	2.3	ND
25	55.9 ± 2.8	58.8	6.4	52.4	10.2 ± 4.3	0.8	ND
26	ND	ND	ND	ND	2.2 ± 0.9	0.6	ND
27	ND	ND	ND	ND	2.6 ± 1.3	0.7	ND

[a] Concentrations determined by averaging the 2 laboratory values. Italics indicate only 1 sample analyzed.
[b] NS = not sampled.
[c] NA = sampled but not analyzed.
[d] ND = not detected.

through 9 are generated from the Hester-Dendy sample data, and metric 10 is based on the qualitative dip-net sample data.

To statistically assess the benthic macroinvertebrate community as related to chemical and physical sediment characteristics, a hierarchical cluster analysis was conducted using taxa abundance data to combine sampling stations into distinct groups containing homogeneous macroinvertebrate assemblages. The hierarchical cluster analysis uses a complete linkage (i.e., farthest neighbor) method and a distance metric of 1 – Pearson correlation coefficient (r). This method is an agglomerative clustering technique that produced tight groups of similar (i.e., homogeneous) samples (Gauch 1982). A linear discriminant analysis was then conducted using the group-associated values for chemical and physical variables (mean particle size, total organic carbon, total arsenic, sulfate, ammonia, and moisture) to describe separation of groups. These variables were used because of their potential to affect arsenic bioavailability, toxicity, and distribution or other effects (e.g., ammonia toxicity). For these statistical analyses, taxa abundance from sites 01 through 04 and 06 through 25 were considered. Macroinvertebrates were not sampled from site 05 (upstream of the BEP discharge) because of an absence of flow. A refined

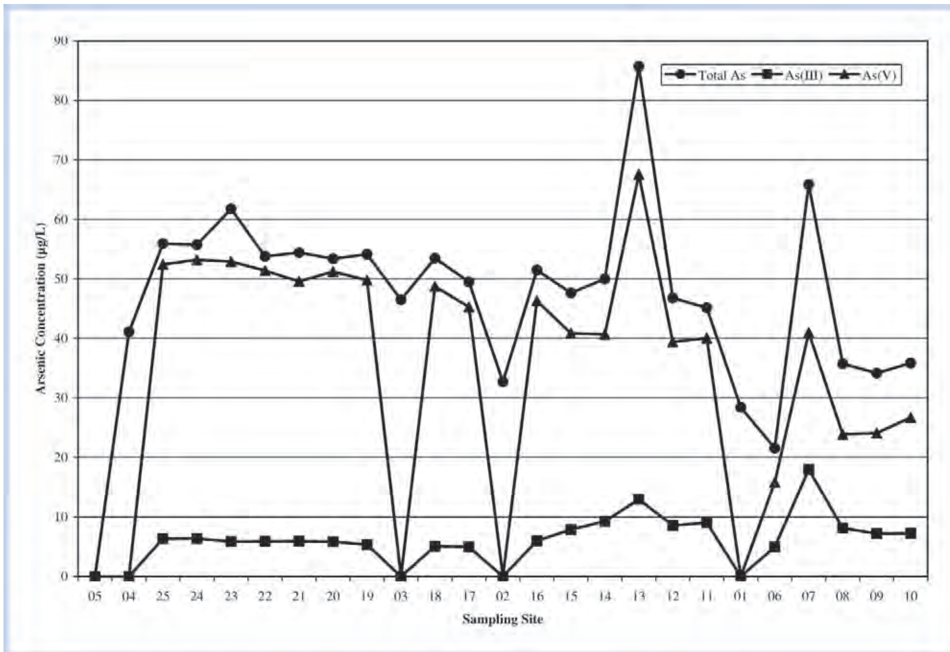

Figure 2. Total arsenic, As(III), and As(V) in surface water samples from Davis Creek. Sampling stations are arrayed from upstream (**left**) to downstream (**right**).

biological characterization of each group was made by conducting univariate analyses of variance for each taxon to test for differences among groups. The purpose of these analyses was to determine which taxa contributed the most information to community structure characteristics of the groups, based on magnitude of the *F* statistic. The *F* statistics were used not for significance testing but rather as the best indicator of the degree to which groups could be defined by each of the species (Green 1979).

A 1-way ANOVA was conducted for each abiotic sediment variable assessed to determine whether groups (clusters of similar benthic invertebrate assemblages) differed from one another by a statistically significant margin in terms of the mean value of the variable. A linear discriminant analysis was then used to elucidate differences between groups based on the chemical and physical variables. Because the abiotic variables were measured on different scales, standardized discriminant coefficients were used to assess group separation. Statistical significance of the discriminant functions was measured by Wilks's lambda.

RESULTS

Surface water

Total arsenic concentrations in Davis Creek surface water samples ranged from 21.6 to 85.7 µg/L (Table 1). Concentrations of arsenic in surface water samples collected within the Ohio River (site 26 and site 27) and upstream of the BEP discharge (site 05) were below detection. The general trend in total arsenic concentrations in Davis Creek was decreasing with increasing distance downstream from the BEP discharge (Figure 2). Total inorganic arsenic concentrations detected in surface water ranged from 20.8 to 80.5 µg/L, while As(III) concentrations ranged from 4.9 to 17.9 µg/L and As(V) concentrations from 15.8 to 67.5 µg/L (Table 1). Total inorganic arsenic concentrations in surface water generally decreased with increasing distance from the BEP outfall; however, the relative percentage of As(III) to As(V) increased downstream (Figure 2). In addition, all aqueous samples collected from the Ohio River had concentrations that were qualified below detection for all forms of arsenic measured (i.e., total, inorganic, As[III], and As[V]).

Surface water pH averaged 7.1, ranging from 6.5 to 8.7 (Appendix A). Water alkalinity varied between sites with values ranging from 39 to 130 mg/L as $CaCO_3$, while hardness values were much more uniform and ranged from 130 to 150 mg/L as $CaCO_3$. Ammonia concentrations ranged from below detection to a maximum concentration of 0.29 mg/L. Total suspended solids concentrations ranged from below detection to 26 mg/L, while total dissolved solids ranged from 260 to 460 mg/L. Total organic carbon concentrations in overlying water ranged from 2.3 to 5.8 mg/L (Appendix A).

After 7-d exposures, there was 100% survival of *C. dubia* observed in all site waters and control waters tested (Table 2). Reproduction in waters from sites 14 to 27 was significantly decreased ($p < 0.05$) compared to reproduction in the DMW control. However, in this series of toxicity tests, reproduction in the DMW control averaged 37.1 young per adult, which was substantially greater than reproduction in other DMW controls and wetland water controls (Table 2). In addition, 37.1 young per adult was also substantially greater than the average reproduction of 20.9 young per adult in DMW controls from reference toxicant tests conducted during the past 4 y. When reproduction in waters from sites 14 to 27 were compared to reproduction in wetland control water, only site 19 water exhibited significantly decreased reproduction.

Survival of fathead minnow after 7 d ranged from 50% in water from site 27 (Ohio River upstream of Davis Creek confluence) to 100% in sites 08, 11, 18, and 22 (Table 2). Survival in all other site waters was not significantly decreased as compared with controls. No significant differences were observed in growth of fathead minnow fry in site waters as compared with controls (Table 2).

Table 2. Results of toxicity tests using *Ceriodaphnia dubia* and *Pimephales promelas* exposed to water from Davis Creek and Ohio River

	C. dubia average % survival	*C. dubia* average reproduction	*P. promelas* average % survival	*P. promelas* average weight (mg)
Laboratory control[a] (replicate a)	100	22.7	92	0.4501
Laboratory control (replicate b)	100	17.0	98	0.5014
Wetland control water	100	25.7	100	0.4683
Site 01	100	28.7	88	0.4672
Site 02	100	26.3	70	0.4381
Site 03	100	27.1	82	0.5001
Site 04	100	31.0	92	0.5261
Site 05	100	20.8	70	0.5314
Laboratory control	100	24.1	100	0.4808
Wetland control water	100	18.0	100	0.4653
Site 06	100	26.9	92	0.5007
Site 07	100	26.1	95	0.4823
Site 08	100	32.0	100	0.4923
Site 09	100	26.7	98	0.4933
Site 10	100	29.1	92	0.4836
Site 11	100	25.2	100	0.4370
Site 12	100	25.5	98	0.4598
Site 13	100	26.2	90	0.4696
Laboratory control	100	37.1	98	0.4848
Wetland control water	100	23.1	100	0.5000
Site 14	100	27.2	98	0.4547
Site 15	100	23.4	98	0.4621
Site 16	100	23.1	88	0.5399
Site 17	100	26.1	92	0.5931
Site 18	100	19.7	100	0.5170
Site 19	100	13.9[b]	98	0.5139
Site 20	100	19.4	90	0.5500
Site 21	100	20.6	95	0.5459
Site 22	100	21.8	100	0.4940
Site 23	100	20.1	98	0.4955
Site 24	100	19.7	95	0.5168
Site 25	100	21.2	92	0.5292
Site 26	100	31.4	98	0.4769
Site 27	100	32.1	50[b]	0.4925

[a] Laboratory control = deionized mineral water.
[b] Significantly different from the wetland control.

Table 3. *Hyalella azteca* average percent survival and weight after 10-d exposures in Davis Creek and Ohio River sediments[a]

	H. azteca average % survival	*H. azteca* average dry weight (mg)	*Chironomus tentans* average % survival	*C. tentans* average dry weight (mg)
Control 1	88	0.156	*63*	*1.090*
Site 01	96	0.086	*94*	*1.918*
Site 02	98	0.099	*94*	*2.577*
Site 03	NT[b]	NT	NT	NT
Site 04	96	0.094	*92*	*2.271*
Site 05	92	0.080	*88*	*1.748*
Control 2	96	0.287	88	1.581
Site 06	95	0.288	68	2.332
Site 07	100	0.297	76	3.388
Site 08	98	0.308	**44**	2.796
Site 09	94	0.302	82	2.594
Site 10	94	0.260	**22**	3.825
Site 11	96	0.218	82	2.708
Site 12	94	0.211	**56**	2.293
Site 13	86	0.304	84	2.473
Control 3	96	0.319	78	2.314
Site 14	98	0.308	98	3.346
Site 15	98	0.321	80	3.777
Site 16	100	0.288	75	4.211
Site 17	98	0.264	95	3.716
Site 18	100	0.286	**10**	1.439
Site 19	100	0.290	75	3.796
Control 4[c]	92	0.259	88/98	1.288/0.987
Site 20	96	0.166	**58**	1.690
Site 21	98	0.187	90	1.783
Site 22	100	0.176	74	2.441
Site 23	92	0.187	82	1.878
Site 24	96	0.200	82	1.978
Site 25	98	0.182	80	1.910
Site 26	98	0.174	84	1.748
Site 27	96	0.170	78	1.983

[a] Italics = insufficient control survival; bold = significant from respective control sample; shaded area = sites retested because of insufficient control survival.
[b] NT = not tested.
[c] Two controls run for *C. tentans*.

Sediment

Total arsenic in sediments collected from Davis Creek ranged from 339.3 mg/kg at site 04 (i.e., BEP outfall) to 6.0 mg/kg at site 05 (upstream of the outfall) (Table 1). In general, total arsenic concentrations increased from upstream to downstream in Davis Creek with the exception of site 04 (Fig. 3). Trivalent arsenic was detected in all sediments analyzed except sites 15, 16, and 18. Pentavalent arsenic was detected in several downstream samples, ranging from 13.5 to 28.8 mg/kg (Table 1).

Based on field observations, Davis Creek possessed 3 distinct morphological areas, or stream reaches:

Reach 1: Downstream reach; depositional sediments (silts and clays); minimal current velocity

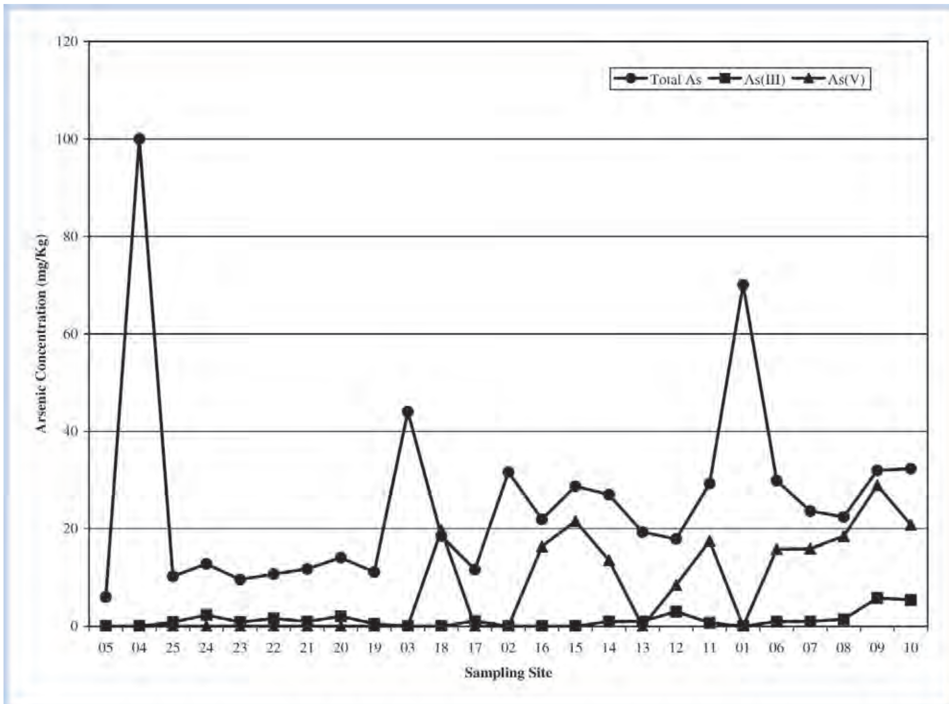

Figure 3. Total arsenic, As(III), and As(V) in sediment from Davis Creek. Sampling stations are arrayed from upstream (**left**) to downstream (**right**).

Reach 2: Transitional area; heterogeneous sediments ranging from clays to gravel; swift riffle sections, runs, and pools that transitioned into wetlands

Reach 3: Upstream reach, well-scoured sediments (sand and gravel), channelized, riparian corridor; swift riffle sections and slower, deeper runs

The sediment physical/chemical characteristics (Appendix B) are described in the context of the observed stream reaches.

Sediment pH ranged from 6.2 to 7.5. Sulfate in sediments ranged from 88.1 to 1038.5 meq/L. Ammonia ranged from 13.4 to 116 mg/kg, and total organic carbon ranged from 0.9 and 3.1%. Average sediment grain size in reach 1 (riffle/run substrate) was 600 µm. Sediment redox potential in reach 1 ranged from +48 to +161 mV. Average sediment grain size in reach 2 (transitional, wetland substrate) was 443 µm. The overall redox potential decreased in reach 2 (–199 to +33 mV), indicating reduced sediment conditions. Average sediment grain size in reach 3 (depositional substrate) was 282 µm. Redox potential indicated that sediments were largely reduced in reach 3 (–204 to +96 mV). In general, stream morphology changed from sand-dominated, oxidized, riffle/run substrate upstream to a silty, reduced, depositional area downstream to the Ohio River confluence.

In whole-sediment toxicity tests conducted in phase 1, no sediment sample exhibited toxicity to *H. azteca* based on survival and growth (average dry weight) compared to controls (Table 3). *Hyalella azteca* survival ranged from 92 to 100% in site sediments, while average dry weight ranged from 0.080 to 0.321 mg/surviving organism compared to control dry weights of 0.156 to 0.319 mg/surviving organism (Table 3).

Sediments from 5 sites (08, 10, 12, 18, and 20) were toxic to C. *tentans* as measured by survival in 10-d whole-sediment

Table 4. Arsenic concentrations in sediments and pore water collected from Davis Creek during phase 2

	Pore water				Sediment		
Sampling site	Total As (µg/L)	Total inorganic As (µg/L)	As(III) (µg/L)	As(V) (µg/L)	Total As (mg/kg)	As(III) (mg/kg)	As(V) (mg/kg)
04	371	390	30.6	360	117	36.4	59.4
22	36.7	33.2	2.1	31.1	27.3	5.5	8.7
15	91.0	93.3	61.3	31.9	25.1	8.6	10.6
12	125	138	89.6	48.5	30.9[a]	11.2	9.3
11	240	246	177	67.8	27.2	13.7	14.2
06	124[a]	129[a]	82.8[a]	46.1[a]	19.2	10.8[a]	9.3[a]
06 Dup	123	128	92.7	34.9	21.1	10.6	9.2

[a] Concentrations determined by taking the average of 2 laboratory values.

Table 5. Benthic macroinvertebrates collected in Davis Creek, Belpre, Ohio, August–September 2000

Phylum	Class	Order	Family	Genus/species
Annelida	Oligochaeta	Tubificida	Naididae	*Dero* sp.
			Tubificidae	*Aulodrilus limnobius*
				Branchiura sowerbyi
				Limnodrilus cervix variant
				Limnodrilus hoffmeisteri
				Limnodrilus udekemianus
				Immature tubificid A
				Immature tubificid B
	Hirudinea	Pharyngobdellida	Erpobdellidae	*Mooreobdella microstoma*
Mollusca	Pelecypoda (Bivalvia)	Heterodonta	Corbiculidae	*Corbicula fluminea*
			Sphaeriidae	*Musculium transversum*
				Pisidium sp.
	Gastropoda	Lymnophila	Planorbidae	*Helisoma anceps*
			Physidae	*Physella* sp.
Arthropoda	Insecta	Ephemeroptera	Ephemeridae	*Hexagenia limbata*
			Caenidae	*Caenis diminuta* gr.
			Heptageniidae	*Stenonema femoratum*
		Odonata	Coenagrionidae	*Argia* sp.
			Libellulidae	*Plathemis lydia*
		Megaloptera	Sialidae	*Sialis* sp.
		Trichoptera	Leptoceridae	*Oecetis* sp.
		Coleoptera	Elmidae	*Dubiraphia* sp.
				Stenelmis sp.
		Diptera	Ceratopogonidae	*Probezzia* sp.
				Ceratopogoniadae sp.
			Tabanidae	*Chrysops* sp.
			Stratiomyidae	*Stratiomys* sp.
			Tipulidae	*Tipula* sp.
			Chironomidae	*Ablabesmyia annulata*
				Ablabesmyia mallochi
				Ablabesmyia monilis
				Chironomus sp.
				Cladopelma sp.
				Cladotanytarsus mancus gr.
				Conchapelopia genus group
				Cricotopus bicinctus
				Crypto-chironomus sp.
				Cryptotendipes sp.
				Dicrotendipes sp.
				Endochironomus subtendens

Table 5. Continued

Phylum	Class	Order	Family	Genus/species
				Glyptotendipes sp.
				Meropelopia group
				Nanocladius crassicornis
				Natarsia sp.
				Paraclado-pelma doris gr.
				Parakiefferiella sp.
				Paratanytarsus sp.
				Phaenopsectra punctipes gr.
				Polypedilum halterale
				Polypedilum halterale gr.
				Polypedilum illinoense
				Polypedilum scalaenum gr.
				Polypedilum simulans/digitifer
				Procladius sp.
				Pseudochironomus sp.
				Stictochironomus annulicrus
				Tanypus neopuncti-pennis
				Tanytarsus sp.
				Chironomini (early instar)
				Tanypodinae (incomplete pupa)

laboratory exposures (Table 3). No significant differences ($p < 0.05$) in organism growth were detected between site sediments and controls. Organism survival in sediments from the remaining sites was either not significantly different from controls or exceeded the minimum survival criterion (70%) and were not considered toxic to C. *tentans*.

In whole-sediment toxicity tests conducted for sites 04, 06, 11, 12, 15, and 22 in phase 2, *H. azteca* survival was statistically decreased at site 04 ($p = 0.0497$) and a duplicate sample of site 06 relative to the control. Survival for the 6 sites (89–98%) exceeded the minimum survival criterion of 80% for *H. azteca*. The average dry weight at test termination for surviving amphipods exposed to sediment at site 04 was significantly decreased compared to controls ($p = 0.0152$). *Hyalella azteca* average dry weights in test sediments ranged from 0.057 to 0.161 mg/surviving organism compared to control dry weights of 0.078 mg/surviving organism. No other statistical differences were observed.

Chironomus tentans survival for the 6 sites ranged from 70 to 85%, which was not significantly different from the control (66% survival), and all met or exceeded the minimum survival criterion of 70% (USEPA 2000). No significant differences in growth of surviving midges were detected for the 6 sites evaluated. Midge growth in test sediments ranged from 0.755 to 1.302 mg dry weight, and growth in the control sediment was 0.936 mg dry weight. This exceeded the minimum growth criterion for controls midges of 0.48 mg dry weight (USEPA 2000).

Sediment pore water

Hyalella azteca survival in pore-water test samples ranged from 80 to 99%. Amphipod growth ranged from 0.095 mg at site 04 to 0.15 mg at site 12. Control and field samples were statistically similar.

Total arsenic in sediment pore water collected from the 6 Davis Creek sampling stations ranged from 37 µg/L at site 22 to 371 µg/L at site 04 (at the BEP outfall) (Table 4). Total inorganic arsenic ranged from 33 µg/L at site 22 to 390 µg/L at site 04. Trivalent arsenic, As(III), was detected in all 6 sediment pore waters, ranging from 2 µg/L at site 22 to 177 µg/L at site 11. The less toxic pentavalent arsenic, As(V), form was also detected in all pore-water samples, ranging from 31.1 µg/L at site 22 to 360 µg/L at site 04 (Table 4).

Benthic community structure

Benthos of Davis Creek sampled in August and September 2000 (phase 1) consisted of 3 phyla (Annelida, Mollusca, and Arthropoda), comprising 20 families and 60 genera (Table 5). None of the metrics (Appendix C) calculated from benthic macroinvertebrate data were strongly correlated with concentrations of total arsenic in sediment; the maximum linear correlation observed was 0.14. Similarly, there was no strong correlation between any metric and the remaining physicochemical parameters measured in Davis Creek sediments.

Hierarchical cluster analysis of the sampling sites in Davis Creek resulted in 4 distinct groups of sampling stations, each

Table 6. Physical description of sampling sites grouped by cluster analysis of benthic macroinvertebrate assemblages in Davis Creek

Group	Sampling site	Description
A	03	Shallow runs with some pooling; large gravel and sandy substrate
	19	
	21	
	22	
	24	
	25	
B	04	Riffles, including turbulent section at the 002 discharge and downstream of beaver dams; large gravel and sandy substrate
	12	
	13	
	14	
	15	
	20	
C	16	Slow-moving, deep runs (1–2-m depth) with adjacent wetlands; substrate ranged from sandy to depositional/detrital
	17	
	18	
	23	
D	01	Pooled areas, including sections upstream of beaver dams and the mouth of Davis Creek; highly depositional sediments (silts and clays)
	02	
	06	
	07	
	08	
	09	
	10	
	11	

consisting of a comparatively homogeneous assemblage of invertebrate taxa (Table 6). Results of univariate ANOVA on each taxon found that only 7 benthic taxa differed significantly among groups and, therefore, could be used as a sufficient biological characterization of group-specific community structure. The 7 species in order of magnitude of their contribution to group separation were *Ablabesmyia mallochi*, *Probezzia* sp., *Polypedilum simulans/digitifer*, *Tanypus neopunctipennis*, *Branchiura sowerbyi*, *Polypedilum scalaenum* gr., and *Cladopelma* sp.

Groups differed significantly for particle size, ammonia, and sediment moisture ($p < 0.05$). No significant differences were found for total organic carbon, total arsenic, or sulfate. Further evaluation and interpretation of group's separation were accomplished using results of the discriminant analysis.

Linear discriminant analysis identified 3 discriminant functions that accounted for all separation of the benthic taxa assemblage groups. The first discriminant function (DF 1) accounted for about 73% of group separation and was found to be statistically significant ($p = 0.0309$). The second and third discriminant functions (DF 2 and DF 3) accounted for an additional 24% and 3% of group separation, respectively. Because of its small percentage, DF 3 was not considered in interpreting results of the analysis. The analysis correctly classified 78% of the sites into groups.

The DF 1 coefficients indicate that moisture, mean particle size, ammonia, and arsenic were the primary variables contributing to group separation based on the absolute values of the coefficients. In general, separation of groups A through D on DF 1 appeared to follow a gradient of decreasing particle size and increasing sediment moisture and ammonia content. While among-group differences in total organic carbon were not found to be statistically significant, the lowest and highest concentrations of organic carbon were found in group A and group D, respectively. Total arsenic was less important in differentiating the groups and did not differ significantly among groups.

The groups were not well separated on DF 2, as reflected in the 24% variation between groups accounted for by DF 2. The coefficients indicated that ammonia and arsenic were the most important contributors in DF 2. Group separation was based largely on differences in arsenic and ammonia concentrations within the groups. The fact that total arsenic did not differ significantly among groups suggested that group separation on DF 2 could be explained by ammonia alone.

Table 7 lists the ICI metrics and scores calculated from data obtained with the Hester–Dendy samplers. The ICI value for HD 01 was 8; according to Ohio water quality standards, the benthic community at this site is narratively classified as poor. The ICI values at HD 02 and HD 03 are 26 and 24, respectively, which are classified as fair. Davis Creek is located in the Western Allegheny Plateau ecoregion of Ohio. The attainment ICI value for warm-water habitat in this ecoregion is 36. Since all the scores were less than 36, none of the Davis Creek station locations achieved attainment of their designated use. Based on habitat evaluations, the stations were characterized by low flow with moderate current velocity, moderate to extensive bank erosion, and limited riffle habitat of poor to fair quality. The stations were located in forested areas with good riparian vegetative zone width. The substrate was primarily coarse gravel at all the sites followed by fine gravel and sand with little cobble. The Ohio EPA Qualitative Habitat Evaluation Index scores were similar at the 3 stations with 67 at HD 01, 73 at HD 02, and 70 at HD 03. These scores are considered to be good for warm-water stream habitat (Ohio EPA 1989).

DISCUSSION

Several lines of evidence were useful in assessing potential adverse effects of arsenic in Davis Creek. Chemical analysis of arsenic in surface water and sediment indicated several trends in arsenic distribution in Davis Creek. While total arsenic concentrations decreased in surface water downstream from the BEP discharge, arsenic concentrations in sediments increased downstream, with the exception of 339.3 mg/kg of total arsenic (the highest concentration observed) detected at the BEP outfall. Concentrations of As(III) in water corresponded with total sediment arsenic concentrations, also increasing downstream from the BEP discharge. This observation could be explained by the transition from the largely erosional, oxidized substrate (sands/gravel) upstream to the depositional, fine particles (silts/clays and detritus) downstream in Davis Creek. The transition in substrate character

Table 7. The invertebrate community index metrics and scores, August–September 2002

	Sampling location		
	HD-01	HD-02	HD-03
Drainage area (square miles)	10	10	10
ICI total[a]	8	26	24
Total number	280	368	156
Number of taxa	18	26	18
Taxonomic score	2	4	2
Number of mayfly	2	3	3
Mayfly score	0	2	2
Number of caddisfly	0	1	1
Caddisfly score	0	4	4
Number of dipteran	11	13	9
Dipteran score	2	2	2
Percent mayflies	1.4	7.3	10.3
Score for percent mayflies	2	2	2
Percent caddisfly	0	1.6	0.6
Score of percent caddisfly	0	6	4
Percent tribe Tanytarsini midges	3.6	16	2.6
Score of percent tribe Tanytarsini midges	2	4	2
Percent other	91.8	71.5	85.9
Score of percent other	0	0	0
Percent tolerant organisms	66.1	26.1	5.1
Score of percent tolerant organisms	0	2	6
Qualitative EPT taxa[b]	1	0	2
Score of qualitative EPT taxa	0	0	0

[a] ICI = Invertebrate Community Index.
[b] EPT = Ephemeroptera, Plecoptera, and Trichoptera.

was indicative of the observed changes in arsenic form (speciation).

Physical and chemical processes play key roles in arsenic speciation and bioavailability in aquatic systems, including oxidation and reduction (redox), biomethylation, coprecipitation with iron and manganese hydroxides, and sorption. In water, arsenic occurs in both inorganic and organic forms as well as dissolved and gaseous states (Eisler 2000). The form of arsenic in water depends on redox potential, pH, organic content, suspended solids, dissolved oxygen, and other variables (USEPA 1985). The primary forms of arsenic existing in water are dissolved ionic species, As(III), and As(V). Particulates generally account for less than 1% of the total measurable arsenic (Eisler 2000). Pentavalent arsenic, the most common arsenic species in water, is favored under conditions of high dissolved oxygen, basic pH, high redox, and reduced content of organic material. Analysis of surface water from Davis Creek indicated that arsenic existed largely as As(V). Trivalent arsenic generally prevails under anoxic conditions (Eisler 2000). However, the kinetics of arsenic redox are slow, so both species are generally present in water (API 1998). As noted, total and inorganic arsenic concentrations decreased in water with increasing distance from the BEP outfall. However, the ratio of As(III) to As(V) increased downstream, likely because of the concomitant increase in total arsenic in sediments.

The increase in As(III) in surface water downstream was likely attributed to chemical and physical processes at the sediment surface. As sediments are buried and become anoxic, Mn(IV) and Fe(III) oxyhydroxides are reduced to Mn(II) and Fe(II) and solubilized. Adsorbed and/or coprecipitated arsenic is then released into the interstitial water. If the surface layer of sediments is oxic, the arsenic that diffuses upward may become resorbed or reprecipitated with Mn or Fe oxyhydroxides, resulting in higher surficial sediment concentrations. Arsenic may then be released to the overlying water if dissolved oxygen is low at the sediment–water interface. Flux of arsenic from sediments to the water column may also be mediated by bioturbation, such as burrowing macroinvertebrates (API 1998). Observed increases in concentrations of As(III) in downstream surface waters of Davis Creek were likely attributed to these mechanisms.

Arsenic associated with sediments is subject to chemically and microbiologically mediated oxidation or reduction and methylation reactions that influence bioavailability (Eisler 2000). In the presence of dissolved sulfide in anoxic sediment, dissolved arsenic, generally As(III), will precipitate as insoluble arsenious sulfide or iron-arsenic sulfides, limiting bioavailability to sediment-dwelling organisms (Huerta-Diaz and Morse 1992; API 1998). The presence of SO_4^{-2} in sediments of Davis Creek, as well as measured redox potentials, indicated that sulfides were likely prevalent in downstream reaches, which would limit arsenic bioavailability. Arsenic also readily adsorbs to iron and manganese oxyhydroxides, mineral particles (silts and clays), and organic matter (API 1998) in addition to forming insoluble precipitates with calcium, aluminum, and barium compounds (Eisler 2000). Total arsenic concentrations were generally greater in sediments from the downstream reaches of Davis Creek compared to upstream, which would be expected given the depositional nature (fine grain size) of the substrate. These factors that influence bioavailability of arsenic in sediments were likely responsible for the absence of toxicity observed in whole-sediment assays.

The pentavalent form of arsenic, which is less toxic than As(III) and predominates in oxic waters (Eisler 2000), was prevalent in Davis Creek water samples collected in phase 1. The phase 2 average concentration of As(V) in surface water was 36.1 μg/L, which is less than the 48-h LC50 of 2540 μg/L reported for *C. dubia* (Boucher and Watzin 1999) and less than the maximum acceptable toxicant concentration (MATC) of 530 μg/L for *P. promelas* (Eisler 2000). This concentration was less than concentrations resulting in reproductive impairment of *Daphnia magna* during chronic exposures (NRCC 1978). The average concentration of As(III) observed in site 04 surface water samples was 0.64 μg/L. This value is less than the 48-h LC50 of 1540 μg/L for *C. dubia* (Boucher and Watzin 1999) and the MATC value of 2100 μg/L for *P. promelas* (Eisler 2000). These data indicated that arsenic in Davis Creek surface waters, regardless of the form, was not toxic to water column–dwelling organisms.

Whole-sediment toxicity tests provided an additional line of evidence of arsenic effects in Davis Creek. Because several sites in Davis Creek had total arsenic sediment concentrations that exceeded sediment screening values (e.g., TEL: 5.9 mg/kg; PEL: 17 mg/kg), adverse effects at most sites might be expected. However, in phase 1 sediment toxicity tests, no adverse effects were observed on *H. azteca* survival and growth. Survival of C. *tentans* was significantly decreased in sediments from 5 of the 25 sites examined in Davis Creek, while no adverse effects on C. *tentans* growth were observed for any site. The average total arsenic concentration in the toxic sediment samples was 21 mg/kg. However, sediments in which no adverse effects were observed averaged 39 mg/kg, nearly twice the average arsenic concentration in the toxic sediments. Additionally, sediments from sites having the highest arsenic concentrations observed (site 01: 70.1 mg/kg; site 04: 339.3 mg/kg) maintained 94% and 92% survival of C. *tentans*, respectively. Thus, effects were likely attributed to arsenic bioavailability or another stressor and not related to total arsenic concentrations. In phase 2, *H. azteca* survival and growth were significantly decreased at site 04 (the BEP outfall) only. No adverse effects were observed on C. *tentans* survival and growth, but control survival was inadequate to validate the tests. Therefore, the C. *tentans* tests were not considered in the study conclusions. Overall, the whole-sediment toxicity assays indicated minimal adverse effects on Davis Creek. Statistically significant adverse effects are limited primarily to the immediate vicinity of the BEP outfall.

Pore-water toxicity tests provided another line of evidence of effects of arsenic in Davis Creek. *Hyalella azteca* assays indicated that pore water extracted from the 6 phase 2 sampling sites was not toxic based on survival and growth endpoints. The total arsenic concentration in site 04 pore water was greater than the USEPA acute (360 μg/L) and chronic (190 μg/L) standards for surface water, although no toxicity was observed. Pentavalent arsenic, which is less toxic than the trivalent form and predominates in oxic waters (Eisler 2000), was present at concentrations similar to As(III) at all sites except sites 04 and 22. The highest concentration of As(V) in pore water (site 04) was 360 μg/L; the 48-h LC50 reported for C. *dubia* is 2540 μg/L (Boucher and Watzin 1999), and the lowest maximum acceptable toxicant concentration (MATC) for *P. promelas* is 530 μg/L (Eisler 2000). The highest concentration of As(III) observed in pore-water samples was 177 μg/L (site 11); the 48-h LC50 reported for C. *dubia* is 1540 μg/L (Boucher and Watzin 1999), and the lowest MATC value is 2100 μg/L for *P. promelas* (Eisler 2000). Although the maximum As(V) concentration at site 04 exceeded the total arsenic criteria, it was below those concentrations of As(V) that have resulted in negative effects on test organisms in published studies. Pore-water As(III) concentrations were also below no-effects levels.

Benthic macroinvertebrate assemblages in Davis Creek provided an additional line of evidence in the assessment of ecological effects. No significant relationships were detected between benthic metrics and abiotic parameters assessed in phase 1. These metrics typically indicate relative ecological health of aquatic ecosystems (Rosenberg and Resh 1993) and can be correlated with contamination or other parameters. We observed using a cluster analysis that biologically defined groups (designated A, B, C, and D) of sampling sites could be distinguished using the occurrence and abundance of 7 taxa out of the total of 60 taxa that were identified.

Group A was dominated by the chironomids *Polypedilum scalaenum* gr. and *Ablabesmyia mallochi* and the oligochaete *Branchiura sowerbyi*. These chironomid species generally cling to the submerged portion of vascular hydrophytes, where they may feed on plant tissue (*Polypedilum*), prey on other biota, or function as detritus collectors/gatherers. *Branchiura sowerbyi* feed head down on organic-rich sediment particles (Matisoff et al. 1998). Group B was also dominated by *P. scalaenum* gr. and *B. sowerbyi*, but no *A. mallochi* were observed. Because *A. mallochi* can be associated with erosional (riffle) and depositional areas, this indicated that the benthic community structure represented in group B was associated primarily with vascular aquatic plants and organic-rich sediments (detritus). Group C was also dominated by *B. sowerbyi*, although other species contributed substantially to the benthic structure: *Probezzia* sp., *Polypedilum simulans/digitifer*, *Cladopelma* sp., *Polypedilum scalaenum* gr., and *A. mallochi*. *Probezzia* sp. is a predatory, burrowing midge that inhabits pooled areas. *Cladopelma* also inhabits slow-moving waters but functions as a detritus collector/gatherer. Group D, also dominated by *B. sowerbyi*, was less diverse with lower overall abundance. However, the chironomid *Tanypus neopunctipennis* was unique to this group. *Tanypus* also inhabits fine sediment particles and vascular hydrophytes, is predacious, and is a detritus collector/gatherer. The habitat preferences and feeding behaviors of these 7 taxa closely followed general differences in the habitats that were sampled, concluding that the cluster analysis successfully recovered essential community structure differences in Davis Creek.

A linear discriminant analysis was then used to describe group separation on the basis of 6 abiotic variables (mean particle size, total organic carbon, total arsenic, sulfate, ammonia, and moisture). The majority of separation (73%) was explained by variations in mean particle size, sediment moisture, and concentration of ammonia among the groups. Among-group differences exhibited by these 3 variables corresponded well with descriptions of sampling sites as being either erosional (i.e., larger particle sizes, lower moisture content, and comparatively low concentrations of ammonia) or depositional (i.e., smaller particle sizes, higher moisture content, and comparatively high concentrations of ammonia). For particle size and moisture content, this gradient most likely reflected current velocity in the creek. In particular, group A sites were characterized as riffle/run habitat, having comparatively greater current velocity than group D stations, which were characterized as depositional habitat. Higher concentrations of ammonia would also be expected in group D, where finer particulate organic material accumulates and degrades. Therefore, differences in invertebrate community structure could be explained largely on the basis of differences in naturally occurring variables along an environmental gradient in Davis Creek. The inference that group separation was driven by changes in particle size, moisture content, and ammonia was supported by the observation that these 3 variables were the only ones found to differ significantly among groups.

Differences in the concentration of total arsenic were not a major determinant of group separation. Comparatively higher concentrations of arsenic were detected in depositional areas (e.g., group D samples) because of preferential binding of arsenic to fine particulate organic material, silt, and clay. Total arsenic did not differ significantly among groups, further supporting the conclusion that benthic community structure was controlled by other variables.

According to the Ohio EPA's ICI, Davis Creek did not attain the state's Warmwater Habitat designation based on this study. The Warmwater Habitat designation is defined as waters "capable of supporting balance, reproducing populations of warmwater fish and associated vertebrate and invertebrate organisms and plants on an annual basis" (Ohio EPA 1988b). This designation is qualitatively defined by the Ohio EPA in general ecological terms in the state's water quality standards, and chemical–numeric criteria are assigned on a parameter-by-parameter basis (Ohio EPA 1988b). Under the agency's system for establishing stream designation, biological performance of a stream is determined by comparing study results to reference data generated from numerous studies in Ohio collected over recent years. Biological performance of a stream is dependent on characteristics within 5 major classes: biotic interactions, energy source, habitat structure, flow regime, and chemical variables (Ohio EPA 1988b). Any of the factors within each of these 5 major classes can influence the ability of a system to meet the warm-water attainment designation. Because surface water arsenic concentrations were below ambient water quality criteria, no aqueous toxicity was observed, and sediment toxicity was very limited, it is unlikely that not achieving the attainment designation was due to the presence of arsenic.

Potential causes for not attaining the warm-water designation could be watershed area or energy sources for Davis Creek. Ohio EPA metrics for Davis Creek were compared to regional reference stream data for watersheds that are 2590 ha. The Davis Creek watershed is 550 ha. The lower 1.29 km of Davis Creek is perennial, while the upper portion of the watershed is ephemeral, likely limiting the recruitment of organisms or the input of nutrients from upstream sources.

This investigation utilized the sediment quality triad approach (Chapman 1990; Chapman et al. 1992) based on multiple lines of evidence to examine ecological effects of arsenic released from the BEP to Davis Creek. The chemical/physical, biological, and toxicological measurements were useful in determining that adverse effects were minimal and were restricted primarily to the immediate vicinity of the BEP outfall. No relationships between arsenic concentrations and benthic macroinvertebrate assemblages were detected. This investigation indicated that Davis Creek was not significantly affected by arsenic despite having measured arsenic concentrations that exceeded sediment screening levels. Direct measurements of toxicity, bioavailability, and community structure were needed to determine whether arsenic was eliciting adverse ecological effects in Davis Creek, as exceeding the TEL and PEL did not predict effects. This study could provide direction for property owners, concerned citizens' groups, consultants, or regulatory agencies faced with limited information (e.g., chemical data) indicating that a site may be problematic (e.g., exceedances of ecological benchmarks), but effects are unknown, and a regulatory ecological risk assessment has not been required. Although no significant ecological risks were identified in this study, a limited sediment remediation was conducted from the BEP discharge to approximately sampling site 25.

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Appendix A. Physical/chemical characteristics of surface water at each of the 27 sampling locations within Davis Creek and the Ohio River

Sampling site	Alkalinity (mg/L)	Hardness (mg/L)	Ammonia (mg/L)	Total dissolved solids (mg/L)	Total suspended solids (mg/L)	Total organic carbon (mg/L)	Temperature (°C)	Dissolved oxygen (mg/L)	Overlying water pH	Salinity (‰)	Conductivity (μS/cm)
01	50	140	0.15	330	ND[a]	3.2	23.1	6.4	6.6	0.2	431
02	51	130	0.11	310	11	3	24.7	7.7	6.9	0.2	422
03	44	130	0.12	290	10	2.7	24.7	7.9	7.3	0.2	424
04	40	130	ND	260	10	3.3	28	6.9	8.7	0.2	417
05[b]	130	150	0.15	280	23	5.8	—	—	—	—	—
06	70	150	0.29	460	11	3.1	32.5	7.0	7.4	0.4	944
07	85	180	0.19	330	7	3.6	31.8	9.0	7.6	0.3	540
08	70	150	ND	260	17	3.1	30.6	8.8	7.6	0.2	471
09	62	150	ND	270	ND	2.6	30.1	8.7	7.4	0.2	406
10	57	150	ND	300	5	2.7	29.9	9.2	7.3	0.2	484
11	42	140	ND	260	ND	2.3	27.1	6.4	7.3	0.2	470
12	42	140	ND	300	7	2.4	26.5	6.0	7.2	0.2	468
13	39	140	0.2	290	26	2.3	26.5	6.1	7.2	0.2	396
14	42	140	ND	280	13	2.6	25.5	6.2	7.4	0.1	275
15	43	140	ND	290	10	4.7	25.8	6.6	7.5	0.2	362
16	43	150	ND	280	16	2.5	25.7	6.5	7.4	0.2	480
17	43	150	ND	280	9	2.6	26.2	6.4	7.4	0.2	482
18	41	140	ND	290	ND	2.6	26.1	7.1	7.2	0.2	480
19	41	150	0.18	290	ND	2.8	25.8	7.1	7.3	0.2	463
20	43	140	0.15	280	ND	2.9	25.8	7.2	6.5	0.2	485
21	45	150	ND	280	ND	2.6	25.9	7.2	7.0	0.2	482
22	44	150	0.12	310	ND	2.5	25.8	7.0	7.1	0.2	491
23	43	150	0.15	310	ND	2.7	26	7.8	7.2	0.2	494
24	41	140	0.13	320	9	2.7	26.1	7.7	7.2	0.2	484
25	45	150	ND	300	11	2.6	26.1	7.7	7.3	0.1	303
26	54	130	0.25	270	9	3	26	5.9	7.1	0.2	464
27	55	130	0.28	270	7	2.9	26	5.7	7.4	0.2	471

[a] ND = not detected.
[b] Some measurements were not collected due to insufficient water depth. Samples were collected from a small pool because there was no flow upstream of the outfall.

Appendix B. Sediment physical/chemical characteristics from Davis Creek and the Ohio River

Sampling site	pH	Cl (meq/L)	SO_4 (meq/L)	CO_3 (meq/L)	HCO_3 (meq/L)	Na (meq/L)	Ca (meq/L)	Mg (meq/L)	K (meq/L)	NO_3-N (mg/kg)	NH_4-N (mg/kg)
01	6.8	30.6	227.0	<0.1	144.4	24.9	116.0	29.3	7.8	0.4	44.8
02	7.2	58.8	187.0	<0.1	94.3	34.9	158.0	27.6	9.3	0.4	85.1
03	7.3	7.8	88.1	<0.1	97.2	11.0	53.2	8.9	2.4	0.5	13.4
04	7.2	58.8	267.0	3.1	127.6	44.4	140.0	29.2	14.1	0.3	116.5
05	7.1	67.1	250.0	<0.1	61.4	22.6	70.8	16.8	5.0	0.7	26.9
06	7.1	90.8	1023.2	<3.1	127.5	110.0	281.0	72.2	11.8	1.0	67.2
07	7.2	80.4	557.2	<3.1	100.2	78.2	234.0	62.1	11.1	0.8	67.2
08	7.1	197.5	462.8	<3.1	45.6	62.9	257.0	60.2	10.9	0.8	71.7
09	7.1	130.0	602.9	<3.1	96.7	48.3	210.0	52.2	8.3	0.8	49.3
10	6.8	203.7	505.4	<3.1	100.0	44.8	220.0	53.4	9.3	0.8	62.7
11	6.5	86.8	1038.0	<3.1	54.0	56.7	251.0	60.7	9.4	0.8	40.3
12	6.7	65.5	455.3	<3.1	57.0	37.1	171.0	40.4	5.9	0.8	35.8
13	6.6	352.9	672.4	<3.1	31.0	50.8	298.0	58.8	24.7	0.8	26.9
14	6.5	226.7	1028.0	<3.1	25.0	49.9	287.0	60.7	18.3	0.8	26.9
15	6.7	217.6	937.7	<3.1	52.8	51.6	309.0	64.5	16.4	0.9	49.3
16	6.8	134.8	1038.5	<3.1	60.0	54.4	361.0	76.4	11.6	0.9	44.8
17	7.5	29.7	844.7	<3.1	72.0	36.1	272.0	31.1	14.4	0.7	13.4
18	6.5	220.5	721.5	<3.1	72.0	59.7	343.0	70.6	13.0	1.2	26.9
19	6.5	155.5	662.5	<3.1	42.0	54.1	309.0	64.0	12.1	0.8	17.9
20	6.5	42.6	459.3	<3.1	66.0	33.9	112.0	25.0	3.4	0.8	22.4
21	6.2	56.1	527.3	<3.1	54.0	41.8	156.5	37.0	6.9	0.9	26.9
22	6.5	46.3	624.5	<3.1	60.0	39.6	155.0	35.5	6.5	0.8	31.4
23	6.7	120.9	413.6	<3.1	111.6	41.0	185.0	36.1	7.9	0.8	22.4
24	6.3	63.0	746.5	<3.1	60.0	46.0	196.0	38.0	11.2	0.9	35.8
25	6.5	43.5	889.6	<3.1	33.0	37.3	178.0	36.2	6.4	0.8	17.9
26	7.0	44.3	837.5	<3.1	46.0	33.6	169.0	30.2	2.8	0.8	40.3
27	7.1	52.4	367.9	<3.1	114.0	36.3	193.0	31.9	4.9	0.8	31.4

Appendix B. Extended

Total organic carbon (%)	Exchangeable acidity (meq/100 g)	Exchangeable Al (meq/100 g)	Redox potential (mV)	% Sand	% Silt	% Clay	Mean particle size (µm)	Saturated paste moisture (%)
1.2	—	<0.1	56	53	24	23	554.8	22.6
3.1	—	<0.1	–199	31	39	30	333.1	49.5
—	—	<0.1	—	82	2	16	846.4	22.5
1.2	—	<0.1	—	37	37	26	394.2	44.4
1.3	—	<0.1	—	48	21	31	502.5	56.5
1.3	<0.1	<0.1	40	19	42	39	210.6	53.4
1.1	<0.1	<0.1	–204	15	54	31	173.1	54.7
1.0	<0.1	<0.1	96	6	55	39	80.8	47.6
1.1	<0.1	<0.1	6	11	48	41	130.1	50.2
1.0	<0.1	<0.1	16	29	32	39	310.4	49.7
1.0	<0.1	<0.1	—	49	16	35	511.2	31.9
0.9	<0.1	<0.1	—	28	33	39	300.4	39.1
0.9	<0.1	<0.1	—	47	14	39	490.0	33.7
1.5	<0.1	<0.1	—	46	19	35	481.3	35.0
1.7	<0.1	<0.1	—	40	23	37	420.8	42.7
1.5	<0.1	<0.1	–199	35	28	37	370.9	45.9
1.5	<0.1	<0.1	33	76	1	23	784.4	20.1
1.0	<0.1	<0.1	—	34	27	39	360.3	42.4
0.6	<0.1	<0.1	78	55	10	35	571.1	29.2
0.9	<0.1	<0.1	161	54	15	31	562.3	32.6
0.8	<0.1	<0.1	—	49	15	36	510.9	39.5
0.8	<0.1	<0.1	161	50	14	36	520.9	40.8
0.7	<0.1	<0.1	48	57	8	35	591.1	31.1
0.4	<0.1	<0.1	136	68	4	28	703.0	22.8
0.5	<0.1	<0.1	—	68	1	31	702.1	23.2
1.5	<0.1	<0.1	—	73	1	26	753.5	30.5
0.9	<0.1	<0.1	—	63	8	29	652.8	34.3

Appendix C. Benthic metrics calculated by sampling site in Davis Creek, Belpre, Ohio

Sampling site	Taxa richness	Nr of EPT taxa[a]	Family richness	Nr of individuals	Ratio of EPT to Chironomidae	% Dominant taxa	% Non-dipterans	Shannon's Diversity Index	% Tolerant organisms (Ohio EPA)	FBI[b] (USEPA)
04	6	0	3	17	0.000	29.412	64.706	1.626	58.824	2.118
25	6	1	6	10	1.000	50.000	90.000	1.498	20.000	1.400
24	20	2	10	138	0.037	26.087	39.130	2.302	5.072	3.826
23	12	0	4	41	0.000	19.512	48.780	2.172	7.317	3.073
22	8	0	3	28	0.000	42.857	50.000	1.445	7.143	3.000
21	12	1	6	36	0.167	27.778	58.333	2.130	2.778	4.000
20	7	1	5	13	0.333	53.846	76.923	1.517	0.000	2.231
19	7	2	6	12	3.000	33.333	83.333	1.792	8.333	3.917
03	11	0	2	36	0.000	55.556	13.889	1.604	61.111	5.722
18	17	1	6	36	0.050	16.667	27.778	2.625	16.667	4.444
17	5	0	2	6	0.000	33.333	66.667	1.561	50.000	2.000
02	22	1	5	44	0.042	13.636	43.182	2.866	38.636	3.500
16	14	1	6	41	0.222	24.390	63.415	2.351	26.829	2.390
15	19	2	11	181	0.333	43.094	89.503	1.826	4.972	0.541
14	9	1	4	43	0.308	25.581	69.767	1.857	16.279	2.465
13	12	0	5	58	0.000	32.759	72.414	1.976	13.793	1.655
12	2	0	2	7	0.000	57.143	100.000	0.683	0.000	0.000
11	10	0	3	41	0.000	29.268	39.024	2.012	51.220	3.659
19	10	0	4	40	0.000	37.500	57.500	1.892	40.000	2.550
09	10	0	4	35	0.000	37.143	65.714	1.815	42.857	2.057
08	8	0	5	27	0.167	25.926	74.074	1.846	33.333	1.704
01	12	0	5	81	0.000	27.160	65.432	1.963	38.272	2.123
07	10	0	3	25	0.000	36.000	72.000	1.942	28.000	1.680
06	14	1	6	23	0.111	13.043	56.522	2.548	30.435	2.783

[a] EPT = Ephemeroptera, Plecoptera, and Trichoptera.
[b] FBI = Family Biotic Index.