Mountaintop Mining's Impact on Watershed and Regional Scale Nitrogen Export

by

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Abstract

Mountaintop removal coal mining with valley fills (MTM) is the largest contributor to land use change in the Central Appalachia Region. MTM uses explosives and draglines to uncover shallow seems of coal from mountaintops and ridgelines. The coal residues and overburden are disposed of into adjacent valleys forming valley fills. The large quantities of unconsolidated rock increase watershed storage potential and vastly increase rates of rock weathering via sulfuric acid generated by coal residues. This leads to high concentrations of coal and rock derived ions in receiving surface waters and causes a number of associated water quality impairments. Alongside known these known impairments, recent studies have also reported high dissolved nitrogen (N) concentrations in samples from affected streams. This project quantifies, for the first time, the magnitudes and persistence of this elevate nitrogen export from MTM affected catchments and investigates how MTM increases N inputs and alters catchment N cycling. Using two years of hydrologic measurements and regular baseflow and storm sampling near the Hobet Mining Complex in West Virginia, this research finds that annual mass flux of nitrate in mined catchments was 9 to 61 times greater than at a reference catchment. Further, the project finds that high levels of nitrate export during active mining declines after reclamation but can remain significantly elevated for at least several decades post mining. Analysis of nitrate isotopes from stream water finds baseflow at mined sits to be highly enriched in both $\delta^{15}N$ and $\delta^{18}O$ compared to the reference site. These isotopic values do not match the signature of any known potential nitrate source but do match with the results of fractionation from denitrification occurring in large pools of NO_3^-. A developed watershed nitrogen budget identifies mining explosives as a sizable mining input of N that could export 9 to 3716 kg N ha^{-1} but also suggests other sources

including fertilizer, weathering derived rock N, and soil mineralization all may play a role in elevated export. Finally, an analysis of regional water quality and surface mining extent indicate a significant correlation between the cumulative extent of surface mining and annual mean nitrate concentrations in the mostly heavily mined regional basin.

Introduction

Humans activities and land use can alter nitrogen (N) cycling and influence watershed N export via streams both by introducing new reactive N to the landscape and by altering N processing and retention in the critical zone. Globally, anthropogenic activities account for approximately half of yearly N fixation, primarily through production of fertilizer and to a lesser degree through biologic nitrogen fixation by agriculture crops and fossil fuel combustion [*Fowler et al*., 2013]. Once fixed, there are numerous pathways that N can take to reach surface and groundwater such as leaching of fertilizers from agricultural and urban areas, direct discharge from sewage and industrial sources, mobilization of soil N through soil and vegetation disturbance, and deposition of N released in emissions from fossil fuel burning and agriculture [*Galloway et al*., 2003]. The effectiveness of landscape accumulation and retention of N in response to increased N loading can be influenced by land cover and land use history. Such disturbances often reduce retention and increase N export. Landscape disturbances such as deforestation, urbanization and agriculture are all often studied at the watershed scale in order to quantify N retention and export [*Likens et al*., 1970; *David et al*., 1997; *Groffman et al*., 2004].

Mountaintop Mining (MTM), a form of surface coal mining, is the largest contributor to land-use change in the Appalachia Coal Region (ACR), which includes parts of West Virginia, Kentucky,

Tennessee, and Virginia [*Drummond and Loveland*, 2010]. Yet how MTM affects N loading and landscape level N retention remains poorly understood. In MTM, tens to hundreds of meters of overlying rock are removed from mountain tops and ridgelines in order to access underlying coal seams. After coal is removed, this waste rock is either placed into valley fills (VF) or used to re-contour and reconstruct the post mining landscape. As of 2016, 5000 km^2 of Central Appalachia have been converted into active, abandoned or reclaimed surface mines, accounting for ~6% of the regions land area [*Periçak et al., 2017*, *in preparation*). Collectively, the valley fills associated with regional MTM activities have buried ~4,000 km of streams and have been linked to a host of water quality concerns in the region [*U.S. Environmental Protection Agency (EPA)*, 2011].

On affected land, MTM and subsequent reclamation drastically reconfigures the critical zone, creating novel landforms and altered hydrologic, geomorphic and biogeochemical states. MTM has been linked to a range of hydrologic changes including higher stormflows during higher intense precipitation events [*Messinger and Paybins*, 2003], changes in infiltration capacity and soil macro-porosity, reductions in evapotranspiration, increased storage, longer flow pathways, and enhanced summer baseflow [*Nippgen et al*., 2017, *in review*; *Messinger and Paybins*, 2003; *Evans et al*., 2015]. The post-mined landscape is significantly flatter, with large amounts of highly fractured rock exposed at the surface and stored in fills [*Ross et al*., 2016]. As water drains through spoils and fills containing this newly exposed rock, it accumulates products from a series of chemical reactions through which sulfuric acid derived from the weathering of coal and shale residues reacts with carbonate bedrock to generate Alkaline Mine Drainage [*Palmer et al*., 2010]. The combination of a strong acid source (shale and coal) together with highly soluble

and mechanically fragmented bedrock (carbonates) has led to among the highest reported rates of rock weathering in the world [*Ross et al.,* 2017, *in review*]. The resulting export of dissolved solutes (e.g. SO4, Mg, Ca) and select metals including selenium causes significant biological impairments to stream ecosystems when as little as 2.2% of the catchment is mined [*Bernhardt et al.*, 2012].

Mountaintop mining (MTM) alters nitrogen stocks, inputs, and export at multiple points through the mining and reclamation process. At the outset of mining, clear-cut logging and removal of existing soils remove standing N stocks [*Simmons et al.*, 2008]. Similar dynamics occur in deforestation experiments, where rapid deforestation followed by the suppression of regrowth has led to reductions in N retention and a corresponding increase in N export [*Likens et al.*, 1970; *Adams and Kochenderfer*, 1999]. Next, explosives and heavy machinery are used to break up and remove overburden [*Wunsch et al.*, 1999]. Explosives commonly contain 20-33% N by weight [*Forsyth et al.*, 1995] and explosive residues have been suggested as a potential source of N found in newly established MTM soils [*Zipper*, 2012] and a cause of elevated nitrate in streams draining MTM catchments [*Bryant et al.*, 2002; *Daniel et al.*, 2015]. Studies focused on other forms of surface and underground mining suggest that 0.2-28% of N in explosives can reach waterways and can depend on the type of explosives used, mining practices and spills, and wetness conditions. [*Ferguson and Leask*, 1988; *Morin and Hutt*, 2009]. However, no known studies to date have addressed how much explosive N sources reaches streams during and after MTM.

Once coal is removed, the reclamation process begins with excess rock placed in VFs and overburden returned to the landscape. Classically, the landscape is regraded and rock spoils are placed on the surface as substitute mine soils. The surface is then revegetated by hydro-seeding of grasses and legumes and fertilized with nutrients [*Zipper*, 2012]. Newer reclamation technique focus on improving forest regrowth by reducing soil compaction, using preferred mine soil mediums such as weathered sandstone or topsoil with lower pH, and reducing but not eliminating fertilizer usage [*Burger et al*., 2009; *Miller et al*., 2012]. Both traditional and new approaches introduce N as fertilizer, which is retained only if converted to organic forms, and encourage the growth of N-fixing vegetation such as legumes or trees [*Zipper et al*., 2011].

Settlement ponds are also constructed on uplands and below VFs to reduce sediment transport and address water quality concerns (Merricks et al. 2007; Griffith et al. 2012). These ponds may play a role in N cycling by being a source of N uptake by algae [*Merricks et al*., 2007] and as potential sites for denitrification given suitable carbon and anoxic conditions. Denitrification in mined landscapes might be further enhanced if saturated conditions exists within the underlying spoil [*Simmons et al*., 2008] or within the VFs. However, denitrification enzyme activity has been found to be reduced in mined soils and also to a lesser degree in the sediments of streams draining MTM impacted catchments [*Burke et al*., 2014].

The high rates of weathering from mine spoils and VFs also raise the potential that geologic N can be a source of N export. In forested catchments underlain by N-rich bedrock, geologic N has been identified as comparable to magnitudes of atmospheric deposition in contributing to soil N [*Morford et al*., 2016]. Elsewhere, N-rich bedrock has been linked to elevated N export

[*Holloway et al*., 1998; *Montross et al*., 2013]. The influence of geology on N export has been observed at Fernow Experimental Forest, WV where one study showed underlying geology was a significant factor, explaining 18% of summer mean nitrate concentrations.[*Williard et al*., 1997]. In fresh mine spoils, 55-86% of N can be of geologic origin, with total N ranging from 250 mg N kg^{-1} spoils in sandstone to 475 mg N kg^{-1} in siltstone [*Li and Daniels*, 1994]. Coal fragments may be the largest contributor of N in spoils as they are N rich (15,876 mg N kg^{-1}) and can comprise from 1-10% of total spoils [*Li and Daniels*, 1994].

Streams downstream from mining in WV have been shown to have significantly higher nitrate concentrations than reference streams [*Bryant et al*., 2002; *Pond et al*., 2008]. Streams draining active mining sites generally exhibit higher N than reclaimed mines [*Lindberg et al*., 2011]. In mining affected streams, both invertebrates [*Daniel et al*., 2015] and sediments [*Fox*, 2009] were reported to have enriched δ15N compared to unmined reaches. Spoil experiments have shown that nitrate concentration in spoil effluent differ significantly based on spoil rock type and decrease over yearly timescales [*Agouridis et al*., 2012]. While N export appears to increase as a result of mining, nitrogen can limit regrowth on the surface of reclaimed mines where soils appear to be initially nitrogen poor relative to forested catchments [*Zipper et al*., 2011]. As previously mined areas are revegetated, N begins to accumulate, particularly in pools in the upper soil layers, litter and vegetation [*Li and Daniels*, 1994; *Nash et al*., 2016].

While MTM has been linked to increased nitrate export, previous studies have only conducted baseflow grab sampling and have not accounted for storm events nor seasonal and temporal changes after mining. Here I quantity for the first time the yearly mass flux of nitrate from a

MTM and VF affected watershed, investigate the persistence and spatial scale of MTM's impact on nitrogen export, and develop new insights into the sourcing and processing of N on affected minelands.

Study Sites and Methods

Methods Overview

This project uses multi-tiered approach to understanding MTM impact on N export. First, I make use of a literature review and measured values to develop a nitrogen budget for a forested and reclaimed watershed. Then I use a paired catchment scale study to compare N export, stormflow N dynamics and isotopic ratios at a reference catchment against mined catchments that have been selected using a space for time substitution approach. I then compare trends in baseflow NO_3^--N concentrations over time at four sites that had been sampled in earlier sampling campaigns in 2000-2001 and/or in 2010. Finally, utilizing published regional water quality and mining extent datasets, I examine whether mining's impact on N export scales from the watershed to the regional basin level.

Site Description

I made use of collected hydrologic measurements and stream chemistry sampling in the Mud River basin in southwestern West Virginia (Figure 1). Four small 1st order watersheds were paired based on the presence or absence of mining and the time since mining. The mined Zero Year watershed (MY0) – 590ha, 90% mined – was mined in sections until 2015 and has not been reclaimed. The stream site is located ~200m below a settlement pond at the base of the mined area. The mined Five Year (MY5) – 68ha, 92% – mined was reclaimed by ~2010. The site is

located at the outlet of a pond draining two VFs. The mined Twenty Year catchment (MY20) – 61ha, 86% mined – was reclaimed by ~1993. All ponds at Twenty Year have been filled in and site is located ~130m below a VF. The reference catchment (REF) is a forested 118ha tributary to the nearby Left Fork River.

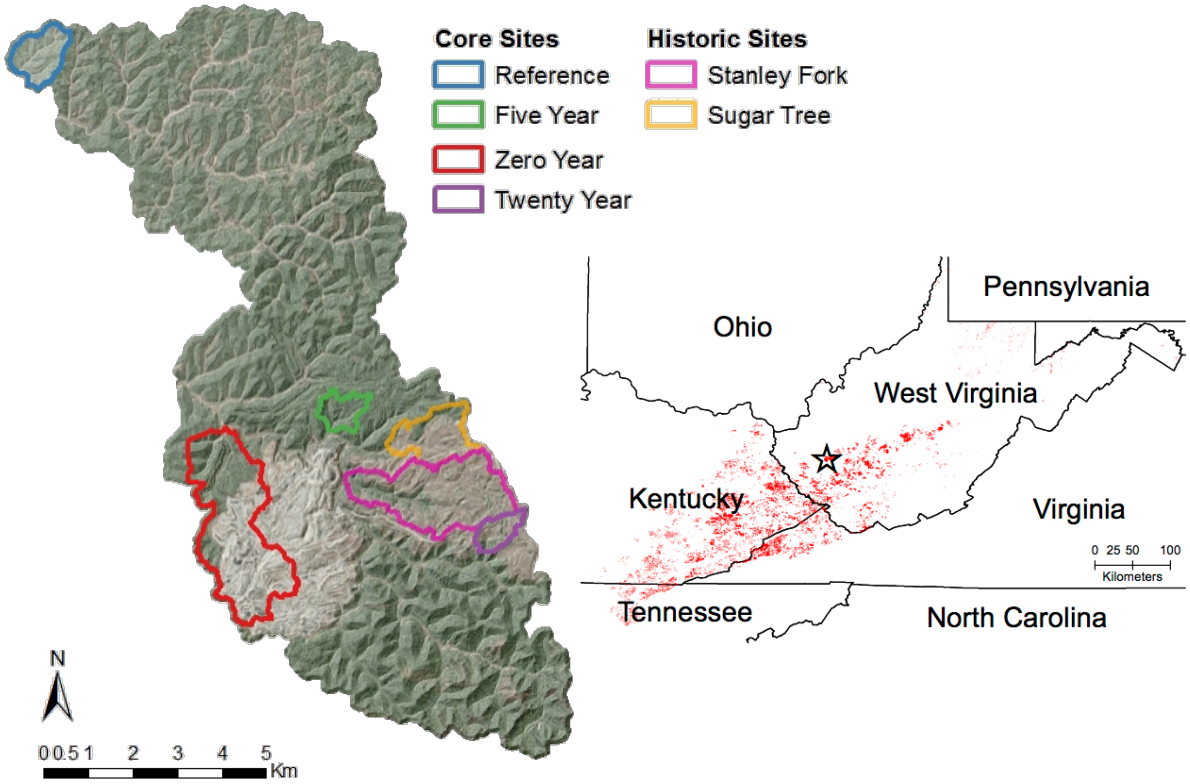

Figure 1: Study Map. Mine catchments are all at the Hobet Mining Complex within the Mud River basin in southwestern West Virginia. The Reference site is in the adjacent Left Fork basin. Red on adjacent regional map shows extent of surface coal mining across the region.

Two additional sites: Sugar Tree (ST) – 158ha, 92% mined– and Stanley Fork (SF) – 439 ha, 86% mined – were sampled at sites nearby to sampling conducted in 2000-2001 [*Bryant et al.*, 2002] and in 2010-2011 [*Lindberg et al.*, 2011] (Table 1). All mined catchments are part of the Hobet Mining Complex, which stopped all active mining activities in 2015. Some of the more recently mined sites have ongoing active reclamation and many have long-term treatment in the form of settlement ponds. Starting in June 2015, Five Year was affected by intermittent pumping

that captured a portion of VF drainage and recycled it back into upland ponds, increasing water residence times and affecting discharge timing. At older sites, ponds have been filled in and no pumping occurs. The study site was chosen in part because no known deep mines are in the study area [*Messinger and Paybins*, 2003].

Table 1: Site Description of Core and Historic Sites.

	Catchment	Abbreviation	Stream Name	Size (ha)	Active Mining Years	% Mined	Year Reclaimed	VF	Pond(s)	Pumping
Core Sites	Reference	Ref	Rich's Branch	118	Not Mined	–	–	–	–	–
	Five Year	MY5	Laurel Branch	68	2005-2009	92	~2010	Yes	Yes	Yes (after 6/2015)
	Zero Year	MY0	Mullin's Branch	590	1999-2015	90	Not Reclaimed	Yes	Yes	Unknown
	Twenty Year	MY20	Left Fork of Ballard Fork	62	1988-1992	86	~1993	Yes	Filled	No
Historic Sites	Sugar Tree	ST	Sugar Tree	158	1993-1996 2002-2007	92	~2009	Yes	Yes	Unknown
	Stanley Fork	SF	Stanley Fork	439	1988-1998	86	~2003	Yes (multiple)	Yes	No

Spatial Analysis:

Pre and post-mining digital elevation models were used to delineate catchments, calculate catchment area post-mining and to estimate VF volumes (see *Ross et al*. [2016] for methods). A yearly mining extent dataset developed by Periçak et al. (manuscript in preparation, 2017) was used to assess peak mining years and percent of catchment mined. Time of reclamation was estimated by identifying the start of regrowth as determined by vegetation canopy heights derived by LIDAR data (see Ross et al. *(*manuscript in preparation, 2017) for methods). Post-mining catchment area estimates for the Zero Year catchment are less certain than other

catchments as Zero Year was undergoing active mining during LIDAR data collection. Geospatial analysis were conducted in ArcMap 10.3.1 and using the Raster [*Hijmans*, 2016], Rdgal [*Bivand et al*., 2016] and Sp [*Bivand et al*., 2013] packages in R.

Hydrologic Measurements and Water Sampling:

At the four core catchments (Reference, Zero Year, Five Year, Twenty Year), stream level was monitored at ten-minute intervals. Reference and Five Year were monitored for both WY15 and WY16, while monitoring at Zero Year and Twenty Year began in July 2015 and continued through the end of WY16. Water level was measured using Onset HOBO loggers at Reference, Five Year, and Twenty Year and a Solinst Levellogger at Zero Year. Rating curves were developed and used to develop continuous stream discharge estimates (see *Nippgen et al*. [2017, *in review]* for methods).

Baseflow samples were collected bi-weekly at Five Year and Reference for WY15 and monthly at all four catchments in WY16. Irregular baseflow sampling was conducted at the historic sites in WY16. Storm sampling was conducted for March, April, and October 2015 at Reference and Five Year and for a June 2016 storm at all sites (Table 2). All water samples were filtered in the field using a 0.45 micron mixed-cellulose fiber filter, frozen onsite and stored frozen until analysis. Samples were analyzed for NO_3^--N utilizing a Dionex ICS-2000 ion chromatograph with IonPac AS-18 analytical column (Dionex Corp., Sunnyvale, CA). Samples from mined sites were diluted 10x prior to analysis and minimum detection was 5ppb. Storm samples from June 2016 were analyzed for NH_4^+-N using a QuikChem8500 flow injection analyzer (Lachat Instruments, Loveland, CO) with detection limit between 0.01-2 mg NH_4^+-N L^{-1}. Total dissolved

nitrogen (TDN) were analyzed for the June 2016 storm using a Shimadzu TOC-VCPH with TNM-1 module (Shimadzu Corp., Kyoto, Japan). Minimum detection for TDN was 0.05 mg N L^{-1}. Below detection values were considered to be zero for all analysis. NO_2^- concentrations are assumed to be negligible and dissolved organic nitrogen (DON) was calculated to be the difference between TDN and measured inorganic species ($NH_4^=$-N + NO_3^--N).

Table 2: Baseflow and Storm Sampling Timing and Analyzed Nitrogen Species

		Baseflow		Storms			
		WY15	**WY16**	**March 2015**	**April 2015**	**October 2015**	**June 2016**
Core Sites	Reference (REF) Five Year (MY5)	NO_3^- (Bi-weekly)	NO_3^- (Monthly)	NO_3^-	NO_3^-	NO_3^--	NO_3^-, NH_4^+ TDN
	Zero Year (MY0) Twenty Year (MY20)	NO_3^- (Irregular)	NO_3^- (Monthly)	NO_3^-	NO_3^-	NO_3^-	NO_3^-, NH_4^+ TDN
Historic Sites	Sugar Tree (ST) Stanley Fork (SF)	–	NO_3^- (Irregular)	–	–	–	–
Rain Gauge	Residence (RS)	–	–	–	–	–	NO_3^-, NH_4^+ TDN

Precipitation was measured at the site RS, located between the reference and mined using a Onset HOBO RG3 rain gauge and data logger recording at 10 minute intervals sites (Table 2). Rain samples were collected and analyzed from gauge RS during the June 2016 storm for NO_3^--N, NH_4^+-N, and TDN.

A one-factor ANOVA was used to test difference in mean NO_3^--N concentrations between mined and unmined catchments. To ensure the equivalency of the between site comparison, only samples collected at all four core catchments during the same sampling period were kept for this

analysis. The Dunnet Test was then used to compare post-hoc pairwise differences between each mined catchment and the reference catchment. The Tukey Honest Differences test was used to test pairwise differences between mined catchments. All results were evaluated using a significance threshold of $p<0.05$.

Nitrate Flux

To develop mass flux estimates, site specific regression models were developed to predict NO_3-N concentration at 10 minute intervals using percent baseflow and season as predictor variables (1.1). Regression models were built using the full NO_3^--N dataset at Zero Year and Twenty Year. At Five Year and Reference, because of changes in sampling frequency and watershed conditions at Five Year, a separate regression model was developed from data collected from each water year (Figure 2). Concentrations and cumulative flux were modeled at Reference and Five Year for WY15 and for all four core sites in WY16.

$$(1.1) \quad Log(NO_3^-\text{-}N\ (mg\ NO_3^-\text{-}N\ L^{-1})) = Baseflow\ (\%\ of\ Total\ Flow) + Season + \varepsilon$$

Baseflow was estimated using a graphical separation approach similar to the *Hewlett and Hibbert* [1965] method and assumes a constant rise in baseflow after precipitation begins (see *Nippgen et al*. [2017, *in review]* for full methods). Percent baseflow was chosen as a predictor rather than the more traditionally used discharge as it was found to be a stronger predictor than discharge at most sites. 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.

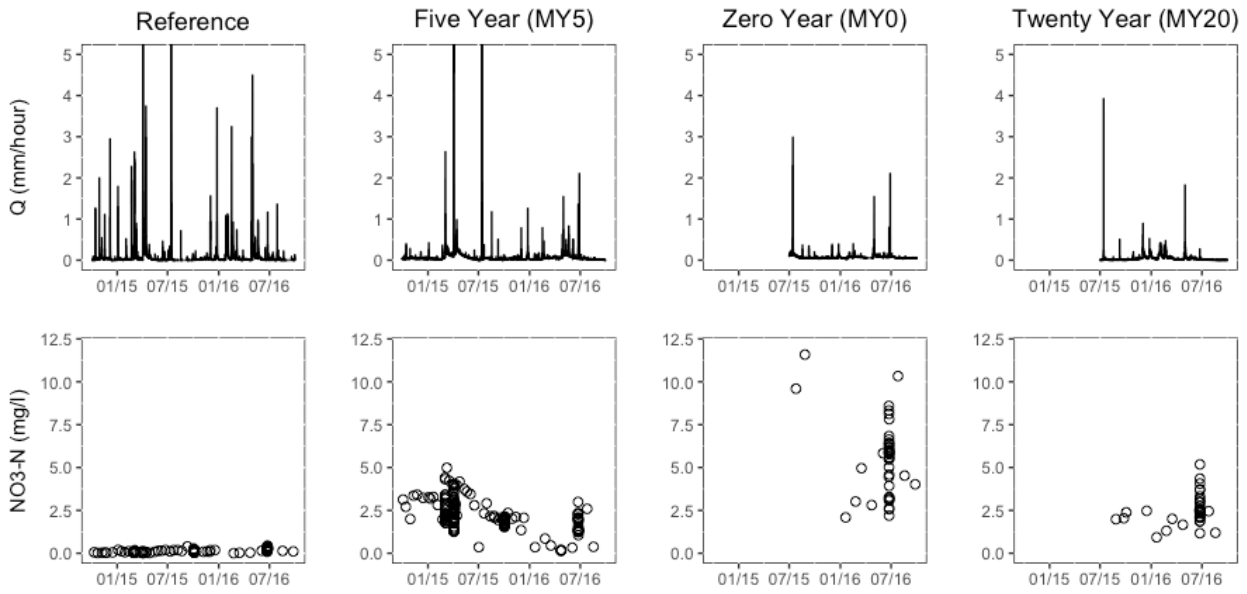

Figure 2: Discharge and NO3--N Concentrations at Core Sites. Peaks of storm hydrographs at REF and MY5 have been cut off to better show overall trends in discharge

Historical Comparison

Grab sampling was conducted near locations used in previous sampling campaigns at Sugar Tree, Stanley Fork, Zero Year & Five Year. Previous site locations were established using geographic coordinates provided by study authors ((T. Lindberg, pers. comm., 2016*);* G. Pond, pers. comm., 2016)). The oldest dataset, published first by *Bryant et al*. [2002], was collected between August 2000 to February 2001 at approximately monthly intervals at sites Sugar Tree and Stanley Fork. Measurements were taken as Nitrate + Nitrite-N. As Nitrite-N was also measured at least once at both sites and was below detection of 0.05 mg N L^{-1}, the measurements are assumed to be comparable to more recent measurements of only NO_3^--N. *Lindberg et al*. [2011] collected samples at Sugar Tree, Stanley Fork, Zero Year and Five Year at monthly intervals from June 2010 to December 2010 (data is missing from August 2010 and November

2010) and reported values as NO_3^--N. PRISM daily rainfall data was compared to historic and current sampling dates to ensure no samples were taken during particularly wet periods [*PRISM Climate Group*, 2016]. Sampling dates with more than 10mm of rainfall in that day or 40mm in the previous 5 days were excluded from the analysis. As sample sizes varied substantially between sampling periods, the nonparametric Kruskall-Wallace test of significance was used to determine if the distribution nitrate concentrations are identical at each site between study periods.

Isotopic Analysis

A subset of stream and rainfall samples from the June 2016 storm were sent to the University of California-Davis Stable Isotope Facility for analysis of NO_3^- isotopes. $\delta^{15}N$ and $\delta^{18}O$ values were analyzed by the bacterial denitrification method [*Sigman et al*., 2001] and reported relative to the standard AIR and VSMOW, respectively. Reported literature values for potential NO_3^- end members such as precipitation, fertilizer, soils [*Kendall et al*., 2008], explosives [*Degnan et al*., 2016], and coal [*Holloway and Dahlgren*, 2002] were used in the analysis. Analysis error was 0.02 ±0.07 (mean ±standard deviation) for $\delta^{15}N$ and 0.06 ±0.27 for $\delta^{18}O$.

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]. Water quality sites were selected by the presence of mining in the river basin and the availability of Nitrate-Nitrite (NO_3^-/NO_2^--N) and Sulfate (SO_4^-) data going back to 1985 (Table 3). Sites within 2.5 km were considered analogous so long as no large tributary affected the downstream location. Catchments

for each site were delineated using TauDEM 5.3 [*Tarboton and Sazib*, 2015]. Yearly mining extent for each basin was extracted from the mining extent dataset developed by Periçak et al. (manuscript in preparation, 2017). The mining extent database provides estimates from 1985 until 2015. For each year, active mining was calculated as the sum of pixels classified as mining in that year and cumulative mining was calculated as the sum of pixels that had been classified as mining at least once by that year. Water quality sites with at least 1% of the basin mined were selected for further analysis. For each selected site, mean solute concentrations (mg L^{-1}) were calculated for each year. A linear regression analysis was then conducted to analyze correlations between mining extent and mean yearly solute concentrations.

Table 3: Regional Basin Characteristics and Linear Regression Results: Linear regression R^2 reflect relationship between mining extent (% of total catchment) and mean annual solute concentration. Only significant results are displayed. Symbol (+ or -) after adjusted R^2 represents sign of correlation coefficient.

			Adjusted R^2			
	Area	Cumulative Mining (2015)	Nitrate/Nitrite-N (annual mean mg/L)		Sulfate (annual mean mg/L)	
	(km^2)	(% catchment)	Active Mining	Cumulative Mining	Active Mining	Cumulative Mining
Coal River	2234	11.8	**0.52+**	**0.52+**	**0.42+**	**0.41+**
Gauley River	3369	3.8		**0.48-**		
Lower Guyandotte	2497	7.9				
Tug Fork	4030	10.3			**0.3**	**0.34+**
Twelvepole River	1109	3.8				**0.23+**

Data Analysis in R:

Unless stated otherwise, all analysis were conducted in R 3.31 [*R Core Team*, 2016] and RStudio 1.0.136.

Results*:*

Nitrogen Budget:

Mountaintop mining activities lead to large exports (timber and coal harvest), large inputs (explosives and fertilizers), and enhanced internal production (high rates of chemical weathering, increase in nitrogen fixation) of N that collectively determine watershed N cycling (Figure 3). To understand these drivers, I developed a simple N budget based on published and measured values for forested, actively mined, and recovering Appalachian catchments (Figure 4). Pre-mined secondary forested catchments that are not N saturated are thought to have high standing N stocks, high retention and low export. 3,000-6,000 kg N ha^{-1} nitrogen is estimated to be stored in forest soils [*Zipper et al*., 2011]. Aboveground stocks depend in part on stand age, but have been measured in reference catchments that were approximately 60 years old as between 353-450 kg N ha^{-1} at Walker Branch in Tennessee and 563 kg N ha^{-1} at Coweeta Hydrologic Laboratory (CHL) in North Carolina [*Adams et al*., 1995]. Nitrogen inputs into forested catchments is primarily through dry and wet atmospheric deposition. In southwest West Virginia (WV), depositional N has been declining over recent decades, with the 2016 yearly input estimated to be between 6-8 kg N ha^{-1} yr^{-1} based on modeled total wet & dry N deposition [*Schwede and Lear*, 2014]. Yearly $NO3^{-}$-N export from the REF catchment in our study was estimated to be 0.43 ± 0.21 kg N ha^{-1} yr^{-1} (Figure 8). Assuming speciation during June measurements is representative of the entire year, then total DIN yearly export was between 0.3 to 0.75 kg N ha^{-1} yr^{-1}. This was lower than DIN export reported at nearby Fernow Experimental Forest (FEF) in northeastern WV (4.3-10.3 kg N ha^{-1} yr^{-1}) but comparable to export from catchments in western NC (0.10 – 1.5 kg N ha^{-1} yr^{-1}) [*Adams et al*., 1995].

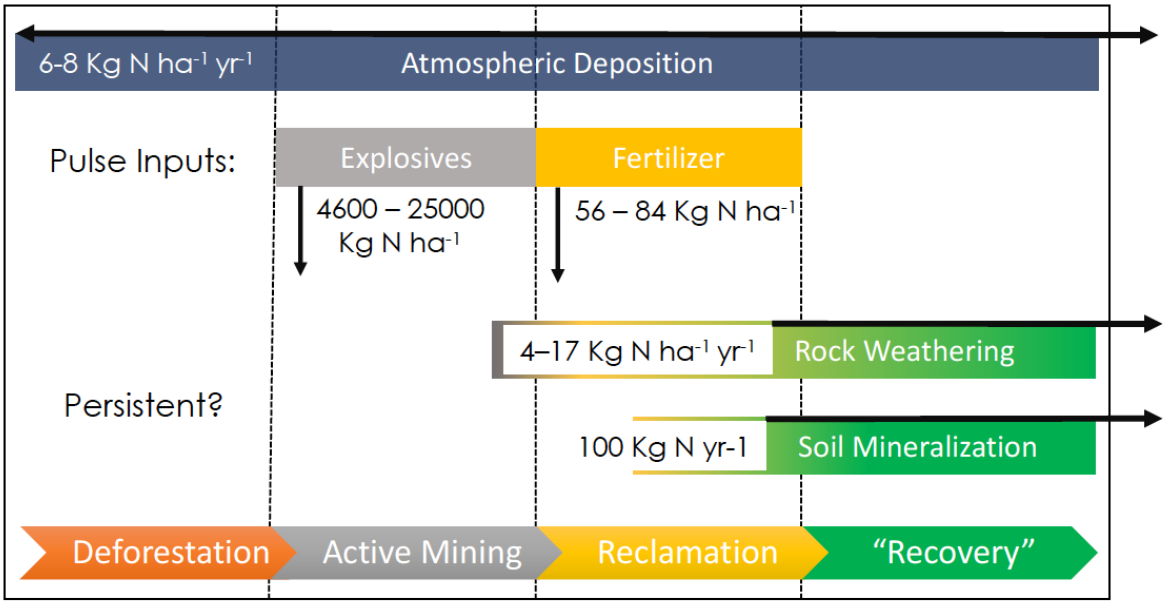

Figure 3: Potential Loading and Timing of N Sources during MTM Activities

Nitrogen pools and inputs are repeatedly altered through the active mining and reclamation process (Figures 3 & 4). To simplify the N budget approach, I considered the N pool sizes at the end of initial reclamation efforts and again after 10 years post-mining. Mining-related N inputs were represented as an input to the recently reclaimed pool and calculated as the cumulative sum of inputs throughout the entire mining process. The removal of vegetation and soils causes N pool sizes after mining to be drastically reduced. Little to no N is present in vegetation or litter immediately after mining. Based on total N concentrations in rock between 249-474 mg N kg in fresh spoils [*Li and Daniels*, 1994], and assuming an average bulk density of 1.2 g cm^{-3} in mined soils [*Zipper et al.*, 2011], total N was calculated in mined soils to be 900-1700 kg N ha^{-1} in the top 30 cm of soil. Unlike forested soil, much of this N is in the form of geologic N and may be unavailable to plants [*Li and Daniels*, 1994].

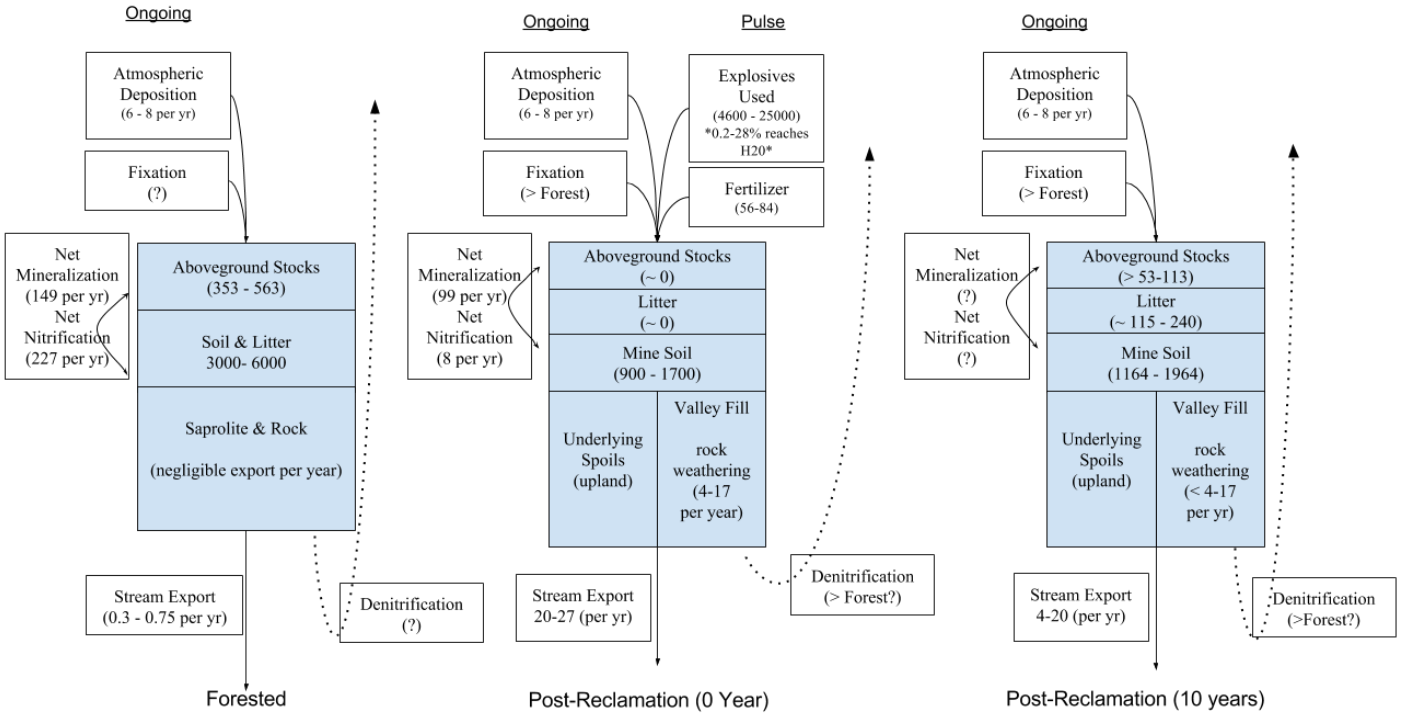

Figure 4: Estimated N Budget for Forested, Recently Reclaimed and 10 Year Post Reclamation Catchments. All values are in kg ha^{-1} and are derived from measured values from this study or a literature review on properties of Appalachian forests, mining practices, and reclaimed surface coal mines.

Together with atmospheric deposition, pulses of N inputs during mining are largely driven by explosive use during mining and fertilizer application during reclamation (Figure 3). Atmospheric N inputs were assumed to be similar to pre-mining forests. Following the guidelines in the Appalachian Regional Reforestation Initiative, fertilizer N inputs were estimated to be a single application of between 56-84 kg N ha^{-1} at the outset of reclamation [*Burger et al.*, 2009]. Earlier reclamation practices likely involved higher application rates and/or multiple applications over several years.

Quantifying explosive N inputs to the catchment produced estimates ranging several orders of magnitude and with high uncertainty.The amount of explosives used would have depended on the amount of rock removed, the powder factor (kg of explosives per m^3 of rock), and the

efficiency of blasting. The nitrogen content of explosives varies with explosive type. The most commonly used form is 94% ammonium nitrate mixed with 6% diesel fuel which contains 33% N by mass [*Forsyth et al*., 1995; *Revey*, 1996]. Alternate explosives types such as watergels or emulsions contain 20% to 30% N by mass (Appendix 1). Nitrogen from explosives is released into the landscape when it is spilled during transportation or charging, leached in wet blastholes, or undetonated explosive residue remains in broken rock. Up to 10 to 20% of explosives in blastholes can misfire and not be consumed in a given blast [*Forsyth et al*., 1995]. While most of N in explosive N is consumed in the explosion, anywhere from 0.2 to 28% can be retained and eventually exported [*Pommen*, 1983; *Ferguson and Leask*, 1988; *Forsyth et al*., 1995; *Morin and Hutt*, 2009]. To estimate the total amount of explosives used per hectare, I used reported powder factors of between 0.33-0.58 kg/m^3 [*English and Luo*, 2001]. I calculated the area normalized amount of total rock exploded by assuming the volume of fill in the VF at Five Year was representative of the rock moved in that catchment. Based on the estimate of a fill volume of 11,000,000 m^3 of rock [*Nippgen et al*., 2017, *in review; Ross et al., 2016]* at Five Year, and reported porosities in mine spoils of between 20-57% [*Wunsch et al*., 1999], I made minimum and maximum estimates of total explosives used (23,000- 75,000 kg ha^{-1}) and N in total explosives (4,600-25,000 kg N ha^{-1}).

Since no studies exist that describe the percentage of explosive N that reaches waterways in MTM, I used 0.2%, 1%, 15% which reflected the range of values reported from other mining types. At 0.2%, estimated inputs ranged from 9-50 kg N ha^{-1}, at 1% from 46-248 kg N ha^{-1} and at 15% from 689-3,715 kg N ha^{-1}. At the lowest range of estimates, inputs were on the same order of magnitude as one to several years of atmospheric deposition but at the higher ranges,

explosive inputs could exceed N standing stocks in catchment soils. Inputs of explosive N are typically both NH_4^+ and NO_3^- but reports have shown that NH_4^+ is lost rapidly via uptake or mineralization and most N measured at mining outlets is in form of NO_3^- [*Morin and Hutt*, 2009; *Jermakka*, 2015]. A container test at the scale of $10m^3$ suggested that explosives leach out in months to a year [*Jermakka*, 2015],while other field studies have suggested there is rapid initial leaching followed by persistent slower leaching and have estimated it could take up to five years for complete leaching to occur [*Morin and Hutt*, 2009]. However, no previous studies on the time scale of leaching are truly relevant to MTM due to the scale and unique landscape position of valley fills in MTM catchments.

To estimate the potential contribution of weathering derived geologic N, I made use of reported estimated total dissolved solutes (TDS) export from Five Year of 8,778 kg ha^{-1} yr^{-1} [*Ross et al*., 2017, *in review*]. I then estimated the N release from congruent weathering given fluxes of co-occurring rock derived elements. Using reported N concentrations in sandstone (250 mg N kg^{-1}), siltstone (475 mg N kg^{-1}) and coal (15,876 mg N kg^{-1}) [*Li and Daniels*, 1994], I bounded the estimate by calculating minimum N export assuming spoil composition was 99% sandstone and 1% coal and maximum export using a composition of 90% siltstone 10% coal. Based on this, I found that from 4 to 17 kg N ha^{-1} yr^{-1} of DIN could have been mineralized from rock weathering within the Five Year catchment (Figures 3 & 4). While potentially a smaller overall input than explosives, the minimum estimate could sustain a 5-13x higher rate of DIN export than observed from our reference catchment. Moreover, as specific conductivities have been observed to be elevated for several decades post mining [*Evans et al*., 2014], rock nitrogen could be a lasting

source that continues to contribute to elevated catchment exports for much longer than the discrete periods of explosive and fertilizer N leaching.

After reclamation, N pools begin to accumulate in vegetation and litter pools, and in the upper layers of soils. *Li and Daniels* [1994] reported that reclaimed surface mining catchments had litter pools between 115.4 – 241.8 kg N ha^{-1}, seven to twelve years post reclamation and that accumulation in soils was 26.4 kg N ha^{-1} per year in the top 10cm of soils. They reported that vegetation varied with age but after about ten years, black locust and white pine began to dominate the canopy cover. Using this estimate of yearly N aggregation in soil, I estimated soil pools after 10 years to have increased to 1164 – 1964 kg N ha^{-1} (Figure 4). This range captures *Simmons et al*. [2008]'s finding of a pool size of 1310 kg N ha^{-1} in mineral soils at a reclaimed surface coal mine in Maryland that had been maintained for ~14 years as mowed grassland. At their site, *Simmons et al*. [2008] also estimated pools of 2.5 kg N ha^{-1} in aboveground biomass, and 132 kg N ha^{-1} in the litter and the O horizon. The large differences in litter pools between the two studies raises the issue that upland management of reclaimed mines can greatly affect N pools. Because no good estimates of the N pool in aboveground vegetation exist for reclaimed minelands managed for forest regrowth, I made use of canopy cover estimates from LIDAR data for a first-order estimation. Canopy cover at 10 year sites average 15-20% of forested areas (Ross et al., 2017, manuscript in preparation) and the vegetation pool was estimated to have recovered to 53-113 kg N ha^{-1}. While I believe this provides an useful estimate, it could be an overestimate of N if canopy cover and biomass do not correlate well.

Mineralization and nitrification rates also are altered by mining. *Simmons et al* [2008] reported net N mineralization rates of 149 kg N yr^{-1} for an unmined forested site in Maryland while the surface mined site was 99 kg N yr^{-1}. Net nitrification rates were much lower in the mined soils, with rates of 227 kg N yr^{-1} at the reference site and only 8 kg N yr^{-1} at the mined site. Since the reclaimed site in the study was managed as a mowed grassland, I assumed similar N processing may be occurring just post-reclamation, prior to the reestablishment of larger litter and vegetation pools. These rates however are likely affected by a number of factors including reclamation practices such as mine soil type and fertilizer applications and it is unclear how net processing might be changing over time.

Stream NO^{3-}-N Concentrations

NO_3^--N concentrations during comparable sampling times were significantly higher at all mined sites than the reference site ($p<0.001$) (Figure 5). Pairwise analysis showed that concentrations at the most recently mined site Zero Year (5.39 ±0.35 (mean ± standard error) mg NO_3^--N L^{-1}) was significantly higher than the two other mined sites ($p<0.0001$). Reclaimed mined sites Five Year (1.52 ±0.12 mg NO_3^--N L^{-1}) and Twenty Year (2.57 ±0.16 mg NO_3^--N L^{-1}) were also significantly difference from each other ($p <0.01$). Mean concentrations at mined sites during comparable sampling times were approximately 6-20x higher than concentrations measured at the Reference site (0.26 ±0.03 mg NO_3^--N L^{-1}). During predominantly baseflow periods (>75% baseflow), the mean concentration at Five Year appeared to decline between WY15 (3.23 ±0.17 mg NO_3^--N L^{-1}) and WY16 (1.40 ±0.22 mg NO_3^--N L^{-1}) while it remained unchanged at Reference with WY15 (0.12 ±0.02 mg NO_3^--N L^{-1}) and WY16 (0.10 ±0.01 mg NO_3^--N L^{-1}).

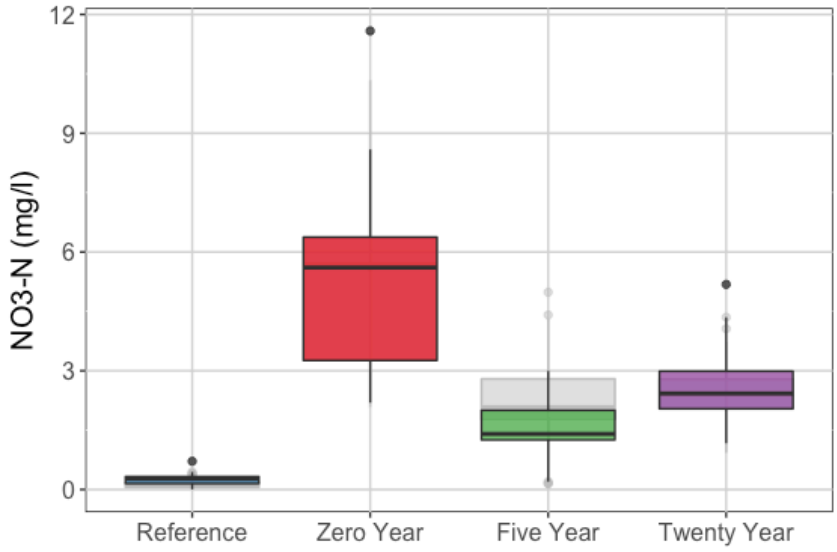

Figure 5: Boxplots of NO_3^--N Concentrations at Core Sites. Only comparable samples collected at similar times at all four sites are displayed in color (boxplots for full datasets for each site are displayed in grey). Line denotes median while the lower and upper hinges represent the first and third quartiles respectively. Whiskers denote ± 1.5 interquartile range,*

Storm Dynamics:

Storm sampling demonstrated that concentration-discharge relationships are altered by mining. During two storm events in March and April of WY15, NO_3^--N concentrations at Five Year diluted as stormflow increased, declining through the early recession and increasing during the latter part of the recession (Figure 6). Although dilution occurred, the instantaneous flux was highly responsive to discharge (Q), peaking around periods of higher flow and remaining elevated during the recession. During a much smaller WY16 October storm, concentrations diluted slightly before returning to pre-storm levels. A lack of peak flow concentration data made a similar analysis at the Reference site not possible for these storms.

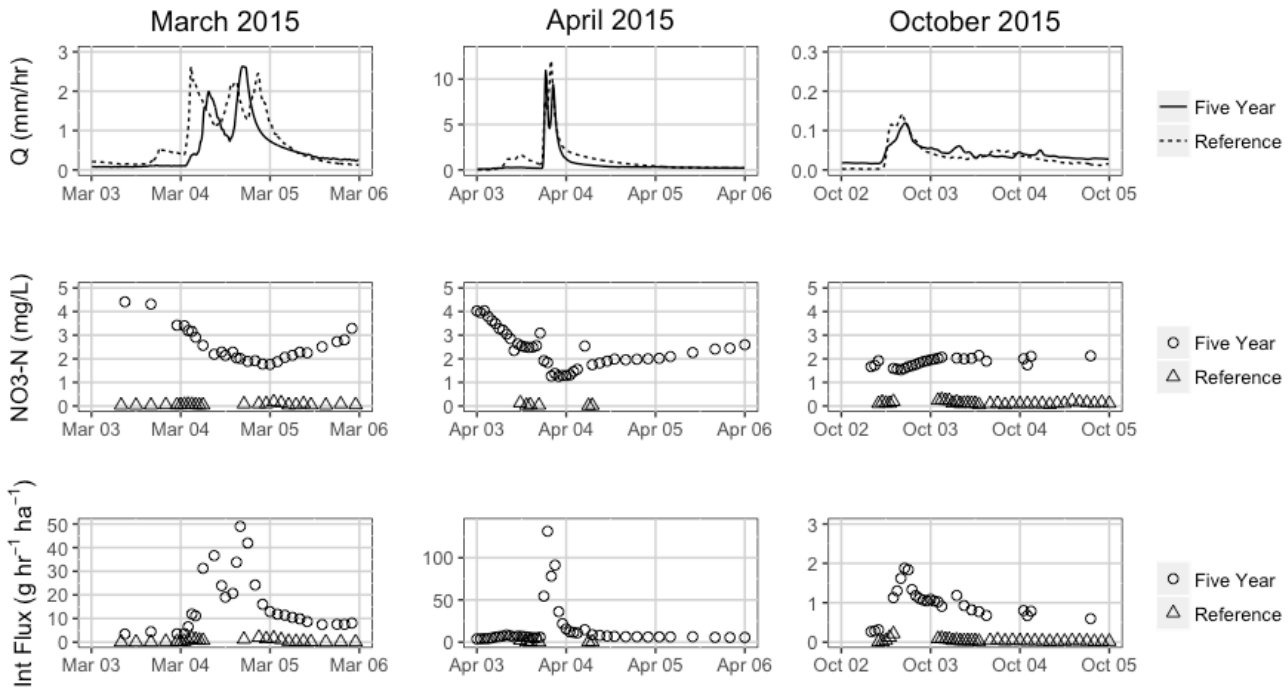

Figure 6: Storm Discharge (Q), NO_3^--N concentrations, and Instantaneous Flux (Int. Flux). March, April and October 2015 storms at MY5 (solid line and circles) and REF (dotted line and triangles) sites. Y-axis for Q and Int Flux vary by storm. Data is missing from peak stormflow for all three storms for REF.

Storm samples, collected at all four core sites during a WY16 June storm, showed between site differences in response during the storm (Figure 7). Five Year had the highest peak Q and the longest recession while Twenty Year and Reference both had much more muted responses. Due both to dry antecedent conditions and the high intensity and short duration of the storm, stormflow response was flashy compared to the other storms observed. Five Year had less dilution than in the previously discussed storms and had relatively high peak instantaneous flux compared to other mined sites. In comparison, Zero Year had lower peak flow but much higher dilution and a slightly lower response in peak instantaneous flux. Twenty Year had a substantially more dampened hydrologic response and unlike other sites, NO_3^--N concentrations increased during peak flows before declining during the latter part of the recession. The Reference sites also had increasing NO_3^--N concentrations during peak flows but both overall

magnitudes and changes in concentrations and the instantaneous flux were relatively small compared to the mined sites.

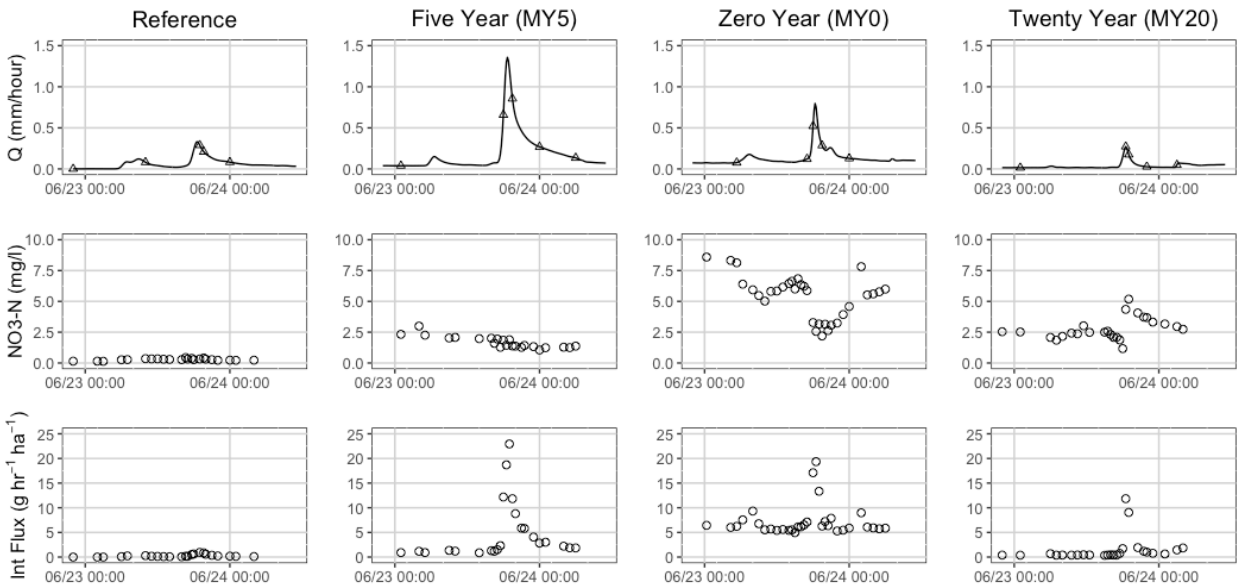

Figure 7: Storm Discharge (Q), NO_3^--N concentrations, and Instantaneous Flux (Int Flux) at June 2016 Storms at Core Sites. Triangles on hydrograph show samples used for nitrate isotope analysis.

Inorganic Nitrogen Species – WY16 June Baseflow and Storm

Across all three mined sites, NO_3^- was the dominant species of dissolved N in June baseflow and storm samples. NO_3^--N as a percentage of total dissolved nitrogen (TDN) averaged 105%, 104% and 100% for Zero Year, Five Year and Twenty Year respectively. That NO_3^--N measurements are above TDN is likely due to error propagation resulting from high NO_3^--N/TDN ratios [*Vandenbruwane et al*., 2007]. Despite this error, the results suggested almost all TDN is in the form of NO_3^--N. NH_4^+-N concentrations were low, averaging between 2-3% of TDN for all three mined sites. During the peak and falling limb of the storm hydrograph, Twenty Year and Five Year had higher TDN than DIN suggesting increased DON export during higher flows. As

measured dissolved inorganic nitrogen (DIN) was greater than TDN during baseflow, very little DON was exported at baseflow. However, due to the described measurement errors, more detailed calculation of DON for mined sites was not possible. Relative N speciation at the Reference site was distinct from mined sites. On average, the concentration of NO_3^--N was 62% of TDN, NH_4^+-N was 11% of TDN and DON was an estimated 27% of TDN for measured samples. Mean NH_4^+-N concentrations (±standard error) were slightly higher at Zero Year (0.10 ±0.01 mg N L^{-1}) than at other sites: Five Year (0.04 ±0.01 mg N L^{-1}), Twenty Year (0.05 ±0.01 mg N L^{-1}), and Reference (0.05 ±0.01 mg N L^{-1}). Precipitation samples analyzed during the June storm from the RS rain gauge had concentrations of NO_3^--N ranging from 0.22 to 0.24 mg N L^{-1}, NH_4^+-N from 0.21 to 0.37 mg N L^{-1} and TDN from 0.46 to 0.60 mg N L^{-1}.

Annual Nitrate Flux

Annual flux estimates followed similar patterns as concentrations with differences both between mined sites and reference and within the mined sites. The site specific regression models were all significant although the strength of the model to capture variance in NO_3^--N concentrations varied, depending on the site and year (Table 4). The model was less able to capture variability at Twenty Year ($R^2 = 0.18$), and stronger for Reference ($R^2 = 0.37$ (WY15) / 0.57 (WY16)), Zero Year ($R^2 = 0.64$) and Five Year ($R^2 = 0.44$ (WY15) / 0.81 (WY16)).

For WY15, annual NO_3^--N flux for Five Year was 20.4 ±2.96 kg N ha^{-1} yr^{-1} (annual mean± aggregate standard error), a 4600% increase in NO_3^--N flux from Reference (0.43 ±0.21 kg N ha^{-1} yr^{-1}) (Figure 8). For WY16, nitrate flux from Five Year sharply declined to 3.91 ±0.71 kg N ha^{-1} yr^{-1} while flux remained nearly identical at Reference at 0.43 ±0.17 kg N ha^{-1} yr^{-1}. Zero Year in

WY16 had the highest flux at 26.40 ±3.79 kg N ha^{-1} yr^{-1} while Twenty Year was slightly lower at 15.6 ±3.67 kg N ha^{-1} yr^{-1}. Across all watersheds, N exports from mined catchments are estimated to be between 9 to 61x higher than the reference. Differences between years in Five Year are attributed to a decrease in overall annual discharge and to active pumping of water out of the valley fill toe pond back onto the mine surface for several months of WY16. Cumulative discharge at Five Year declined 30% from 676.6 mm to 473.5 mm between WY15 and WY16. A similar but smaller decrease was observed at Reference where cumulative discharge decreased 15.7% from 608.9 mm in WY15 to 512.8 mm in WY16.

Table 4: Linear Modeling Results for Site Specific Flux Models

Sites		Adjusted R^2	P-value
Five Year	WY15	0.44	<0.0001
	WY16	0.81	<0.0001
Reference	WY15	0.37	<0.0001
	WY16	0.57	<0.0001
Zero Year	WY16	0.64	<0.0001
Twenty Year	WY16	0.18	<0.05

At most sites, the timing of the nitrate flux was strongly controlled by the timing of discharge at the mined and reference watersheds, although proportionally, nitrate flux tended to be elevated compared to water flux during the growing season (May to October) (Figure 9). At the Reference site, between 19% (WY 15) to 37% (WY16) of water and 31% (WY15) to 54% (WY16) of the nitrate flux was exported during the growing season (Figure 9). Of the mined sites, Twenty Year was most similar with 23% of water and 26% of nitrate exported during the growing season. Zero Year had higher export with 51% of water and 64% of nitrate exported during the growing

season. Five Year had more variable dynamics with from 32% (WY15) to 53% (WY16) of water and 29% (WY15) to 61% (WY16) of nitrate exported during the growing season.

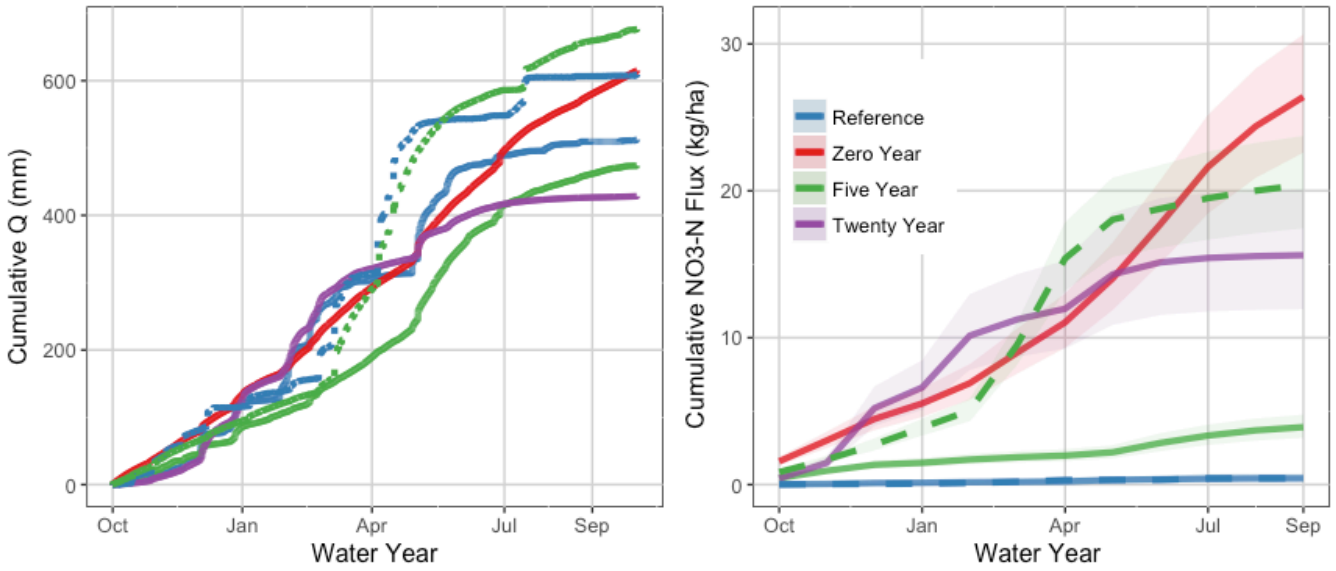

Figure 8: Cumulative Discharge (Q) and Cumulative Area Normalized NO_3^-–N Modeled Flux (kg ha^{-1}) for WY15 (dotted) and WY16 (solid) at Core Sites. WY15 only available for MY5 and REF.

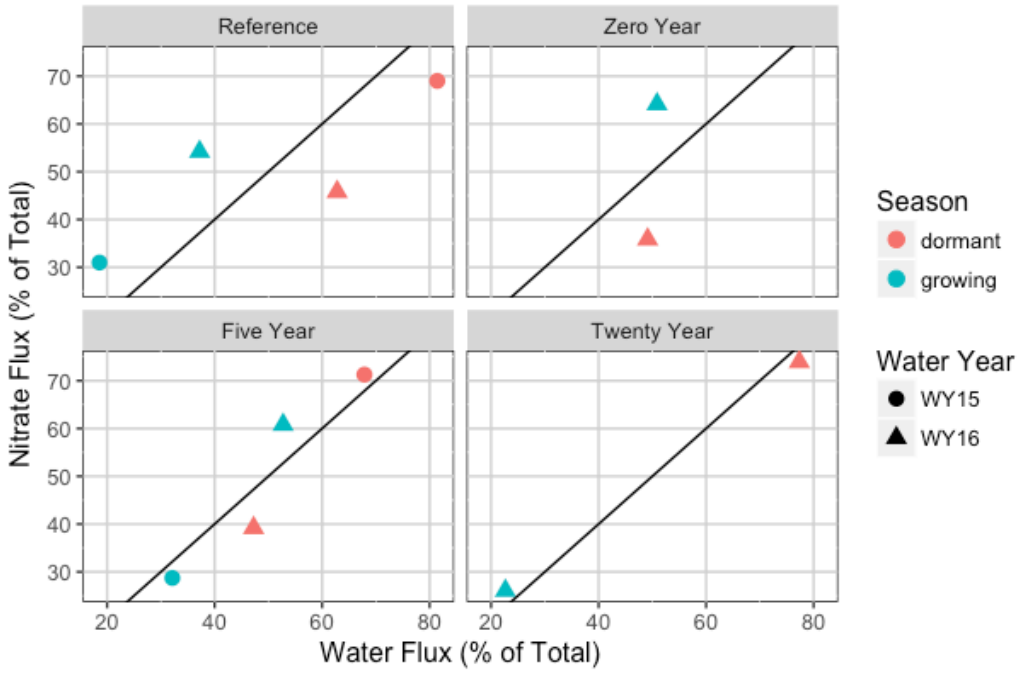

Figure 9: Seasonality of Water Flux and Modeled Annual NO_3^--N Mass Flux at Core Sites. Dormant (red) season is from November until April while growing season (blue) is from May to October. Black line is the 1:1 line.

Historic Observations

Comparison of sampling dates with PRISM rainfall data revealed historic sampling data was all taken during baseflow periods. However, the screening process did remove all storm samples and several grab samples from the 2015-2016 sampling campaign due to wet conditions. A pattern of declining mean NO_3^--N concentrations at baseflow was observed for all analyzed sites and at three sites, Sugar Tree ($p<0.001$), Stanley Fork ($p<0.001$) and Zero Year ($p<0.01$), there were significant declines in mean concentrations between the study periods (Figure 10). In 2001, Sugar Tree (last mined in 2007) had very high mean concentrations of 13.5 ±2.1 mg NO_3^--N L^{-1}, which declined by 2010 to 1.9 ±0.2 mg NO_3^--N L^{-1}, and continued to decline to 0.6 ±0.1 mg NO_3^--N L^{-1}in 2015-2016. The first sampling in Stanley Fork (last mined in 1998) reported mean NO_3^--N concentrations of 3.4 ±0.16 mg/L in 2001, which declined to 1.4 ±0.1 mg NO_3^--N L^{-1} in 2010, and to 0.7 ±0.1 mg NO_3^--N L^{-1}in 2015-2016. In Zero Year (last mined in 2015) mean NO_3^--N concentrations were very high when sampled during the active mining phase 14.2 ±1.6 mg NO_3^--N L^{-1}in 2010 and still quite elevated when sampled 5 years later (5.7 ±1.0 mg NO_3^--N L^{-1}in 2015-2016). At Five Year, no significant change in mean concentrations was observed between 2010 (3.3 ±1.0 mg N L^{-1}) in and 2015-16 (2.4 ±0.2 mg NO_3^--N L^{-1}). No matter the number of years post mining, all samples collected from mining impacted streams had mg NO_3^--N concentrations above the mean DIN concentrations of our reference catchment.

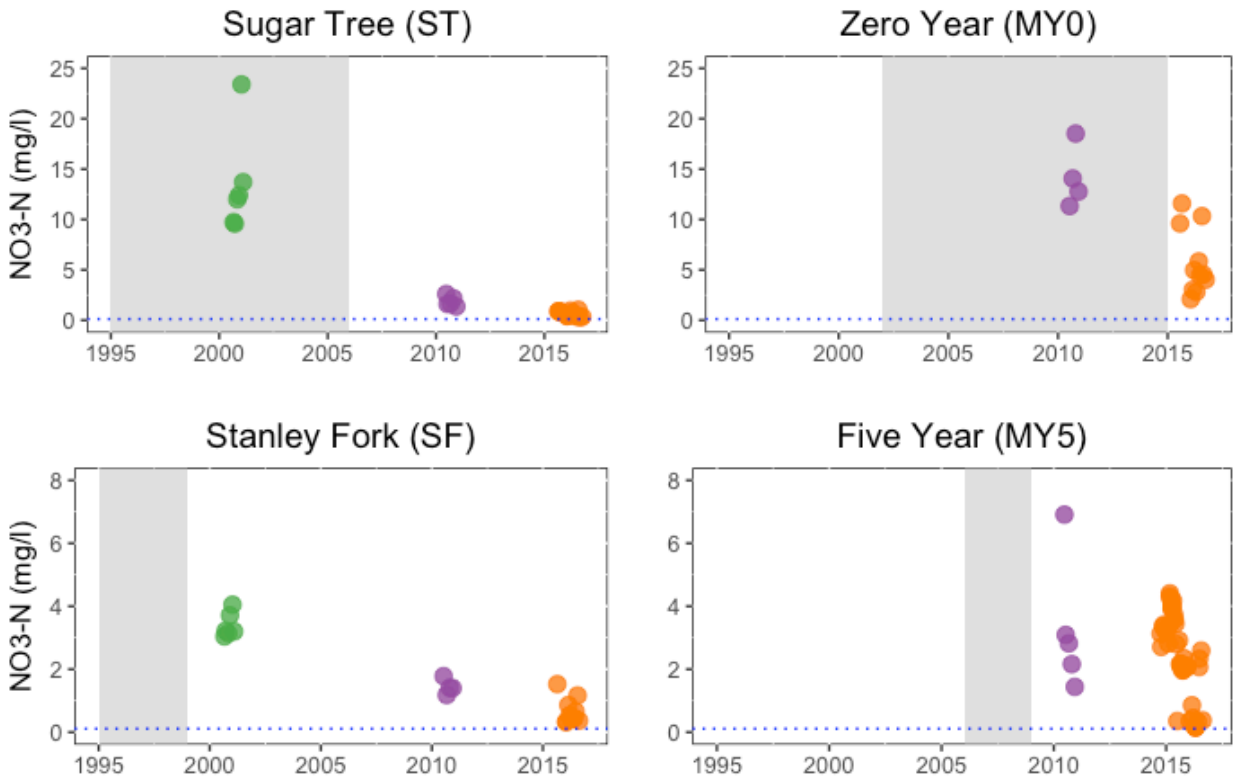

Figure 10: Baseflow Concentrations over Time. Historic data was collected by Bryant et al. (green) in 2000-2001, Lindberg et al. (purple). Data from the current study (orange) ranges from 2014-2016. The grey box shows periods where ongoing active mining was occurring and the dotted blue line represents the mean concentration at REF.

DIN Export in Nitrogen Budget

Based on this studies' analysis of NO_3^--N concentrations over time (Figure 10), I assumed (Figure 4) that rapid declines occurred after active mining ended, followed by more gradual declines after reclamation. Assuming negligible export of NH_4^+ compared to NO_3^-, I bounded the estimated DIN export for a recently reclaimed site to between 20 to 27 kg N ha^{-1} yr^{-1} with the low value being the Five Year WY15 flux and the high value as the Zero Year WY16 flux (Figure 8). The results from Five Year and Twenty Year were used to create a range of yearly DIN export for a watershed mined 10 years ago (4 to 20 kg ha^{-1} yr^{-1}).

Isotopic Analysis

Isotopic ratios of $\delta^{15}N$ in stream water at mine sites were enriched at baseflow relative to known N sources and were enriched in both $\delta^{15}N$ and $\delta^{18}O$ relative to the stream water at the Reference site (Figure 11). At baseflow, more recently mined sites were also more enriched than older sites with Zero Year having the most enriched ratios ($\delta^{15}N$ of NO_3^- was +24.03‰ and $\delta^{18}O$ of NO_3^- was +19.02‰). In comparison, during baseflow, NO_3^- isotopic ratios at the Reference site were much less enriched (+3.03‰ $\delta^{15}N$ and +3.73‰ δ18O). The combined enriched $\delta^{15}N$ / $\delta^{18}O$ signal at mined sites was unlike any endmember expected based on reported potential source ratios. Reported $\delta^{15}N$ values for N in coal from other regions range between -0.7‰ to +10.7‰ [*Holloway and Dahlgren*, 2002]. Nitrate from explosives and synthetic fertilizer both have high + $\delta^{18}O$ (20‰ to 22‰ (explosives), 20‰ to 26‰ (fertilizer)) and low + $\delta^{15}N$ (2‰ to 3‰ (explosives), -2‰ to 2 ‰ (nitrogen)) while nitrified ammonium from these sources would more resemble soils and have low $\delta^{15}N$ (-10‰ to +5‰) & $\delta^{18}O$ (-15‰ to + 15‰) [*Kendall et al*., 2008; *Degnan et al*., 2016]. Given the potential source pools, the highly enriched signal observed in our mined streams seems to be consistent with strong fractionation during denitrification which selects for the light isotopes of NO_3^- and thus enriches both $\delta^{15}N$ and $\delta^{18}O$ in remaining nitrate pools on a slope between 1:1 and 2:1. Fractionation from denitrification has been found to be more pronounced when nitrate pool sizes are large [*Kendall et al*., 2008], a condition the seems likely to be the case in mined landscapes given the findings of this study.

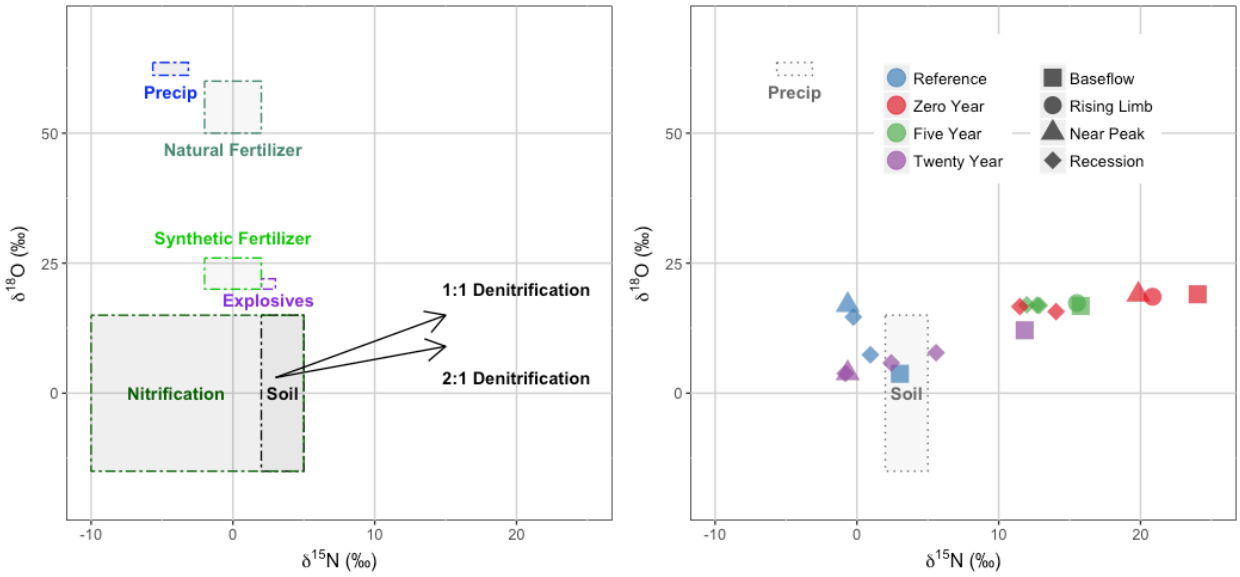

Figure 11: Nitrate Isotope Ratios for Endmembers (left) and June Storm (right). Core sites are identified by color and relative hydrograph position of sample is identified by shape. Baseflow (square) were sampled prior to storm, rising limb (circle) were taken before peak flow, near peak (triangle) were collected just before or after peak flow, and recession (diamond) were collected post peak flow. Precipitation (Precip) endmember is derived from samples taken from RS rain gauge during storm. Other end members are derived from literature values.

Two precipitation samples collected at the RS rain gauge from the June storm had $\delta^{15}N$ ranging from -5.65‰ to -3.14 ‰ and $\delta^{18}O$ from 61.12‰ to 63.58‰, falling within reported ranges for precipitation $\delta^{15}N$ (–15‰ to +15‰) and just at the low end of reported ranges for precipitation $\delta^{18}O$ (+63‰ to +94‰) [*Kendall et al.*, 2008]. During the June storm sampling, $\delta^{15}N$ at Reference became more depleted (range: -0.65‰ to 0.95‰) while $\delta^{18}O$ became further enriched (range: 7.38‰ to 16.95‰) relative to baseflow (Figure 11). Ratios at Reference were most similar to rainfall during the peak and falling limb of the storm. At Zero Year, during the storm, $\delta^{15}N$ depleted from baseflow (range: 11.49‰ to 20.85‰) while $\delta^{18}O$ had smaller depletion (range: 15.89‰ to 18.95‰). Five Year had similar, but smaller depletion in $\delta^{15}N$ (range: 11.98‰ to 15.51‰) but enrichment in $\delta^{18}O$ (range: 16.87‰ to 17.33‰). Twenty Year exhibited different behavior with large depletions in both $\delta^{15}N$ (range: –0.82‰ to 5.58‰) and $\delta^{18}O$ (range: 3.81‰

to 7.78‰). Ratios at Twenty Year during the peak streamflow and falling limb fall in ranges similar to reported soil and nitrification pools.

Regional Analysis:

Analysis of regional trends indicated significant positive correlations between mining extent and sulfate in three basins, but only Coal River had a corresponding positive correlations between mining extent and mean annual Nitrate-N (Table 3, Figure 12). Both active mining and cumulative mining were equally strong predictors of NO_3^--N concentrations in Coal River (R^2 = 0.52). Coal River had the highest percent cumulative mining (11.8% of basin) of any basin by the end of the study period (2015) and also the highest active mining extent (~6% of basin). No other basin had more than ~4% of the basin actively mined in a given year. A declining significant correlations was found between cumulative mining and mean annual NO_3^--N in the Gauley River, although only 3.8% of the catchment had been mined by 2015. For sulfate, which is a more conservative tracer, known to be associated with coal mining [*Palmer et al*., 2010], two basins, Coal River and Tug Fork had significant correlations between mean annual sulfate concentrations and both active and cumulative mining extent while Twelvepole had a significant correlation only with cumulative mining.

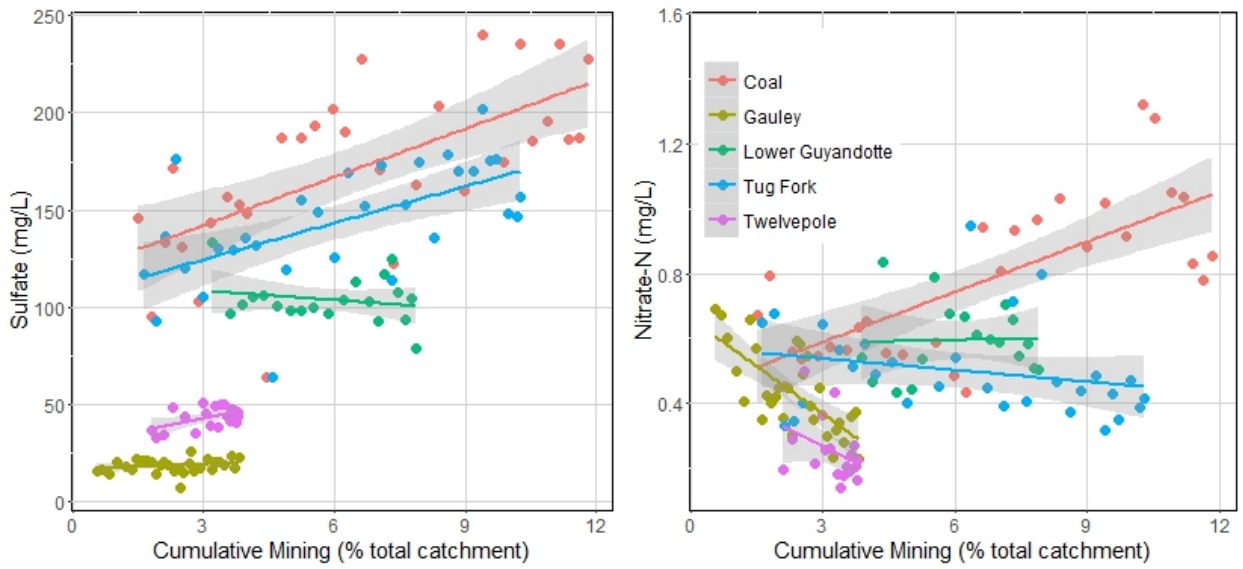

Figure 12: Scatterplot of Mean Annual Sulfate (left) and Nitrate-N (right) Concentrations Compared to Cumulative Mining (% of total catchment). Solid lines represent linear relationship and grey ribbon is the 95% confidence interval. Basins are represented by differing colors.

Discussion

The results show that MTM alters nitrogen export, dramatically increasing NO_3^--N concentrations and mass flux in mined streams compared to a reference site. Temporal trends were observed between the most recently mined site Zero Year and the older mined sites. Zero Year had significantly higher concentrations and higher annual flux that the older mined sites, which themselves both still had significantly elevated concentrations and annual flux compared to the Reference. More revealing are the findings from comparing baseflow concentrations between 2000, 2010, and 2015-2016, which document significant declines in baseflow NO_3^- concentrations and export over time following mining. At Sugar Tree and Zero Year, steep declines in NO_3^--N were observed between samples collected during periods of active mining and subsequent sampling efforts. This supports Lindberg et. al (2010)'s space-for-time inferred conclusion that actively mined sites have significantly higher nitrate concentrations than

reclaimed sites. Neither Stanley Fork nor Five Year were sampled during active mining which may explain why NO_3^--N concentrations were lower overall at these sites.

The variation in mean NO_3^--N concentrations between years at Five Year coupled with the lack of significant declines between 2010 and 2015 at Five Year suggest that factors influencing export rates are more complex than simply time since mining. At Five Year, some of the variation is likely due to active reclamation efforts like the observed pumping that occurred in WY16. Additionally, other studies have shown there are limitations in using space-for-time approaches between MTM sites to understand temporal patterns in solute fluxes because between inter-site variability in mined catchments can be quite high [*Evans et al*., 2014]. Catchments can differ in mining and reclamation practices, valley fill size and fill materials, topography and microclimate. Nevertheless, the result that the WY16 flux at Twenty Year was over an order of magnitude higher than Reference demonstrates elevated NO_3^--N export can persist for more than two decades after the cessation of active mining.

This raises the question of what is driving this persistence of this elevated N export. The development of the N budget strongly suggests that N residues of explosives could drive high N export during active mining (Figure 3 & 4). Other sources are either too low to explain the observed flux (atmospheric deposition, rock weathering) or are not important inputs until later in the mining process (fertilizer, N fixation by planted legumes). However, the budget does not reveal whether long-term sources are lingering residuals of pulse inputs or the result of persistent sources that are generating and then mobilizing nitrate in-situ in the watershed. Another consideration is that different N sources are heterogeneously distributed in the watershed.

Atmospheric deposition, fertilizer and mineralization/nitrification in soils all are inputs occurring at or near the surface and as such are affected by vegetative uptake and microbial immobilization. As soils are initially N poor and see relatively rapid N aggregation rates, it seems likely that a large fraction of these inputs could be retained by vegetation and within surface soils.

Residue from explosives mixed into waste rock and rock weathering derived nitrogen both will be present below the rooting depth, deeper in the subsurface in the spoils and exposed to water moving through valley fills. Some large fraction of these nitrogen rich residues are likely to be inaccessible to surface vegetation, making it more easily mobilized and exported. One potential explanation for the persistence of export over time is that instability and weathering in valley fills may cause shifting in the rock and altered preferential flow pathways, allowing for nitrogen in previously hydrologically inactive areas to become mobilized. If deeper subsoil conditions are at least sometimes anoxic and contain sufficient carbon, another potential pathway is for this nitrogen to be denitrified. Denitrification may help explain why we do not observe even greater export given the very large potential loading from explosives.

Supporting the concept that landscape position of N sources may matter, at a surface coal mine without a valley fill, *Simmons et al*. [2008] found significantly lower N export in a reclaimed catchment than a reference catchment and ascribed this difference to the reduction of nitrification and limitation of N in the reclaimed soils. At first, this result may appear contradictory to increased N export from mining reported here. However, just as hydrologic changes at surface mines may be controlled by the presence of a valley fill [*Nippgen et al.,* 2017, *in review*], I

speculate that the valley fill might be also be a controlling factor as to whether N export is elevated, particularly once reclamation is complete and new vegetation becomes established in the catchment.

Our isotopic analysis of stream water NO_3^- also qualitatively suggests that subsurface sourcing and cycling might be the dominant driver of observed N export, particularly in more recently mined sites. At baseflow, all the mined catchments had elevated nitrate concentrations and similarly enriched isotopic signatures when compared to the reference site (Figure 11). At mined catchments, baseflow reflects drainage through spoils and valley fills. 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. At the newer mine sites (Zero Year and Five Year), the dilution pattern during storms (Figures 6 & 7) and the depletion during June stormflow of only $\delta^{15}N$ but not $\delta^{18}O$ (possibly suggesting mixing with rainwater) provide further evidence that the primary nitrate source is from the subsurface. In contrast, at Twenty Year, there is also evidence of an altered or additional source of loading during stormflow not found at the other mined sites. NO_3^--N concentrations at Twenty Year increased during the June storm and remained elevated during the stormflow recession. Simultaneously, the isotopic ratio strongly depleted in both $\delta^{15}N$ and $\delta^{18}O$ during the stormflow, more strongly matching endmembers for a soil pool source for NO_3^--N. As Twenty Year has had increased time for soil and vegetation redevelopment and increases in their respective N pool sizes and cycling rates, I speculate that this storm mobilized NO_3^--N from soil pore water in addition to N sources within the fill.

At the regional scale, of the three basins where sulfate concentrations were significantly correlated with mining extent, only one, the Coal River basin, also had a significant correlation between nitrate and mining. Given that nitrate is non-conservative, and many other sources of N loading (wastewater, fertilizers) exist in these larger basins, it is not surprising that more sites had significant correlations for sulfate. Sulfate is both exported at rates over an orders of magnitude higher than nitrate and, at these concentrations, should saturate any biological demand within receiving streams. Coal River had both the most cumulative mining impact and the highest % of the catchment being actively mined, making it the most likely candidate for downstream effects to be observable, particularly if highest N export occurs during active mining phases.

Conclusion

This study reports, for the first time, the magnitude and persistence of enhanced stream N loading resulting from mountaintop removal coal mining. In a region that otherwise is predominantly forested, mining represents a new source of N loading to headwater streams and downstream receiving waters. Mining introduces large pulsed inputs of nitrogen from explosive and fertilizer while creating hydrologic, geological, and ecological conditions that enable in-situ production and flushing of soluble nitrogen. Elevated nitrate in streams can disrupt local ecological function and likely exacerbates ecological impairments caused by other mining derived solutes and pollutants. It also creates increased risks of eutrophication in downstream lakes and reservoirs and has been measured in some mined streams at levels above EPA safe drinking water standards.

The study also raises new concerns about the use and management of explosives at surface coal mines. There is a lack of peer reviewed research on the nutrient impacts on streams and groundwater from explosives from coal mining or even from other uses (although see *Degnan et. al* [2016] for an example). Moreover, as most states in the United States lack comprehensive nitrogen standards and regulating nitrogen in NPDES permits remains rare, there is also a lack of regulatory frameworks to address the issue. More research is needed to better identify if persistently elevated nitrate export is being driven by residual inputs or in-situ generation. Better understanding the nitrate source will help in the development and implementation of prevention and/or mitigation strategies. Lastly, more research and monitoring is needed at other MTM sites to better understand how factors such as rock lithology, mining and reclamation practices and valley fill construction affect N loading and export. More in-depth studies at instrumented MTM and valley fills should also be conducted to both better quantify N inputs and stocks, and better trace the fate of nitrogen through the landscape.

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