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Flooding and arsenic contamination: Influences on ecosystem structure and function in an Appalachian headwater stream

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Abstract

We investigated the influence of flooding and chronic arsenic contamination on ecosystem structure and function in a headwater stream adjacent to an abandoned arsenic (As) mine using an upstream (reference) and downstream (mine-influenced) comparative reach approach. In this study, floods were addressed as a pulse disturbance, and the abandoned As mine was characterized as a press disturbance. We further addressed chronically elevated As concentrations as a ramp disturbance, in which disturbance intensity was ramped by increasing proximity to the As source. Stream ecosystem structure and biogeochemical functioning were characterized monthly over a period ranging from July to December 2004. Influence of the press disturbance was evident in the mine-influenced reach, where As concentrations (254 ± 39 μg L^{-1}) were more than 30 times higher than in the reference reach (8 ± 1 μg L^{-1}). However, in almost all cases the presence of the abandoned As mine appeared to exert little influence on reach-scale measures of ecosystem structure and function (e.g., organic matter [OM] standing crops, phosphorus [P] uptake). Conversely, floods significantly influenced OM standing stock in both study reaches. Interactions between press and pulse disturbances influenced P uptake in the mine-influenced reach. Within the mine-influenced reach, P uptake across a gradient of As concentrations correlated with Michaelis–Menton models of enzyme kinetics in the presence of a competitive inhibitor. These results indicate that As competitively inhibits P uptake by microbial assemblages.

Disturbances occur when potentially damaging forces, such as forest fires, floods, and anthropogenic activities, are imposed upon habitat space occupied by a population, community, or ecosystem (Lake 2000). Disturbances differ in their temporal pattern of intensity and duration and can be separated into three primary categories: pulse, press, and ramp disturbances (Lake 2000). Pulse disturbances exert discrete, short-term influences on an ecosystem, while press disturbances are characterized by long-term, sustained influences. The concept of a ramp disturbance was first introduced by Lake (2000) to describe a case in which disturbance intensity increases steadily with time.

Specific disturbance frequency and intensity may dictate ecosystem stability and successional recovery. However, many ecosystems experience a mix of disturbance types simultaneously; thus, understanding responses to disturbance may require knowledge of disturbance interaction and history (Ross et al. 2004). In some cases the magnitude and duration of responses to major pulse disturbances can depend on the presence or absence of an underlying press disturbance (Collier and Quinn 2003), or the influence of a press disturbance may only be evident after a pulse disturbance (Parkyn and Collier 2004).

Stressors on aquatic ecosystems resulting from mining can persist for extended periods of time (Courtney and Clements 2002). Mining potentially imposes a template of multiple disturbances on aquatic ecosystems; these disturbances include increased acidity and heavy metal concentrations, precipitation of metal oxides on sediments, and sedimentation (Kelly 1988; Courtney and Clements 2002). These stressors often represent a press disturbance, although they may also be pulsatile as a result of discrete events such as storms or toxic spills.

The effects of disturbances may be manifested at all levels of biological organization. Because preservation of biological integrity includes protecting higher levels of biological organization, some researchers (e.g., Gessner and Chauvet 2002) have suggested that field responses of ecosystem structure and function are more ecologically relevant than are effects at lower levels. Functional metrics, such as rates of metabolism and measures of nutrient cycling, integrate a wide variety of ecosystem characteristics, are sensitive to ecosystem perturbation, and show both lower variability and higher sensitivity than commu-

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nity-level metrics (Niemi et al. 1993). Therefore, functional measures potentially provide insight with regard to the reasons for which why stream communities are perturbed and the causes of environmental degradation.

Recently, Chaffin et al. (2005) demonstrated that elevated levels of arsenic (As) decreased leaf decomposition rates in a headwater stream as a result of the toxic effects of As on the macroinvertebrates. As is a metalloid linked to human skin, bladder, and other cancers (National Research Council 1999) and is toxic to many prokaryotes and eukaryotes (Oremland and Stolz 2003). Arsenate (AsO_4^{-3}), the dominant form of As in aquatic ecosystems, is a molecular analog to phosphate (PO_4^{-3}; Oremland and Stolz 2003; Mkandawire et al. 2004). Studies on PO_4^{-3} uptake by plants have indicated that AsO_4^{-3} competes with PO_4^{-3} for the same uptake carriers, which may explain the reduction of phosphorus (P) uptake in plants when As is present (Mkandawire et al. 2004). Speir et al. (1999) demonstrated that although elevated As caused a significant decrease in phosphatase activity in soils, there were no negative effects of As on either microbial respiration or biomass. As a result, Speir et al. (1999) concluded that the decline in phosphatase activity conformed to Michaelis–Menton (M-M) kinetics and was a response to competitive inhibition of phosphatase activity by As resulting from the chemical similarities between AsO_4^{-3} and PO_4^{-3}.

In the current study, we address the general hypothesis that individual disturbances do not act as single discrete entities but rather interact to alter ecosystem structure and function. More specifically, we focus on how flooding (i.e., a natural disturbance) and chronic As contamination (i.e., an anthropogenic disturbance) influence a headwater stream discretely and how they interact with one another. Along with structural attributes (i.e., organic matter [OM] standing crops, hydrogeomorphic characteristics), we used ecosystem metabolism and nutrient spiraling (i.e., linked transport, uptake, and release; Webster and Patten 1979) to address how disturbances may interact to organize ecosystem structure and function.

Methods

Study site—Research was conducted in a headwater stream located at the site of the former Brinton Arsenic Mine (BAM) in southwestern Virginia. From 1903 to 1919, arsenopyrite was mined within a few hundred meters of the stream, and several tailing piles were deposited adjacent to the stream channel. Tailings consist primarily of unconsolidated sediment containing arsenopyrite, scorodite ($FeAsO_4*2H_2O$), and As-rich iron oxides (Harvey et al. 2006), as well as minerals from the host rock, a quartz sericite schist (Dietrich 1959). Tailing piles and adjacent areas exhibit extensive signs of erosion and mass wasting into the stream channel. Stream flow originates approximately 200 m above the tailing piles. Baseflow velocity (0.06–0.11 m s^{-1}), width (0.55–0.58 m), depth (0.010–0.015 m), and discharge (0.5–0.8 L s^{-1}) were consistent along the entire stream channel (Chaffin et al. 2005; this study). No distinct pool-riffle sequences are evident in the stream, and channel gradient is approximately 4% (Brown 2006).

The study site (Fig. 1) includes a 120-m upstream reference reach and a 90-m downstream mine-influenced reach. The reference reach is not influenced by the prior mining activities and is heavily forested with deciduous trees (Chaffin et al. 2005). The mine-influenced reach begins at the upstream extent of the tailing piles and is constrained to 90 m as a result of a property boundary downstream. Approximately 60 m of the mine-influenced reach is devoid of vegetation along the side of the stream adjacent to the tailing piles. Riparian vegetation on the opposing side of the channel is typical of the watershed. The remaining 30 m of the reach includes riparian vegetation on both sides of the stream, similar to the composition and abundance exhibited along the reference reach. Although As concentrations increase significantly along the 90-m reach, concentrations of other toxic elements (i.e., copper, zinc, and cadmium) are not comparably elevated (Chaffin et al. 2005).

Due in part to the detrimental nature and scarcity of surface As mining, our study sites are not replicated, and study reaches are not independent as a result of integration by flowing water. This is often the reality of ecosystem-scale studies (Carpenter 1989), and our approach has been used successfully elsewhere and in the present study site (Chaffin et al. 2005).

Stream chemistry—Filtered water samples (Whatman GF/F) for anion analysis were collected at 10-m intervals within each reach on a monthly basis from July through December 2004. Water samples were analyzed for anions (chloride [Cl^-], nitrogen [as NO_3-N], and P [as PO_4-P]) using a Dionex DX-500 following the standard methods of the U.S. Environmental Protection Agency (1993). We were unable to use colorimetric techniques, which have lower detection limits, to quantify P because of As interference (American Public Health Association 1995).

Additional water samples were collected for determination of As at 20-m intervals within each reach. Samples for As analysis were preserved with nitric acid and analyzed for total As using a Graphite Furnace Atomic Absorption Spectrophotometer with Zeeman background correction (U.S. Environmental Protection Agency 1992).

Stream reach structure: Light, temperature, geomorphology, and biological characteristics—Channel insolation (as % incident light) was determined by 1-min integration of light intensity at 5-m intervals within each reach using the HOBO-Light Intensity Logger (Onset Computer Corp.). A separate data logger was placed in an area with no canopy cover to determine maximum insolation. Water temperature was recorded at 2-min intervals using an automated sonde (Hydrolab model 4A) for the 24-h period encompassing each sampling event. Sediment particle distribution was determined from 100 random samples collected in July and December 2004 within each reach using granulometry techniques (Bunte and Abt 2001).

The volume of large wood and wood mass as ash-free dry mass (AFDM) was quantified using the methods of

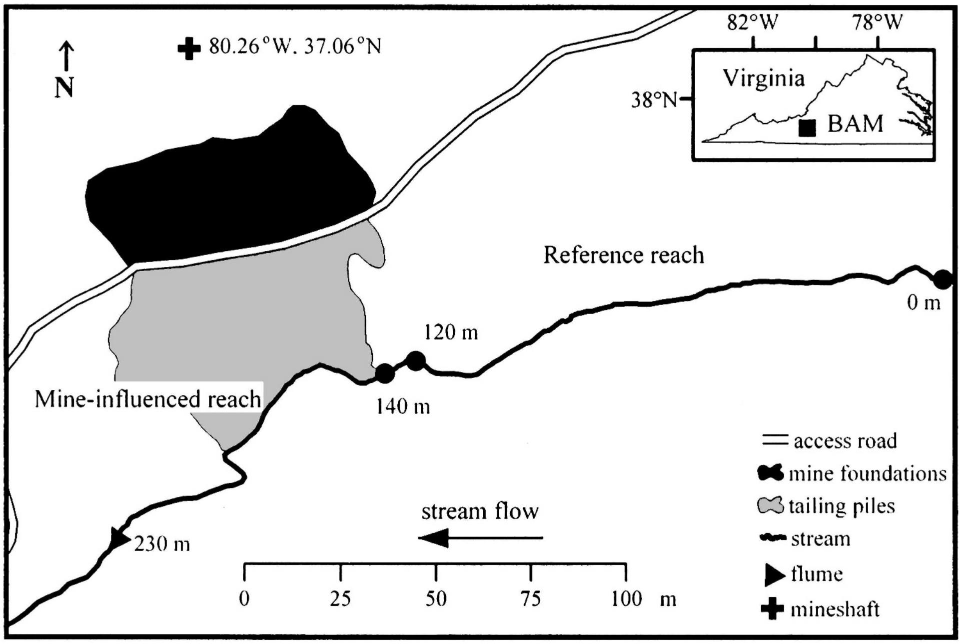

Fig. 1. Site location map for Brinton Arsenic Mine (BAM) study. The reference reach extends from 0 to 120 m downstream. The mine-influenced reach begins at the top of the tailing piles (140 m) and extends 90 m (to 230 m) downstream to a flume with a continuous stage recorder.

Wallace and Benke (1984) and Wallace et al. (2000), respectively. Wood dams were defined as collections of wood (i.e., several pieces) with a single piece measuring at least 5 cm in diameter that extended the width of the stream (Valett et al. 2002) and were enumerated once in each reach.

Epilithic OM, chlorophyll *a* (Chl *a*), fine benthic organic matter (FBOM, particles <1 mm), and coarse particulate organic matter (CPOM, wood and leaves >1 mm) were quantified as the mean of five samples collected from random locations along each reach during each sampling event. Rock scrapings of a known area were used to determine epilithic OM, as AFDM following combustion at 550°C for 45 min, and Chl *a* using hot ethanol extraction (Sartory and Grobbelaar 1984). CPOM was collected from each location using a cylindrical sampling device (0.05 m^2), and standing crops were quantified as AFDM. FBOM was sampled by sealing the same cylindrical sampling device to the stream bottom, determining the average depth of stream water in the sampling device, agitating sediments to 5-cm depth, determining AFDM concentration in a 250-mL subsample, and calculating standing stock as the product of concentration and depth.

Solute injections—A conservative tracer (NaCl) and a biologically active solute (KH_2PO_4) were released simultaneously under base-flow conditions at approximately monthly intervals (six in each reach) throughout the study to determine reach scale P uptake and hydrogeomorphic characteristics (Stream Solute Workshop 1990). Target enrichment concentrations for solutes were 3 mg L^{-1} Cl^- and 50 μg L^{-1} PO_4^{-3}. A single water sample for anion analysis was collected at 10-m intervals within each reach prior to each injection, and duplicate samples were collected from the same locations during plateau, as described previously. Specific conductance (SC) was recorded during each injection at 2-min intervals using an automated sonde.

Solute injections: Solute transport modeling—Dilution gauging techniques (Stream Solute Workshop 1990) and one-dimensional modeling of solute transport (Bencala and Walters 1983), including inflow and transient storage, were used to characterize the hydrologic variables in each study reach. Wetted channel width was measured at 5-m intervals along each reach prior to solute injections. Average discharge was calculated using dilution at each transect (Stream Solute Workshop 1990). Dilution gauging discharge estimates were similar to continuous discharge measurements from a flume located at the base of the mine-influenced reach. Lateral inflow was calculated as the change in discharge from the head to the base of the reach, normalized to a 1-m distance. Lateral inflow in the system is representative of groundwater discharge (Brown 2006), although it could potentially encompass some hyporheic return flow from upstream transient storage flow paths.

Cl^- and SC relationships were developed using standard solutions across the range of Cl^- concentrations anticipated, and background-corrected SC data (converted to Cl^- concentrations) were used to analyze solute transport (Runkel 1998). Although we did not correct for potential influences of uptake of PO_4^{-3} on SC (Gooseff and McGlynn 2005), the experiments were designed such that the maximum contribution of PO_4^{-3} to SC was less than

2% (0.2–0.3 μS cm^{-1}) of the target SC increase. Damkohler coefficients (Wagner and Harvey 1997) calculated for injection experiments ranged from 0.65 to 4.23, with a mean of 1.82, and were within the range suggested by Harvey and Wagner (2000) for adequate estimation of model parameters. Quantified surface parameters included cross-section area, stream velocity, and dispersion. Depth was calculated from average discharge, stream width, and velocity. Output variables for the storage zone include cross-sectional size and exchange coefficient, a measure of the percentage of water entering the storage zone per unit time. Normalized storage zone area was used to represent the storage zone size relative to the channel cross-sectional area. The proportion of median travel time due to storage was calculated using an empirical formula provided by Runkel (2002). Mean storage residence time was calculated after the method of Gooseff and McGlynn (2005).

Solute injections: Calculation of P uptake—Dilution- and background-corrected plateau P samples from each reach were natural log-transformed and analyzed as a function of distance downstream using linear regression. The regression coefficient was used to determine the P uptake velocity (v_{f-PO_4}) using the method of the Stream Solute Workshop (1990).

Ecosystem metabolism—Gross primary production (GPP) and ecosystem respiration (R) were determined using the diel dissolved oxygen (O_2) mass balance technique concurrent with solute injections (Bott 1996). Dissolved O_2 concentrations and temperature were recorded at 10-min intervals for 24 h with a single automated sonde located at the base of each reach. Exchange of dissolved O_2 with the atmosphere was calculated from the average O_2 saturation deficit within the study reach, temperature, barometric pressure, and reaeration rates determined from the dilution-corrected decline of sulfur hexafluoride during steady-state conditions. GPP and R were calculated using the single station technique (Bott 1996).

Sediment P sorption characteristics—To assess the potential for abiotic control (i.e., sorption to sediments) of P uptake, benthic sediment cores (1.5-cm diameter, 5-cm depth) were collected for laboratory sorption assays along both reaches from areas consisting of fine sediments (<4 mm). Within the reference reach, 10 cores were collected randomly along the entire reach length. In the mine-influenced reach, 10 cores were collected within areas characteristic of low, medium, and high As concentrations. Filtered stream water was obtained from each location and used as the matrix for sorption assays. A second water sample was also collected, filtered, and preserved with nitric acid at each location for determination of dissolved As.

P uptake/sorption was determined on five unamended (live) and five mercuric chloride ($HgCl_2$)–amended (killed) sediment cores to assess biotic and abiotic influence on P sorption capacity (Lottig and Stanley 2007) from each sampling area. Filtered stream water from each sample location (100 mL) was added to 20–30 g of wet sediments and enriched to 50 μg L^{-1} P (similar to field enrichment concentrations). Samples were shaken for 10 s every 15 min. After 1 h, a 15-mL aliquot was removed, filtered, and analyzed for change in P.

Analysis of natural and anthropogenic disturbance regimes—The BAM site is influenced by multiple disturbances that span several spatial and temporal scales (Fig. 2). We did not address every possible disturbance but rather chose to focus on several natural and anthropogenic disturbances that may interact to organize ecosystem structure and function. For the purposes of this study, floods were characterized as natural pulse disturbances (Lake 2000). Although we recognize that contaminant transport and biological structure and function are influenced during storms (Resh et al. 1988), the focus of this research was to address long-term characteristics that integrate the effects of storms. Base flow discharge in the study stream is approximately 0.5 L s^{-1} during summer and fall (Chaffin et al. 2005). Increased flow was classified as a 'flood' when discharge exceeded the competent flow required to move more than 50% of the benthic sediment. Water velocity required to move a particle of this size was determined after Gordon et al. (2004), and relationships between discharge and velocity were established using a power relationship between the two variables. In this study, flows exceeding 8 L s^{-1} (i.e., the flow required to mobilize a particle of 5.6-mm diameter, or approximately 50% of the stream bed) were defined as floods. Scouring of epilithic algae and sediment was visible after floods of this magnitude and greater.

The presence of the abandoned As mine was characterized as a press disturbance and was analyzed by comparing reach-scale measures of ecosystem structure and function. Increasing As concentrations within the mine-influenced reach were used to assess how a ramp disturbance influences P uptake, assuming space-for-time substitution. For this analysis, the mine-influenced reach was separated into three 30-m subreaches (0–30, 30–60, and 60–90 m) representing a gradient of increasing As concentration. All subreaches contained sections of variably open canopy, although the amount varied. Average As concentration and measures of v_{f-PO_4} were determined from replicate samples collected from four preestablished transects (10-m intervals) within each subreach in a similar fashion to the methods used for prior reach-scale analyses.

Nutrient uptake in streams has been shown to conform to M-M kinetics (Earl et al. 2006), in which areal uptake (U) increases asymptotically to a maximum with increasing nutrient concentration. Because spiraling metrics are mathematically related, applying the M-M model to U also dictates how uptake velocity (v_f) will respond to increasing nutrient concentration (Earl et al. 2006). v_f is thus described by a nonlinear, hyperbolic decline with increasing nutrient concentration, thus:

$$v_f = \frac{U_{\max}}{K_m + C} \tag{1}$$

where $U_{\max}$ = maximum uptake, K_m = half-saturation constant, and C = nutrient concentration (Earl et al. 2006).

Disturbance type	Disturbance form: Chemical	Physical	Riparian
Press	Reference reach • None Mine-influenced reach • Elevated [As] from abandoned arsenic mine Time scales • Long (100 years)	Reference reach • None Mine-influenced reach • Loss of large wood and debris dams Time scales • Linked to source – riparian zone	Reference reach • Loss of riparian cover from natural tree death Mine-influenced reach • Loss of riparian cover from natural tree death • Loss of riparian cover from tailing piles Time scales • Varies (growing season to years)
Pulse	Reference reach • None Mine-influenced reach • Potential variation in [As] due to flooding Time scales • Short-term (hours)	Reference reach • Episodic floods • Benthic particle movement as a result of floods Mine-influenced reach • Episodic floods • Benthic particle movement as a result of floods Time scales • Short-term (hours)	Reference reach • Erosion of bank sediments during storms Mine-influenced reach • Erosion of bank sediments during storms (may be more substantial due to lack of riparian vegetation) Time scales • Short-term (hours)
Ramp	Reference reach • None Mine-influenced reach • In stream [As] gradients Time scales • Long (100 years)		

Fig. 2. Types and forms of disturbances that are potentially influencing the reference and mine-influenced reaches at the Brinton Arsenic Mine.

In this study, P concentrations were always at or below detection limits (bdl = 5 μg L^{-1}) and thus are represented as a constant (5 μg L^{-1}). Consequently, for a given stream condition, $U_{\max}$ and v_f are constants.

Within the mine-influenced reach, the subreach analysis of P uptake provided a potential range of v_{f-PO_4} across a gradient of As concentrations. A M-M model for v_{f-PO_4} that takes into account the presence of a competitive inhibitor (AsO_4^{-3}) was used to assess if AsO_4^{-3} inhibits microbial P uptake. In the presence of a competitive inhibitor, K_m increases by a factor of

$$1 + \frac{I}{K_I} \tag{2}$$

where I = concentration of the inhibitor and K_I = the dissociation constant for the enzyme-inhibitor complex (Campbell 1999). The M-M model for v_f can then be adjusted to account for the presence of a competitive inhibitor:

$$v_f = \frac{U_{\max}}{K_m\left(1 + \frac{I}{K_I}\right) + C} \tag{3}$$

To fit this model, we assumed that the half-saturation constants for PO_4^{-3} and AsO_4^{-3} were similar (i.e., $K_m = K_I$) and that the P concentration was constant (5 μg L^{-1}). Based on these assumptions, v_{f-PO_4} should decline hyperbolically with increasing AsO_4^{-3} concentration. Model output ($U_{\max}$, K_m) estimates were derived from a nonlinear fit of Eq. 3 using Sigma Plot 9.0 (Systat Software, 2004).

Statistical analysis—Hydrologic stability was assessed by comparing the coefficients of variation (CV) for all hydrologic parameters. The CV for each hydrologic parameter was determined (n = 6 for each parameter) in each reach, and a paired t-test grouped by hydrologic variable was completed in order to address directional trends in temporal variability. Sediment sorption characteristics in the reference and mine-influenced reaches were compared using two-way analysis of variance (ANOVA) using reach (reference and mine-influenced) and treatment (live vs. killed) as main effects. The influence of As concentrations on sediment P sorption capacity was determined using one-way ANOVA. Physical and chemical properties, biotic structure, and ecosystem function were completed using paired t-tests. Relationships between

Table 1. Characterization of chemical, hydrologic, and organic matter standing stock features of the reference and mine-influenced reaches at the Brinton Arsenic Mine. p values derived from paired t-tests are given in the final column. Dashes indicate no reach-scale replication.

Steam reach characteristics	Reference reach	Mine-influenced reach	t,df	p
Chemical characteristics†				
Arsenic (As, μg L^{-1})	08 ± 1	254 ± 39	6.50,5	0.001*
PO_4-P (μg L^{-1})	<5	<5	—	—
NO_3-N (μg L^{-1})	781 ± 63	497 ± 59	12.7,5	0.001*
Hydrologic characteristics†				
Discharge (Q, L s^{-1})	1.7 ± 0.4	2.4 ± 0.8	2.01,5	0.101
Lateral inflow (Q_L, L s^{-1} m^{-1})	0.004 ± 0.001	0.009 ± 0.002	2.53,5	0.052
Wetted width (w, m)	0.66 ± 0.04	0.74 ± 0.06	3.79,5	0.013*
Depth (z, m)	0.05 ± 0.01	0.04 ± 0.01	2.75,5	0.040*
Stream x.s. area (A, m^2)	0.03 ± 0.01	0.03 ± 0.01	2.16,5	0.083
Velocity (u, m s^{-1})	0.06 ± 0.01	0.09 ± 0.01	4.65,5	0.006*
Storage zone x.s. area (A_s, m^2)	0.05 ± 0.01	0.03 ± 0.01	2.10,5	0.090
Exchange coefficient (α, s^{-1})	0.0005 ± 0.0001	0.0008 ± 0.0003	1.15,5	0.302
Normalized transient storage zone area (A_s/A, m^2 m^{-2})‡	1.72 ± 0.03	1.56 ± 0.08	0.40,5	0.704
F_{med}^{100} (%)‡	40.6 ± 0.20	24.6 ± 0.40	3.48,5	0.018*
Physical characteristics				
Mean particle size Jul 2004 (mm)	4	4	—	—
Mean particle size Dec 2004 (mm)	4	12	—	—
Insolation (%)‡	4.34	10.92	—	—
Temperature (°C)†	11.4 ± 2.2	12.2 ± 2.5	1.91,5	0.114
Organic matter standing stocks				
Wood mass (kg m^{-2})	0.85	0.82	—	—
Wood dam frequency (No. per 100 m)	8.33	3.33	—	—
Chlorophyll a (mg m^{-2})§	0.15 ± 0.96	1.52 ± 1.32	1.12,4	0.326
Epilithic OM (g m^{-2})§	0.17 ± 0.03	1.22 ± 0.80	1.34,4	0.250
FBOM (g m^{-2})§	68 ± 13	37 ± 80	2.65,4	0.057
CPOM (g m^{-2})§	116.6 ± 35.50	54.0 ± 13.8	2.34,4	0.079

† Data are mean ± SE for six reach averages from July–December 2004.
‡ Mean and SE were calculated on square-root transformed data; tabular values were back-transformed.
§ Data are mean ± SE for five reach average values from August–December 2004. OM, organic matter; FBOM, fine benthic organic matter; CPOM, coarse particulate organic matter.
* $p < 0.05$.

structure, function, and responses to disturbance were assessed using linear regression models. Comparisons of regression parameter estimates between reaches were completed by assessing the interaction term between variables. SAS (version 9.1, SAS Institute) was used for all statistical analyses.

Results

Chemical, physical, and hydrogeomorphic characteristics—Across all sampling dates, average As concentration within the reference reach was 8 μg L^{-1} (Table 1), with little spatial variation along the reach (3–26 μg L^{-1}; Fig. 3). Average As concentrations in the mine-influenced reach were more than 30 times the reference values (Table 1) and increased dramatically along the reach (Fig. 3). Average NO_3-N concentrations were generally >500 μg L^{-1} in both reaches and were significantly higher in the reference reach (t = 12.7, df = 5, $p < 0.001$; Table 1). A preliminary nutrient injection indicated that there was no significant NO_3-N uptake in either reach, In contrast to the relatively high NO_3-N concentrations, P was at or below detection limits (<5 μg L^{-1}) throughout the study (Table 1).

Insolation was relatively constant in the reference reach, averaging <5% incident light. Insolation values at the head and base of the mine-influenced reach were similar to values in the reference reach (~5%), where canopy cover existed. However, adjacent to the sparsely vegetated tailings, insolation increased to over 80% of incident light.

At the beginning of the study, no major differences in stream sediment particle size distribution were observed between reaches. Over the period of the study, median particle size did not change significantly within the reference reach, and proportions of particles within size classes remained relatively constant. However, in the mine-

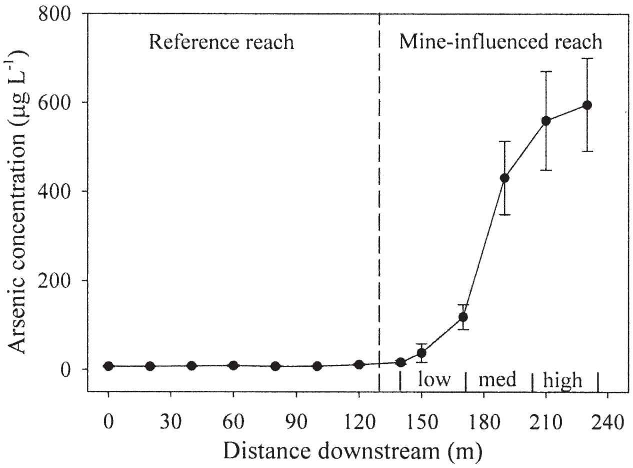

Fig. 3. Arsenic concentrations (mean ± standard error [SE]) from July through December 2004 for the reference and mine-influenced reaches at the Brinton Arsenic Mine. Data represent mean ± SE for six monthly values at each site (error bars may be within point symbols). Monthly values were determined from triplicate samples at each location. Subreaches within the mine-influenced reach are identified as 'low,' 'medium,' and 'high' in reference to average arsenic concentration.

influenced reach, the proportional abundance of fine (<4-mm) sediments declined 20% across the study period, resulting in increased median particle size (12 vs. 4 mm; Table 1).

Discharge at the base of the mine-influenced reach varied from 0.8 L s^{-1} to >44 L s^{-1} during the study (Fig. 4). The greatest discharge values corresponded to Hurricanes Frances (08 September 2004), Ivan (17 September 2004), and Jeanne (28 September 2004) and to two flash floods (13 October and 24 November 2004). Average depth and velocity were numerically similar but differed significantly between reaches (Table 1). Lateral inflow in the mine-influenced reach was more than double that in the reference reach (t = 2.53, df = 5, p = 0.052). Channel cross-sectional area was similar for the two reaches

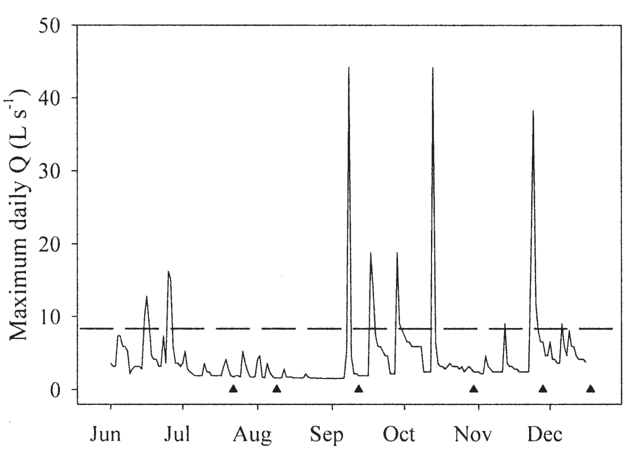

Fig. 4. Maximum daily discharge determined from a Tracon fiberglass H-flume at the bottom of the mine-influenced reach at Brinton Arsenic Mine. Triangles indicate when stream sampling occurred. Floods are defined as maximum daily discharge in excess of 8 L s^{-1} (i.e., above the dashed line).

(Table 1), but discharge was higher in the mine-influenced reach and was evident as higher velocity (Table 1). Average absolute size of the transient storage zone was approximately 1.7 times greater in the reference reach, but mean values were not significantly different (t = 2.19, df = 5, p = 0.090; Table 1). When normalized to channel cross-sectional area, normalized storage zone size was only 1.1 times greater in the reference reach (Table 1). The percent of median residence time spent in storage varied from 9% to 58% and was significantly greater in the reference reach (t = 3.48, df = 5, p = 0.018; Table 1).

Hydrogeomorphic characteristics, including velocity, depth, and transient storage (Table 1), in the mine-influenced reach were significantly more temporally variable than in the reference reach (t = 2.89, df = 10, p = 0.016). CVs for all hydrogeomorphic variables varied from 14% to 80% and were generally higher in the mine-influenced reach (51.7%) than the reference reach (41.7%).

The number of floods (Q > 8 L s^{-1}) and the magnitude of floods observed in each reach differed over the course of the study. Correlations between discharge at the base of the reference reach and mine-influenced reach indicated that mean discharge in the reference reach was approximately 46% lower than in the mine-influenced reach (r^2 = 0.97, p < 0.001, n = 6). Six floods occurred in the reference reach, two with a maximum discharge of 24 L s^{-1}. A total of nine floods occurred in the mine-influenced reach, two with a maximum discharge >44 L s^{-1}.

Large wood and benthic standing stocks—Standing stocks of large wood were similar in the reference and mine-influenced reaches (Table 1). While reach estimates of wood mass differed by <5%, distribution of wood within the two reaches was very different. Wood dam frequency within the reference reach (8.33 100 m^{-1}) was nearly three times that in the mine-influenced reach (3.33 100 m^{-1}; Table 1). No significant differences in mean organic matter biomass were observed for Chl a, FBOM, or CPOM among the reaches over the entire study period.

Following floods, temporal change was evident for several OM characteristics. No floods were observed in the 73 d prior to Hurricane Frances (first major flood during study), and 29 d prior to Hurricane Frances, Chl a standing crops were 0.53 mg m^{-2} and 6.79 mg m^{-2} in the reference and mine-influenced reaches, respectively. After Hurricane Frances, Chl a standing crops were extremely low (<0.01 mg m^{-2}). Chl a then increased with days postflood (DPF) in the reference (r^2 = 0.39, p = 0.378, n = 5) and mine-influenced (r^2 = 0.96, p = 0.020, n = 5) reaches, although they never reached pre–Hurricane Frances levels in either reach. Maximum standing crops observed 17–25 d after Hurricane Frances were an order of magnitude smaller than those observed prior to the hurricane. FBOM in the reference reach also increased significantly with DPF (r = 0.97, p = 0.005, n = 5). A similar trend observed in the mine-influenced reach was not statistically significant (r^2 = 0.063, p = 0.684, n = 5).

Sediment P sorption characteristics—Using data from all cores, P uptake values on 'live' and 'killed' sediment cores

Table 2. Ecosystem respiration, phosphorus uptake, and sediment assays in the reference and mine-influenced reaches at Brinton Arsenic Mine.

Stream reach characteristics	Reference reach	Mine-influenced reach	t,df	p
Ecosystem metabolism†				
Ecosystem respiration (R, g O_2 m^{-2} d^{-1})	4.4 ± 0.4	3.3 ± 0.5	1.90,5	0.116
Phosphorus uptake metrics‡				
Uptake velocity (v_{f-PO_4}, mm s^{-1})	0.027 ± 0.004	0.027 ± 0.003	0.27,5	0.796
Sediment sorption characteristics§				
50 μg L^{-1} enrichment (mg m^{-2} h^{-1})	9 ± 0	11 ± 00	2.71,29	0.011*

† Data are mean ± SE for five reach averages from August–December 2004. p values derived from paired t-tests given in the final column.
‡ Data are mean ± SE for six reach averages from July–December 2004. p values derived from paired t-tests given in the final column.
§ Data are mean ± SE of both live and killed sediment assays from the reference and mine-influenced reaches. p values derived from t-tests given in the final column.
* $p < 0.05$.

averaged 11 mg m^{-2} h^{-1} and were not significantly different ($F_{1,27} = 0.40$, $p = 0.533$) between treatments at spiking concentrations similar to those created by P additions to the stream. 'Live' and 'killed' sorption capacity estimates were therefore combined to characterize each reach. Sediment from the mine-influenced reach had significantly greater potential to sorb P ($t = 2.71$, df = 29, $p = 0.011$; Table 2), and by extrapolation, sediment uptake in either reach could result in P uptake in the range of 9–11 mg m^{-2} h^{-1}.

Within the mine-influenced reach, sediment sorption characteristics varied across a range of As concentrations ($F_{2,20} = 3.61$, $p = 0.046$). No significant differences (Tukey's honestly significantly different [HSD] $t_{critical} = 2.09$, df = 20, $p > 0.05$) were observed between the sorption capacity of sediments from near the head (263 μg L^{-1} As) and at the base (2,822 μg L^{-1} As) of the mine-influenced reach. Sediment from the middle region (823 μg L^{-1}) of the mine-influenced reach had significantly lower (Tukey's HSD $t_{critical} = 2.09$, df = 20, $p < 0.05$) P sorption potential.

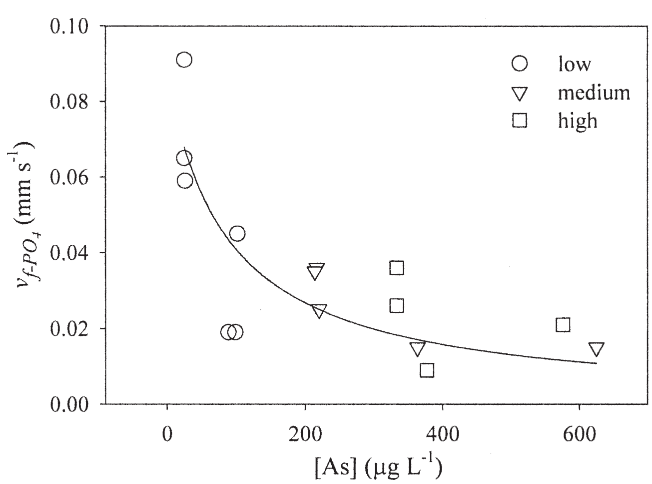

Fig. 5. Hyperbolic relationship between phosphorus uptake efficiency (v_{f-PO_4}, mm s^{-1}) and mean arsenic (As, μg L^{-1}) in the mine-influenced reach at the Brinton Arsenic Mine ($R^2 = 0.86$, $p < 0.001$, $n = 15$). Values of v_{f-PO_4} and mean As concentrations were calculated from 30-m subreaches representing low, medium, and high As concentrations. Estimates of M-M parameters from Eq. 3 were $U_{max} = 31$ mg m^{-2} h^{-1} and $K_m = 113$ μg L^{-1}.

Ecosystem metabolism and P retention—No detectable GPP was observed throughout the study in either reach. R varied from 1.3 to 5.6 g O_2 m^{-2} d^{-1} and was not significantly different ($t = 1.90$, df = 5, $p = 0.116$; Table 2) between reaches or correlated to standing stocks of CPOM, FBOM, or Chl *a* ($p > 0.05$).

Mean v_{f-PO_4} for each reach was identical (0.027 mm s^{-1}; Table 2). v_{f-PO_4} increased with decreasing relative storage zone (A_s/A, $r = -0.70$; $p = 0.011$, $n = 12$) and F^{100}_{med}($r = -0.68$; $p = 0.015$, $n = 12$) and did not significantly correlate with the mean storage residence time. v_{f-PO_4} was also positively related to CPOM standing crops in the reference ($R^2 = 0.91$, $p = 0.013$, $n = 5$) and mine-influenced ($R^2 = 0.78$, $p = 0.046$, $n = 5$) reaches. Relationships between CPOM and v_{f-PO_4} for each reach did not differ from each other ($p > 0.05$). Regression models, including both CPOM and DPF, explained 99% of the variance in v_{f-PO_4} in the mine-influenced reach ($R^2 = 0.989$, $p = 0.023$, $n = 5$), while DPF did not significantly add explanatory power to the regression model in the reference reach. No significant relationships were observed between v_{f-PO_4} and other standing stock estimates.

P uptake also varied as a function of As concentration. Average As concentrations within 30-m subreaches of the mine-influenced reach ranged from 25 to 625 μg L^{-1} (Fig. 3). However, across the sampling period (six dates), As concentrations varied within the stream as a function of groundwater discharge (Brown 2006), and, consequently, subreach As concentrations varied such that overlap was observed between the mid- and high–As concentration subreaches (Fig. 5). Values of v_{f-PO_4} calculated for the 30-m subreaches ranged from 0.009 to 0.091 mm s^{-1}. At high As concentrations, v_{f-PO_4} was always low; similarly, at low As concentrations, v_{f-PO_4} was generally high. Overall, a hyperbolic model best explained (i.e., greatest r^2) the relationship between v_f and As in the mine-influenced reach ($R^2 = 0.86$, $p < 0.001$, $n = 15$; Fig. 5). Model estimates of M-M parameters from Eq. 3 were $U_{max} = 31$ mg m^{-2} h^{-1} and $K_m = 113$ μg L^{-1}.

Discussion

Ecosystem metabolism and P uptake—We found no detectable GPP. Other studies of forested, headwater streams have similarly found very low GPP, most likely as a result of light limitation (e.g., Mulholland et al. 2001). However, the values of R (1.3–5.4 g O_2 m^{-2} d^{-1}) observed here are similar to values reported for other headwater streams (e.g., Mulholland et al. 1997, 2001). Recent studies (e.g., Hall and Tank 2005) have suggested that minor groundwater inputs influence oxygen mass balance and bias measures of ecosystem metabolism. Groundwater inputs are potentially a source of error for metabolism estimates in our study. On the other hand, work by Brown (2006) demonstrated that while groundwater characteristics were temporally variable at the study site, longitudinal variation in groundwater discharge along the stream was minimal. Accordingly, our estimates may be biased, but comparisons between stream reaches are likely still valid.

Streams in the southern Appalachian Mountains are often P limited (Webster et al. 1995), and the demand for P is higher than for nitrogen (Webster et al. 1991). Many studies have suggested that v_f is an useful metric for biological comparisons of nutrient demand among systems because it accounts for hydrologic variation (e.g., stream depth and velocity) (Davis and Minshall 1999; Valett et al. 2002). v_{f-PO_4} in both the reference and mine-influenced reaches in this study are relatively close to many other reported v_{f-PO_4} values (e.g., 0.01–0.08 mm s^{-1}) for P-limited streams (Mulholland et al. 1997; Davis and Minshall 1999), but they were substantially lower than those reported for old-growth forest streams in the southern Appalachians (Valett et al. 2002).

Although we are able to estimate P uptake using solute injections, we cannot isolate the mechanisms responsible for uptake because P may be sequestered by both biotic and abiotic processes. If P uptake is driven by sediment sorption, we would expect that increased interaction with sediment (measured as interaction with transient storage zones) would result in increased P uptake. However, the results from this study indicate that P retention occurs in association with benthic surfaces, a notion supported by (1) significant correlations between benthic CPOM standing stocks and P uptake along with (2) negative correlations between P uptake and transient storage zone characteristics and (3) lack of any significant correlation with transient storage residence time. In this study 78–91% of the variation in v_{f-PO_4} was explained by CPOM standing stocks, and v_{f-PO_4} in both reaches was greatest when CPOM standing stocks were maximal.

Press and pulse disturbance influence on reach structure and function—Although several studies have shown that functional measures are sensitive to disturbance (e.g., Gessner and Chauvet 2002; Chaffin et al. 2005), specific functional responses to toxic stressors may differ. This study indicates that ecosystem responses to chronic As pollution depend largely on whether specific processes are mediated by primarily metazoan or microbial biota. Macroinvertebrates, especially shredders (i.e., organisms that process CPOM) play an important role in detrital breakdown (Wallace et al. 1982) and are adversely affected by elevated As (Chaffin et al. 2005). However, functional characteristics, such as ecosystem metabolism and nutrient uptake, are primarily mediated by microbial assemblages (Hall and Meyer 1998).

Other studies at the BAM demonstrate that processes controlled by metazoans are drastically altered by As (Chaffin et al. 2005; Valenti et al. 2005), whereas our study indicates that those controlled by microbial communities are less affected, even at As concentrations that are nearly 70 times greater than toxic levels of metazoans (U.S. Environmental Protection Agency 2002). This conclusion is supported by prior studies of As influence on microbial assemblages. It is well documented that many microbial species are capable of using AsO_4^{-3} as a terminal electron acceptor (Oremland and Stolz 2003). Speir et al. (1999) demonstrated that the presence of elevated As did not inhibit microbial respiration or decrease microbial biomass in soils. Chaffin et al. (2005) also noted that chronic As pollution appeared to exert little influence on microbial leaf disk respiration. Further, Turpeinen et al. (2004) concluded that exposure to high levels of As resulted in reduced microbial diversity, but at the same time observed that soil metabolic activity was not altered.

Pulse disturbances such as floods have long been recognized as dominant factors controlling stream ecosystem structure and function (e.g., Resh et al. 1988), and floods played a significant role in structuring the physical characteristics of both the reference and mine-influenced reaches at the BAM. Although floods changed sediment particle size distribution and OM standing stocks, they did not have a similar effect on ecosystem function (i.e., P uptake and ecosystem metabolism).

Interactions between press and pulse disturbances—Similar to other studies (e.g., Parkyn and Collier 2004; Ross et al. 2004), interaction between pulse and press disturbances was evident for both structural and functional characteristics. Comparison of sediment particle size distribution indicates that the mine-influenced reach was less resistant to flooding than was the reference reach, most likely as a result of the lack of wood dams (Bilby and Likens 1980). The decreased resistance to floods was also evident as increased temporal variation in hydrogeomorphic characteristics in the mine-influenced reach. These patterns indicate that the mine-influenced reach, under the influence of an active press disturbance, was less resistant to flood (i.e., pulse) disturbances.

Additionally, multiple linear regression models indicate that floods and CPOM influenced P uptake in the mine-influenced reach, while floods had no influence on P uptake in the reference reach. P uptake was greatest immediately after a flood and may be due to an influx of new sediment from mine tailings and higher abiotic uptake on open sorption sites of imported sediments (Brown 2006). This interaction indicates that in order to understand P uptake dynamics in an ecosystem exposed to a press disturbance, relationships with additional disturbance regimes may need to be considered.

Ramp disturbance influence on P uptake—As a result of the wide range of As concentrations observed in this study, we employed a subreach analysis within the mine-influenced reach to examined P uptake across a gradient of As concentrations and to assess how the 'ramp disturbance' model (Lake 2000) applies to As influence on P uptake.

We applied a M-M approach to understanding As–P interaction in the mine-influenced reach, and the primary result of this analysis was that the data were best described by our derived model of competitive inhibition of P uptake typical of enzyme kinetics (sensu Speir et al. 1999). This approach generated reasonable M-M estimates similar to those obtained in other studies. However, the decline in P uptake could also be due to a downstream decrease in abiotic sorption potential as a result of increased quantities of As sorbed to sediment surfaces. As a result of similarities between AsO_4^{-3} and PO_4^{-3}, AsO_4^{-3} competes for the same binding sites on sediment (Rubinos et al. 2003; Stollenwerk 2003). However, no significant decline in sediment P sorption potential was observed across a wide gradient of As concentrations, indicating that sediment sorption sites are saturated with As and are likely not contributing to P uptake. Further, we observed that low v_{f-PO_4} values occurred in conjunction with elevated As concentrations regardless of whether these concentrations occurred in subreaches characterized by low, medium, or high As concentrations. Finally, we observed strong correlations between P uptake and CPOM standing stocks, but not with increased interaction with the transient storage zone, the former emphasizing association with biotically active particles and the latter reflecting sediment–pore water interaction. Together, these results indicate that As may not alter microbial P uptake as a toxin but rather as a chemical inhibitor.

Ecosystem implications—Streams are typically organized by multiple factors, and we emphasize that in this system, multiple disturbances and their corresponding regimes exist simultaneously (Fig. 2). Disturbances are complex, interactive, and can be difficult to separate. In recognition of these facts, this study attempts to address how combined natural and anthropogenic disturbances simultaneously influence stream structure and function across temporal and spatial scales.

In addition to demonstrating that disturbances interact and should to be considered as a combined regime, we suggest that in order to assess the influences of a toxin at an ecosystem scale, a range of functional characteristics need to be considered. Here we emphasize that processes associated with microbial assemblages (i.e., ecosystem metabolism) are highly resistant to elevated concentrations of As. On the other hand, in their study Chaffin et al. (2005) demonstrated a lack of resistance in the macroinvertebrate community and its implications for organic matter processing. These authors also highlighted the fact that As altered ecosystem function indirectly as a result of its toxic nature, while here we suggest that As may also alter ecosystem function (e.g., P uptake) as a consequence of its chemical characteristics.

Results from this study along with others (Parkyn and Collier 2004; Ross et al. 2004) continue to highlight the fact that disturbance regimes interact to alter ecosystem structure and function. Therefore, in light of Clements' (2000) call for ecotoxicological studies to take place at the ecosystem scale, such studies should not only consider contaminant influences but should also place their implications within the extant disturbance regimes from both natural and anthropogenic causes.

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