Isotopic Imprints of Mountaintop Mining Contaminants

Avner Vengosh,*† T. Ty Lindberg,‡ Brittany R. Merola,† Laura Ruhl,§ Nathaniel R. Warner,† Alissa White,† Gary S. Dwyer,† and Richard T. Di Giulio‡

†Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States
‡Division of Environmental Sciences and Policy, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States
§Department of Earth Sciences, University of Arkansas at Little Rock, Little Rock, Arkansas 72204, United States

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 (δ34S_SO4), carbon isotopes in dissolved inorganic carbon (δ13C_DIC), and strontium isotopes (87Sr/86Sr). The data show that δ34S_SO4, δ13C_DIC, Sr/Ca, and 87Sr/86Sr 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 87Sr/86Sr characterize tributaries that originated from active MTM areas, while tributaries from reclaimed MTM areas had low Sr/Ca and high 87Sr/86Sr. Leaching experiments of rocks from the watershed show that pyrite oxidation and carbonate dissolution control the solute chemistry with distinct 87Sr/86Sr 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 87Sr/86Sr 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...
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 mineral19−21 (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 (δ13C_DIC) and sulfur isotopes for dissolved sulfate (δ34S_SO4). We also used dissolved strontium isotopes (87Sr/86Sr) 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 δ13C_DIC, δ34S_SO4, and 87Sr/86Sr in surface water streams and tributaries originated from MTM sites. On the basis if 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 87Sr/86Sr 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 ARL 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.
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 VF in the watershed of the Mud River, we define two types of tributaries: those originated from areas draining VF of active and current MTM areas 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, $\delta^{34}$SO₄, DIC, and $\delta^{13}$C_DIC variations are indistinguishable between tributaries originated from active and reclaimed MTM areas (Figure S4, Supporting Information) but differ in their Sr/Ca and $\delta^{87}$Sr/$\delta^{86}$Sr (Table 1, Figures 2, 3, and Figure S1, Supporting Information).

The variations of $\delta^{13}$C_DIC and $\delta^{34}$SO₄ (Figures 4, 5) indicate that DIC and SO₄ were derived from two major sources: (1) diluted tributaries depleted in $\delta^{13}$C_DIC ($\delta^{13}$C_DIC < −6‰) and slightly enriched in $\delta^{34}$SO₄ ($\delta^{34}$SO₄ > +5‰) and (2) saline tributaries enriched in $\delta^{13}$C_DIC ($\delta^{13}$C_DIC > −6‰) and slightly depleted in $\delta^{34}$SO₄ ($\delta^{34}$SO₄ = −2 to +2‰). The respective low $\delta^{13}$C_DIC and high $\delta^{34}$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 $\delta^{13}$C_DIC and low $\delta^{34}$SO₄ in the saline tributaries reflect the composition of the source DIC and sulfate in VF. The positive $\delta^{13}$C_DIC signature of the DIC-enriched tributaries is substantially different from the negative carbon isotope composition typical to the Appalachian coal ($\delta^{13}$C range of −22 to −27 ‰) [27]. The positive $\delta^{13}$C_DIC also differed from measurements of total soil samples for MTM reclaimed soils, forest soils, and grassland soils that all yielded low $\delta^{13}$C (−25 to −28‰) [33].

### RESULTS AND DISCUSSION

#### Geochemical and Isotopic Characterization of VF Effluents

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The high $\delta^{13}$C_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 CO₂ depletion [22, 24]. In contrast,
relatively positive $\delta^{13}$C 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. The high $\delta^{13}$C composition (a range of 2 to 5) is typical for Pennsylvanian marine carbonate rocks, which is equivalent to the Allegheny and Kanawha Formations. These values are consistent with the $\delta^{13}$C 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 inorganic carbonates with a positive $\delta^{13}$C imprint due to sulfuric acid originated from pyrite oxidation. The linear correlation between $\delta^{13}$C in DIC and inorganic carbonates suggests that the bulk DIC in AMD is derived from the dissolution of inorganic carbonates.
correlation between DIC and δ¹³CDIC in Figure 5 therefore reflects a mixing between two DIC sources: (1) organic carbon in soil that generates ¹³C-depleted CO₂ 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 δ¹³C (> +6‰).

Likewise, we attribute the slightly elevated δ³⁴SSO₄ (≈ +5‰) in the diluted tributaries to a meteoric source, which is consistent with the δ³⁴SSO₄ of bulk precipitation and pristine stream waters in the upland forested catchments within the Appalachian Plateau region of West Virginia and other inland basins (Figure 4). In contrast, the saline tributaries with high SO₄ had lower δ³⁴SSO₄ (−2 to +2‰), originated from oxidation of pyrite from within the bedrock, which typically has a similar low δ³⁴S range. These results are also consistent with an elevated SO₄ and an apparent δ³⁴S end member of ≈−1‰ measured in stream waters of Yellow Creek, West Virginia, also associated with coal mining.

**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. The dilute upstream section of river is characterized by low δ¹³CDIC and high δ³⁴SSO₄ 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 δ¹³CDIC and the decrease in δ³⁴SSO₄ and ⁸⁷Sr/⁸⁶Sr (Figures S6, S7, S8, Supporting Information) in the downstream river clearly reflect the effect of the tributaries’ inflows, regardless of their absolute concentrations. The ⁸⁷Sr/⁸⁶Sr 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 ⁸⁷Sr/⁸⁶Sr ratios, respectively (Figure 6 and Figure S6, Supporting 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.

A mass-balance calculation, using the Sr and ⁸⁷Sr/⁸⁶Sr 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 μg/L in the nonimpacted section (MR-2) to 1672 μg/L in the first MTM tributary that enters the Mud River, corresponds to an overall 80% accumulative input of dissolved Sr from MTM tributaries (Figure 6)
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. In order to characterize the chemistry and 87Sr/86Sr 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. 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 813C values measured in VF effluents (Figure 5).

In contrast, soluble strontium and 87Sr/86Sr 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 87Sr/86Sr ratio in the Allegheny Formation (mean = 0.71611 ± 0.00124, n = 11) was higher than that of the Kanawha Formation (mean = 0.71342 ± 0.00338, n = 13) (Figure 7). The leaching experiments reveal therefore two distinctive soluble rock sources: (1) low Sr/Ca and high 87Sr/86Sr in the shallow rocks of the Allegheny Formation and (2) high Sr/Ca and low 87Sr/86Sr in the deeper rocks of the Kanawha Formation. It should be noted that the 87Sr/86Sr ratios of rock samples containing coal were almost identical in both the Allegheny and Kanawha Formations (~0.7126, Table 1). Similar 87Sr/86Sr 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 87Sr/86Sr 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 87Sr/86Sr 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 SO4 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 sulfurous 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 δ13C and δ34S in the 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.

AUTHOR INFORMATION

Corresponding Author
*Phone: (919) 681-8050. Fax: (919) 684-5833. E-mail: vengosh@duke.edu.

Notes
The authors declare no competing financial interest.

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