DISSOLVED AND TOTAL COPPER IN A COAL ASH EFFLUENT AND RECEIVING STREAM: ASSESSMENT OF *IN SITU* BIOLOGICAL EFFECTS

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Abstract. An *in situ* chemical and biological study was conducted in the lower Muskingum River (southeast Ohio, U.S.A.) to evaluate potential effects of copper (Cu) discharged from a coal ash effluent. Effluent total Cu, dissolved Cu, TSS and pH measurements were performed monthly during January–December 1995. Benthic macroinvertebrates were sampled at five river locations using artificial substrate samplers, and *in situ* Cu analyses were conducted. Effluent Cu (total) ranged from 8 to 142 μg L^{-1} (mean = 58 μg L^{-1}), but dissolved Cu never exceeded 78 μg L^{-1} (mean = 20 μg L^{-1}). The mean ratio of dissolved Cu to total Cu in these samples was 32%. Total Cu concentrations at the biological sampling sites adjacent to the effluent discharge were higher than levels at ambient sites, but dissolved Cu levels were similar among all sites. The macroinvertebrate community proximal to the coal ash effluent had the highest number of taxa and total number of individuals; a high number of mayfly and caddis fly taxa; and the highest Invertebrate Community Index score. The high water velocity of the discharge (which likely contained particulate organic matter) apparently created a favorable microhabitat that, combined with Cu-complexing constituents in the discharge, superceded potential adverse effects of high Cu levels. This study emphasizes the importance of instream biological data when obtained in conjunction with chemical analyses.

Keywords: bioassessment, bioavailability, coal ash, copper, macroinvertebrates

1. Introduction

Chemical speciation is now recognized as a principal determinant affecting the bioavailability of trace metals (Allen and Hansen, 1996: Peijnenburg *et al.*, 1997). This acknowledgement has prompted a shift in the regulation of trace metals discharged to receiving water bodies. Since 1993, U.S. EPA's policy on metals regulation has been that the dissolved form is a more accurate predictor of potential toxic effects, and thus appropriate effluent limitations should be based on the dissolved fraction of the metal (U.S. EPA, 1992). From a regulatory standpoint, the dissolved form of metal is often synonymous with the bioavailable form, though more precise analytical determinations have been shown to more accurately represent the true bioavailable fraction (i.e., concentration of free metal ion; Deaver and Rodgers, 1996). While the current practice of regulating the dissolved form of metal has many technical advantages, sample contamination is a concern when total metal

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levels approach the Method Detection Limit (MDL). Moreover, it should be noted that metals can also incur adverse effects through exposure modes other than through the water column (e.g., sediment pore water exposure, bioaccumulation). Site-specific hydrological and habitat factors can be important determinants of risks from these exposure routes.

In both polluted and unpolluted waters, the bioavailablility of trace metals varies along spatial and temporal scales. In many cases, variation in pH and amount of complexing agents (both organic and inorganic) has a strong effect on the dissolved fraction of metals. Indeed, biological exposure and uptake is a complex process in field settings. A metal or suite of metals may have a relatively high *in situ* dissolved concentration, but chemical uptake, transformation, and depuration rates eventually dictate the degree of bioaccumulation or toxic effect. In many cases, assessments of exposure in field settings can only be approximated. Study designs that incorporate both biological and instream chemical analyses can minimize the uncertainty of instream exposure, and determine if the biological effect is consistent with the pollutant's mode of action.

When coal combustion occurs at power generating facilities, two types of ash are produced; fly ash (lighter than air) and bottom ash (often referred to as slag). At many coal-fired power plants, the ash produced during combustion is transported to large settling ponds. In these ponds, sedimentation and precipitation removes trace metals from the water column. The supernatant effluent is often discharged to a water body. Coal ash effluents are comprised principally of inorganic constituents (trace metals and salts), but relative levels of these constituents vary considerably due to natural differences in coal composition (Coleman *et al.*, 1993; Finkelman and Gross, 1999). Most of the elemental mass in coal is converted to fly ash during combustion. Thus, fly ash ponds typically contain higher concentrations of trace metals compared to bottom ash ponds. Trace metals in these effluents can exceed applicable water quality criteria. The speciation of the metal, therefore, dictates the probability of toxic effects to biota in the receiving stream.

In this study, an instream biological and chemical study was conducted to assess potential adverse effects of a coal-fired power plant coal ash discharge. Elevated levels of total copper (Cu) were previously measured in the discharge. Both total Cu and the more bioavailable form (dissolved Cu) were measured in the wastewater and receiving stream. Macroinvertebrate communities were sampled at locations proximal to the wastewater discharge, and at locations without discharge influence. The goal of the study was to determine if elevated Cu levels were associated with community-level shifts in proximal near-shore invertebrate assemblages.

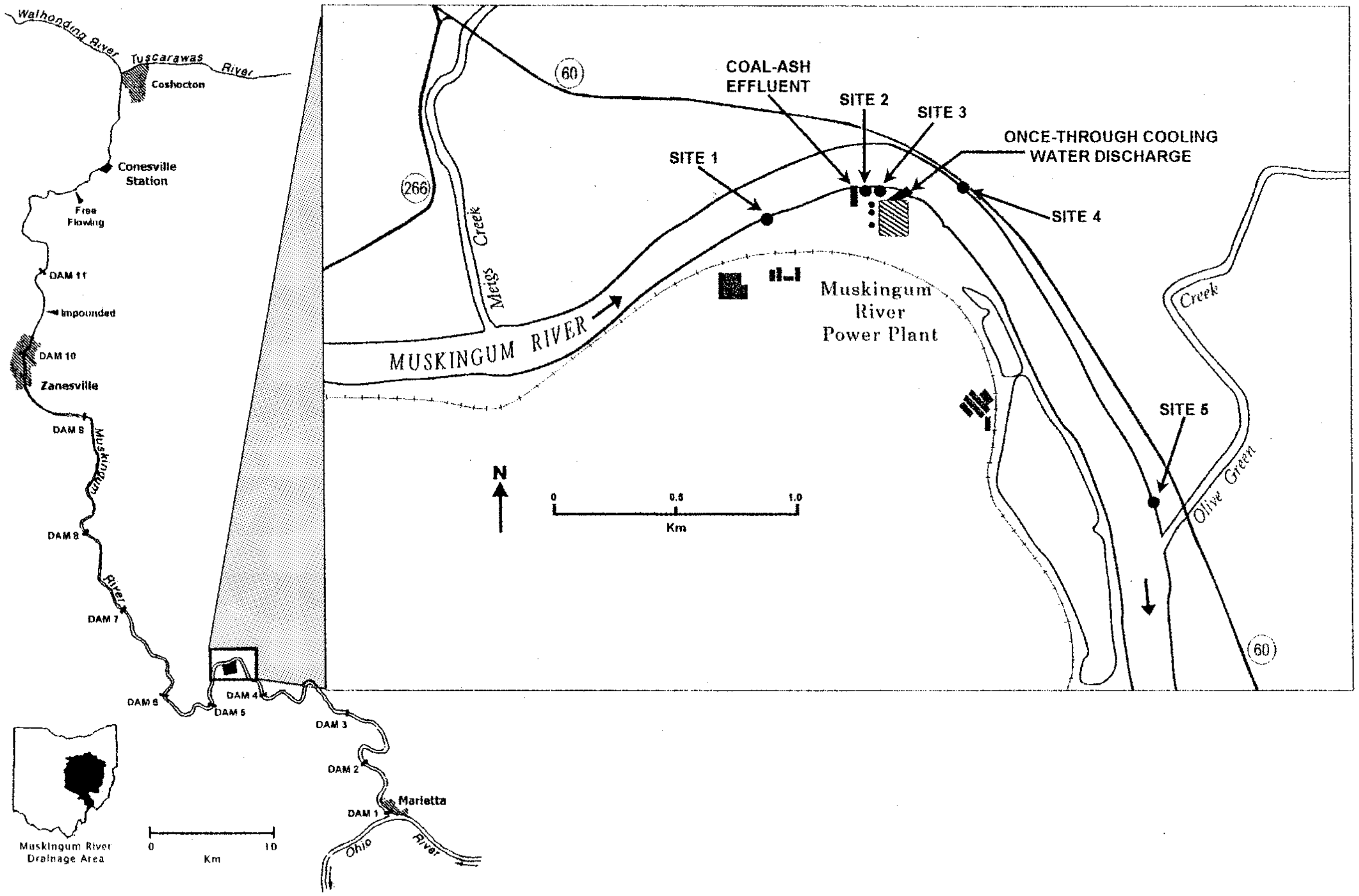

Figure 1. Location of Muskingum River, Muskingum River power plant, and five biological sampling locations. Instream copper measurements were taken at Sites 1–3.

2. Materials and Methods

2.1. STUDY SITE

The study was conducted adjacent to Ohio Power Company's Muskingum River power plant, in the lower Muskingum River (southeast Ohio, U.S.A.; Figure 1). Muskingum River Plant generates electrical power by burning coal transported from a nearby coal mine. There are five generating units, with a combined generating capacity of 1625 megawatts. The lower portion of the Muskingum River is interrupted by a series of low-head dams, thus forming discrete navigation pools between the dams. Muskingum River Plant is located approximately halfway between Dam 5 and Dam 4 on the lower river, about 46 km upstream from the confluence of the Muskingum River and Ohio River (Figure 1). During the study period, the mean daily flow of the Muskingum River near the power plant was 63.5 m^3 s^{-1}.

During the electrical generation process, both fly ash and bottom ash is produced. Coal ash wastewater effluent is discharged to the Muskingum River just upstream of the plant's cooling water intake structure (Figure 1). This effluent is actually comprised of numerous process wastewaters (bottom ash, fly ash, coal pile runoff, cooling tower blowdown, and low volume sewage treatment plant). The long-term mean flow rate of the discharge is 0.21 m^3 s^{-1}. Prior to discharge to the river, suspended solids in the combined wastestreams are precipitated out by settling within a large pond. Elevated levels of total copper (>100 μg L^{-1}) were measured in the effluent discharge during 1990–1994. The primary source of the copper in the pond was cooling tower blowdown (river water with highly concentrated constituents due to long-term evaporative cooling of the water). No other metals in the effluent appeared to approach applicable freshwater acute (or chronic) thresholds as determined by hardness-specific water quality criteria (U.S. EPA, 1995).

Five instream locations were selected for biological assessments (Figure 1). Water velocity data (measured with a Marsh-McBirney 201 meter) and substrate composition observations are provided in Table I. Site 1 was located upstream of Muskingum River Plant, about 0.75 km upstream of the coal ash effluent. This site had somewhat unique substrate characteristics (large-diameter constituents). Site 2 was located about 10 m downstream of the effluent discharge. Water velocity was highest at Site 2 due to turbulence effects of the effluent discharge. This site represented the location nearest to the effluent having suitable habitat for immobile aquatic life.

Site 3 was located about 20 m downstream from Site 2, where the effluent was more completely mixed. This site was considered to be influenced by the coal ash effluent, although to a lesser extent than Site 2. The substrate composition at Sites 2 and 3 were similar. Site 4 was located on the opposite shore of the plant's once-through cooling water discharge. The samplers were placed near emergent

TABLE I

Physical habitat characteristics at five near-shore macroinvertebrate sampling sites, lower Muskingum River, August 1995

	Sampling site				
	1	2	3	4	5
Water velocity (m s^{-1})[a]	0.04	0.11	0.06	0.04	0.02
Substrate composition (% of total)[b]					
Boulder	30	–	–	–	–
Bedrock	20	–	–	–	–
Cobble-gravel	40	40	50	25	30
Sand	–	30	40	25	30
Silt	10	30	10	50	40

[a] Measured at time of sampler placement.

[b] Based on visual observations at 0.5–1 m depth.

vegetation, about 7 m from shore. Site 5 was located about 1.5 km downstream of the once-through cooling discharge, on the shore opposite the power plant. Sampler placement at this site was underneath overhanging vegetation canopy; water velocity was lowest compared to other sites, and the substrate composition was similar to that at Site 4. Both Sites 4 and 5 were considered downstream reference sites, i.e., they were located outside the influence of the coal ash effluent.

2.2. ANALYTICAL METHODS

Coal ash effluent water samples were collected during the period December 1994–December 1995. Total Cu, dissolved Cu, total suspended solids (TSS), and pH were measured monthly. During August–September 1995 weekly samples were taken, as this coincided with the instream biological study. Samples for copper analysis were collected in 1 L polyethylene containers. Each sample was iced and, upon delivery at the laboratory, two split aliquot samples were obtained. One aliquot was immediately acidified to $pH < 2$ using HNO_3, while the other was filtered (0.45 μ filter) and then acidified to $pH < 2$. For both samples, total recoverable copper was determined using inductively coupled plasma atomic emission spectroscopy (U.S. EPA Method 200.7; U.S. EPA, 1983). The MDL was typically 1 $\mu g\ L^{-1}$, though some analyses had an MDL of 0.5 $\mu g\ L^{-1}$. Quality assurance procedures consisted of analyses of Cu in duplicate, spiked, laboratory blank, and field blank samples. Effluent total suspended solids (TSS) and pH were measured in split samples at the same time Cu samples were collected.

During 1995, bimonthly water samples were collected at the effluent discharge and plant intake (ambient water) for analysis of dissolved salts (Ca^{2+}, K^+, Mg^{2+}), trace metals (Al, Cd, Ni, Zn), and total hardness. Copper was also measured in plant intake samples. Chloride (Cl^-) was measured biannually at both locations. The pH of intake samples was determined on a quarterly basis in 1995.

2.3. INSTREAM BIOLOGICAL ASSESSMENTS

An instream biological assessment was conducted from August–September 1995 at Sites 1–5. A study of near-shore macroinvertebrate communities was chosen because: (1) the abundance and faunal diversity of macroinvertebrates is a valuable indicator of recent exposure to water quality conditions; (2) some macroinvertebrate taxa (e.g., mayflies) are known to be particularly sensitive to Cu; and (3) fish are highly mobile, thus assessing exposure of a pollutant to these organisms is very difficult in field settings. To minimize potential effects of substrate differences, modified Hester-Dendy samplers were used as colonization substrates. At each biological assessment site, five replicate Hester-Dendy samplers were attached to a large cinder block per standardized Ohio EPA procedures (Ohio EPA, 1989). The samplers were placed in the river in early August 1995 (1 m depth) and recovered six weeks later. Sample collection, processing, and taxa identification generally followed Ohio EPA (1989) procedures.

Macroinvertebrate results were evaluated using a modification of the Invertebrate Community Index (ICI), a multi-metric criterion that encompasses structural (total number taxa; number of mayfly, caddis fly, and dipteran taxa), functional (percent mayfly, caddis fly, Tanytarsini midges, and non-insects), and pollution tolerance (percent tolerant organisms) attributes (Ohio EPA 1987; DeShon, 1995). For each metric, a numeric score of six, four, two, or zero is assigned based on metric scores for undisturbed regional reference sites. One metric of the ICI evaluates the number of taxa collected by qualitative depletion sampling. Because the study site was on a large impounded river, this metric (typically conducted in shallow free-flowing habitats) was not included in the overall score. ICI values were compared between sites to evaluate potential effects of the coal ash effluent on *in situ* aquatic life.

The faunal similarity of macroinvertebrate communities sampled at the five sites was assessed using the Index of Similarity (S) (U.S. EPA, 1990). Percent similarity of taxa collected was calculated using the following formula:

$$S = 100 \times [2\, C/A + B]$$

where

A = number of taxa collected at Site A;
B = number of taxa collected at Site B;
C = number of taxa collected at both Site A and B.

Similarity values were used to assess potential shifts in faunal composition in relation to proximity to the effluent discharge, relative to most upstream and downstream locations.

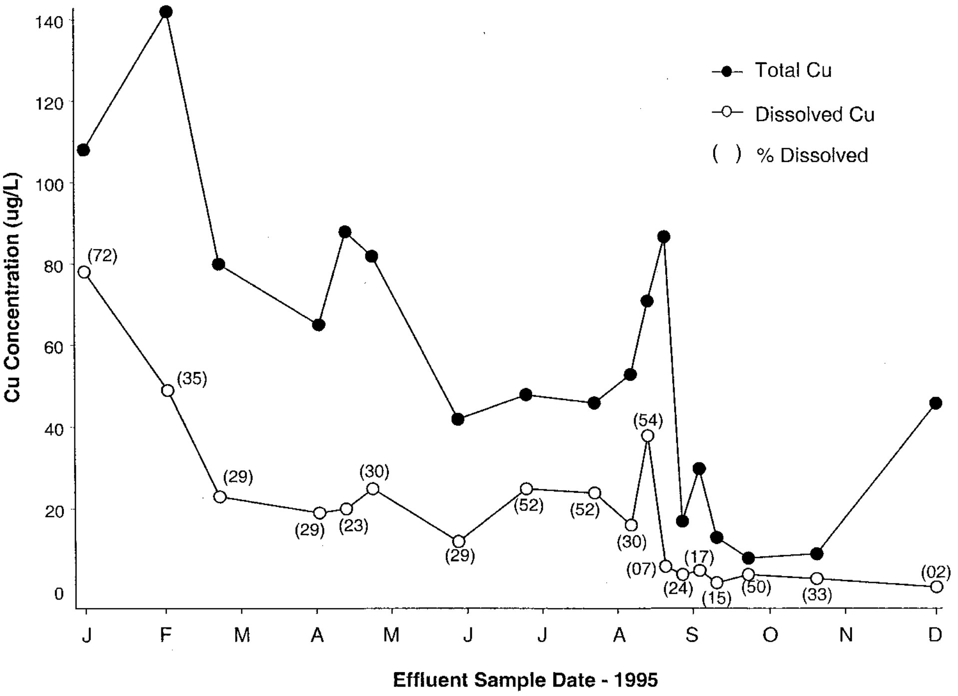

Figure 2. Total and disolved coper concentrations in the coal ash effluent discharge, January–December 1995. In parentheses, the percentage of dissolved copper (relative to total) is indicated.

Weekly samples for total recoverable and dissolved copper were taken at Sites 1–3 during the macroinvertebrate colonization period to compare instream sample concentrations to effluent concentrations and estimate the portion of Cu that was bioavailable to near-shore aquatic life. Samples were not collected at Sites 4 and 5, as it was assumed that Cu levels at these locations were similar to background (Site 1) levels. Water samples were collected just next to the instream macroinvertebrate samplers during August and September 1995, and were processed for total and dissolved Cu analysis as described above.

3. Results

3.1. ANALITICAL RESULTS

Summary statistics for all Cu analyses (effluent discharge and instream sites) and effluent pH and TSS are provided in Table II. Paired total recoverable and dissolved Cu concentrations at the coal ash effluent discharge are provided in Figure 2. Total Cu concentrations varied seasonally, and there was a gradual trend of lowered Cu concentrations during the study period (Figure 2). The high Cu levels observed in January and August were likely due to peak electrical output during extreme

TABLE II

Results of copper analyses for the coal ash effluent discharge (December 1994–December 1995) and three instream locations (August–September 1995). TSS and pH analyses also provided for effluent samples. For all parameters, mean values (minimum and maximum values in parentheses) are indicated

Parameter	Sample location			
	Effluent discharge (N = 18)	Instream Site 1 (N = 6)	Insteam Site 2 (N = 7)	Insteam Site 3 (N = 6)
Total recoverable Cu (μg L^{-1})	58 (8–142)	4 (3–7)	11 (4–22)	10 (2–20)
Dissolved Cu (μg L^{-1})	20 (1–78)	2 (0.5–5)	3 (1–6)	4 (0.5–13)
Percent dissolved Cu	32 (2–72)	53 (2–100)	37 (14–75)	31 (10–65)
TSS (mg L^{-1})	14 (4–25)	–[a]	–[a]	–[a]
pH (S.U.)	7.9 (7.4–8.7)	–[a]	–[a]	–[a]

[a] No measurements taken.

weather conditions; increased amounts of coal ash produced during peak generation periods typically result in temporary, lowered settling efficiency of ash particles in the treatment pond.

Effluent total recoverable Cu levels varied from 8 μg L^{-1} (October 1995) to 142 μg L^{-1} (February 1995); the mean concentration was 58 μg L^{-1}. Dissolved Cu levels ranged from 1 μg L^{-1} (December 1995) to 78 μg L^{-1} (January 1995), and had a mean concentration of 20 μg L^{-1}. Dissolved Cu levels were highly correlated with total Cu concentrations ($P < 0.001$; r = 0.75) (Figure 2). As expected, total recoverable concentrations were always higher than dissolved levels. The percentage of Cu in the dissolved phase was highest in the initial sample (72%), but never exceeded 52% in subsequent samples (Figure 2). The overall mean percentage of dissolved Cu was 32%. The percent of dissolved Cu was correlated with dissolved Cu concentrations ($P < 0.001$; r = 0.71).

TSS levels were relatively low in the effluent samples (mean = 14 mg L^{-1}), and effluent pH was consistently circumneutral (geometric mean = 7.88). Cu concentrations (total and dissolved) were not correlated with effluent pH, but total Cu was highly correlated with TSS ($P < 0.001$; r = 0.73). Dissolved Cu concentrations were weakly correlated with TSS ($P < 0.05$; r = 0.48), however the percentage of dissolved Cu showed no relationship with either effluent pH or TSS concentration.

TABLE III

Chemical analysis results for biomonthly ambient (upstream) Muskingum River and coal ash effluent samples, 1995. N = 6 or 7. Metal concentrations (except Al) are in μg L^{-1}; other constituents are in mg L^{-1}. Values are mean (± SD)

Location	Hardness ($CaCO_3$)	Ca	Mg	K	Cl	Al	Cd	Cu	Ni	Zn
Muskingum	236	62.3	19.4	4.8	45[a]	1.04	0.3	6	4	18
River	(45)	(10.9)	(4.3)	(1.1)	–	(0.74)	(0.18)	(2)	(2)	(11)
Coal ash	371	105.3	26.7	12.1	62[a]	0.57	1.5	58[b]	23	53
Effluent	(52)	(14.2)	(5.1)	(1.9)	–	(0.31)	(1.0)	(36)	(10)	(36)

[a] N = 2.
[b] N = 18.

A total of 19 instream samples for paired total/dissolved Cu measurements were obtained from Sites 1–3 (Table II). The highest total Cu measurement (22 μg L^{-1}) was found at Site 2 (adjacent to the effluent discharge). Mean total Cu values at Sites 2 and 3 were about 2.5 times higher than the mean concentration at Site 1. Mean dissolved Cu levels at the three sites were similar, with only marginal increases at sites influenced by the effluent. In the instream samples, the percentage of Cu in the dissolved phase was low at Sites 2 and 3 (mean = 37 and 31%, respectively), but somewhat higher (57%) at the upstream location. This difference, however, should be regarded with caution. The sample size of paired samples at all sites was low. In addition, most of the dissolved Cu measurements at Site 1 were at, or slightly above, the MDL. At these low analytical levels, the ratio of dissolved Cu to total Cu is very sensitive to small changes in measured values.

Routine water chemistry analysis results indicated that the effluent had higher mean levels of dissolved salts and trace metals compared to ambient river samples (Table III). Total hardness, not surprisingly, was higher in the effluent discharge. Aluminum was the only constituent that was higher in ambient samples. Though not presented in the table, the geometric mean pH of plant intake samples (measured quarterly) was 8.2 S.U.; ambient water pH was, thus, slightly more basic than the effluent (geometric mean = 7.9 S.U.).

3.2. INSTREAM BIOLOGICAL RESULTS

Appendix I indicates macroinvertebrate taxa collected in artificial substrate samplers at five near-shore sampling locations. A total of 49 taxa were collected during the study. Taxa richness (all sites combined) was highest for midges (Diptera: Chironomidae) and mayflies (Ephemeroptera), with 13 and 9 taxa collected, respectively.

TABLE IV

Similarity values for macroinvertebrate communities collected on Hester-Dendy samplers at five locations on the Muskingum River, August–September 1995. Percent similarity (S) calculated by multiplying value by 100

Site	Sample site 1	2	3	4	5
1	–	0.56	0.77	0.72	0.61
2		–	0.66	0.57	0.56
3			–	0.65	0.64
4				–	0.67

The proximity of the effluent discharge did not result in lowered attributes of macroinvertebrate composition and function. Site 2 (adjacent to the effluent) had the highest number of total individuals (1196), the highest number of taxa (31), and the highest number of mayfly taxa (7; same as for Site 1). The elevated total abundance of individuals at Site 2 was largely attributed to high numbers of two caddis fly taxa (*Hydropsyche orris* and *Potamyia flava*) and the midge *Glyptotendipes*.

Taxa collected exclusively at Site 2 (total of 8) represented five taxonomic groups (a bryozoan and four insect orders) encompassing a range of pollution tolerance; thus, increased taxa richness at Site 2 was not attributed exclusively to greater diversity of pollution-tolerant taxa. The amphipod *Gammarus fasciatus* was collected exclusively at sites near the effluent discharge, and was most abundant at Site 2.

Site 1 (upstream reference) was characterized by high richness (and abundance) of mayfly taxa, and low richness of chironomid taxa. Only four chironomid taxa were collected at Site 1, whereas 5–11 taxa were collected at other sites. Sites 3, 4, and 5 were similar in taxa richness (25 to 27 total taxa collected). Sites 4 and 5 had a lower abundance of mayflies relative to the three upstream sites; Site 5 had the fewest number of these taxa collected (4). Taxa that were particularly abundant at Site 5 were the damselfly *Argia tibialis*, and the chironomid midge *Dicrotendipes neomodestus*. Site-specific habitat features at this location (overhanging vegetation, low water velocity) may have been particularly favorable for these abundant taxa.

Invertebrate Community Index values were similar among Sites 1, 3, 4, and 5 (ICI = 24 to 28; Appendix I). The highest ICI value was found at Site 2 (ICI = 34). High metric scores for taxa richness attributes (i.e., total number of taxa and total number of mayfly, caddis fly, and dipteran taxa) were most influential in causing the relatively high ICI value at this site.

Community similarity values indicated that, from a taxa presence/absence measure, Sites 1 and 2 were relatively dissimilar (S = 0.56) (Table IV). Similarity values between Site 1 and Sites 3 and 4 were relatively high (S = 0.77 and 0.72, respectively), indicating a more homogenous faunal composition (with Site 1) downstream of the immediate effluent mixing zone. The faunal similarity among downstream sites indicated relatively dissimilar communities between Site 2 and Sites 4–5, with higher levels of faunal similarity found among Sites 3, 4, and 5. Thus, the faunal assemblage at Site 2 was relatively unique compared to all other sites.

4. Discussion and Conclusion

Concentrations of dissolved salts measured in ambient and effluent samples were within the range of values measured at ambient water quality stream locations in the Muskingum River basin, which drains many coal-bearing geological formations (USGS, 1993). Levels of dissolved salts and trace metals were higher in the effluent discharge, but coal ash effluents are typically enriched with these constituents (Rowe *et al.*, 2002). With the exception of Cu, the concentrations of other measured trace metals did not approach applicable chronic toxicity criteria for protection of aquatic life. Assuming an instream hardness value of 300 mg L^{-1} $CaCO_3$, the applicable total recoverable chronic criterion values are 5.8 μg L^{-1} (Cd), 24 μg L^{-1} (Cu), 130 μg L^{-1} (Ni), and 300 μg L^{-1} (Zn) (U.S. EPA, 1995). However, the mean Cu concentration at the effluent discharge (58 μg L^{-1}), exceeded both the chronic and acute water quality criterion (acute criterion = 39 μg L^{-1}). Thus, Cu was the only metal that had the potential to cause some toxic effect at locations near the discharge point.

The macroinvertebrate community in the Muskingum River, adjacent to a coal ash effluent discharge, had the highest number of taxa, the highest total abundance, and the highest multi-metric community score relative to nearby upstream and downstream locations. Thus, the proximity of the effluent discharge appeared to promote a more diverse, functionally complex fauna compared to other sites. The relatively dissimilar community similarity of this location, relative to Sites 1, 4, and 5, provides evidence that the effluent discharge promoted a unique, but spatially limited, invertebrate community. A complex composite of habitat and physicochemical conditions presumably enabled the establishment of this unique community.

Measured Cu concentrations at Site 2 were highest among the three instream sites. While the mean Cu copper concentration (11 μg L^{-1}) was not particularly elevated at this location, previous researchers have reported adverse effects to sensitive macroinvertebrates when Cu exposures were in the range 10–15 μg L^{-1}. Schultheis *et al.* (1997) found that taxonomic richness and total abundance of macroinvertebrates was reduced in a stream receiving mining effluent (range of total Cu levels = 12–32 μg L^{-1}). Leland *et al.* (1989) documented shifts in macroinvertebrate community structure in a Sierra Nevada stream that was artificially dosed to achieve stream concentrations of total filterable Cu levels of 2.5–15 μg L^{-1}. The authors elucidated a Cu threshold value of 2.5–10 μg L^{-1} for most taxa.

In both laboratory and field exposures, Clements *et al.* (1990) exposed macroinvertebrate taxa to acid-soluble Cu concentrations ranging from 12–50 μg L^{-1}. Macroinvertebrates was considerably more sensitive in laboratory exposures. During field exposures, however, total mayfly abundance, total community abundance, and taxa richness decreased by 25, 44, and 10%, respectively, during Cu exposures at 12 μg L^{-1}. In a related study, Clements *et al.* (1989) exposed macroinvertebrates to ambient river water dosed with Cu to achieve exposure levels of 6, 12, and 25 μg L^{-1}. The sensitivity of macroinvertebrates differed between the two water sources, owing to water chemistry differences. Certain taxa showed reduced densities at exposure levels of 12 μg L^{-1} (*Baetis brunneicolor, Isonychia bicolor, Stenonema modestum*, Tanytarsini chironomids), and total abundance of macroinvertebrates was also reduced. Other taxa (net-spinning caddisflies, Orthocladiini chironomids) were quite tolerant to elevated Cu levels. While these and other studies indicate the potential of toxic effects upon freshwater macroinvertebrates at Cu exposure concentrations between 10–20 μg L^{-1}, the absence or presence of effects are clearly taxa-specific, and dependent on water quality characteristics.

The observation of a more diverse community adjacent to the effluent discharge was likely explained by low bioavailablility of Cu, and site-specific habitat characteristics. Dissolved Cu levels near the discharge were elevated compared to other sites, but were likely not high enough to cause toxic effects. Brix *et al.* (2001) summarized Cu acute and chronic toxicity to freshwater organisms and predicted that chronic effects to insects were unlikely at dissolved Cu concentrations less than 10 μg L^{-1}. Moreover, natural Cu-complexing constituents in the ash treatment pond (and the Muskingum River) likely bound a significant portion of the dissolved Cu that was released at the discharge point. The effluent was shown to have elevated (compared to background) concentrations of dissolved salts, which is typical of coal ash wastewaters (Suloway *et al.*, 1983, El-Mogazi *et al.*, 1988). Some dissolved cations (Ca^{2+}, Na^{2+}) are known to compete with Cu for adsorption onto biological receptor sites, making Cu less bioavailable (Mansilla-Rivera and Nriagu, 1999). Empirical evidence for this relationship (e.g., Erickson *et al.*, 1996) is the basis of the Biotic Ligand Model, which predicts that toxic effects will occur when the metal-biotic ligand complex reaches a critical concentration (Di Toro *et al.*, 2001). While the presence of particulate organic matter in the effluent is only anecdotal, the presence of abundant filter-feeding insect taxa near the discharge point strongly suggests that such constituents were present in the discharge. Biological uptake of Cu is negligible when it is adsorbed to complex organic molecules (Dodge and Theis, 1979; Buckley, 1983; Van Veen *et al.*, 2002). Presumably, bioavailability (and hence biological uptake) of Cu was negligible when the effluent initially mixed with the receiving stream.

The increased water velocity at Site 2, caused by the effluent discharge, could have contributed to the higher taxa richness at this location. In addition, the ash treatment pond changed to a green-colored condition during summer months. The coloration change was assumed to be caused by algal and diatom productivity. The dominant taxa found at Site 2 (*Hydropsyche orris, Potamyia flava, Glyptotendipes* sp.) are considered to be collector-flilterers regarding trophic function; principal food items consumed by these taxa are diatoms, algae, and detritus (Merritt and Cummins, 1984). Van Hassel and Wood (1984) documented high abundances of filter-feeding caddis flies (Cheumatopsychidae) and chironomid dipterans below a fly ash impoundment. Phytoplankton and heterotrophic bacteria are often present in coal ash impoundments (e.g., Larrick *et al.*, 1981). The high abundance of dominant filter-feeding taxa at Site 2 was likely due to a combination of suitable food material (pond-derived primary producers and fine particulate organic matter), combined with high water velocity.

In conclusion, an instream chemical and biological study near a power plant effluent discharge indicated that near-shore macroinvertebrates were not adversely affected by elevated Cu levels in the discharge. A more taxa-rich community was found near the discharge, and this increased diversity resulted in the establishment of a relatively unique community (i.e., low faunal similarity) compared to other locations. Carlisle and Clements (1999) evaluated various macroinvertebrate responsive variables to heavy metal exposure, and found that taxa richness parameters were the most sensitive in explaining shifts in community composition. Thus, potential *in situ* effects of the coal ash discharge were evidently not measurable in this study, considering the community metrics examined. High water velocity of the effluent discharge (which appeared to contain suitable food material for filter-feeding invertebrates) appeared to promote a site-specific diverse community. Potential toxic effects of Cu, if present, were unimportant relative to unique habitat factors.

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Appendix

Appendix I

Total number of macroinvertebrate taxa collected in Hester-Dendy samplers at five locations on the Muskingum River, August–September 1995

Taxon	Total number collected in composite sample				
	Site 1 (upstream effluent)	Site 2 (adjacent to effluent)	Site 3 (20 m from effluent)	Site 4 (downstream of plant)	Site 5 (downstream of plant)
Platyhelminthes					
Planariidae					
Dugesia tigrina		1	2		10
Bryozoa					
Plumatellina					
Hyalinella punctata				1	1
Plumatella sp.		1			
Mollusca					
Gastropoda					
Pleuroceridae					
Elimia livescens	5		5	3	
Viviparidae					
Lioplax sp.					1
Physidae					
Physella sp.			1		4
Planorbidae					
Micromenetus dilatatus					1
Bivalvia					
Corbiculidae					
Corbicula fluminea	1	2	2		
Annelida					
Oligochaeta					
Tubificidae					
Limnodrilus sp.					2
Arthropoda					
Crustacea					
Amphipoda					
Gammarus fasciatus		18	3		
Insecta					
Ephemeroptera					
Caenidae					
Caenis hilaris	12	27	4		

Appendix I

(continued)

Taxon	Total number collected in composite sample				
	Site 1 (upstream effluent)	Site 2 (adjacent to effluent)	Site 3 (20 m from effluent)	Site 4 (downstream of plant)	Site 5 (downstream of plant)
Insecta *(continued)*					
Ephemeridae					
Hexagenia sp.	33	6	13	5	15
Heptageniidae					
Stenacron interpunctatum	41	12	48	7	8
Stenonema exiguum				1	
Stenonema integrum	67	57	23	12	10
Stenonema modestum		1			
Stenonema terminatum	1				
Stenonema vicarium	1	9	1	3	
Tricorythidae					
Tricorythodes sp.	14	51	6	4	2
Odonata					
Aeschnidae					
Boyeria vinosa			1		
Coenagrionidae					
Argia tibialis		7	7	12	58
Coenagrion sp.		3			
Corduliidae					
Neurocordulia molesta	2		1		2
Libellulidae					
Celithemis sp.			1		
Macromiidae					
Macromia taeniolata		1			
Trichoptera					
Hydropsychidae					
Cheumatopsyche sp.		6			
Hydropsyche orris	34	218	2	2	
Hydropsyche simulans		6			
Potamyia flava	5	348	12	6	2
Leptoceridae					
Nectopsyche sp.		2	1		3
Polycentropodidae					
Cyrnellus fraternus	203	78	132	70	47
Neureclipsis sp.		1			
Coleoptera					
Elmidae					
Ancyronyx variegata					2
Macronychus glabratus	2	4	5	2	10
Stenelmis humerosa-sinuata	9	42	5	6	11

Appendix I

(continued)

Taxon	Total number collected in composite sample				
	Site 1 (upstream effluent)	Site 2 (adjacent to effluent)	Site 3 (20 m from effluent)	Site 4 (downstream of plant)	Site 5 (downstream of plant)
Insecta *(continued)*					
Coleoptera *(continued)*					
Gyrinidae					
Dineutus sp.		2	1		
Diptera					
Chironomidae					
Ablabesmyia mallochi	2		1	7	7
Ablabesmyia ramphe	10	6	11	25	12
Cryptochironomus sp.				1	
Dicrotendipes neomodestus			1	22	22
Dicrotendipes sp.		3			
Glyptotendipes sp.	246	274	78	183	626
Nanocladius sp.		1		1	2
Parachironomus sp.		1		2	3
Polypedilum (P.) illinoense		2			4
Stenochironomus sp.				6	
Tanytarus sp.				1	
Thienemannimyia gr.		6		6	
Tribelos sp.	34		3	19	‘15
Total number individuals	727	1196	370	407	880
Total number taxa	20	31	27	25	26
Total mayfly taxa	7	7	6	6	4
Total mayfly individuals (% of total abundance)	169(23.2)	163(13.6)	95(25.7)	32(7.9)	35(4.0)
Invertebrate Community Index (ICI)	26	34	26	28	24

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