Cumulative impacts of mountaintop mining on an Appalachian watershed

T. Ty Lindberg[a,1], Emily S. Bernhardt[b], Raven Bier[b], A. M. Helton[b], R. Brittany Merola[a], Avner Vengosh[a], and Richard T. Di Giulio[a]

[a]Nicholas School of the Environment, Duke University, Durham, NC 27708; and [b]Department of Biology, Duke University, Durham, NC 27708

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Mountaintop mining is the dominant form of coal mining and the largest driver of land cover change in the central Appalachians. The waste rock from these surface mines is disposed of in the adjacent river valleys, leading to a burial of headwater streams and dramatic increases in salinity and trace metal concentrations immediately downstream. In this synoptic study we document the cumulative impact of more than 100 mining discharge outlets and approximately 28 km^2 of active and reclaimed surface coal mines on the Upper Mud River of West Virginia. We measured the concentrations of major and trace elements within the tributaries and the mainstem and found that upstream of the mines water quality was equivalent to state reference sites. However, as eight separate mining-impacted tributaries contributed their flow, conductivity and the concentrations of selenium, sulfate, magnesium, and other inorganic solutes increased at a rate directly proportional to the upstream areal extent of mining. We found strong linear correlations between the concentrations of these contaminants in the river and the proportion of the contributing watershed in surface mines. All tributaries draining mountaintop-mining-impacted catchments were characterized by high conductivity and increased sulfate concentration, while concentrations of some solutes such as Se, Sr, and N were lower in the two tributaries draining reclaimed mines. Our results demonstrate the cumulative impact of multiple mines within a single catchment and provide evidence that mines reclaimed nearly two decades ago continue to contribute significantly to water quality degradation within this watershed.

environmental impact | alkaline mine drainage | total dissolved solids | water chemistry

Mountaintop mining (MTM) is a relatively new form of surface coal mining adapted to mountainous terrain that has enabled individual mines to expand considerably in size (1). The United States Environmental Protection Agency (EPA) estimates that by 2012, these mines will have impacted 6.8% of the largely forested 4.86-million-hectare portion of the Appalachian Coalfield Region (ACR) within West Virginia (WV), Kentucky, Virginia, and Tennessee (1). MTM involves accessing shallow coal seams by removing up to 300 vertical meters of overlying mountain summits and ridges with explosives and heavy machinery (1–3). The resulting noncoal rock spoil or overburden is then used for regrading or is pushed into adjacent valleys to create fills, permanently burying headwater streams under tens to hundreds of meters of waste rock (3, 4). Based on complete utilization of fill permits issued between 1992 and 2002, the EPA estimated that 1,944 km of headwater streams were buried during this period and predicted that the extent of buried stream length will double to almost 4,000 km by 2012 (1, 5).

This fundamental change in the topography and morphology of the watershed has important consequences for the water quality of downstream ecosystems. Mining exposes previously buried coal minerals to both oxygen and water, leading to the dissolution of pyrite (FeS_2) within the coal wastes to produce sulfuric acid (H_2SO_4) that dissociates to hydrogen and sulfate ions (SO_4^{2-}). As a result of mining activities, directly impacted streams in WV often have a 30- to 40-fold increase in SO_4^{2-} concentrations (6–10). Throughout much of the central Appalachians, the presence of significant carbonate and base cations in parent material neutralizes the acidity caused by hydrogen ions released from weathered coal deposits, such that stream water exiting surface mines exhibits high concentrations of calcium, magnesium, and bicarbonate (Ca^{2+}, Mg^{2+}, and HCO_3^-) ions with accompanying high SO_4^{2-} concentrations. The resulting alkaline mine drainage has elevated pH, electrical conductivity, and concentrations of total suspended solids compared to reference streams (7–9, 11). Typical specific conductance levels in low order WV streams measured in previous research ranged from 13 to 253 $\mu S\,cm^{-1}$ while valley fill impacted streams were found to far exceed these values (502–2540 $\mu S\,cm^{-1}$) (7, 8, 11). The abundance of the elements Fe, Al, Mn, K, and Se may also be elevated in surface coal mine drainage (7, 8, 11). Of particular concern is the increase in surface water concentrations of the known fish toxin selenium (12–14) due to the Se-enriched coal formations in the regions where MTM is most prevalent and the enhanced solubility of Se in alkaline waters (15).

Individual mines profoundly impact stream water quality, community structure, and ecosystem functions immediately downstream of valley fills. Thus, there is good reason to expect that multiple mining operations within larger watersheds will have cumulative effects on larger downstream rivers through increased loading of dissolved substances derived from alkaline mine drainage. This information is, however, lacking, and individual permitting decisions are typically made without consideration of the extent of historic mining impacts that have occurred within a watershed (4). Petty et al. demonstrated that the extent and intensity of mining were clearly linked to the degree of degradation of stream biological communities, providing strong evidence of cumulative impacts (16).

In this synoptic study, we measured stream conductivity and collected water samples along the Upper Mud River and its tributaries for subsequent chemical analyses. The headwaters of the Mud River begin in Boone County, West Virginia, and flow northwest into Lincoln County as a third order stream until its impoundment in the Mud River reservoir, approximately 25 km downstream. From river km (Rkm) 4.9 to 14.3, the stream passes through the Hobet surface mine complex, which has been active since the early 1970s. There are currently 105 active National Pollutant Discharge Elimination System (NPDES) permitted outlets related to surface coal mining within the 56.5 km^2 catchment. These permits are issued and enforced by the state under the federal Clean Water Act (CWA) with the intent of limiting the release of pollutants into waters of the United States. By the time

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[1]To whom correspondence should be addressed. E-mail: tl93@duke.edu.

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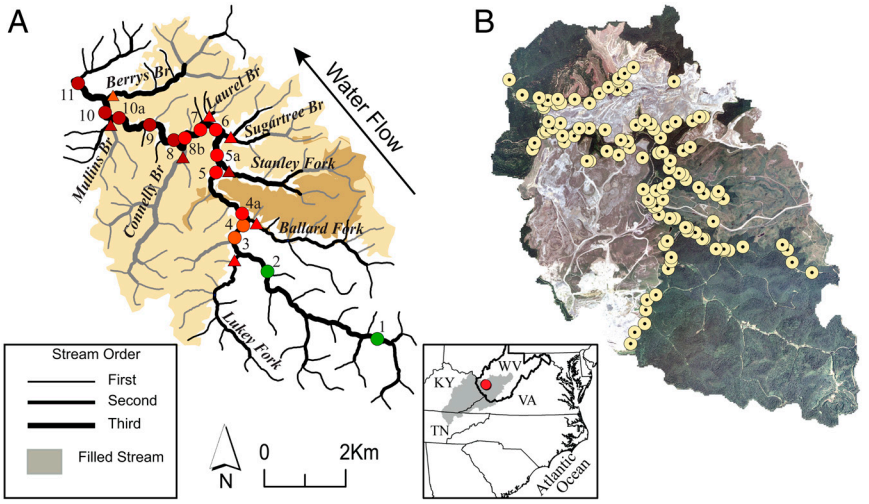

Fig. 1. Map of study area depicting Upper Mud River and associated tributaries with aerial photo on right. Sampling sites consisted of 15 mainstem (circles) and eight named tributary locations (triangles). Sites 1 and 2 were located upstream of current and historic MTM activity. The remaining sites were chosen so as to bracket each confluence of the Upper Mud River and an MTM-affected tributary. Marker color denotes median conductivity level in mainstem during survey (green <300, orange 301 to 500, red 501 to 1,000, and dark red >1,000 $\mu S\,cm^{-1}$). Brown shaded areas reflect surface mining with darker area representing reclaimed mines. Aerial photo on right shows location of 105 active surface-mining-related outlets within the watershed that are regulated through eight NPDES permits. Inset of US mid-Atlantic states shows Appalachian coalfield region as gray shaded area with relative location of study site in red (not to scale).

the Upper Mud River exits the active surface mining area following its confluence with Berrys Branch, it has received mining effluent from eight MTM-affected tributaries that contain 68 NPDES permitted discharge points (Fig. 1 and Table 1). This detailed survey allowed us to quantify the cumulative impact of many separate discharge permits on downstream water quality and to clearly demonstrate that measured increases in conductivity and concentrations of major and trace elements were directly proportional to the upstream areal extent of surface mining.

Table 1. Sampling site attributes for mainstem and MTM affected tributaries on the Upper Mud River

Sample site	River km or location of confluence	Watershed area upstream (km^2)	% mined watershed area upstream	No. of NPDES permitted outlets upstream
Mainstem				
1	0.31	2.45	0	0
2	4.02	10.02	0	0
3	5.37	16.91	16.52	9
4	5.88	17.13	16.45	11
4a	6.07	23.63	20.46	27
5	7.88	25.71	25.27	37
5a	8.11	30.55	34.61	48
6	8.97	34.54	39.20	60
7	9.43	35.79	40.77	64
8b	10.25	36.31	41.32	68
8	10.51	42.84	49.55	69
9	11.58	44.06	50.27	74
10a	12.75	44.83	50.69	81
10	12.97	47.79	50.96	86
11	14.30	56.52	49.14	105
Tributaries				
Lukey Fork	4.91	5.14	33.88	11
Ballard Fork	5.94	6.46	31.21	16
Stanley Fork	8.00	4.62	86.41	11
Sugartree Branch	8.78	3.59	77.74	4
Laurel Branch	9.28	0.99	91.30	2
Connelly Branch	10.31	6.44	95.87	1
Mullins Branch	12.81	2.80	55.03	5
Berry Branch	13.36	5.81	57.61	18

All sites are in order from upstream to downstream position as in Fig. 1.

Results and Discussion

A suite of stream solutes consistently and significantly increased in concentration between the upstream and the downstream sites (Fig. 2 and Table S1). Conductivity measurements throughout the surface mining impacted section of the Upper Mud River always exceeded 300 $\mu S\,cm^{-1}$ (Fig. 2 *A* and *B*), a level recently deemed harmful to aquatic life in the central Appalachians by the EPA (17). Upstream of mining, conductivity measurements did not vary much seasonally or spatially, averaging $156.1 \pm 11.6\ \mu S\,cm^{-1}$ ($\pm$standard error), a range consistent with values reported by the WV Department of Environmental Protection (WVDEP) for state reference sites within the Upper Guyandotte watershed (Fig. 2*C*) (10). Immediately below the confluence with Lukey Fork, the most upstream MTM-impacted tributary to the Upper Mud River, conductivity increased significantly to $620.4 \pm 198.6\ \mu S\,cm^{-1}$. The average conductivity for the 72 measurements taken on the 13 mining-affected mainstem sampling sites was $1{,}293.9 \pm 59.6\ \mu S\,cm^{-1}$. Average conductivities for the eight MTM-affected tributaries ranged from 990 $\mu S\,cm^{-1}$ to 2,210 $\mu S\,cm^{-1}$ (Fig 2*C*). Sulfate concentrations were highly correlated with conductivity (Fig. 3*A*), and the increase in SO_4^{2-} throughout the Upper Mud River mainstem mirrored increases in conductivity (Fig. 2 *D* and *E*).

Dissolved selenium concentrations on the mainstem (Fig. 2*G*) followed the same trend with samples from upstream sites below our detection limit (1.1 $\mu g\,L^{-1}$) while downstream sites exceeded the EPA's freshwater chronic criterion concentration of 5.0 $\mu g\,Se\,L^{-1}$ (18) for 43 of 52 samples. The highest mainstem Mud River concentration of 19.1 $\mu g\,L^{-1}$ was measured at site 11 on September 2, 2010. Tributaries draining active MTM operations had Se concentrations ranging from at or below our detection limit in Ballard Fork, a stream draining older surface mines reclaimed in the early 1990s, to $28.1 \pm 3.5\ \mu g\,L^{-1}$ from Mullins Branch, an actively mined watershed (Fig 2*I*). Selenium concentrations in MTM-affected tributaries exceeded the chronic criterion in 26 of 31 samples. We collected the highest recorded Se concentration of the study, 35.7 $\mu g\,L^{-1}$, from Mullins Branch on September 2, 2010.

Stream water conductivity was significantly positively associated with constituents typically derived from rock and coal weathering (SO_4, Ca, Mg, Li, Rb and U) in the mainstem as well as the MTM-affected tributaries (Fig. 3 *A* and *B* and Table S1). Selenium and total dissolved nitrogen (TDN) concentrations

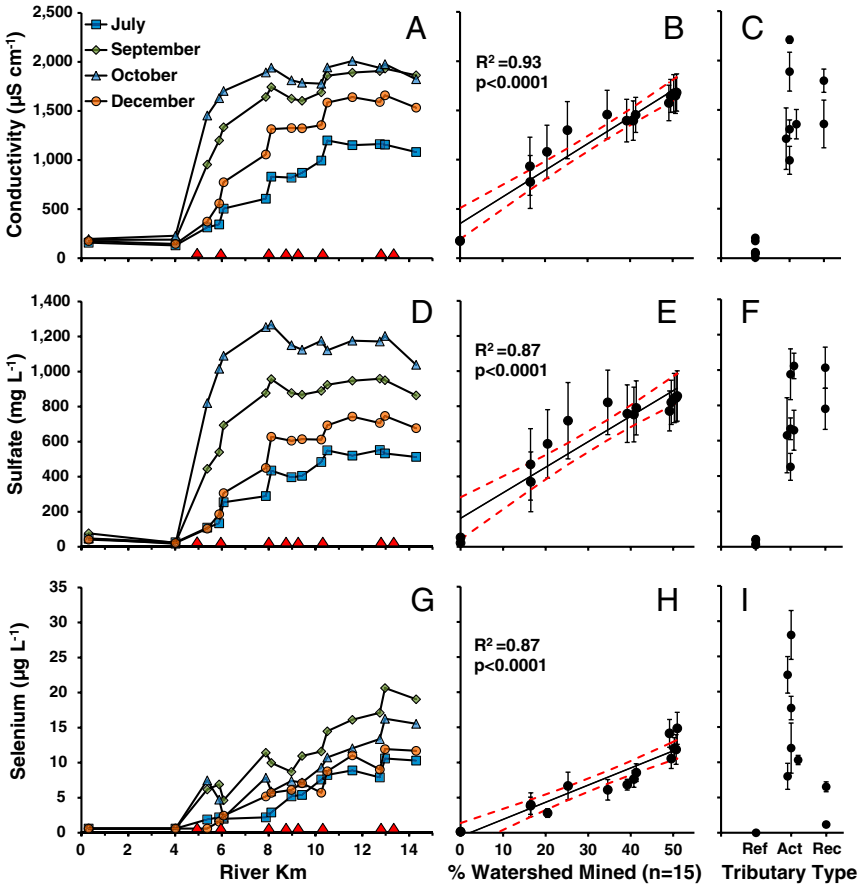

Fig. 2. Longitudinal patterns of conductivity and stream solutes and their correlation to the areal extent of upstream surface mining. Increases in conductivity (*A*), sulfate (*D*), and selenium (*G*) on the mainstem of the Upper Mud River are shown for the four most complete survey months in the study. The locations of MTM-impacted tributary inflows are indicated by red triangles on the *x* axis. The proportion of the contributing watershed in surface mines explains a significant fraction of the variation in stream water conductivity (*B*) sulfate (*E*), and selenium (*H*) concentrations in the mainstem of the Mud River (error bars denote standard error of the mean for the four monthly measurements, red dashed line is the 95% confidence interval for the regression line). The variation in conductivity and solute concentrations in the mainstem are directly compared to data over the same four dates for the eight state reference streams (Ref) within the Upper Guyandotte watershed (data from WVDEP) (10) and tributaries within the Mud River that drained either watersheds with active MTM (Act) or watersheds with historic surface mines reclaimed nearly 20 years ago (Rec). Our detection limit for selenium was 1.1 µg L^{-1}.

were highly correlated to conductivity and its constituent ions in the mainstem ($R^2 = 0.69$ and 0.57, respectively; $p < 0.0001$, Fig. 3*C*), but they lacked any significant relationship to conductivity levels in the samples taken from the MTM-affected tributaries (Fig. 3*D*). In contrast Se and TDN concentrations were highly correlated to the weathering-derived element Sr in both the mainstem ($R^2 = 0.76$ and 0.81, respectively; $p < 0.0001$, Fig. 3*E*) and the affected tributaries ($R^2 = 0.69$, 0.76, respectively; $p < 0.0001$, Fig. 3*F*). For the two tributaries draining only reclaimed surface coal mines, the average Se concentrations were lower than for the six tributaries draining active surface mining operations (Fig. 2*I*). This relationship was also generally true for Sr and TDN (Fig. S1). However, conductivity and SO_4^{2-} levels were similar in all affected tributaries regardless of reclamation status in their contributing watersheds (Fig. 2 *C* and *F*). One possible explanation for this difference in solute export is that Se, Sr, and N mobility decline following mine reclamation while exports of pyrite and carbonate weathering-derived solutes (especially SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+}) continue to be exported at high concentrations even decades after surface mines have been reclaimed (19). Because these weathering-derived ions are the dominant source of high conductivity in draining streams, our data suggest that current reclamation strategies will have limited success in reducing ionic stress for downstream organisms. Alternative explanations for this pattern may be that differences in the Sr, N, and Se content of parent rocks within the basin drive these spatial patterns (15, 20) or that earlier surface coal mining approaches may not have accessed additional selenium-enriched coal strata occurring in deeper formations. We found little evidence, however, of differences in parent geology across the watershed that would support the former hypothesis. The study area is dominated by the middle Pennsylvanian Allegheny and upper Kanawha coal seams that generally contain the highest concentrations of Se in WV (15). Furthermore, leachate experiments conducted on spoil samples from three surface mines that targeted different formations within the ACR showed no systematic difference in water chemistry, which is predominantly controlled by SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, K^+, and Na^+, much like the stream chemistry of the Upper Mud River (21). Further research on the patterns of solute export from reclaimed surface coal mines is necessary to help differentiate between these alternatives.

The consistent increases in a variety of stream water solutes along the Upper Mud River were found to be highly correlated with the cumulative amount of upstream surface mining disturbance. The extent of upstream watershed area that has been mined explains greater than 85% of the longitudinal increases in conductivity and the concentrations of SO_4^{2-} and Se in mainstem sampling sites; we show strong linear correlations between these dissolved constituents and the proportion of the contributing watershed area in surface mines ($R^2 = 0.93$, 0.87, and 0.87, respectively; $p < 0.0001$ in all cases; Fig. 2 *B*, *E*, and *H*). The water quality impacts of the most upstream MTM-affected

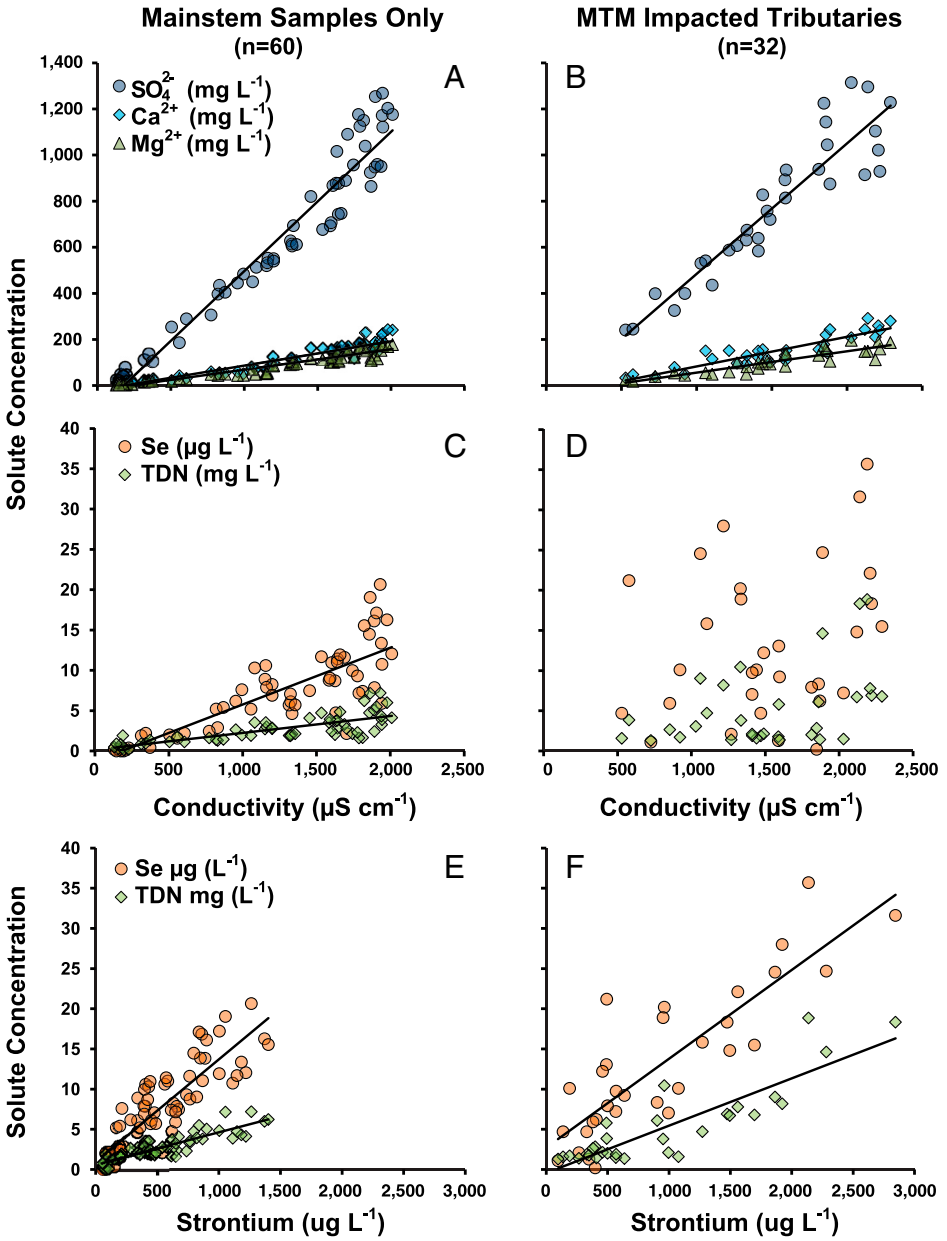

Fig. 3. Correlations between a variety of stream solutes are compared for the mainstem and eight MTM-impacted tributaries. Sulfate, magnesium, and calcium concentrations are strongly correlated to conductivity in both the mainstem ($R^2 = 0.93, 0.90, 0.88$, respectively; $p < 0.0001$) (*A*) and in the affected tributaries ($R^2 = 0.83, 0.78, 0.81$, respectively; $p < 0.0001$) (*B*). Total dissolved nitrogen (TDN) and selenium are strongly related to conductivity in the mainstem ($R^2 = 0.57, 0.69$, respectively; $p < 0.0001$) (*C*) but not across the MTM-impacted tributaries (*D*). TDN and selenium concentrations are more strongly associated with strontium in both the mainstem ($R^2 = 0.81, 0.76$, respectively; $p < 0.0001$) (*E*) and the MTM-impacted tributaries ($R^2 = 0.76, 0.69$, respectively; $p < 0.0001$) (*F*). Differences in sample size are a result of there being 15 mainstem sites and eight tributary sites each sampled four times.

tributary (Lukey Fork) were sufficient to raise the conductivity of the Upper Mud River to an average 620 ± 198 µS cm^{-1} and the Se concentration to 4.0 ± 1.6 µg L^{-1}. EPA water quality data from Lukey Fork prior to the initiation of surface coal mining in its watershed recorded no detectable Se in this stream (EPA detection limit of 3.0 µg L^{-1}) (11). During our 2010 survey, Lukey Fork selenium concentrations ranged from 4.7 to 13.1 µg L^{-1} (this study's detection limit is 1.1 µg L^{-1}). Additional MTM-impacted tributaries further altered water quality such that just downstream of the confluence with Berry Branch, the last MTM-affected tributary, conductivity averaged $1{,}525 \pm 127$ µS cm^{-1} and selenium concentrations averaged 14.1 ± 2.0 µg L^{-1}. Once the river leaves the Hobet mine complex it receives input from multiple unmined tributaries including the Left Branch of the Mud River. The confluence of these two third-order streams is now the site of the 124-hectare Mud River reservoir. Despite the large influx of water from the Left Branch with chemistry similar to the most upstream sampling sites (average conductivity 153 µS cm^{-1} and Se below our detection limit from five sampling sites along the left fork sampled 12/2010), we measured selenium concentrations of 6.5 and 4.0 µg L^{-1} in samples taken from the tailrace below the reservoir in September and December of 2010, respectively.

Increased conductivity, SO_4^{2-} and selenium concentrations in MTM-affected streams have been linked to losses of sensitive aquatic biota throughout the central Appalachians (4, 5, 8). The Mud River reservoir (located 11 km downstream of the last Hobet Mine outfall) has a very high incidence of Se-related developmental deformities in the larvae of bluegill sunfish *(Lepomis macrochirus)* and largemouth bass (*(Mircopterus salmoides*) (22). Instances of adults with physical deformities consistent with

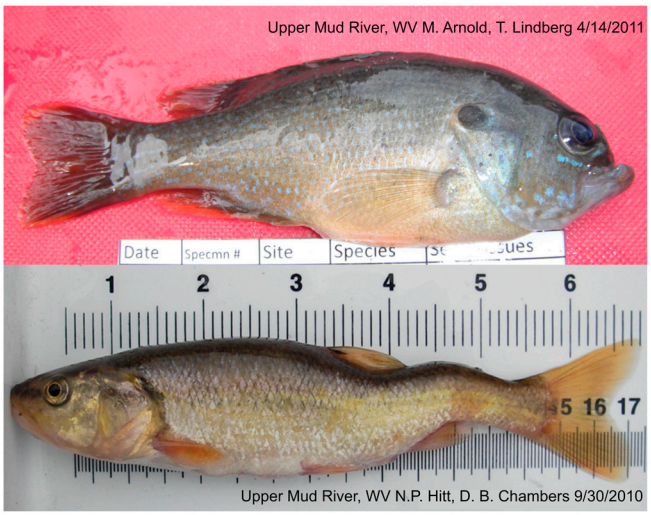

Fig. 4. Effects of selenium toxicity on two species of fish. (*Upper*) One of two Lepomis sp. hybrids caught at site 7 showing cranial-facial deformities typical of selenium toxicity. (*Lower*) Female creek chub (*Semolitus atromaculatus*) from site 10 with lordosis deformity typical of selenium toxicity.

selenium toxicity have been observed on the mainstem of the Upper Mud River (Fig. 4). Analysis of state monitoring efforts over a 10-year period documents a strong negative correlation between stream water conductivity and SO_4^{2-} concentrations and the diversity of sensitive macroinvertebrate taxa in the Guyandotte, the receiving watershed of the Mud River (Fig. S2), a result entirely consistent with trends documented for the entire central Appalachian region (5, 9, 17).

Efforts to link MTM operations to downstream water quality degradation and biological impairment have typically relied on benthic macroinvertebrate surveys (5, 8, 16, 23) and water chemistry analysis (11, 24) with conductivity and SO_4^{2-} concentrations used as major indicators of current and historical mining activity (7, 25). While it is accepted that SO_4^{2-} is a reliable indicator of upstream mining activity (26–28) and that SO_4^{2-} and conductivity are highly correlated in streams receiving surface mining effluents (Fig. 3 *A* and *B* and Fig. S3), to date the direct link between the areal extent of upstream mining activities and conductivity has not been well established. Some studies have shown that increases in concentrations of solutes such as SO_4^{2-} are positively correlated to the amount of coal mined from the watershed and provide evidence for a link between land use among multiple mined watersheds and downstream water quality (6, 16, 26). Our synoptic survey approach conclusively demonstrates that the observed increases in conductivity and Se concentration can be attributed directly to the areal extent of surface coal mining occurring in the watershed. The extensive number of permitted effluent discharges also appears to play a major role in the transport of mining related pollutants into receiving streams (Fig. S4). Our results suggest that the concentrations of some metals and ions related to MTM operations may differ between tributaries draining active versus reclaimed surface mines, while high conductivity and the constituent weathering-derived salts that contribute to conductivity are not ameliorated nearly two decades after reclamation. Additional studies are needed to better understand how the placement and treatment of rock spoil, during all phases of mining and reclamation, affects the mobility and transport of pollutants in impacted watersheds.

Methods

Field Sampling. We measured stream conductivity and collected water samples for subsequent chemical analyses at 23 locations along the Upper Mud River and its tributaries. The sampling locations consisted of two sites upstream of all active and historic (nonactive) MTM and 21 sites along the mainstem and its major tributaries. At each confluence, samples were taken from the tributary and from the mainstem at points above and below the confluence. A suite of major and trace elements were measured including SO_4^{2-}, nitrogen, magnesium, calcium, and selenium (Table S1). This detailed survey allowed us to quantify the cumulative impact of many separate mining permits and associated outlets on downstream water quality and to compare the chemical signatures of MTM-impaired streams based on the amount of upstream mining activity and when it occurred (i.e., current or historical).

Sample Handling and Analysis. A total of 152 samples were collected from tributaries and mainstem of the Mud River in WV at 23 locations (Fig. 1) from May to December 2010. Water sampling strictly followed United States Geological Survey (USGS) protocol (29). Samples for metals and major ions were filtered with a 0.45-μm syringe disk filter. Dissolved metals samples were preserved with 0.2% v/v trace metal grade nitric acid with all sample bottles placed on ice prior to storage at 4.0 °C at the laboratory. Water quality measurements were taken either midstream or from a grab sample with a Beckman Coulter Phi 470 multimeter (Beckman Coulter Inc.). Trace elements were measured with a VG PlasmaQuad-3 (Thermo Fisher Scientific Inc.) inductively coupled plasma mass spectrometry (ICP-MS) and major elements with an ARL SpectraSpan 7 (Thermo Fisher Scientific Inc.) direct current plasma optical emission spectrometry (DCP-OES). Both instruments were calibrated to the National Institute of Standards and Technology 1643e standard, which was used at varying concentrations before, after, and throughout sample runs. Internal standards of In, Th, and Bi were spiked into all samples prior to measurement on the ICP-MS. The detection limit (DL) of the ICP-MS was determined by taking three times the standard deviation of repeated blank measurements and dividing by the slope of the external standard. The resulting values were then averaged ($n = 4$) and are reported for trace elements measured on the ICP-MS in Table S1. Analytical precision was calculated as the relative percent difference (RPD) of the results of duplicate sample measurements and is also reported in Table S1. Sulfate and chloride anions were analyzed using a Dionex ICS-2000 ion chromatograph with an AS-18 column (Dionex Corporation). For both anions, the lowest standard used was 0.01 mg L^{-1}. Total dissolved nitrogen (TDN) and nonparticulate organic C (NPOC) were measured on a Shimadzu TOC-V total carbon analyzer with a TNM-1 nitrogen module (Shimadzu Scientific Instruments). The lowest standards used for TDN and NPOC were 0.05 mg L^{-1} and 0.25 mg L^{-1}, respectively.

Land Cover Classification and Watershed Delineation. Spatial data were collected from the West Virginia GIS Technical Center (available online: http://wvgis.wvu.edu/). Rkm was calculated by measuring distances between sampling locations along the Mud River with the 1:24,000 USGS National Hydrography Dataset. Watersheds for each sampling location were delineated using a 30-meter digital elevation dataset (USGS National Elevation Dataset) and spatial analyst hydrology tools in ArcMap 10.0. Mining and reclaimed areas were delineated from areal imagery (1-meter color orthophotos from the US Department of Agriculture's National Agriculture Imagery Program).

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