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Key Points:

- Nitrate fluxes from mined watersheds were 1-2 orders of magnitude higher than an adjacent forested watershed, impacting regional water quality
- Nitrate export declined after the cessation of active mining but persisted above reference levels for decades post-mining
- The persistence of mining-associated N export suggests N sources are linked to deeper flow paths within constructed valley fills

Supporting Information:

- Supporting Information S1

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Excess Nitrate Export in Mountaintop Removal Coal Mining Watersheds

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Abstract Throughout the Central Appalachian ecoregion, mountaintop removal coal mining (MTM) is the predominant form of land use change. The streams draining MTM impacted watersheds have been reported to contain high stream nitrate (NO_3^-) concentrations, yet the source and persistence of elevated NO_3^- remains unknown. Here we compiled data from multiple sources to conduct a regional evaluation of the impact of mining on stream NO_3^- , examine NO_3^- persistence after mining cessation, and identify potential N sources. Using water quality data from six large watersheds, we observe elevated NO_3^- in watersheds with the highest active mining density. At four small MTM watersheds with repeat sampling, we found that high levels of NO_3^- concentrations declined after mining cessation but remain elevated above reference after several decades. At MTM watersheds, we found annual mass flux of NO_3^- was 3.68 to 26.4 kg $\text{N ha}^{-1} \text{ year}^{-1}$, which is 1 to 2 orders of magnitude higher than a nearby forested reference watershed. Stream water NO_3^- isotopic ratios at these sites did not match previously suggested NO_3^- sources such as explosives used during mining and fertilizer applied during reclamation but were highly enriched in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ compared to the reference watershed suggesting high rates of NO_3^- retention. Explosive residue could account for the bulk of watershed NO_3^- export during active mining phases but other mining related N sources including fertilizer and rock-derived N, the construction of valley fills, and alterations in watershed NO_3^- cycling likely contribute to the persistence of elevated NO_3^- export observed in this study.

Plain Language Summary Mountaintop removal coal mining, a form of surface coal mining common in Central Appalachia, causes deep transformations of previously forested mountain landscapes. Previous studies demonstrated that mining adversely impacts downstream water quality including causing high levels of dissolved nitrate, a form of nitrogen. Excessive stream water nitrate can damage stream food webs, trigger algal blooms, and pose a threat to human health. This work identifies elevated nitrate as a widespread problem caused by mountaintop removal coal mining. We sought to identify the sources of this nitrate and how long the problem persists after mining stops. We found evidence that nitrate levels in Central Appalachian rivers increased with the amount of active mining in their watersheds. In heavily mined watersheds, we found the level of nitrate exported was 1 to 2 orders of magnitude higher than at an adjacent forested watershed. Nitrate levels remained higher in mined watersheds even several decades after mining ended. Our work identifies explosives as a likely source of stream water nitrate during active mining. In addition, changes to the physical structure of the landscape and the increased chemical breakdown of newly exposed rock may also contribute to persistent high nitrate levels in affected streams.

1. Introduction

Mountaintop removal coal mining (hereafter, MTM) is the dominant driver of land use change in the Central Appalachian ecoregion with active, abandoned and reclaimed surface mines covering 7% of the 83,000 km² region (Pericak et al., 2018). Mountaintop mining is an exceptionally intense disturbance that alters multiple layers of the critical zone, from vegetation and soils to up to 100 s of meters of underlying bedrock (U.S. Environmental Protection Agency, 2011). Mining operations start with logging forests and clearing vegetation, then explosives and heavy machinery are used to remove rock layers on top of shallow coal seams. Ridges are lowered as mining progresses, while valleys are filled as excess rock is deposited into

headwater valleys. The resulting landscapes are regraded, but resulting watersheds are significantly flatter and more porous than before mining (Miller & Zégre, 2014; Ross et al., 2016). The resulting changes in topography, subsurface structure, and porosity alter hydrologic flow paths and can turn intermittent headwaters into perennial streams (Evans et al., 2015; Nippgen et al., 2017). These alterations coupled with the increased surface area of mine spoils drive high mineral weathering rates, leading to shifts in stream chemistry that propagate downstream of the mine permit boundaries as alkaline mine drainage (AlkMD) (Lindberg et al., 2011; Ross et al., 2018). Alkaline mine drainage is the result of pyrite dissolution within coal and shale residues that in return accelerates weathering of primary carbonate and silicate minerals (Ross et al., 2018). The resulting mine effluent is alkaline with exceptionally high concentrations of a variety of weathering derived ions, particularly Ca^{2+} , Mg^{2+} , and SO_4^{2-} , which increases stream salinity and electrical conductivity, and elevates levels of the toxic metalloid Se. These effects can persist for decades (Evans et al., 2014; U.S. Environmental Protection Agency, 2011). The large spatial footprint of MTM and the persistent AlkMD problems have resulted in biological impairments in a substantial fraction of all rivers in southern West Virginia (Bernhardt et al., 2012).

Several studies have also reported water quality impairments due to high nitrate (NO_3^-) concentrations in AlkMD effluent from MTM sites, yet none have explored the persistence nor the source of this elevated nitrogen (N) (Bryant et al., 2002; Lindberg et al., 2011; Pond et al., 2008). The reported NO_3^- concentrations (means of 3.4–4.8 mg N L⁻¹) from streams draining mined watersheds are 3 to 4 times the maximum concentration observed in unmined streams in the Central Appalachian ecoregion (95th percentile, 1.0 to 1.6 mg N L⁻¹) (U.S. Environmental Protection Agency, 2000). Maximum NO_3^- concentrations observed in MTM effluents (16.5–18.5 mg N L⁻¹) well exceed the EPA drinking standard of 10 mg N L⁻¹ (Lindberg et al., 2011; Pond et al., 2008). The exceptionally high NO_3^- concentrations in MTM systems rival the nutrient pollution downstream of agricultural runoff (Groffman et al., 2004) but have not yet been directly linked to possible sources of N pollutants.

Previous authors have suggested that excess N associated with MTM could be from sources not present in most unmined watersheds and have speculated that explosives used during mining to remove overburden, could be a major contributor of N (Bryant et al., 2002; Krenz et al., 2018). However, these previous efforts did not attempt to identify the source directly. One common approach for discriminating among possible N sources is the NO_3^- isotopic ratio method, utilizing the signatures of known end members (e.g., fertilizer, septic system wastewater, and atmospheric deposition) (Kendall et al., 2008). Previous work found that both biota (Daniel et al., 2015) and particulate N (Fox, 2009) in MTM streams were enriched in $\delta^{15}\text{N}$, suggesting that the source might be identifiable through signatures of stream water NO_3^- isotopic ratios.

Given the severity and large regional footprint of MTM's disturbance on critical zone processes, accumulating evidence of elevated stream NO_3^- concentrations in small mined watersheds, and the uncertainty over the sources of this NO_3^- , we pose the following questions:

1. Is elevated stream water NO_3^- a consistent, regional response to upstream mining activities?
2. How long do elevated NO_3^- concentrations persist after the cessation of mining?
3. How do elevated NO_3^- concentrations translate into watershed NO_3^- fluxes?
4. Do NO_3^- isotopic ratios in MTM streams have a signature consistent with likely N sources?

To investigate these questions, we integrated water quality monitoring data from six large watersheds to examine relationships between area mined and stream nitrate. To examine persistence, we compared current baseflow concentrations at four small headwater watersheds to data from previous sampling campaigns at the same site. Further, to identify possible mechanisms, at four smaller watersheds, more detailed analysis was conducted using more extensive sampling, hydrologic measurements as well as NO_3^- isotopic data.

2. Methods

2.1. Regional Analysis

Regional water quality was downloaded from the West Virginia Department of Environmental Protection Water Quality Data Reporting Tool (State of West Virginia, 2017) and the Water Quality Portal (NAQMC, 2018). Water quality sites were selected by the presence of mining in the river basin and the availability of

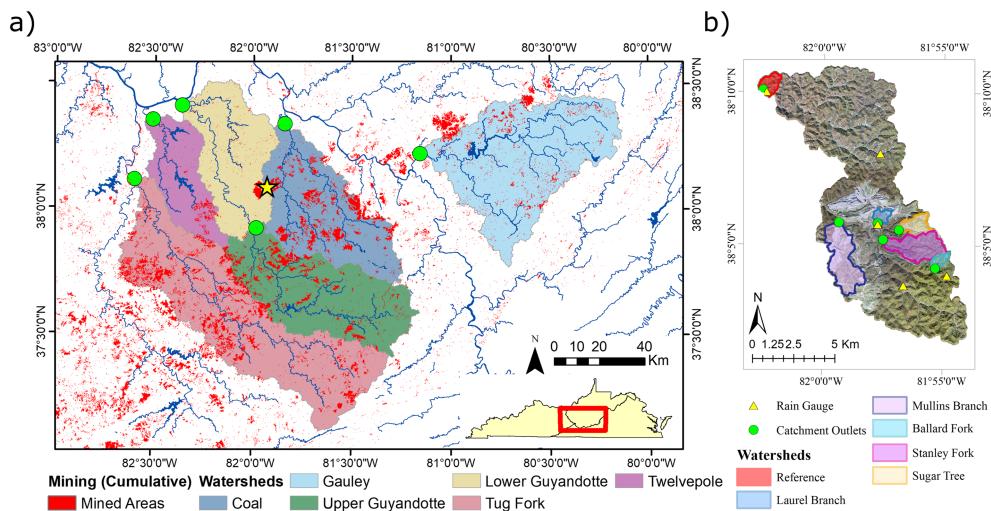


Figure 1. (a) Regional water quality study basin. Green circles denote water quality sites, red on map indicates extent of surface coal mining across the region, and the yellow star is the Hobet Mine location. (b) Small watershed study layout. Mined watershed is at the Hobet Mining Complex within the Mud River basin in southwestern West Virginia. The Reference watershed is in the adjacent Left Fork basin.

nitrate-nitrite ($\text{NO}_3^- + \text{NO}_2^-$) and/or nitrate (NO_3^-) and sulfate (SO_4^{2-}) data going back to 1985 (Figure 1a and Table S1 in the supporting information). We include SO_4^{2-} because it is a known tracer of aquatic MTM impacts (Lindberg et al., 2011) and provides a point of comparison to nitrate dynamics. For each selected site, minimum, median, and max solute concentrations (mg L^{-1}) were calculated for years that contained four or more samples. Samples below detection were included with a value of 50% of the detection limit (SO_4^{2-} : 2.5 mg $\text{SO}_4^{2-} \text{ L}^{-1}$, NO_3^- : minimum detection limits ranged between 0.005 and 0.05 mg N L^{-1}). Regional watersheds for each site were delineated using TauDEM 5.3 (Tarboton & Sazib, 2015). Yearly active and cumulative mining extent for each basin was extracted from a recently published remotely sensed mining extent data set (Pericak et al., 2018). The mining extent database provides estimates from 1985 to 2015. Water quality sites with at least 1% cumulative mining cover were selected for further analysis. Watersheds were additionally screened for alternative land use change by comparing dominant land use classes in each watershed using 2001 and 2011 National Land Cover Data Sets (Table S1). We identified six water quality sites within five river basins that met our criteria in southern West Virginia (Figure 1a). All sites had at least 90 samples in the record. Four sites (Coal, Gauley, Lower Guyandotte, and Tug Fork) have records dating to 1985 while two sites (Upper Guyandotte and Twelvepole) have records dating to 1998 (Table S1). No site had more than 3 years within the record removed due to insufficient samples during the year (less than four samples). All basins were between 79% and 83% forested and 1% and 3% developed with little change in landcover (between 2001 and 2011) apart from mining (Table S1).

To analyze relationships between mining and solutes, for each watershed, we identified the 5 years with the highest active and cumulative mining and calculated means of annual max, min, and mean concentrations of solutes for the selected years. We then regressed the mean percent active mining and percent cumulative mining over the selected 5 years against the mean NO_3^- and SO_4^{2-} concentration statistics to identify the strength of mining area metrics as predictors of both SO_4^{2-} and NO_3^- in stream water.

2.2. Repeat Sampling of Stream Water NO_3^-

To examine persistence of NO_3^- over time, we collected stream water grab samples near locations used in previous sampling campaigns at the outlet of four watersheds with extensive mining: Laurel Branch, Mullins Branch, Stanley Fork, Sugar Tree (Bryant et al., 2002; Lindberg et al., 2011; Pond et al., 2008) (Figure 1b). All mined watersheds included here are part of the Hobet Mining Complex but differ in time since the cessation of mining (Table 1). Baseflow stream water grab samples were collected intermittently across the 2015 and 2016 water years. Stream water NO_3^- concentrations were then compared with those

Table 1
Study Watershed Description, Mining Activity, and Presence of Valley Fills, Ponds, and Ongoing Pumping

Watershed	Stream name	Size (ha)	Active mining year	% Mined	Year reclaimed	VF ¹	Pond (s) ²	Pumping ³
<i>Core Sites</i>								
Reference Laurel Branch	Rich's Branch Laurel Branch	118 68	Not Mined 2005–2009	– 92	– ~2010	– Yes	– Yes	– Yes (after June 2015)
Mullins Branch	Mullins Branch	590	1999–2015	90	Not Reclaimed	Yes	Yes	Unknown
Ballard Fork	Left Fork of Ballard Fork	61	1988–1992	86	~1993	Yes	Filled	No
<i>Historic Sites</i>								
Sugar Tree	Sugar Tree	158	1993–1996, 2002–2007	92	~2009	Yes	Yes	Unknown
Stanley Fork	Stanley Fork	439	1988–1998	86	~2003	Yes (multiple)	Yes	No

¹Presence/absence of constructed valley fills in watershed. ²Presence/absence of treatment ponds in watershed. In some cases, previously existing ponds were later filled in. ³Presence/absence of pumping that moved water from treatment ponds to higher parts of watershed (or to locations outside of the watershed).

from two previous sampling campaigns. The oldest data set, published first by Bryant et al. (2002), was collected between August 2000 and February 2001 at approximately monthly intervals at sites Sugar Tree and Stanley Fork. Lindberg et al. (2011) collected samples at all four watersheds at monthly intervals from June 2010 to December 2010. To ensure comparability between sampling campaigns, sampling dates of all three data sets were screened for wet periods using PRISM daily rainfall data (PRISM Climate Group, 2016). Sampling dates with more than 10 mm of rainfall during the day of sampling or 40 mm in the previous 5 days were excluded from the analysis. Final sample sizes varied substantially between both sampling periods and sites (ranged between 4 and 47 samples; see Table S2).

2.3. Modeled Watershed NO₃[−] Fluxes

To explore how increased NO₃[−] concentrations in MTM watersheds translated into mass fluxes, we intensively instrumented and sampled three mined and one adjacent reference watershed across the 2015 and 2016 water years (Figure 1b and Table 1) in West Virginia's Mud River basin. The three heavily mined watersheds were selected to capture a range of timespans since the cessation of mining. Mullins Branch (590 ha, 90% mined) was mined in sections until 2015 and had not been reclaimed by the end of this study. Laurel Branch (68 ha, 92% mined) was last mined in 2009 and was reclaimed by ~2010. Ballard Fork (61 ha, 86% mined) was last mined in 1992 and was reclaimed by ~1993. Recently mined sites have ongoing active reclamation and both Mullins Branch and Laurel Branch have long-term treatment in the form of settlement ponds between the mined areas and downstream sampling sites. All settlement ponds at Ballard Fork had been filled in by the time of the study. The Reference watershed is a forested 118-ha tributary to the nearby Left Fork Mud River and was selected for its comparable size and geology to the Laurel Branch watershed (Nippgen et al., 2017). Unfortunately, there are no other long-term watershed studies in this region to provide additional estimates of NO₃[−] flux; however, mean NO₃[−] concentrations for our Reference site (0.24 mg N L^{−1}) are similar to mean concentrations at unmined watersheds reported in other studies in the region: 0.22 mg N L^{−1} (Lindberg et al., 2011) and 0.4 mg N L^{−1} (Pond et al., 2008).

Premining and postmining digital elevation models were used to delineate watersheds, calculate watershed area postmining, and estimate valley fill volumes (see Ross et al., 2016 for methods). Peak mining years and percent of watershed mined were assessed using a yearly mining extent data set (Pericak et al., 2018). We monitored stream stage at ten-minute intervals and developed rating curves to generate continuous streamflow records (see Nippgen et al., 2017, for details). From these records, we separated stormflow and baseflow using a graphical hydrograph separation approach similar to the Hewlett and Hibbert (1965) method which assumes a constant rise in baseflow after precipitation begins (Nippgen et al., 2017). Precipitation was measured at three rain gauges distributed across the Mud River watershed for the 2015 water year (WY15) and at

five sites for the 2016 water year (WY16) (Figure 1b). Precipitation was recorded at 10-min intervals and spatially interpolated to develop watershed specific rainfall estimates (see Nippgen et al., 2017, for details).

We collected stream water grab samples twice monthly at Laurel Branch and Reference for WY15 and monthly at all four watersheds in WY16. Storm sampling was conducted for March, April, and October 2015 at Reference and Laurel Branch and for a June 2016 storm at all four sites at dynamic sampling intervals ranging from 30 min to several hours with the densest sampling during the rising limb and peak flows. All water samples were field filtered using 0.45 micron mixed cellulose fiber filters, frozen onsite, and stored frozen until analysis. All samples were analyzed for cations and anions including NO_3^- utilizing a Dionex ICS-2000 ion chromatograph with IonPac AS-18 analytical column with a minimum detection of 0.005 mg N L⁻¹ (see Ross et al., 2018, for details). To identify if N species other than NO_3^- were measurable components of N export, we further analyzed June 2016 storm samples for NH_4^+ and total dissolved nitrogen (TDN). NH_4^+ was analyzed using a QuikChem8500 flow injection analyzer (Lachat Instruments, Loveland, CO). NH_4^+ detection limits were between a minimum of 0.01 to a maximum of 2 mg N L⁻¹. TDN was analyzed using a Shimadzu TOC-VCPh with TNM-1 module (Shimadzu Corp., Kyoto, Japan). Minimum detection was 0.05 mg N L⁻¹. Dissolved organic nitrogen (DON) was calculated to be the difference between TDN and measured inorganic species ($\text{NH}_4^+ + \text{NO}_3^-$). Instantaneous NO_3^- flux was calculated as the product of measured NO_3^- concentrations and discharge at the sampling time. Rain samples were also collected and analyzed during the June 2016 storm for NO_3^- , NH_4^+ , and TDN.

Mean NO_3^- concentrations were then compared between mined and unmined watersheds. To ensure the equivalency of the between site comparison, only samples collected at all four watersheds during the same sampling period and under similar streamflow conditions were kept for this analysis. Sample sizes ranged from $n = 31$ at Ballard Fork to $n = 41$ at Mullins Branch due to unequal sampling frequency during storm conditions (Table S2).

To develop yearly mass flux estimates, site specific regression models were developed to predict NO_3^- concentration at 10-min intervals using discharge and season as predictor variables (1).

$$\text{Log (PConc)} = \text{Log}(Q) + \text{Season} + \varepsilon \quad (1)$$

where PConc is the predicted NO_3^- concentration (mg N L⁻¹), Q is calculated discharge at the time of sampling, season is calendar season, and ε is the regression error. Regression models were built using the full NO_3^- data set at Mullins Branch and Ballard Fork. At Laurel Branch and Reference, two models were developed at each site, one for each water year. Separate yearly models were necessary because of changes in sampling frequency and the initiation of pumping from the settlement pond at Laurel Branch. Concentrations and cumulative flux were modeled at Reference and Laurel Branch for WY15 and for all four sites in WY16. Discharge and season are commonly used predictors of nitrate flux and were selected because they were the strongest predictors at the majority of sites (Robertson & Roerish, 1999). Mean flux and uncertainty calculations were completed using the linear regression approach in the Loadflex R package (Appling et al., 2015). Uncertainty was calculated as the standard error of prediction, which is the square root of the sum of the variance of the fit in addition to the residual error variance (estimated as the mean of the squared residuals). Mean flux and standard errors were aggregated through each water year to produce cumulative yearly flux and uncertainty estimates.

2.4. NO_3^- Source Dynamics

To investigate source dynamics, a subset of stream and rainfall samples from the June 2016 storm was analyzed for ^{15}N and ^{18}O values by the bacterial denitrification method (Sigman et al., 2001) at the UC Davis Stable Isotope Facility. Reported values are relative to the standard air (AIR) and Vienna Standard Mean Ocean Water (VSMOW), respectively. Reported literature values for potential NO_3^- isotope end members such as fertilizer, soils (Kendall et al., 2008), explosives (Degnan et al., 2016), and coal (Holloway & Dahlgren, 2002) were used in the analysis (Figure S1). The precipitation endmember was derived from measured rainfall samples taken during storm periods. Lab analysis error was 0.02 ± 0.07 (mean \pm standard deviation) for $\delta^{15}\text{N}$ and 0.06 ± 0.27 for $\delta^{18}\text{O}$.

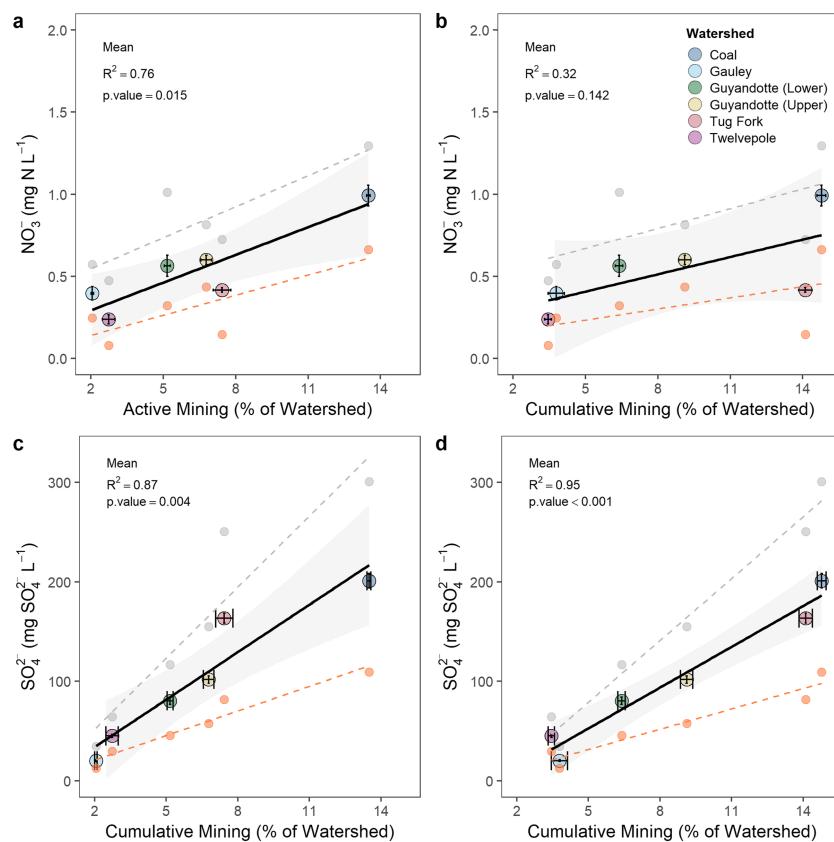


Figure 2. MTM water quality signals in regional watersheds. Y axis for all sites is shown as mean value of the five peak mining years for mean annual values (large points colored by watershed), maximum annual values (small grey points), and minimum annual values (small orange points). X axis is the mean value of the five peak mining years for active mining % (a, c) and cumulative mining % (b, d). Error bars indicate the standard error of the mean value. Regression lines are also shown for mean (solid black line), maximum (dotted grey), and minimum (dotted orange). Active mining % and cumulative mining % is derived from yearly mining estimates from LANDSAT imagery (Pericak et al., 2018). Nitrate and SO₄²⁻ data are from public data sets available through the Water Quality Portal and the State of West Virginia.

3. Results

3.1. Is Elevated Stream Water NO₃⁻ a Consistent Response to Upstream Mining Activities?

Regression analysis showed that both SO₄²⁻ and NO₃⁻ had significant positive correlations with percent active mining but only SO₄²⁻ had a significant positive relationship with cumulative mining at a significance level of 0.05 (Figure 2). For SO₄²⁻, this relationship was significant regardless of which annual summary statistic was used (all *p* values <0.01), although variation explained by the regression differed by mining metric and by statistic. Sulfate concentrations had a stronger correlation with % cumulative mining (%CM) than % active mining (%AM) for the mean of annual means (adj R²: 0.95 (%CM) to 0.87(%AM)) and for the mean of annual maximums (adj R²: 0.97 (%CM) to 0.86 (%AM) (annual maximum), while for the mean of annual minimums, the fit for %AM (adj R²: 0.92) was slightly higher than for %CM (adj R²: 0.90). Relationships were weaker between mining metrics and NO₃⁻ concentrations although still significant for %AM for mean of annual means (adj R²: 0.76, *p* value = 0.015) and mean of annual maximums (adj R²: 0.69, *p* value = 0.026) but just above the 5% significance level for the mean of annual minimums (adj R²: 0.55, *p* value = 0.057). Models between %CM and NO₃⁻ concentrations were not significant with model *p* values >0.1.

3.2. Do Elevated NO₃⁻ Concentrations Persist Over Time?

Comparison of baseflow NO₃⁻ concentrations from this study with previously reported concentrations (Bryant et al., 2002; Lindberg et al., 2011), reveal that NO₃⁻ concentrations in streams declined with

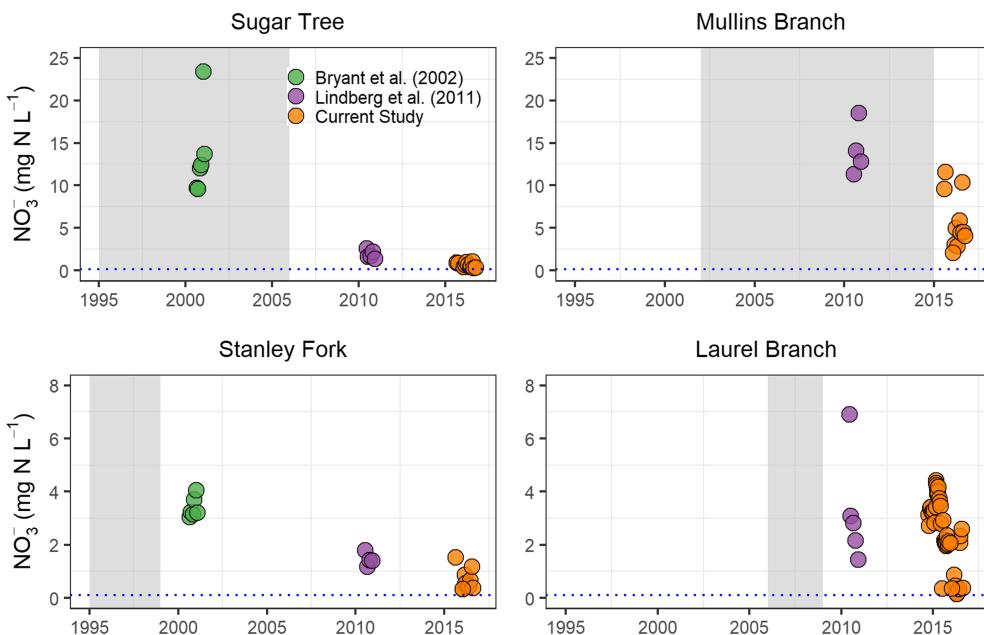


Figure 3. Baseflow concentrations over time. Historic data were collected by Bryant et al. (2002) (green) from August 2000 to February 2001 and by Lindberg et al. (2011) from June to December 2010. (purple). Data from the current study (orange) ranges from 2014 to 2016. The grey box indicates periods when ongoing active mining was occurring and the dotted blue line represents the mean NO₃⁻ concentration at the Reference watershed. Note that the y axis scale differs between top and bottom panels.

increasing time since mining. Yet, all the samples at mined watersheds remained above mean NO₃⁻ baseflow concentrations at the Reference site (0.11 mg N L⁻¹) (Figure 3). In 2001, Sugar Tree (last year mined (l.y.m.): 2007) had high mean NO₃⁻ concentrations of 13.5 ± 2.1 (mean \pm standard error) mg N L⁻¹, which declined by 2010 to 1.9 ± 0.2 mg N L⁻¹, and continued to decline to 0.6 ± 0.1 mg N L⁻¹ in 2015 and 2016. Three years after mining ceased in Stanley Fork, reported mean 2001 NO₃⁻ concentrations were 3.4 ± 0.16 mg N L⁻¹, which declined to 1.4 ± 0.1 mg N L⁻¹ by 2010, and to 0.7 ± 0.1 mg N L⁻¹ in 2015 and 2016. At Mullins Branch (l.y.m.: 2015), mean NO₃⁻ concentrations were high when sampled during the active mining phase 14.2 ± 1.6 mg N L⁻¹ in 2010 and still relatively elevated when sampled 5 years later (5.7 ± 1.0 mg N L⁻¹ in 2015 and 2016). At Laurel Branch (l.y.m.: 2009), modest declines in mean concentrations were observed between 2010 (3.3 ± 1.0 mg N L⁻¹) and 2015 and 2016 (2.4 ± 0.2 mg N L⁻¹).

3.3. How Do Elevated NO₃⁻ Concentrations Translate Into Watershed N Fluxes?

At the three instrumented mined watersheds, mean NO₃⁻ concentrations were consistently higher than concentrations measured at the Reference site (0.26 ± 0.03 mg N L⁻¹). Nitrate concentrations at the most recently mined site, Mullins Branch (5.39 ± 0.35 (mean \pm standard error) mg N L⁻¹), were higher than at reclaimed mined sites Laurel Branch (1.52 ± 0.12 mg N L⁻¹) and Ballard Fork (2.57 ± 0.16 mg N L⁻¹). During baseflow sampling periods (discharge at sampling time was $>75\%$ baseflow), the mean concentration at Laurel Branch declined by more than 50% between WY15 (3.23 ± 0.17 mg N L⁻¹) and WY16 (1.40 ± 0.22 mg N L⁻¹). Mean baseflow NO₃⁻ concentration at the Reference site remained unchanged over this period (0.12 ± 0.02 mg N L⁻¹ in WY15 and 0.10 ± 0.01 mg N L⁻¹ in WY16).

Between watershed differences in annual area normalized discharge were larger than observed differences in annual precipitation. Annual precipitation averaged across all watersheds was 20% higher in WY15 (1,284 mm) than WY16 (1071 mm). The maximum difference in annual precipitation between watersheds was 6.7% in WY15 and 4.3% in WY16. In contrast, annual area normalized discharge at the instrumented mined watersheds exhibited diverging patterns relative to the reference site with annual discharge at mined sites ranging between 16.5% lower and 20% higher than Reference (WY15 609 mm and WY16 513 mm). In WY16, Mullins Branch had the highest annual discharge (615 mm) while Ballard Fork had the lowest

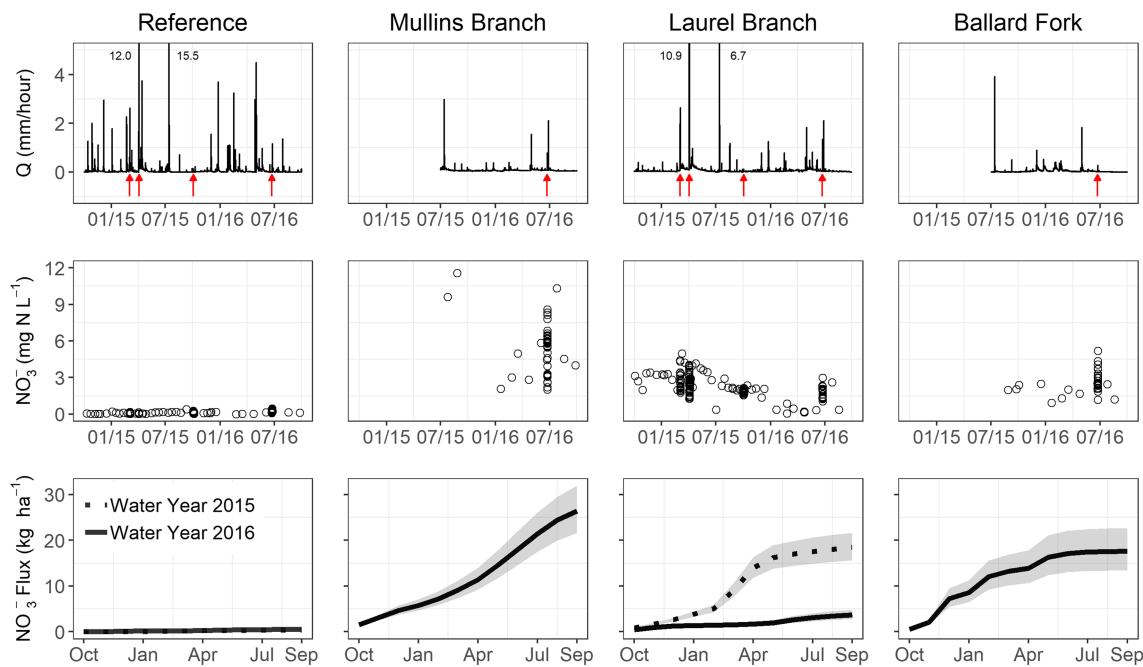


Figure 4. (a) Discharge at Reference, Mullins Branch, Laurel Branch, and Ballard Fork. Storm runoff hydrographs at Reference and Laurel Branch exceed Y axis ranges shown (values indicated). Mined watersheds are arranged left to right from the most recently mined to the oldest mined site. Red arrows denote storm sampling periods (b) NO₃⁻ concentrations across WY15 and WY16. (c) Cumulative area normalized NO₃⁻ modeled flux (kg ha⁻¹) for WY15 (dotted) and WY16 (solid). WY15 data is only available for Laurel Branch and Reference. Shaded region is the 95% confidence interval of modeled fluxes.

annual discharge (428 mm). Annual discharge at Laurel Branch declined 31% from 676.6 to 470.0 mm between WY15 and WY16 and the runoff ratio (the ratio of total yearly discharge to total precipitation) declined from 0.51 in WY15 to 0.45 in WY16. A similar but smaller decrease was observed at Reference, where cumulative discharge decreased 15.7% from WY15 to WY16, while the runoff ratio decreased slightly from 0.49 in WY15 to 0.47 in WY16. In comparison, the WY16 runoff ratio was 0.57 at Mullins Branch and 0.40 at Ballard Fork.

An analysis of N speciation during June baseflow and stormflows confirms that at the mined watersheds, N export was predominantly from high NO₃⁻ while Reference had higher proportions of both NH₄⁺ and DON. At mining sites, NO₃⁻, as a percentage of TDN, averaged 105%, 104%, and 100% for Mullins Branch, Laurel Branch, and Ballard Fork, respectively. Because of error propagation, values greater than 100% are possible when the ratio of NO₃⁻ to TDN is near one (Vandenbruewane et al., 2007). Consistent with this result, NH₄⁺ concentrations averaged between 2% and 3% of TDN for all three mined sites. Nitrogen speciation at the Reference site was distinct from mined sites. On average, NO₃⁻ was 62% of TDN, NH₄⁺ was 11% of TDN, and DON was calculated as 27% of TDN for measured samples. Analysis of N speciation reveals export at mined watershed is overwhelmingly NO₃⁻ while DON and NH₄⁺ contribute substantial portions to N export at the Reference watershed. Based on these findings, we focused our flux modeling efforts on NO₃⁻ since that was the dominant species in mined watersheds.

Modeled NO₃⁻ flux followed similar patterns to NO₃⁻ concentrations because between watershed differences in concentration were proportionally much larger than the differences in discharge. Large differences were observed in NO₃⁻ flux between mined sites and the Reference site and within the mined sites (Figure 4). The regression models, which modeled NO₃⁻ concentration as a function of Q at 10-min intervals and season, were all significant, although model strength in capturing variance in NO₃⁻ concentrations varied depending on the site and year (Table S3). The reference watershed exported an estimated 0.41 kg N ha⁻¹ year⁻¹ in WY15 and 0.52 kg N ha⁻¹ year⁻¹ in WY16. All of the mined watersheds had higher annual rates of N export than Reference. The highest NO₃⁻ fluxes were generated in the recently mined Mullins Branch site in WY16 (26.4 kg N ha⁻¹ year⁻¹) followed by Laurel Branch (18.4 kg N ha⁻¹ year⁻¹) in WY15 and then Ballard Fork (17.6 kg N ha⁻¹ year⁻¹) in WY16 (Figure 4). In WY16, NO₃⁻ flux at Laurel Branch

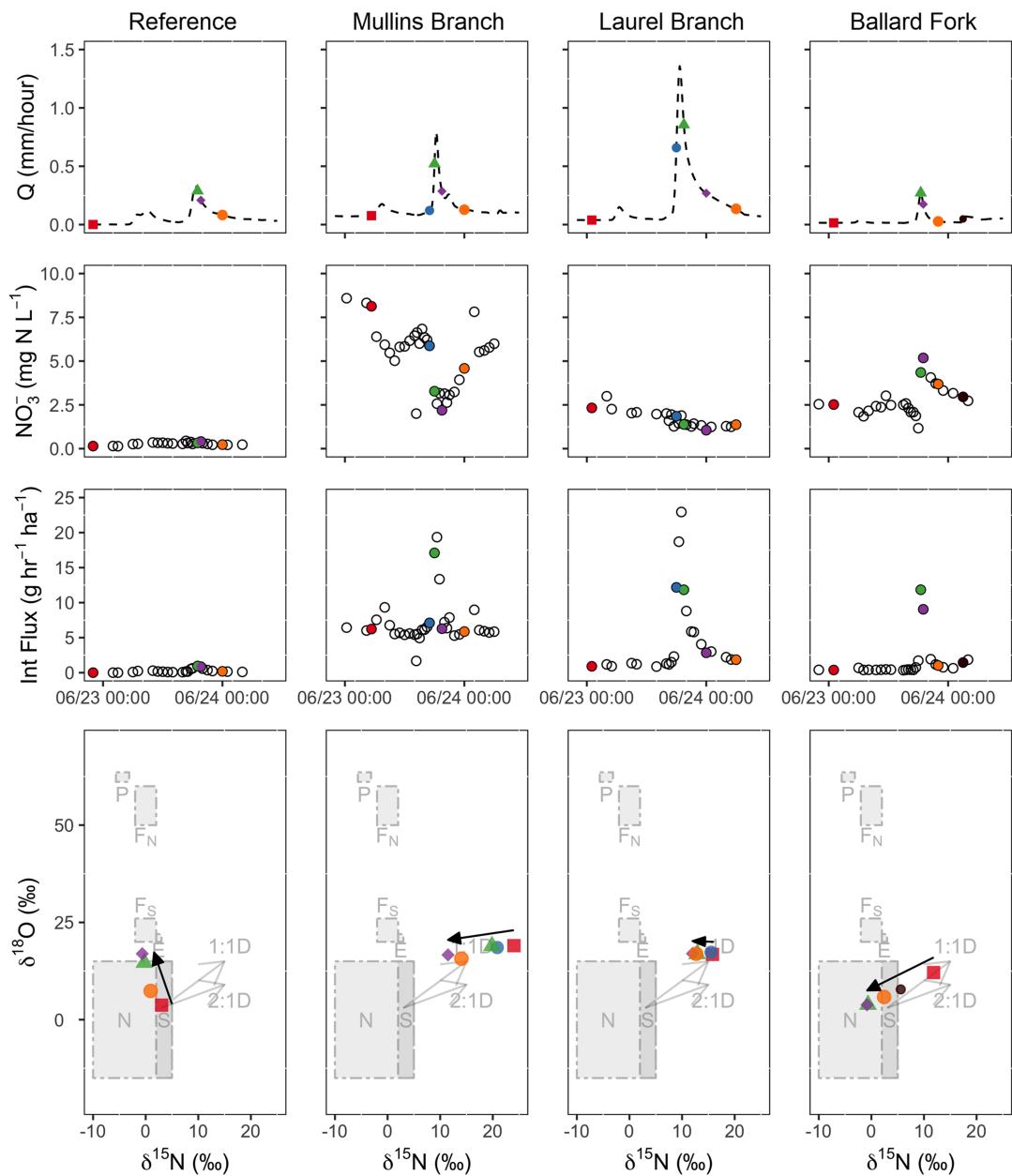


Figure 5. (a) Storm discharge (Q), (b) NO_3^- concentrations, (c) NO_3^- flux, and (d) NO_3^- isotopes at June 2016 storm. Shapes on hydrograph indicate sampling times used for nitrate isotope analysis. Shapes and/or color represent samples analyzed for isotopes. Red square is baseflow sample, blue circle is rising limb, green triangle is nearest to peak, purple diamond is falling limb, and orange and maroon circles are during the later recession. Black arrow denotes direction and magnitude of change of isotopic ratios between baseflow and falling limb. Isotope endmembers are shown in grey boxes: Precipitation (P), Natural Fertilizer (Fn), Synthetic Fertilizer (Fs), Nitrification (N), Soil (S), Explosives (E), and Denitrification (1:D and 2:D).

sharply declined to $3.68 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Differences between WY15 and WY16 at Laurel Branch are attributed to a decrease in overall annual discharge and to active pumping of water out of the valley fill settlement pond back onto the mine surface for several months during WY16.

3.4. Do NO_3^- Isotopic Ratios in MTM Streams Have a Signature Consistent With Potential N Sources?

Isotopic analysis of NO_3^- suggests N source differences between the Reference and the mined sites at baseflow, but the source was not identifiable given known source signatures. Isotopic ratios of $\delta^{15}\text{N}$ in

stream water at mined sites were higher at baseflow relative to expected N sources such as mining explosives and fertilizer used to promote revegetation (Figure 5). Both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were higher at mined sites than at the Reference site (Figure 5). At baseflow, more recently mined sites were higher in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ than the reclaimed older mine sites. Mullins Branch had the highest isotopic ratio (+24.03‰ $\delta^{15}\text{N}$ and +19.02‰ $\delta^{18}\text{O}$) relative to the reference site (+3.03‰ $\delta^{15}\text{N}$ and +3.73‰ $\delta^{18}\text{O}$).

Isotopic ratios were responsive to the June storm but the directionality of the response varied between sites. Precipitation samples collected during the June storm had $\delta^{15}\text{N}$ ranging from -5.65‰ to -3.14‰ and $\delta^{18}\text{O}$ from 61.12‰ to 63.58‰, falling within reported ranges for precipitation $\delta^{15}\text{N}$ (-15‰ to +15‰) and just at the low end of reported ranges for precipitation $\delta^{18}\text{O}$ (+63‰ to +94‰) (Kendall et al., 2008; Figures 5 and S1). During the June storm runoff sampling, relative to baseflow, $\delta^{15}\text{N}$ at Reference became lower (range: -0.65‰ to 0.95‰) while $\delta^{18}\text{O}$ became higher (range: 7.38‰ to 16.95‰) (Figure 5). Ratios at Reference were most similar to rainfall during the peak and falling limb of the storm. Isotopic ratios at the mined watersheds did not show a similar clear shift toward a precipitation signature. At mined watersheds, while $\delta^{15}\text{N}$ was lower in storm samples than at baseflow, particularly at Ballard Fork and Mullins Branch, $\delta^{18}\text{O}$ did not substantially increase, rather it decreased at Ballard Fork and to a lesser degree at Mullins Branch (Figure 5). Changes in the signature at Laurel Branch were more muted with small decreases in $\delta^{15}\text{N}$ and small increases in $\delta^{18}\text{O}$. Overall, at baseflow, all mined sites had substantially higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ than the reference site but responses to the June storm event differed among mined watersheds.

4. Discussion

4.1. Persistence of Elevated NO_3^- Across Spatial and Temporal Scales

We found that elevated stream water NO_3^- concentrations are a long-term water quality impact of surface coal mining in Central Appalachia. Prior studies in the region have documented increases in rock weathering derived solutes that contribute to heightened conductivity in mining impacted streams (Ross et al., 2018). The production of NO_3^- pollution from these watersheds appears to be derived from different sources and under a different set of controls. We find that NO_3^- concentrations and watershed exports are high during periods of active mining and that these inorganic N losses decline over time while remaining elevated above unmined watersheds. Isotopic evidence suggests that little of the reactive nitrogen inputs to these mined watersheds (as explosives or fertilizers) are directly lost to receiving streams. Instead the enriched $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ signatures may be consistent with extremely high rates of N cycling and denitrification within watershed soils and valley fills.

In our mined watersheds, we observed that NO_3^- concentrations peaked during active mining but remained elevated for decades post mining. Based on analysis of resampled sites between 2000, 2010, 2015, and 2016, we observed elevated but declining baseflow NO_3^- concentrations over time following the cessation of mining (Figure 3). Even with these observed declines, concentrations at all mined sites remained elevated above Reference site concentrations throughout 2015 and 2016. Other studies have shown there are limitations in using space-for-time approaches between MTM sites to understand temporal patterns in solute fluxes because intersite variability in mined watersheds can be quite high (Evans et al., 2014). For example, watersheds can differ in mining and reclamation practices (Burger, 2015), valley fill size (Ross et al., 2016) and fill materials (Hester et al., 2019), topography (Ross et al., 2016), and microclimate. Despite this, WY16 fluxes in our mined watersheds were 7 to 50 times higher than our Reference watershed, demonstrating that elevated NO_3^- exports are both a significant and persistent impact of MTM.

Regional analysis of public water quality data sets revealed that water quality signals of MTM can be observed at the scale of river basins ($2,500\text{--}7,000 \text{ km}^2$). Sulfate concentrations were strongly correlated with both cumulative and active mining %, which is unsurprising given that SO_4^{2-} is a known product of AlkMD and relatively stable in streams, enabling its transport down network from headwater mining areas (Bryant et al., 2002; Lindberg et al., 2011). Nitrate concentrations were also significantly correlated with active mining but not with cumulative mining, despite evidence of long-term NO_3^- export at small watersheds. The weaker signal for NO_3^- relative to SO_4^{2-} is likely due, at least in part, to biological demand for and retention of inorganic N in streams (Alexander et al., 2007). In addition, the larger number of anthropogenic N sources in most watersheds could obscure the MTM NO_3^- signal. This additional complexity at river

basin scales made it difficult to determine whether the persistence of mining related NO_3^- export at small watersheds continues to impact regional rivers after the cessation of active mining.

4.2. Source Dynamics of Elevated N Export

We found that sources of N export at MTM watersheds were distinct from the forested Reference watershed. At baseflow, all the mined watersheds had elevated NO_3^- concentrations and similarly enriched isotopic signatures when compared to the Reference site (Figure 5). Since baseflow in MTM watersheds is largely generated via flow paths through constructed valley fills (Nippgen et al., 2017), our observation of elevated baseflow NO_3^- concentrations indicates NO_3^- sourcing is likely occurring within the valley fills. During the observed June storm, isotopic signatures at MTM watersheds did not indicate significant mixing with rainwater NO_3^- . This again suggests that NO_3^- sourcing was dominated by subsurface processes. The differing storm response at Ballard Fork as compared to the other MTM watersheds does indicate there may be differences in water and solute sourcing among MTM watersheds. During the observed storm, Ballard Fork exhibited increasing NO_3^- concentrations and NO_3^- isotopic signatures that match soil/nitrification endmembers (Figure 5), both suggesting an additional NO_3^- source in soils that is active along shallower, more rapid subsurface flow paths. This suggests that some redevelopment of soil and vegetation could have occurred since reclamation, which is consistent with observations at other surface coal mining sites that N pools in soils, litter, and vegetation redevelop post-reclamation (Li & Daniels, 1994, Simmons et al., 2008; Table S5).

While our comparison of NO_3^- isotopic signatures with known NO_3^- endmembers was inconclusive, our findings of high NO_3^- export during mining and post-mining declines lend credence to speculation from previous studies (Bryant et al., 2002; Krenz et al., 2018) that N residues from explosives are a key driver of high N loading and export from MTM. To further explore this possibility, we calculated estimates of potential loading of N from explosive residue onto the mined landscape (see Table S4). Typical explosives are comprised of 20%–33% N (Forsyth et al., 1995; Revey, 1996). A large quantity of explosives is needed to remove rock contained in valley fills (English & Luo, 2001), which have a mean volume across the region of 75,000 m³ (Ross et al., 2016) and reported porosity from 20–57% (Wunsch et al., 1999). Given this, if even a small fraction of N in explosives reaches waterways, explosive related N export would represent a substantial increase in N export over reference conditions (Table S4, Ferguson & Leask, 1988; Morin & Hutt, 2009; Pommen, 1983). Despite this, there remains a dearth of peer reviewed research on the nutrient impacts on streams and groundwater from explosives from coal mining or even from other uses of explosives (although see Degnan et al. (2016) and Mahmood et al. (2017) for examples). The scale of the use of explosives in MTM highlights the need to better consider and study the use, management, and fate of explosives at surface coal mines. Despite their likely impact on N export, since explosives are only used during active mining, it is not clear if explosives alone can explain the decadal persistence of elevated N export observed in this study.

In addition to explosives, there are multiple sources that could contribute substantially to large N watershed pools long after active mining has ceased (Table S4). For example, nitrogen fertilizer is applied during reclamation (Burger et al., 2009; Zipper et al., 2011) and AlkMD related rock N weathering may liberate a substantial amount of N (see Table S4 for estimation methods; Holloway et al., 1998; Montross et al., 2013 for examples of rock derived N in streams). In addition, annual atmospheric deposition can be substantial (Schwede & Lear, 2014) while N uptake may be reduced due to the removal of vegetation. Based on examination of the sources, it emerges that the real puzzle may not be why there is high stream NO_3^- export associated with MTM but rather why watershed NO_3^- exports are not substantially higher. High NO_3^- export is likely only a fraction of potential N loading during mining and reclamation. If so, there must be high watershed retention of N which is consistent with the observed enriched isotopic signature of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. This enriched signal is in line with previous work that found that trophic positions in mined streams were enriched in $\delta^{15}\text{N}$ (Daniel et al., 2015; Voss & Bernhardt, 2017) as was particulate N in mining sediment (Fox, 2009). The enriched signal does not fit potential source endmembers but does match the result of denitrification occurring from a stock with a large pool size (Figure 5; Kendall et al., 2008). This is consistent with observations that headwater watersheds with high N loading from land use can have higher denitrification rates in sediments than forested watersheds (Inwood et al., 2005). Further, the flatter topography of MTM

watershed (Ross et al., 2016) and valley fill construction could promote saturated conditions conducive to denitrification. If denitrification rather than simply retention explains the gap between inputs and observed stream exports, then these watersheds may be exporting sizable amounts of gaseous N in addition to their elevated exports of dissolved NO₃.

Our analysis does not reveal whether long-term sources are time lagged residues of singular pulse inputs or the result of an ongoing altered biogeochemical regime in a manmade landscape. While anthropogenic disturbances often cause elevated N export, the lag times and persistence of this export can vary widely. For example, in intensive agricultural watersheds with long term N loading, elevated N export can last decades after the cessation of the application of fertilizer (Van Meter et al., 2016) while N export after timber harvest can return to preharvest levels after only several years of recovery (Hornbeck et al., 1986). At MTM watersheds in recovery, even as vegetation and soils redevelop, there remains a legacy of anthropogenic N inputs and long-term alterations to N pools sizes and internal processing. Moreover, despite some surface recovery, in the postmined landscape, substantial proportions of streamflow come from flow through the valley fill at depths inaccessible to plant roots (Nippgen et al., 2017). Both residue from explosives mixed into waste rock and rock weathering derived N could accumulate along these deeper, slower flow paths and then be released to the stream in baseflow. As valley fills weather and hydrologic flow paths shift (Evans et al., 2015; Hester et al., 2019; Ross et al., 2018), N in previously hydrologically inactive areas could be mobilized. As a result, we speculate that valley fills might serve as a source of elevated N export long after reclamation is complete and vegetation is reestablished on the watershed surface.

5. Conclusion

This study demonstrates that mountaintop mining activities can cause large increases in N export that can persist above pre&mining conditions for at least decades after mining cessation. In a region that otherwise is predominantly forested, this source of N loading to headwater streams can raise mean concentrations by as much as 2000% of reference concentrations, disrupt local ecological function, and likely exacerbates ecological impairments caused by other mining derived solutes and pollutants. As mining is widely distributed across the region's headwaters and headwater loading of N often disproportionately affects downstream waters (Alexander et al., 2007), N pollution from mining is a regional water quality concern. We found evidence that this signal is observable even at large regional scales when active mining activities are widespread enough to overwhelm interference from other sources and sinks of nitrate. At the small watershed scale, our finding of peak N concentrations during active mining and declines over time in nitrate concentrations post-mining suggest that cessation of mining reduces N export. However, we found no evidence of sites where export had reduced to reference levels. In fact, our observation indicate that mining associated elevated N can last at least multiple decades. More research is needed to better identify if this is the legacy of external N inputs such as explosives added during mining and fertilizer during reclamation activities or if the geomorphic restructuring of the watersheds has created an altered biogeochemical state where watersheds remain persistently leakier than unaltered forested watersheds due to changes in hydrologic storage, weathering surfaces, and runoff flow paths.

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