Supporting Information

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SI Methods

Instrument Detection Limit = (3 × standard deviation of repeated blank measurements)/slope of the plot of the external standard.

Detection Limit = Average of four instrument detection limit calculations from different analytical runs.

$\text{RPD} = \text{abs}[(A - B)/((A + B)/2)] \times 100$, where A and B are the values of the original and duplicate samples, respectively.

Data for Figs. S2 and S3 was provided by Jeff Bailey of the West Virginia Department of Environmental Protection (Division of Water and Waste Management) on March 27, 2009.

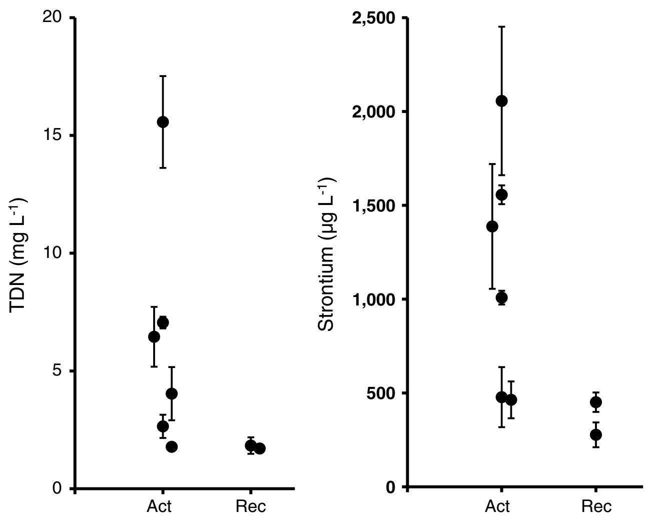

Fig. S1. Charts comparing average total dissolved nitrogen (TDN) and strontium concentrations in active (Act) and reclaimed (Rec) MTM-impacted tributaries to the Upper Mud River. As in Fig. 2, concentrations of TDN and Sr are generally lower in the tributaries draining reclaimed surface mines than in those draining active surface mines.

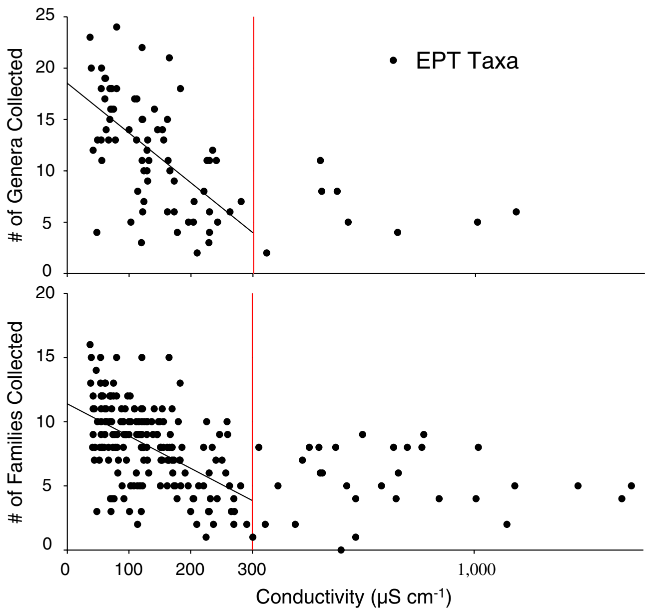

Fig. S2. This represents all stream macroinvertebrate data collected by the West Virginia Department of Environmental Protection for the Upper Guyandotte from 1998 through 2008. In the top graph there are 70 sites with conductivity < 300 and eight sites with conductivity > 300. In the bottom graph there are 180 sites with conductivity < 300 and 31 with conductivity > 300. The red line at conductivity = 300 is the EPA's aquatic life benchmark (1).

1 Cormier SM, Suter GW, Yuan LL, Zheng L (2011) *A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams* (US Environmental Protection Agency, Washington) EPA/600/R-10/023F.

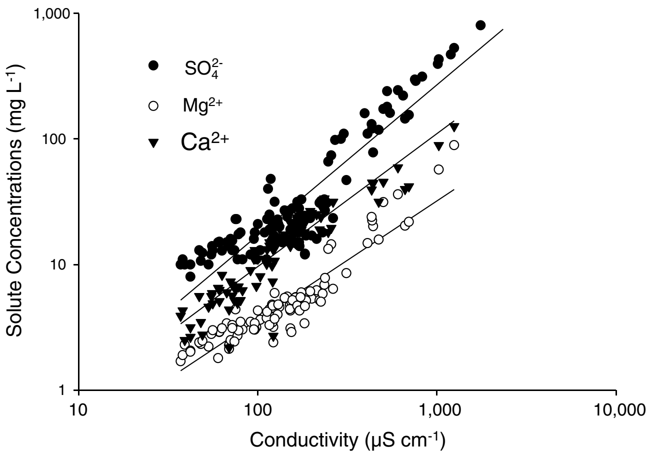

Fig. S3. Scatter plot and correlations for three major ions and conductivity on the Lower Guyandotte using sample data from the West Virginia Department of Environmental Protection database. The relationship between sulfate and conductivity on this larger watershed is nearly identical to that found on the Upper Mud River watershed ($R^2 = 0.94$, $p < 0.0001$, $n = 83$). SO_4^{2-} $R^2 = 0.95$, $p < 0.0001$ $n = 122$; Mg^{2+} $R^2 = 0.89$, $p < 0.0001$, $n = 100$; Ca^{2+} $R^2 = 0.91$, $p < 0.0001$, $n = 96$.

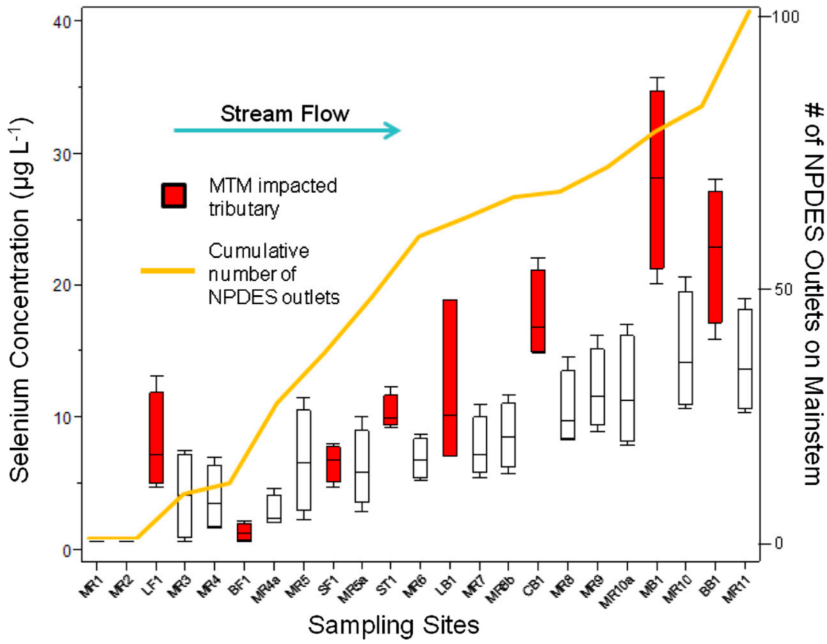

Fig. S4. Box plot showing range and mean stream selenium concentrations during four surveys in 2010 on the Upper Mud River. The cumulative number of active National Pollutant Discharge Elimination System permitted outlets is represented by a yellow line with the scale on the right side of the graph. The red box plots denote the selenium concentrations for MTM-impacted tributaries, with the remainder representing mainstem sampling sites.

Table S1. Summary of measured solutes and correlations to areal upstream mining and conductivity

		Upstream of Hobet Mine Complex	Within Hobet Mine Complex		Correlations		
Measured Solute or Parameter	Method DL RPD(%)	Median (min—max) 2 sites	Median Mainstem (min—max) 13 sites	Median MTM Tributary (min—max) 8 sites	R^2 Median All Mainstem Sites to % Area Mined	R^2 All Mainstem Sites to Conductivity	R^2 MTM Tributary Sites to Conductivity
Conductivity ($\mu S\ cm^{-1}$)	Field Probe	151.8 (88.1–229.0)	1329.5 (182.6–2010.0)	1480.0 (529.0–2290.0)	**0.96 *n* = 15**		
SO4 (mg/L)	IC	26.7 (16.6–76.9)	692.8 (47.8–1268.0)	785.0 (240.7–1314.1)	**0.91 *n* = 15**	**0.94 *n* = 83**	**0.86 *n* = 32**
Cl (mg/L)	IC	7.2 (4.1–19.9)	4.9 (3.4–12.7)	5.6 (1.2–15.3)	**–0.41 *n* = 15**	0.02 *n* = 83	**0.19 *n* = 32**
TN (mg/L)	TOC-TN	0.4 (0.2–1.9)	2.7 (0.9–7.2)	3.0 (1.0–18.9)	**0.70 *n* = 15**	**0.58 *n* = 60**	0.10 *n* = 32
NPOC (mg/L)	TOC-TN	3.0 (1.7–3.4)	4.2 (1.8–5.3)	3.9 (1.1–8.1)	**0.70 *n* = 15**	**0.35 *n* = 60**	0.11 *n* = 32
Ca (mg/L)	DCP	13.0 (11.8–22.4)	128.7 (22.3–242.7)	149.9 (33.3–291.5)	**0.98 *n* = 15**	**0.90 *n* = 72**	**0.81 *n* = 32**
Mg (mg/L)	DCP	6.1 (4.4–9.3)	110.1 (16.3–179.9)	101.2 (18.2–195.9)	**0.93 *n* = 15**	**0.91 *n* = 72**	**0.81 *n* = 32**
Sr (μg/L)	DCP	69.4 (57.0–109.8)	550.3 (81.8–1402.5)	636.6 (96.3–2845.1)	**0.85 *n* = 15**	**0.75 *n* = 72**	**0.26 *n* = 32**
Na (mg/L)	DCP	6.7 (5.5–18.4)	8.0 (2.5–19.6)	9.2 (0.8–53.7)	**0.48 *n* = 15**	**0.23 *n* = 72**	0.00 *n* = 32
Fe (μg/L)	DCP	175.8 (29.8–536.7)	37.7 (2.4–201.6)	39.3 (6.1–382.5)	**–0.42 *n* = 15**	**–0.26 *n* = 72**	0.02 *n* = 32
Ba (μg/L)	DCP	27.6 (17.2–53.6)	35.6 (15.4–63.1)	31.3 (8.1–73.2)	0.05 *n* = 15	**0.16 *n* = 72**	0.00 *n* = 32
Mn (μg/L)	DCP	88.8 (37.2–682.6)	91.3 (27.7–438.8)	122.0 (0.0–1765.4)	**–0.28 *n* = 15**	0.03 *n* = 72	0.04 *n* = 32
Si (mg/L)	DCP	4.2 (3.7–4.8)	1.8 (0.3–3.7)	1.9 (0.9–3.0)	**0.75 *n* = 15**	**0.53 *n* = 72**	0.00 *n* = 32
Li (μg/L)	ICP-MS DL = 0.4 RPD = 1.9	1.7 (1.2–4.6)	21.9 (3.3–33.1)	25.3 (6.7–40.8)	**0.98 *n* = 15**	**0.90 *n* = 60**	**0.49 *n* = 32**
B (μg/L)	ICP-MS DL = 7.0 RPD = 1.8	15.7 (7.8–20.0)	26.1 (11.0–125.9)	38.9 (8.9–252.5)	**0.55 *n* = 15**	**0.24 *n* = 60**	0.04 *n* = 32
Al (μg/L)	ICP-MS DL = 1.9 RPD = 18.1	5.4 (BDL–13.5)	3.9 (BDL–16.3)	3.5 (BDL–66.4)	0.14 *n* = 15	**–0.16 *n* = 60**	0.02 *n* = 32
V (μg/L)	ICP-MS DL = 0.06 RPD = 1.3	0.2 (0.2–0.4)	0.15 (BDL–3.5)	0.11 (BDL–0.4)	–0.19 *n* = 15	0.00 *n* = 60	0.09 *n* = 32
Cr (μg/L)	ICP-MS DL = 0.3 RPD = 3.4	0.5 (BDL–1.0)	BDL	0.15 (BDL–0.7)	**–0.70 *n* = 15**	**–0.20 *n* = 60**	0.03 *n* = 32
Co (μg/L)	ICP-MS DL = 0.04 RPD = 9.1	0.3 (0.1–1.8)	0.5 (0.3–2.0)	0.55 (0.25–7.8)	0.06 *n* = 15	0.01 *n* = 60	0.04 *n* = 32
Ni (μg/L)	ICP-MS DL = 0.9 RPD = 9.5	BDL	4.7 (1.0–9.6)	5.93 (1.6–60.8)	**0.80 *n* = 15**	**0.52 *n* = 60**	0.00 *n* = 32
Cu (μg/L)	ICP-MS DL = 0.6 RPD = 7.5	BDL	1.2 (BDL–3.9)	1.35 (BDL–3.3)	**0.77 *n* = 15**	**0.48 *n* = 60**	**0.29 *n* = 32**
Zn (μg/L)	ICP-MS DL = 1.0 RPD = 13.8	4.0 (BDL–11.0)	6.4 (BDL–35.2)	8.89 (BDL–15.5)	**0.58 *n* = 15**	**–0.27 *n* = 60**	**0.20 *n* = 32**
As (μg/L)	ICP-MS DL = 0.06 RPD = 2.2	0.2 (BDL–0.3)	0.1 (BDL–0.3)	0.09 (BDL–0.2)	**–0.80 *n* = 15**	**0.06 *n* = 60**	0.00 *n* = 32
Se (μg/L)	ICP-MS DL = 1.1 RPD = 5.0	BDL	7.9 (BDL–20.7)	10.1 (BDL–35.7)	**0.87 *n* = 15**	**0.68 *n* = 60**	0.07 *n* = 32
Rb (μg/L)	ICP-MS DL = 0.04 RPD = 0.9	2.0 (1.0–2.4)	15.3 (2.6–23.0)	19.24 (6.5–27.4)	**0.99 *n* = 15**	**0.92 *n* = 60**	**0.56 *n* = 32**
U (μg/L)	ICP-MS DL = 0.01 RPD = 11.6	BDL	3.6 (0.4–6.6)	3.5 (0.2–9.3)	**0.97 *n* = 15**	**0.91 *n* = 60**	**0.69 *n* = 32**

Detection limits (DL) for ICP-MS were calculated based on the average instrument detection limit and precision by the relative percent difference (RPD). Both are described further in *SI Methods*. For statistical purposes a value equal to one half of the DL was used when the concentration in the sample was undetected or below the detection limits (BDL). If the median value for a solute was below the DL, then it was considered undetected for all instances at that sampling location. Bold correlation values are highly significant ($p < 0.05$). For other methods the reported concentrations were above the lowest calibration standard.