

Isotopic Imprints of Mountaintop Mining Contaminants

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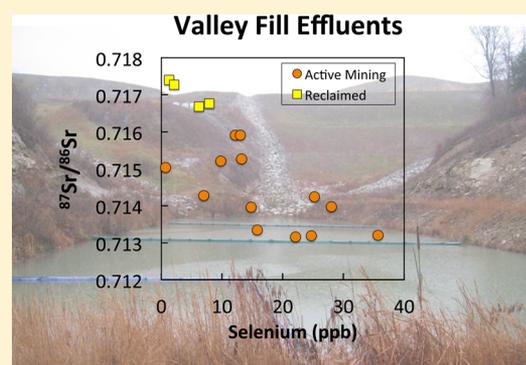
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Supporting Information

ABSTRACT: Mountaintop mining (MTM) is the primary procedure for surface coal exploration within the central Appalachian region of the eastern United States, and it is known to contaminate streams in local watersheds. In this study, we measured the chemical and isotopic compositions of water samples from MTM-impacted tributaries and streams in the Mud River watershed in West Virginia. We systematically document the isotopic compositions of three major constituents: sulfur isotopes in sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$), carbon isotopes in dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$), and strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$). The data show that $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{13}\text{C}_{\text{DIC}}$, Sr/Ca, and $^{87}\text{Sr}/^{86}\text{Sr}$ measured in saline- and selenium-rich MTM impacted tributaries are distinguishable from those of the surface water upstream of mining impacts. These tracers can therefore be used to delineate and quantify the impact of MTM in watersheds. High Sr/Ca and low $^{87}\text{Sr}/^{86}\text{Sr}$ characterize tributaries that originated from active MTM areas, while tributaries from reclaimed MTM areas had low Sr/Ca and high $^{87}\text{Sr}/^{86}\text{Sr}$. Leaching experiments of rocks from the watershed show that pyrite oxidation and carbonate dissolution control the solute chemistry with distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios characterizing different rock sources. We propose that MTM operations that access the deeper Kanawha Formation generate residual mined rocks in valley fills from which effluents with distinctive $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca imprints affect the quality of the Appalachian watersheds.



INTRODUCTION

In the eastern United States, surface mountaintop mining (MTM) has become the dominant technique for coal exploration, particularly in the central Appalachian coalfields of Kentucky, Virginia, West Virginia, and Tennessee, which cover about 48,000 km².¹ As part of the MTM operations, several layers of sedimentary rocks are removed to access the underlying coal seams. The residual mined rocks, or overburden, are then typically placed in stream channels adjacent to the surface mines, creating valley fills (VF). These fills permanently bury headwater streams and alter the hydrology, chemistry, and biotic composition of source waters that feed the local streams and river systems.^{2–18}

Carbonate mineral dissolution within the VF buffers the acidity that is generated from the oxidation of pyrite, and consequently, alkaline (pH typically >7) and saline (TDS > 1500 mg/L) effluents are generated in VF outflows. The VF effluents are characterized by high concentrations of Ca, Mg, Sr, SO₄, and HCO₃.^{15–17} The VF effluents also contain elevated concentrations of trace elements such as Se, As, and Mn that pose serious ecological risks to receiving streams, including toxic effects observed in fish in local watersheds.^{1,11,12,15,18} Recent findings show a cumulative aspect to discharge effluents

from both active and reclaimed surface coal mines in West Virginia, where the increases in salinity, sulfate, and selenium are proportional to the upstream aerial extent of mining.¹⁵ A survey quantifying the extent of surface mining in southern West Virginia revealed that the extent of surface mining disturbance within a catchment is highly correlated with the ionic strength and sulfate concentrations of the receiving streams.¹⁴

The majority of coal production from surface mines in the southern Appalachian of West Virginia is derived from the Middle Pennsylvanian Kanawha and Allegheny formations (Figures S1, S2, Supporting Information). The Kanawha Formation is composed mostly of sandstone, gray and black shale (Carbolith), siltstone, and hosts several coal seams, including the high quality Coalburg and Stockton coals. These coal seams represent 42% of West Virginia's original coal resources. The overlying Allegheny Formation is composed of cyclic sequences of sandstone, siltstone, shale, limestone, and

Received: March 25, 2013

Revised: August 2, 2013

Accepted: August 2, 2013

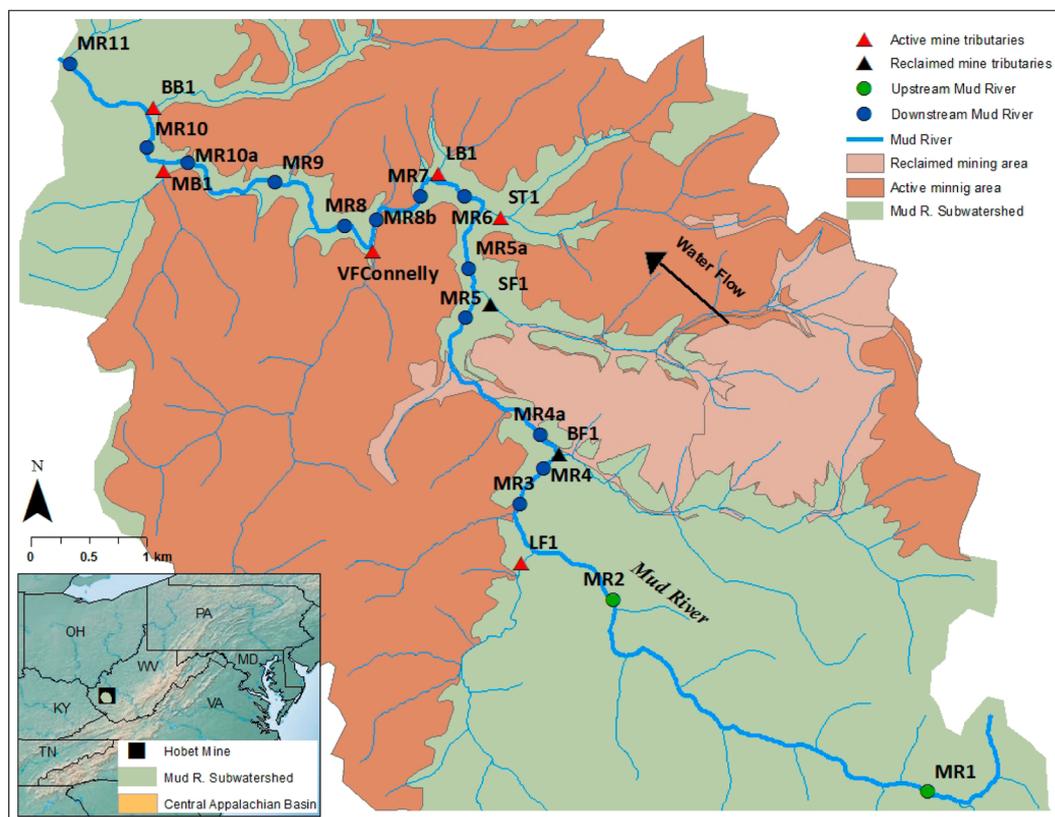


Figure 1. Sampling location map along the Mud River watershed in West Virginia. Note the distinction between the sampling sites of the upper (unaffected) Mud River (green circles), downstream Mud River (blue circles), tributaries from reclaimed mines (black triangles), and active mines (red triangles).

coal, including the No. 5 and No. 6 coal seams. Both formations contain a wide range of sulfur content (0.01–10%) in the forms of organic sulfur and pyrite mineral^{19–21} (Figure S1, Table S1, Supporting Information).

Previous studies have evaluated the chemical and isotopic compositions of acid mine drainage that originated from subsurface coal mining.^{22–31} This study explores, for the first time, the stable isotope ratios of the major constituents in VF effluents and their impact on the isotopic variations in the receiving stream waters. We used stable carbon isotopes to delineate the sources of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) and sulfur isotopes for dissolved sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$). We also used dissolved strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) as a proxy for selenium contamination, given the high correlation between Sr and Se previously observed in MTM-impacted streams.¹⁵ The study was conducted in the Mud River watershed in Lincoln and Boone Counties of West Virginia (Figure 1) and was based on two components. The first was systematic measurements of the chemical composition and $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{34}\text{S}_{\text{SO}_4}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ in surface water streams and tributaries originated from MTM sites. On the basis of their spatial distribution, we divided the sample locations into four subcategories including tributaries draining both active and reclaimed sections of MTM operations as well as the upstream and downstream sections (with respect to MTM drainage areas) of the main stem of the Mud River (Figure 1). A second component of the study was measurements of major elements, selenium, and $^{87}\text{Sr}/^{86}\text{Sr}$ in leachates of rocks of the lower section of the Allegheny Formation and the upper section of the Kanawha Formation collected from a 70 meter core drilled in the Hobet 21 mine in West Virginia

(Figure 1 and Figures S1 and S2 and Table S1, Supporting Information²⁰). The objective of this study is to determine whether MTM effluents have distinctive stable isotopic imprints relative to unaffected stream waters and to test their application as diagnostic tools for tracing the impact of MTM effluents on stream chemistry and ecology in the Appalachian Basin.

METHODS

Water samples were collected monthly from May to December 2010 from 23 locations on the main stem of the Mud River and its tributaries in West Virginia (Figure 1). Water sampling strictly followed U.S. Geological Survey (USGS) protocol.³² Samples for metals and major ions were filtered with a 0.45 μm syringe disk filter. Dissolved metal 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 in the laboratory. Trace elements were measured with a VG PlasmaQuad-3 (Thermo Fisher Scientific, Inc.) inductively coupled plasma mass spectrometer (ICP-MS) and major elements with an ARS SpectraSpan 7 (Thermo Fisher Scientific, Inc.) direct current plasma optical emission spectrometer (DCP-OES) and ion chromatography (IC) at Duke University. The detection limit of Se (1.1 ppb) was determined by dividing three times the standard deviation of repeated blank measurements by the slope of the external standard. Analytical precision for Se (5%) was calculated as the relative percent difference (RPD) of the results of duplicate sample measurements.

Strontium isotopes were analyzed by thermal ionization mass spectrometry (TIMS) on a ThermoFisher Triton at the TIMS

Table 1. Mean Values of Water Quality and Isotopic Tracers of Water Samples Collected from the Upstream Section of the Mud River, Downstream of the Mud River, Tributaries from Reclaimed MTM Areas, and Tributaries from Active MTM Areas^a

	EC	pH	Ca (ppm)	Mg (ppm)	SO ₄ (ppm)	Se (ppb)	Sr (ppb)	Sr/Ca	⁸⁷ Sr/ ⁸⁶ Sr	δ ³⁴ S	δ ¹³ C-DIC
Mud River watershed											
upstream Mud River	155	7.1	13.7	5.7	34.3	BDL	78.9	0.0057	0.71426	3.91	-6.9
downstream Mud River	1291	7.3	118	95	653	8.4	710	0.0061	0.71487	0.4	-1.1
tributaries from reclaimed MTM	1512	7.8	129	126	856	3.5	391	0.0032	0.71703	0.1	-1.3
tributaries from active MTM	1369	7.1	132	84	657	15.5	1235	0.0089	0.71452	0.3	-0.2
Rock leaching											
Allegheny Fm., combined	709	3.8	140	48	1882	683	568	0.0047	0.71611	-	-
Allegheny Fm., noncoal	260	4.5	144	61	774	809	413	0.0032	0.71830	-	-
Allegheny Fm., coal	1249	2.9	132	23	2712	454	852	0.0075	0.71265	-	-
Kanawha Fm., combined	994	3.9	277	113	1605	348	6458	0.0247	0.71342	-	-
Kanawha Fm., noncoal	768	4.4	321	143	1455	430	7769	0.0259	0.71409	-	-
Kanawha Fm., coal	1252	3	213	72	1755	220	4623	0.0233	0.71262	-	-

^aThese variations are compared to mean values measured in water-soluble salts extracted from rocks (see lithology information in Table S1, Supporting Information) as part of leaching experiments in this study. The rock samples from the Allegheny and Kanawha Formations represent the surface geology in the area of the Hobet #21 mine.

lab at Duke University. The average ⁸⁷Sr/⁸⁶Sr of the SRM-987 standard measured during this study was 0.710266 ± 0.000005 (SD). The carbon isotope ratio of dissolved inorganic carbon was analyzed by acid digestion on a ThermoFinnigan GasBench II, feeding a ThermoFinnigan Delta+XL isotope ratio mass spectrometer (IRMS) at Duke University. The δ¹³C of the resulting CO₂ was normalized vs Vienna Pee Dee Belemnite (VPDB) using NBS19, IAEA CO-8 standards, and an internal CaCO₃ standard and were expressed as δ¹³C_{DIC}. Sulfur isotopes were measured in a continuous-flow gas-ratio mass spectrometer (ThermoQuest Finnigan Delta PlusXL) at the Environmental Isotope Laboratory at the University of Arizona. The system was calibrated by using international standards OGS-1 and NBS123. Precision was estimated to be ±0.15‰. The ³⁴S/³²S ratio was normalized to the standard VCDT (Vienna Canyon Diablo Troilite) and expressed as δ³⁴S_{SO₄}.

Surface geology was examined through leaching experiments of powder-crushed rocks from a core collected from the Hobet 21 mine (457 m north of the Hobet 21 main office, between Bragg Fork and the right fork of Long Branch, Scott District; latitude, 38.11900; longitude, 81.87806) in Boone County, West Virginia (Figure 1 and Figure S2, Supporting Information). The 70 m core (depth interval of 40 to 110 m) was composed of coal and noncoal rocks from the Middle Pennsylvanian Allegheny and Kanawha formations (Figure S2, Table S1, Supporting Information²⁰). Four to five grams of each powdered rock sample was combined with 40–50 mL of deionized water (>18 MΩs; liquid to solid ratio of ~10) in a HDPE trace-metal free centrifuge tube. The combined samples were shaken for 24 h and then removed from the shaker. The samples were centrifuged; the liquid was then decanted and filtered through 0.45 μm filters into new 50 mL HDPE trace-metal free centrifuge tubes. The control samples followed this same procedure only with deionized water and no rock sample. Leachates were measured for pH, electric conductivity, major ions, Se, and strontium isotope ratios.

RESULTS AND DISCUSSION

Geochemical and Isotopic Characterization of VF Effluents. The major dissolved constituents in tributaries of the Mud River (Figure 1) that determine the overall salinity were Ca, SO₄, and DIC (Figure S3, Supporting Information). On the basis of systematic sampling of tributaries originating

from VFs in the watershed of the Mud River,¹⁵ we define two types of tributaries: those originated from areas draining VFs of active and current MTM activities and those from nonactive reclaimed MTM areas (Figure 1). The definition of MTM refers to the timing of operation; reclaimed areas are MTM operations of mostly, but not exclusively, of coal from the overlying Allegheny Formation in the eastern part of the Mud River watershed. Active MTM refers to current MTM activities of mostly the deeper Kanawha Formation in the central and western section of the watershed (Figure 1 and Figure S1, Supporting Information). Our data show that both types of tributaries are characterized by relatively high salinity and sulfate concentrations but differ with higher concentrations of Sr and Se observed in tributaries draining active MTM (Table 1, Figures 2 and 3). Additionally, sulfate, δ³⁴S_{SO₄}, DIC, and δ¹³C_{DIC} variations are indistinguishable between tributaries originated from active and reclaimed MTM areas (Figure S4, Supporting Information) but differ in their Sr/Ca and ⁸⁷Sr/⁸⁶Sr (Table 1, Figures 2, 3, and Figure S1, Supporting Information).

The variations of δ¹³C_{DIC} and δ³⁴S_{SO₄} (Figures 4, 5) indicate that DIC and SO₄ were derived from two major sources: (1) diluted tributaries depleted in ¹³C_{DIC} (δ¹³C_{DIC} < -6‰) and slightly enriched in ³⁴S_{SO₄} (δ³⁴S_{SO₄} > +5‰) and (2) saline tributaries enriched in ¹³C_{DIC} (δ¹³C_{DIC} ~ +6‰) and slightly depleted in ³⁴S_{SO₄} (δ³⁴S_{SO₄} = -2 to +2‰). The respectively low δ¹³C_{DIC} and high δ³⁴S_{SO₄} of the diluted tributaries mimic the natural background conditions (soil processes and meteoric sulfate) and were also observed in the upstream section of the Mud River without any mining influence, prior to the river flow through the MTM affected area. In contrast, we suggest that the high δ¹³C_{DIC} and low δ³⁴S_{SO₄} in the saline tributaries reflect the composition of the source DIC and sulfate in VFs. The positive δ¹³C_{DIC} signature of the DIC-enriched tributaries is substantially different from the negative carbon isotope composition typical to the Appalachian coal (δ¹³C range of -22 to -27‰;^{28,29}). The positive δ¹³C_{DIC} also differed from measurements of total soil samples for MTM reclaimed soils, forest soils, and grassland soils that all yielded low δ¹³C (-25 to -28‰³³). The high δ¹³C_{DIC} signature is also different from the composition that characterizes natural waters (a range of -21‰ to -10‰) in which DIC dissociation and carbonate dissolution are derived from carbonic acid originated from organic matter oxidation and ¹³C-depleted CO₂.³⁴ In contrast,

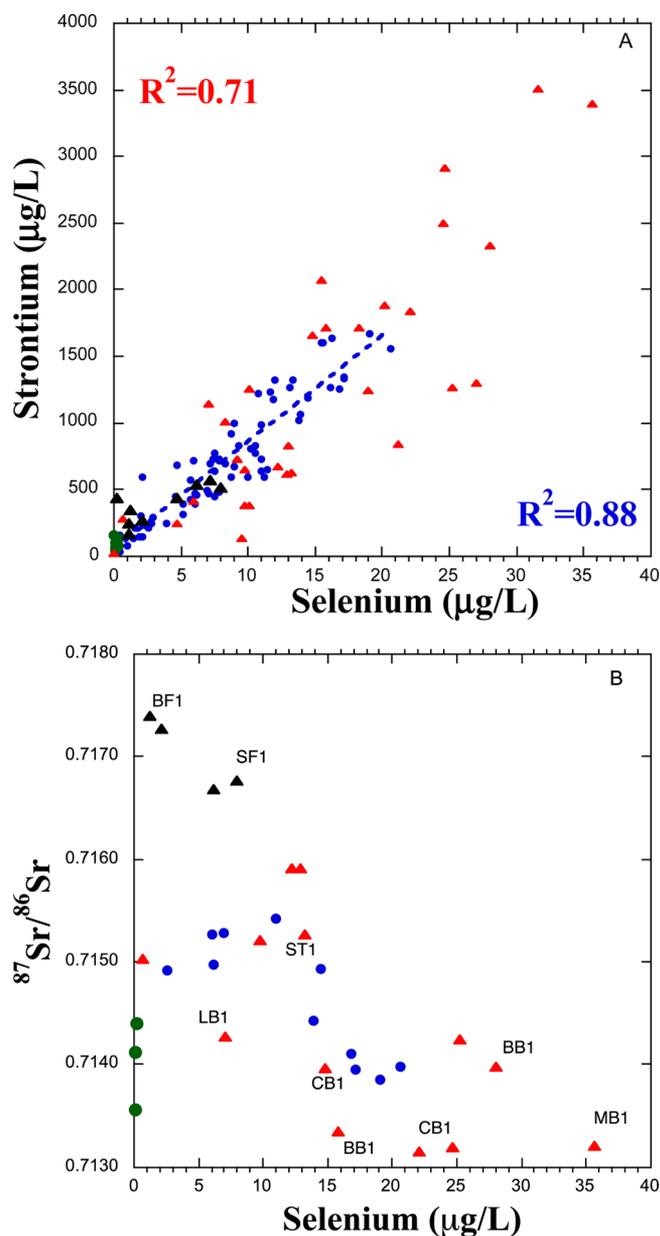


Figure 2. (A) Strontium versus selenium concentrations and (B) $^{87}\text{Sr}/^{86}\text{Sr}$ versus selenium concentrations in tributaries draining reclaimed MTM areas (black triangles), active mines (red triangles), upstream section of the Mud River (green circles), and downstream of the Mud River (blue circles). See sample locations in Figure 1. Note the linear correlation between Se and Sr and the inverse correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and selenium.

relatively positive $\delta^{13}\text{C}_{\text{DIC}}$ values (a range of -10% to $+0.8\%$) were measured in acid mine drainage (AMD) from Pennsylvania that was attributed to dissolution of carbonate minerals by sulfuric acid originated from pyrite oxidation.³¹ The high $\delta^{13}\text{C}$ composition (a range of 2 to 5‰) is typical for Pennsylvanian marine carbonate rocks,³⁵ which is equivalent to the Allegheny and Kanawha Formations. These values are consistent with the $\delta^{13}\text{C}_{\text{DIC}}$ values of the apparent high DIC end member presented in Figure 5.

Our leaching experiments (see below) demonstrate that indeed pyrite oxidation generates sulfuric acid that apparently dissolves calcium carbonate in VFs. We conclude that the bulk DIC in effluents derived from VF is derived from dissolution of

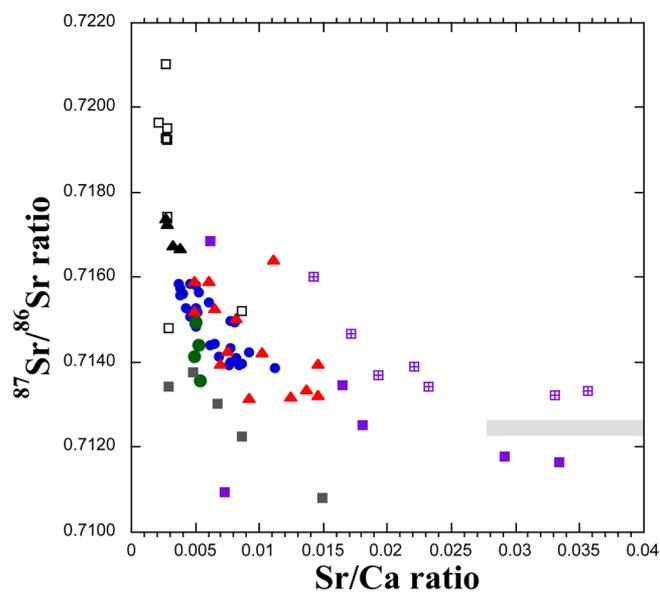


Figure 3. $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr/Ca ratios in tributaries from reclaimed MTM areas (black triangles), active mines (red triangles), upstream section of the Mud River (green circles), and downstream of the Mud River (blue circles) as compared to water-soluble fractions from leaching of coal rocks (gray squares) and noncoal rocks (open black squares) from the shallow Allegheny Formation and coal rocks (purple squares) and noncoal rocks (purple checkers) from the deeper Kanawha Formation. Note that leachates from coal-containing rocks from both formations and noncoal rocks from the Kanawha Formation had typically lower $^{87}\text{Sr}/^{86}\text{Sr}$, similar to tributaries from active mines VFs with high Sr/Ca and lower $^{87}\text{Sr}/^{86}\text{Sr}$. This $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (~ 0.7124) seems to represent a common soluble strontium isotopic imprint for Appalachian coals (marked as gray area).

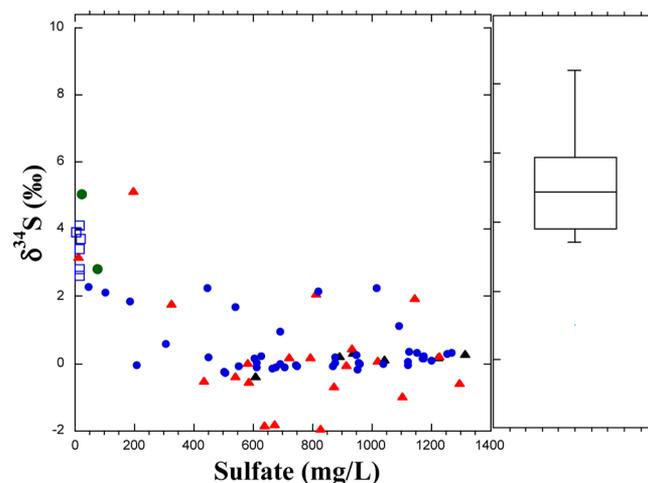


Figure 4. $\delta^{34}\text{S}$ (normalized to Vienna Canyon Diablo Troilite) versus sulfate concentrations in tributaries from reclaimed MTM areas (black triangles), active mines (red triangles), upstream section of the Mud River (green circles), and downstream of the Mud River (blue circles) as compared to uncontaminated streams from West Virginia (open blue square³⁶). On the right panel is the distribution of $\delta^{34}\text{S}$ in typical meteoric water.³⁷ Note that waters with low sulfate contents from the upper section of the Mud River and tributaries had higher $\delta^{34}\text{S}$, which is consistent with previous reports for $\delta^{34}\text{S}$ in meteoric water. In contrast, the sulfate-rich waters had a lower $\delta^{34}\text{S}$ signature.

inorganic carbonates with a positive $\delta^{13}\text{C}$ imprint due to sulfuric acid originated from pyrite oxidation. The linear

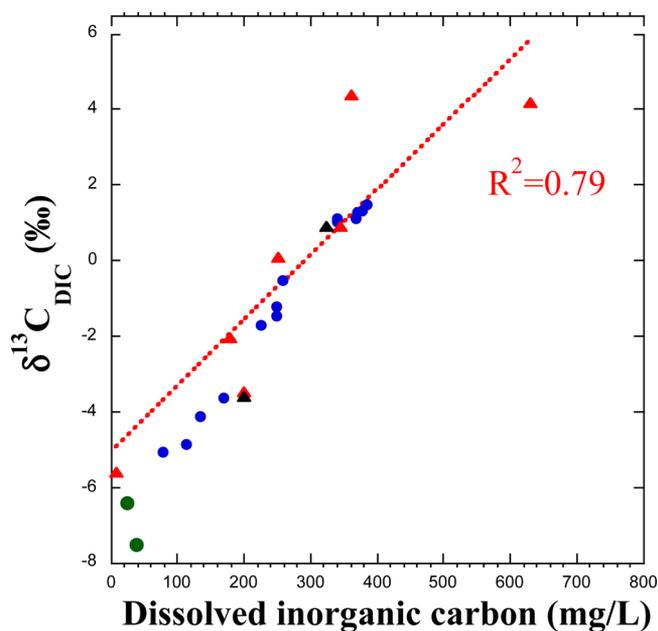


Figure 5. $\delta^{13}\text{C}_{\text{DIC}}$ (normalized to Vienna Pee Dee Belemnite) versus dissolved inorganic carbon (DIC) concentrations in tributaries from reclaimed MTM areas (black triangles), active mines (red triangles), upstream section of the Mud River (green circles), and downstream of the Mud River (blue circles). Note the linear correlation that reflects a conservative mixing between low DIC with depleted $\delta^{13}\text{C}$ and high DIC with high $\delta^{13}\text{C}$.

correlation between DIC and $\delta^{13}\text{C}_{\text{DIC}}$ in Figure 5 therefore reflects a mixing between two DIC sources: (1) organic carbon in soil that generates ^{13}C -depleted CO_2 that is indicative of pristine natural waters with low DIC and (2) dissolution of carbonates in the residual rock materials in VFs with a positive $\delta^{13}\text{C}$ ($> +6\text{‰}$).

Likewise, we attribute the slightly elevated $\delta^{34}\text{S}_{\text{SO}_4}$ ($\sim +5\text{‰}$) in the diluted tributaries to a meteoric source, which is consistent with the $\delta^{34}\text{S}_{\text{SO}_4}$ of bulk precipitation and pristine stream waters in the upland forested catchments within the Appalachian Plateau region of West Virginia³⁶ and other inland basins (Figure 4).³⁷ In contrast, the saline tributaries with high SO_4 had lower $\delta^{34}\text{S}_{\text{SO}_4}$ (-2 to $+2\text{‰}$), originated from oxidation of pyrite from within the bedrock, which typically has a similar low $\delta^{34}\text{S}$ range.³⁷ These results are also consistent with an elevated SO_4 and an apparent $\delta^{34}\text{S}$ end member of $\sim 1\text{‰}$ measured in stream waters of Yellow Creek, West Virginia, also associated with coal mining.³⁶

Impact on the Mud River. The chemical and isotopic variations of the mining-impacted tributaries are notably different from those of the upper Mud River, above any current mining activity (Table 1 and Figure 1). Data demonstrating the gradual and accumulative increase of salinity (Figure S5, Supporting Information), sulfate, Sr, and Se contents with higher intensity of MTM were reported previously.¹⁵ The dilute upstream section of river is characterized by low $\delta^{13}\text{C}_{\text{DIC}}$ and high $\delta^{34}\text{S}_{\text{SO}_4}$ that are distinguished from the composition of the downstream section of the Mud River (Figures S7, S8, Supporting Information). Temporal variations in salinity (Figure S5, Supporting Information), sulfate, bicarbonate, selenium, and strontium concentrations showed seasonal fluctuations in the Mud River, resulting from dilution. Yet, the increase in $\delta^{13}\text{C}_{\text{DIC}}$ and the

decrease in $\delta^{34}\text{S}_{\text{SO}_4}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Figures S6, S7, S8, Supporting Information) in the downstream river clearly reflect the effect of the tributaries' inflows, regardless of their absolute concentrations. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of tributaries that drain reclaimed mining areas are different from those draining current MTM watersheds. This ratio fluctuates as the river flows downstream depending on the mining status of the contributing watershed (Figure S6, Supporting Information); river waters downstream from tributaries from reclaimed and active VFs are characterized by relatively high and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, respectively (Figure 6 and Figure S6, Supporting

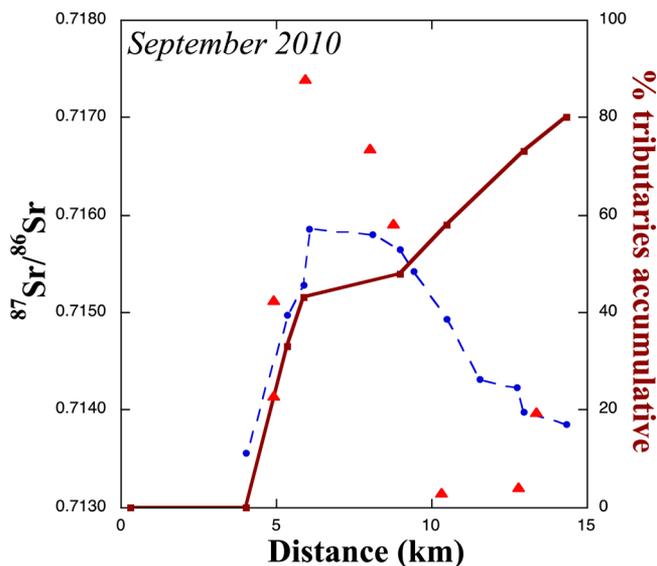


Figure 6. Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ in the Mud River (blue circles) and calculated accumulated contribution of the external tributaries (red line, see calculations in Table 1) during September 2010 sampling as compared to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of tributaries (red triangles) along the Mud River flow. Distance (km) refers to the flow of the Mud River from the initial sample (Figure 1). Note that the changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ of the tributary inflows modify the $^{87}\text{Sr}/^{86}\text{Sr}$ in river water in downstream samples.

Information). The preservation of the chemical and isotopic variations in the downstream Mud River (e.g., the linear correlation between Sr and Se; Figure 3A) indicates that the major and minor constituents, including selenium, behave conservatively in the river system without retention or attenuation. These results are consistent with earlier observations that the salinity, sulfate, and Se concentrations in MTM streams are linearly proportional to the extent of surface mining in the watershed.^{14,15}

A mass-balance calculation, using the Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in a mixing model, provides a sensitive evaluation of the fraction of the tributaries contributing to each of the downstream sampling points along the Mud River (Figure 1). We estimate that the tributaries provide between 5% and 33% of the dissolved constituents in the mainstem at different sampling locations along its flow (Figure 1 and Table S3, Supporting Information). The rise of Sr concentrations in the Mud River from $95 \mu\text{g}/\text{L}$ in the nonimpacted section (MR-2) to $1672 \mu\text{g}/\text{L}$ in the downstream site (MR-11), about 10 km downstream from the first MTM tributary that enters the Mud River, corresponds to an overall 80% accumulative input of dissolved Sr from MTM tributaries (Figure 6).

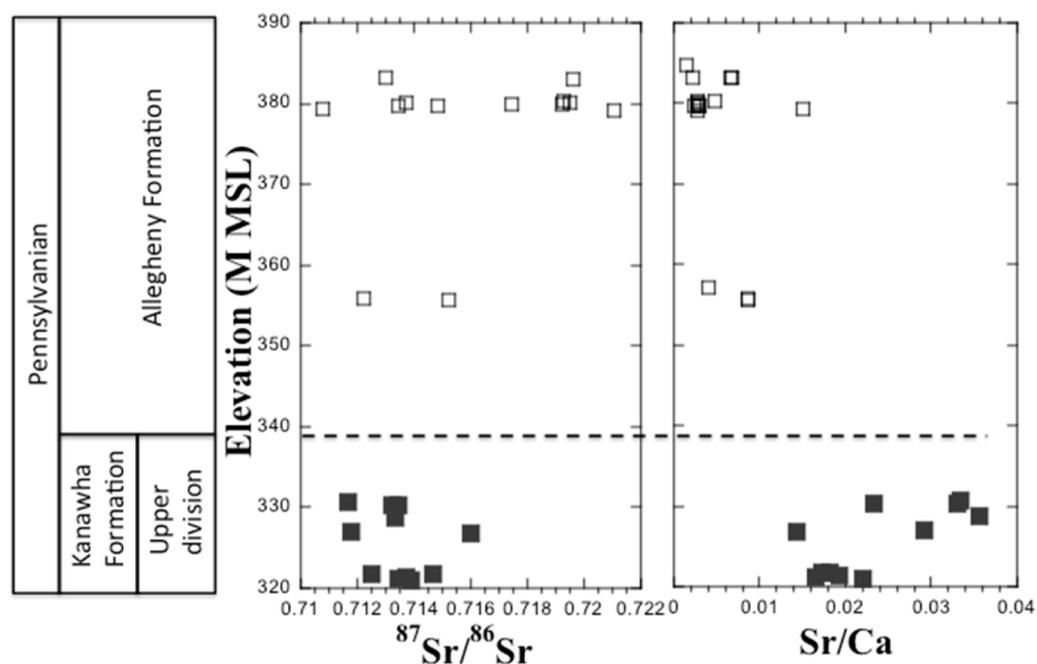


Figure 7. Variations of water-soluble $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca in leachates from rocks of the Allegheny and Kanawha Formations, revealed by a 70 m core from Hobet #21.²⁰ Note the wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ and lower Sr/Ca ratios in water-soluble salts extracted from the upper Allegheny Formation relative to lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher Sr/Ca in the lower Kanawha Formation.

Leaching Experiments of Local Bedrock from the Hobet #21 Mine. The lower and upper sections of the Middle Pennsylvanian Allegheny and Kanawha Formations represent the surface geology within the permitted area of the Hobet #21 mine^{19–21} (Figure 7 and Figures S1, S2, Table S1, Supporting Information). In order to characterize the chemistry and $^{87}\text{Sr}/^{86}\text{Sr}$ variations of soluble salts that are mobilized from the watershed rocks, we conducted leaching experiments on rocks obtained from a core sample of the Allegheny and Kanawha Formations (Table S1, Figure S2, Supporting Information). Our data show that the salinity (as expressed as EC) of the water-soluble salts in rocks from the Allegheny and Kanawha Formations is high (Table 1), similar to the field EC values measured in VF effluents, and inversely correlated with the leachates' pH (Figure S9, Supporting Information). On the basis of our leaching experiments, we suggest that the oxidation of pyrite, which evidently exists in all rock types from the Allegheny and Kanawha Formations (Figure S9, Supporting Information), generates both elevated sulfate (Figure S10, Supporting Information) and acidity. Yet, calcium variations were not correlated directly with the total salinity (i.e., EC) relative to sulfate (Figures S10, S11, Supporting Information). This suggests that calcium was derived by dissolution of calcium carbonate minerals. We observed that leachates from rocks containing coal tend to generate higher sulfate (and acidity), while leachates from noncoal rocks have higher calcium, magnesium, and strontium contents (Table 1). These results are consistent with the overall high soluble TDS reported for leaching experiments of MTM overburden spoils and coarse/fine coal refuse.³⁸ The inverse correlation between EC (and sulfate) and pH (Figures S9, S10, Supporting Information) confirms that sulfuric acid generated during the oxidation of pyrite is responsible for dissolution of the carbonate minerals in VFs and not from carbonic acid that originated from the oxidation of organic matter in the soil. This

is further verified by the elevated $\delta^{13}\text{C}_{\text{DIC}}$ values measured in VF effluents (Figure 5).

In contrast, soluble strontium and $^{87}\text{Sr}/^{86}\text{Sr}$ were different in leachates from the rocks representing the two formations, with significantly lower strontium in the shallower Allegheny Formation (mean = 567 ± 400 ppb, $n = 17$) relative to the deeper Kanawha Formation (mean = 6458 ± 4919 ppb, $n = 12$) (Table 1). Likewise, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Allegheny Formation (mean = 0.71611 ± 0.00338 , $n = 13$) was higher than that of the Kanawha Formation (mean = 0.71342 ± 0.00124 , $n = 11$) (Figure 7). The leaching experiments reveal therefore two distinctive soluble rock sources: (1) low Sr/Ca and high $^{87}\text{Sr}/^{86}\text{Sr}$ in the shallow rocks of the Allegheny Formation and (2) high Sr/Ca and low $^{87}\text{Sr}/^{86}\text{Sr}$ in the deeper rocks of the Kanawha Formation. It should be noted that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of rock samples containing coal were almost identical in both the Allegheny and Kanawha Formations (~ 0.7126 , Table 1). Similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were also reported in coal impoundments from the West Virginia (0.7124)²⁵ and Pittsburgh coal (0.71168),³¹ which seem to represent a common soluble strontium isotopic imprint for the Appalachian coals (Figure 3). In contrast, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in leachates from noncoal rocks from both formations were different, with higher ratios in the shallow Allegheny Formation (0.71830) relative to the deeper Kanawha Formation (0.71409, Table 1).

While we observed differences in Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in leachates from the different formations, the Se concentrations were indistinguishable (Table 1). Nonetheless, we show that Se concentration in leachates increases with higher Ca/EC ratio (Figure S7, Supporting Information). A high Ca/EC ratio reflects a larger Ca contribution fraction from carbonate dissolution (i.e., high Ca/EC) relative to the contribution of SO_4 that is generated from pyrite oxidation (i.e., low Ca/EC). Thus, the leaching experiments suggest that Se mobilization is associated with carbonate dissolution and not

pyrite oxidation in both the Allegheny and Kanawha Formations. This conclusion is consistent with the high correlations observed between Se and Sr in the tributaries (Figure 2) that seem to reflect a common carbonate source for both Sr and Se in VF effluents. This is also consistent with the observations of Vesper et al.,²¹ who showed that Se abundance is not associated with sulfur content in the rocks of Kanawha Formation and Se is distributed in both coal and noncoal rocks.²¹

The inverse relationship of Sr/Ca and ⁸⁷Sr/⁸⁶Sr observed in the rock leaching experiments overlap with the variations observed in the MTM tributaries, particularly the distinction between tributaries draining active (high Sr/Ca and low ⁸⁷Sr/⁸⁶Sr) and reclaimed MTM sites (low Sr/Ca and high ⁸⁷Sr/⁸⁶Sr, Figure 3). In contrast, the bulk salt concentrations of ions such as Ca and SO₄ were indistinguishable in tributaries from active and reclaimed MTM areas. This is consistent with the uniformly high soluble salt concentrations found in leachates from both the Allegheny and Kanawha Formations (Table 1). Given the overlap of these geochemical trends (Figure 3), we propose that the low Sr/Ca and high ⁸⁷Sr/⁸⁶Sr signatures of the reclaimed MTM tributaries reflect past mining of the predominantly shallow coal seams of the Allegheny Formation, while more recent and active mining incorporates a deeper section of the geological strata, including the Kanawha Formation with its distinctive Sr/Ca and ⁸⁷Sr/⁸⁶Sr signatures. Because these geological materials are mixed in the VFs, one would expect that the effluents that are generated by interactions of the blended rock materials would contain the geochemical fingerprints of the most abundant rock materials. It seems, therefore, that modern forms of MTM surface mining have been more effective in targeting and extracting the deeper coal seams (e.g., Stockton) of the Kanawha Formation (Figure S2, Supporting Information).

The increased contribution of the deeper coal seams is also reflected by current coal production statistics, showing the increased exploitation of coals associated with the Kanawha Formation over time.¹⁹ Historic data show that between 1983 and 1997 coal production from the Kanawha Formation doubled from about 40 million tons to over 80 million tons, while coal production from the overlying Allegheny Formation was not changed and remained below 40 million tons.¹⁹ The high correlation between Sr and Se observed in the tributaries¹⁵ (Figure 2) suggests that the deeper rocks of the Kanawha Formation also have higher Se contents. This is consistent with the high Se contents reported for noncoal rocks of the Kanawha Formation in Boone County, West Virginia.²¹ However, our leaching experiments did not show higher selenium concentrations in water-soluble leachates from the Kanawha Formation (Table 1). These results are probably due to the difference on water chemistry; the Se-rich VF effluents are characterized by a neutral to high (6–8) pH, while the water-soluble leachates from the laboratory experiments were much more acidic (Table 1). Given that selenium mobilization is expected to intensify under elevated pH conditions,³⁹ we posit that the generation of sulfuric acid from pyrite oxidation would trigger carbonate dissolution, which would buffer the pH of VF effluents and further enhance selenium mobilization from the carbonate phases. We conclude that the geochemical and isotopic changes we observed in leachates from rocks spanning the transition from Allegheny to Kanawha Formations are representative of the expected composition of the blended rock

found in VFs and the resulting chemical influence they have on the headwaters flowing to the Mud River.

This study reveals distinct geochemical fingerprints of $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{13}\text{C}_{\text{DIC}}$, Sr/Ca, and ⁸⁷Sr/⁸⁶Sr in MTM effluents compared to those of the unimpacted and upper section of the Mud River, representing a typical Appalachian watershed. The changes in water quality in the downstream section of the river, in particular the increase in salinity, SO₄, and Se, are directly associated with isotopic modifications of DIC, sulfate, and strontium, reflecting the cumulative effect of the dissolved constituents derived from VF effluents. Given the linear correlation between Se and Sr, we posit that Sr isotopes can be used as a valuable geochemical proxy for tracing Se origin and mobilization in impacted Appalachian watersheds. In particular, one can apply the Sr isotope tool for quantification of *dilution* (i.e., with no change in isotopic ratio) versus *mixing* of different sources for evaluating the processes that control Se occurrence in contaminated water sources. A mixing model, using Sr and ⁸⁷Sr/⁸⁶Sr variations in tributaries and along the 10 km segment of the downstream river water, shows an ~80% increase of dissolved constituents originating from predominantly active MTM operations. Leaching experiments of the local watershed rocks confirm that the elevated salinity, high Ca and SO₄ contents, and Sr/Ca and ⁸⁷Sr/⁸⁶Sr fingerprints of the leachates directly reflect the compositions of MTM effluents. These results provide new geochemical tools to delineate and monitor the mobilization and potential impact of dissolved constituents derived from leaching of residual rocks in VFs associated with surface MTM operations.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional details on the watershed geology, core stratigraphy, and chemical and isotopic variations of the Mud River and tributaries from the valley fills, along with chemical data of the leaching experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank William Chameides, the Dean of the Nicholas School of Environment, for supporting this research. We also thank three anonymous reviewers and the editor for improving the manuscript. We gratefully acknowledge the long-term financial support from Fred and Alice Stanback to the Nicholas School of Environment.

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