

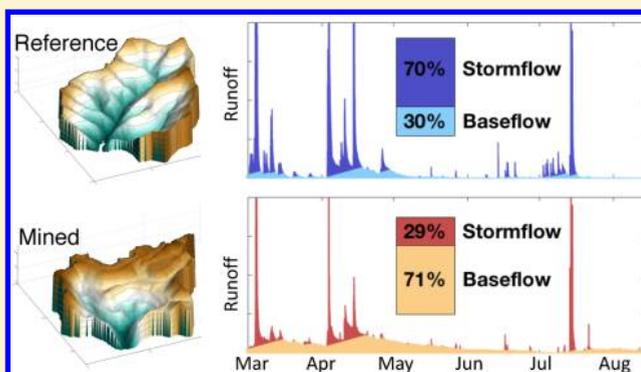
## Creating a More Perennial Problem? Mountaintop Removal Coal Mining Enhances and Sustains Saline Baseflows of Appalachian Watersheds

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**ABSTRACT:** Mountaintop removal coal mining (MTM) is a form of surface mining where ridges and mountain tops are removed with explosives to access underlying coal seams. The crushed rock material is subsequently deposited in headwater valley fills (VF). We examined how this added water storage potential affects streamflow using a paired watershed approach consisting of two sets of mined and unmined watersheds in West Virginia. The mined watersheds exported 7–11% more water than the reference watersheds, primarily due to higher and more sustained baseflows. The mined watersheds exported only ~1/3 of their streamflow during storms, while the reference watersheds exported ~2/3 of their annual water yield during runoff events. Mined watersheds with valley fills appear to store precipitation for considerable periods of time and steadily export this alkaline and saline water even during the dry periods of the year. As a result, MTMVs in a mixed mined/unmined watershed contributed disproportionately to streamflow during baseflow periods (up to >90% of flow). Because MTMVs have both elevated summer baseflows and continuously high concentrations of total dissolved solids, their regional impact on water quantity and quality will be most extreme and most widespread during low flow periods.



### INTRODUCTION

Humans have manipulated their environment on a detectable scale for thousands of years since at least the onset of agriculture.<sup>1,2</sup> Today, the anthropogenic impacts on the landscape include, among others, large-scale deforestation,<sup>3</sup> agriculture,<sup>4</sup> under- and above-ground mining for coal and other natural resources,<sup>5,6</sup> tar sand mining,<sup>7</sup> damming of major rivers,<sup>8,9</sup> urbanization,<sup>10</sup> and wars.<sup>11,12</sup> The earth layer affected by those disturbances has recently been referred to as the critical zone<sup>13</sup> and includes vegetation, soils, and groundwater-bearing bedrock. Disturbances of the critical zone occur across the planet,<sup>14</sup> so it is important to understand how physical and biological parameters are altered in order to evaluate the ramifications for encompassing ecosystems. Assessing the quantitative and qualitative change in hydrologic fluxes during and after these landscape alterations is often a crucial first step for understanding ecosystem wide transformations, as hydrology has been recognized as a driver for multiple ecosystem processes throughout the critical zone, such as nutrient or contaminant export,<sup>15,16</sup> aquatic biodiversity,<sup>17,18</sup> and human well-being.<sup>19</sup>

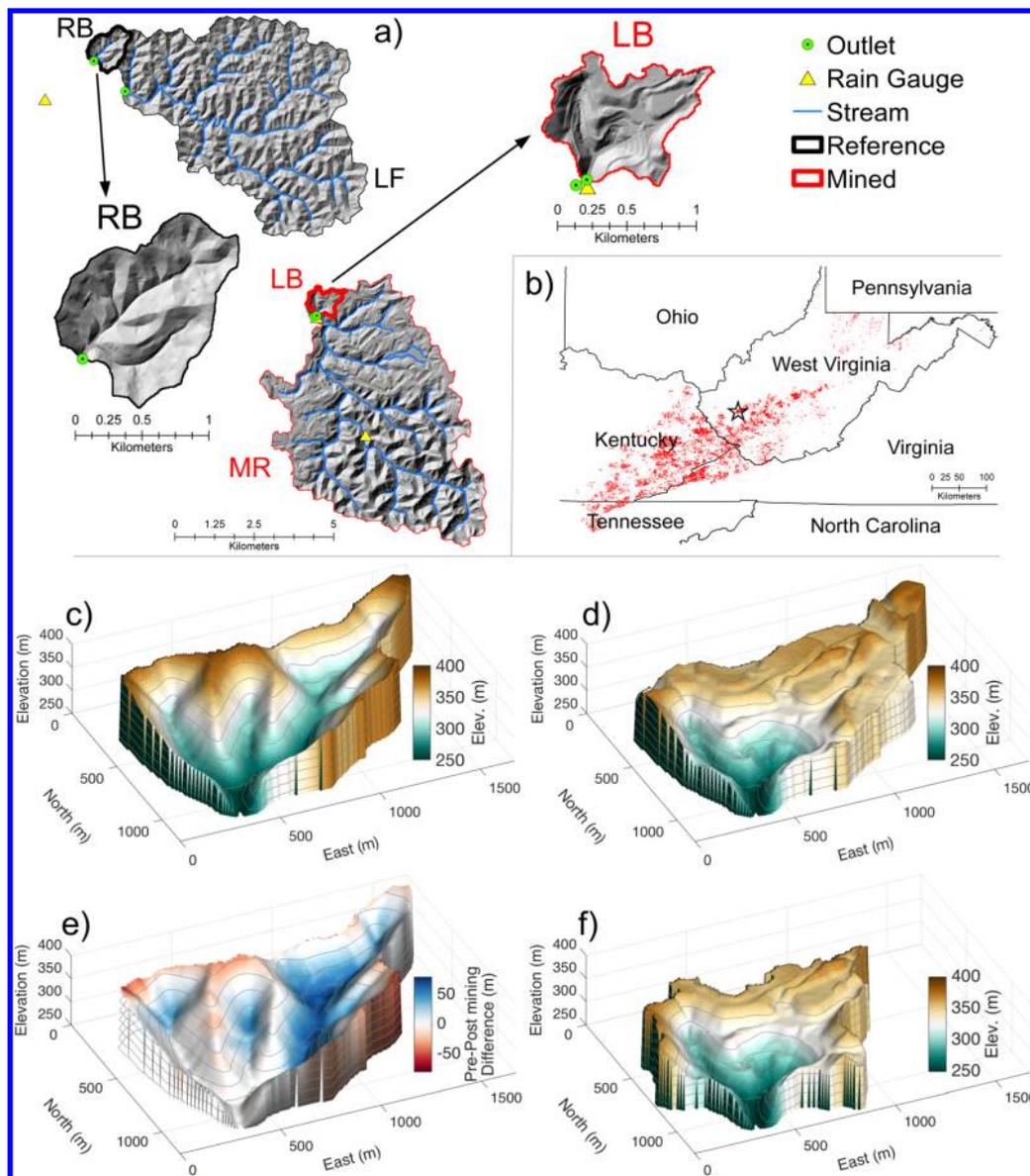
Here, we present an example of hydrologic change from a large-scale mining disturbance, which is common in the USA but is also practiced in other parts of the world, e.g., Canada<sup>20</sup> and China.<sup>21</sup> Mountaintop removal coal mining with valley fills

(MTMVF) is a surface-mining procedure during which the tops of mountains and ridges are removed to access underlying coal seams. The resulting rock material is subsequently deposited into adjacent valleys.<sup>22</sup> These valley fills (VF), designed as permanent storage for excess spoil and to reduce landslides on reclaimed mine areas,<sup>23</sup> are estimated to have buried up to 4000 km of headwater streams.<sup>24</sup> MTMVF is endemic to the Appalachian coal region of Kentucky, Tennessee, Virginia, and West Virginia (Figure 1b), where it became more prevalent in the 1990s. The US Environmental Protection Agency estimated that as of 2012 surface mines would cover approximately 7% of the region.<sup>24</sup> In contrast to many other disturbances that either do not extend into the bedrock at all or only to a limited degree (e.g., deforestation, urbanization, agriculture) and mainly affect vegetation or infiltration capacities,<sup>25</sup> MTMVF can disturb the critical zone hundreds of meters deep.<sup>24,26</sup> This disturbance happens both in former mountaintop and ridge areas where bedrock is removed up to hundreds of meters deep through explosion and in the valleys, where the crushed rock is deposited on the ground surface, essentially adding a highly

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**Figure 1.** a) Location of the four study watersheds relative to other. Red outline denotes mined watersheds, black outline reference watersheds; b) Appalachian coal region, highlighted in red are mining impacted areas; c) LB topography pre-mining; d) LB topography post-mining; e) elevation changes in LB from pre- to post-mining; f) LB with post-mining delineated watershed boundaries. Maps of the mined watersheds were generated using LiDAR data made available by the West Virginia Department of Environmental Protection (<http://tagis.dep.wv.gov/home>). Maps of the reference sites were generated using elevation data from the National Elevation Dataset (<https://lta.cr.usgs.gov/NED>).

disturbed layer to the critical zone.<sup>26</sup> Despite the scale and nature of the disturbance, MTMVF has only recently received more focused attention from the hydrologic community,<sup>27–32</sup> but basic knowledge gaps remain as to how the dramatic changes in topography and critical zone associated with MTMVF affect hydrologic response and long-term hydrologic regimes of watersheds.

While some forms of surface mining (e.g., strip and contour mining) lead to increased peak flows and overall water export due to the compaction of soils and spoil during reclamation,<sup>33–36</sup> MTMVF areas feature large volumes of crushed rock, which could increase watershed storage. Ross et al.<sup>26</sup> estimated volumes of ~1500 Appalachian valley fills and conservatively concluded that mining could increase the water storage capacity of mined watersheds by a factor of 10 but that individual valley fills were highly variable in size.

Empirical evidence for this enhanced-storage effect is limited, relatively recent, and in parts confounded by other disturbances present in the study watersheds. Messenger and Paybins<sup>30</sup> reported increased runoff volumes in a small first-order mined watershed in West Virginia relative to an unmined watershed and attributed the increase in baseflow to the greater storage potential of the mined watershed. Somewhat surprisingly, they also found that during large events, the mined watershed would export more water than the unmined watershed. On a larger scale, Zegre et al.<sup>28</sup> did not detect significant changes in annual streamflow in a 1000 km<sup>2</sup> watershed in West Virginia over a 16-year period despite increasing mining activities. It was noted by the authors that only a limited area was affected by mining (9% of the surface area). When they extended the time series to ~40 years, Zegre et al.<sup>31</sup> were able to detect decreases in streamflow maxima and small but statistically significant increases in

baseflow contributions for the same watershed that were consistent with Messinger and Paybins.<sup>30</sup> However, in addition to mountaintop mining, their research watershed was also affected by extensive subsurface mining, making direct inferences to mountaintop mining difficult.<sup>31,37</sup>

In addition to changes in water yield, the disturbance of the critical zone caused by mountaintop mining also leads to degraded streamwater quality. Precipitation that enters MTMVF watersheds flows through a reactive matrix of pyrite and calcareous bedrock that, via strong acid weathering, releases large amounts of various ions, such as  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  (e.g., ref 38), as well as the toxic pollutant selenium.<sup>20,39</sup> Together, these constituents increase the salinity and pH of streams draining mines in a well-documented phenomenon of alkaline mine drainage.<sup>38,40,41</sup> Alkaline mine drainage has been shown to negatively impact stream biota<sup>42–45</sup> in as much as 22% of streams in central Appalachia.<sup>40</sup> However, the mechanisms and timing of stream impairment caused by mountaintop mining are tightly coupled to hydrologic processes and are hence not well understood.

We quantified water yield and water quality changes in stormflow and baseflow behavior for two sets of mined and unmined watersheds in West Virginia. MTMVF was the dominant disturbance present in our research watersheds, allowing for direct inferences of observed changes to the critical zone disturbance. We used high-resolution streamflow gauging, high-resolution specific conductance monitoring (a proxy for salinity), precipitation monitoring, landscape analysis, and empirical baseflow separation methods for 12 months of rainfall, runoff data, to address the following questions:

- (1) To what degree does mountaintop mining alter baseflow and stormflow contributions to total runoff and does this effect change with increasing watershed scale?
- (2) How does MTMVF affect the export of total dissolved solids?
- (3) How do mined and unmined portions of partially mined watershed contribute to runoff across hydrologic seasons?
- (4) How do hydrologic changes associated with MTMVF compare to other disturbances?

## METHODS

**Site Description.** The Mud River watershed is located in southwestern West Virginia, approximately 40 km southwest of Charleston. The four study watersheds were paired (first and fourth order) based on size and the presence or absence of mining (Figure 1a). The 68 ha Laurel Branch (LB) watershed, a tributary to the Mud River, is approximately 95% mined, while 46% of the 3672 ha Mud River (MR) watershed into which LB flows is in active or reclaimed mines. The majority of mining in MR (>90%) happened between 1985 and 2005. The youngest mines are located in the northern part of MR—which contains the LB subwatershed—where mining began after 2005.<sup>39</sup> The unmined reference sites include the 3463 ha Left Fork (LF) of the Mud River and the 118 ha Rich's Branch (RB), a tributary to the Left Fork River. There are no known deep mines in the area<sup>29</sup> that could confound the analyses and interpretations through legacy effects.<sup>37,46</sup> We were not able to collect data in the mined watersheds before the mining activity started. However, since the watersheds were similar in size and topography and are close to one another, we will refer to the unmined watersheds as the reference watersheds.

Soils in the unmined areas of the four watersheds are generally shallow (<2 m), well-drained silty loams or sandy loams with moderate to rapid permeability ratings.<sup>47,48</sup> The underlying geology consists of alternating layers of siltstone, sandstone, and shale.<sup>49</sup> Vegetation in the unmined areas is mixed mesophytic forest,<sup>50</sup> and the mined portions are either barren or with herbaceous and shrub cover. Median vegetation height derived from Lidar data (first returns minus last returns) was 0.3 m in LB and 0.4 m in MR. The Lidar data did not cover the reference watersheds. However, median vegetation height in the unmined parts of MR, which are representative for the vegetation in the reference sites, was 24 m. Average annual precipitation in the base period 1981–2010 was 1183 mm.<sup>51</sup> Precipitation is relatively homogeneously distributed over the year with slightly wetter months during the summer. Average annual air temperature for the 1981–2010 base period was 12.7°. The growing season in this area extends from May through October (data from the Fernow Experimental Forest, about 230 km northeast of our study sites<sup>52</sup>).

**Spatial Analysis.** We used pre- and postmining digital elevation models and methods developed by Ross et al.<sup>26</sup> to quantify the geomorphic changes associated with MTMVF in LB and MR (slope, change of watershed area pre- to postmining, estimate of VF volumes).

**Hydrologic Measurements.** The study period encompassed the 2015 water year (10/01/2014–10/01/2015). Precipitation was measured at three different locations (Figure 1a) using *Onset* HOBO RG3 rain gauges and data loggers recording at 10 min intervals. The small watersheds (RB and LB) were assigned the precipitation of the closest rain gauge, while the larger LF and MR were assigned precipitation values based on inverse distance weighting with the two closest rain gauges. The rain gauges had on average ~11% missing data; however, the gauge near LB was swept away during a major flooding event in April and had ~30% of the data missing. Missing data at each rain gauge were detected and filled using double mass curves with adjacent rain gauges.<sup>53</sup>

Open-channel streamwater levels and specific conductance (SC), a measure of the ionic strength of a water sample, were recorded at 10 min intervals with *Onset* HOBO Water Level loggers and *Onset* HOBO Specific conductance loggers, respectively, during the entire period, with redundant *Decagon* CTD sensors connected to *Campbell Scientific* CR1000 data loggers beginning January 2015. We developed stage–discharge rating curves at each gauging site with >13 manual runoff ( $Q$ ) measurements over a range of observed discharge. At LB, we manually measured the maximum observed runoff of the water year. At RB, LF, and MR, bank-full Gauckler–Manning<sup>54</sup> estimates of  $Q$  were used to restrict the rating curves at high water levels. Water levels were above bank for <3% of the water year at LF, and <1% at RB and MR. Missing data at RB from 10/14/2014 to 10/26/2014 was filled by interpolation since no precipitation was recorded during this time. During a major precipitation event on April 3, both RB and LF experienced backflow from the Mud River Reservoir downstream of the gauging sites, affecting the falling limbs of the hydrographs. The affected time periods were corrected using two-term exponential regression models. The LB gauging site experienced backflow from the Mud River during the falling limb of three storms (March 4, April 3, and July 14), which were corrected using a regression with water level data from a sensor approximately 100 m upstream.

Throughout the study period, the specific conductance sensors experienced drift caused by either deposition of dissolved particulates onto the electrodes or by becoming covered in sediment. We assumed a linear drift in the SC data and corrected the drift using measurements from a hand-held SC meter at biweekly intervals.

From 06/27/2015 to 07/20/2015, the mining company began intermittently pumping water out of a small retention pond 150 m upstream of the gauging station, thereby affecting the LB stream levels. The water was pumped to another pond uphill of the LB valley fills. We believe the water remained in the LB watershed.

**Hydrologic Analysis.** We used three different hydrograph-based methods to separate baseflow from stormflow. The first method was similar to the approach proposed by Hewlett and Hibbert,<sup>55</sup> where baseflow rises at a constant rate after the onset of precipitation. The rate of baseflow rise was the same for each watershed and was chosen so that the small reference watershed exhibited a baseflow percentage that corresponds to the ~30% USGS estimate of baseflow for the Mud River watershed.<sup>56</sup> The second method was the “local minimum” method, which searches the hydrograph for local minima over specified periods of time.<sup>57</sup> For this method, the 10 min data was aggregated to daily values. The third method was an adaptation of the “constant- $k$ ” method proposed by Blume et al.<sup>58</sup> The approach initially requires the computation of a modified recession constant,  $k^*$ , as

$$k^* = \frac{dQ}{dt} \times \frac{1}{Q_{\text{mean}}}$$

Assuming an exponential recession curve in the case of a linear groundwater reservoir,  $k^*$  should become approximately 0 (or constant) when the stormflow portion of the hydrograph ends. Baseflow was then delineated as a straight line with slope 0 from the beginning of the runoff event to the end of stormflow (the time during which  $k^* \neq 0$ ). Originally developed for event-hydrograph separation, we extended the method to the length of the study period. Since  $k^*$  fluctuates around 0 rather than becoming 0, even during long periods without precipitation, we assumed constancy in  $k^*$  when  $-0.001 \leq k^* \leq 0.001$ . To attenuate sensor-related jumps in the  $Q$  time series, we calculated  $k^*$  using a 4-h running average.

Further, we calculated flow duration curves for all watersheds as well as cumulative  $Q$  totals to compare peak and baseflow behavior between the reference and the mined sites as well as potential changes in the seasonal timing of water delivery.

In addition to the hydrograph separation to distinguish between stormflow and baseflow, we estimated the contributions from the mined and unmined areas in MR with a simple two-component hydrograph separation using specific conductance of RB (reference) and LB (mined) as the two endmembers, following Pinder and Jones<sup>59</sup>

$$Q_{\text{MR}} = Q_{\text{unmined}} + Q_{\text{mined}}$$

$$Q_{\text{MR}} SC_{\text{MR}} = Q_{\text{unmined}} SC_{\text{unmined}} + Q_{\text{mined}} SC_{\text{mined}}$$

$$Q_{\text{mined}} = Q_{\text{MR}} \left( \frac{SC_{\text{unmined}} - SC_{\text{MR7}}}{SC_{\text{unmined}} - SC_{\text{mined}}} \right)$$

with  $Q$  being runoff and  $SC$  being specific conductance. This approach has been applied in many geographic regions using different chemical signatures to distinguish endmembers,<sup>60–62</sup>

including specific conductance.<sup>63–67</sup> Similar to the baseflow separation we calculated cumulative fluxes for the mined and unmined areas for the entire water year and broken up into baseflow and stormflow periods using the Hewlett and Hibbert baseflow separation.

## RESULTS

**Spatial Analysis.** The size of LB changed from 99 ha premining to 68 ha postmining, a 31% reduction in area (Figure 1c–f). MR increased in size from 3582 ha premining to 3672 ha after mining. Both watersheds experienced a large reduction in mean slope; the mean slope in LB decreased from 20.5° to 13.3°, the slopes in MR decreased from 21.1° to 17.3°. The mean slopes in the reference watersheds RB and LF are 19.5° and 17.5°, respectively. We estimate that 10–14 million m<sup>3</sup> of mine spoil were deposited in VFs in LB, while the VFs in the larger MR watershed contain 162–185 million m<sup>3</sup> of overburden. Spread out over the watersheds the crushed rock material would cover LB about 15 m and MR 4 m deep.

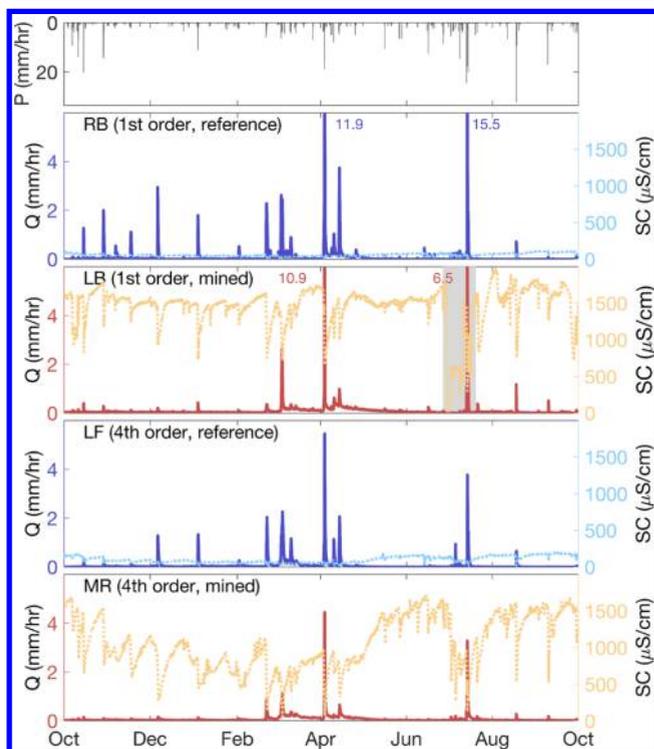
**Hydrology.** Precipitation for the study period ranged from 1254 mm in RB to 1358 mm in MR. The 104 mm difference between the small reference watershed and the larger mined watershed is likely due a 75 m difference in mean elevation between the two watersheds and is consistent with the 1981–2010 PRISM data that indicate an average 51 mm difference between the two watersheds. Precipitation in Charleston, WV, was 1166 mm for the 2015 WY (data provided by the Utah Climate Center). The 1996–2015 annual mean at this station (Charleston WSFO) is 1191 mm, which makes the 2015 WY an average precipitation year.

Runoff in the mined first-order watershed was 68 mm (11.2%) higher than runoff in the first-order reference watershed (677 and 609 mm, respectively), and runoff in the mined fourth-order watershed was 40 mm (7.3%) higher than in the fourth-order reference watershed (585 mm and 545 mm, respectively; see Table 1).

**Table 1. Precipitation, Runoff, and Runoff Ratios for the 2015 Water Year for the Four Study Watersheds as Well as Baseflow and Event Flow Proportions Derived from Three Different Empirical Baseflow Separation Methods**

	RB (1st order reference)	LB (1st order mined)	LF (4th order reference)	MR7 (4th order mined)
precipitation (mm)	1254	1339	1293	1358
runoff (mm)	609	677	545	585
runoff Ratio (–)	0.49	0.51	0.42	0.43
Hewlett and Hibbert (1967)				
baseflow	0.30	0.71	0.41	0.69
event flow	0.70	0.29	0.59	0.31
Pettyjohn and Henning (1979)				
baseflow	0.30	0.72	0.33	0.65
event flow	0.70	0.28	0.67	0.35
Blume et al. (2007)				
baseflow	0.29	0.75	0.30	0.71
event flow	0.71	0.25	0.70	0.29

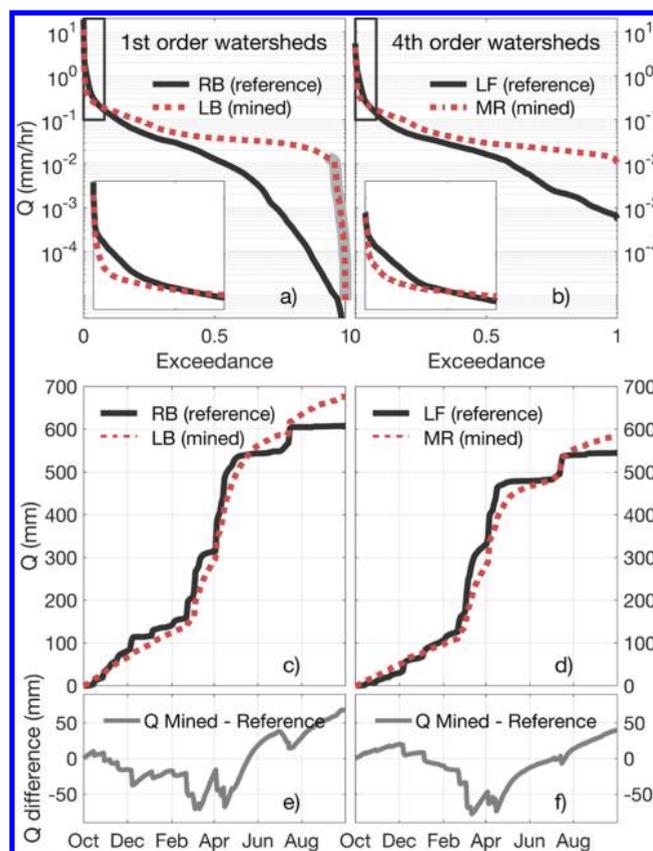
The hydrographs demonstrate differences in hydrologic response between the mined and reference watersheds, with both reference watersheds exhibiting generally higher peakflows than the mined watersheds during runoff events (Figure 2).



**Figure 2.** Precipitation ( $P$ , top panel), runoff ( $Q$ , solid lines), and specific conductance ( $SC$ , dotted lines) for the four watersheds. Mined watersheds are denoted in red, unmined/reference watersheds in blue hues. The gray shading denotes the time period when the mining company pumped water out of the small sedimentation pond below the valley fill and does not represent a natural decrease in conductivity. Interactive versions of the figures and additional information accompanying this publication can be found at <https://mtm-hydro.web.duke.edu/>.

The flow duration curves (FDCs) further highlight the mining impact for both mined sites with increased low flows and attenuated high flows (Figure 3, top panel). Flow in RB ceased several times during the growing season (Figure 3, left top panel), while the slightly smaller LB sustained streamflow throughout the year.

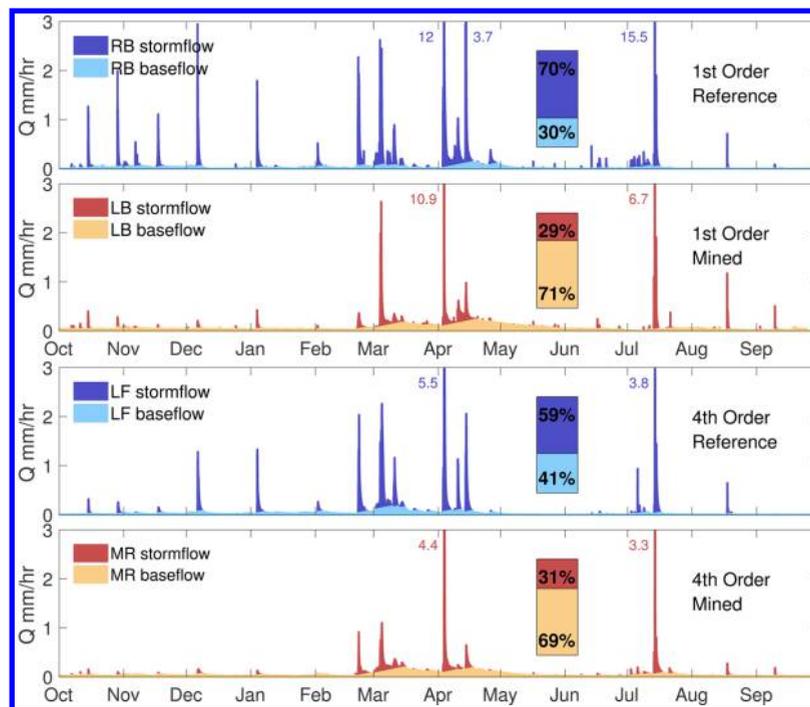
Water export in the mined and reference first-order watersheds was largely similar from December 10 through April 30 (~415 mm). However, the reference watershed exported more water during larger runoff events, while the mined watershed exported more water following events (enhanced hydrograph recessions) (Figure 2 and Figure 3 middle and bottom panels). The greatest differences occurred from May 1 through the end of the study period in early October, when the mined headwater–watershed exported 2.4 times more water than the headwater reference site (184 mm from LB and 77 mm from RB). The mined watershed also exported more water over the first 1.5 months of the study period following the previous year's low-flow period. The dynamics in the fourth-order watersheds were generally similar to the first-order watersheds, while the overall difference in  $Q$  after 12 months was lower than in the first-order watersheds (Figure 3).



**Figure 3.** Flow duration curves (FDCs) for the first-order watersheds (left column) and fourth-order watersheds (right column). The insets are enlarged sections of the high flows denoted by the black rectangles (top panel); cumulative runoff for the first-order watersheds (left column) and fourth-order watersheds (right column) (middle panel); runoff difference between mined and reference watershed for the first-order watersheds (left column) and fourth-order watersheds (right column) (bottom panel). Note that the shaded portion in the top left panel represents the time periods affected by the mining company pumping water out of the retention pond below the valley fill and does not represent a natural decrease in streamflow.

The baseflow separations yielded consistent results for all three baseflow separation methods and across watershed scales (Table 1 and Figure 4). The baseflow portion across all three methods in the reference watersheds was ~30% of annual streamflow in the small reference watershed and 35% in the larger reference watershed, while baseflow constituted ~73% and ~68% of annual streamflow in the small mined watershed and the larger mined watershed, respectively.

**Specific Conductance.** Specific conductance ( $SC$ ) was on average 10 times (MR to LF) to 25 times (LB to RB) higher in the mined watersheds than in the associated reference watersheds (Figure 2 and Table 2). The lowest  $SC$  values were observed in RB (<10  $\mu\text{S}/\text{cm}$ ), where  $SC$  never exceeded 111  $\mu\text{S}/\text{cm}$ .  $SC$  in the fourth-order reference watershed was slightly higher and more variable than the values for RB but never exceeded 195  $\mu\text{S}/\text{cm}$ . The highest  $SC$  values were measured in LB, ranging from 660 to 1977  $\mu\text{S}/\text{cm}$  (omitting the period of greatest pump influence from 06/27/2015 through 07/20/2015). MR, the partially mined fourth-order watershed, had  $SC$  values that ranged from a minimum value of 53  $\mu\text{S}/\text{cm}$  during a major winter storm to a maximum of 1705  $\mu\text{S}/\text{cm}$  during summer baseflows. In all watersheds,  $SC$



**Figure 4.** Hydrographs and baseflow separation with constant slope method (Hewlett and Hibbert, 1967)<sup>55</sup> for first-order watersheds (top half) and fourth-order watersheds (bottom half). Reference watersheds are depicted in blue; mined watersheds in red.

**Table 2.** Specific Conductance (SC) Statistics for the Four Experimental Watersheds<sup>a</sup>

SC ( $\mu\text{S}/\text{cm}$ )	RB (unmined)	LB (mined)	LF (unmined)	MR7 (mined)
mean	58	1504	102	1053
median	52	1530	89	1005
standard dev	20	198	43	367
minimum	8	660	19	53
maximum	111	1977	195	1705

<sup>a</sup>LB statistics were calculated omitting the period of greatest pump influence (06/27/2015–07/20/2015).

decreased during runoff events. In the unmined watersheds, event flows could dilute SC to as low as 8  $\mu\text{S}/\text{cm}$  or RB and 19  $\mu\text{S}/\text{cm}$  for LF. In contrast, even the largest storms were unable to dilute the mining associated SC signal in LB to a similar degree, where even during the highest flow event SC remained above 650  $\mu\text{S}/\text{cm}$ . Stormwater dilution in the larger mined watershed was more effective than in the small mined watershed, diluting SC to as low as 53  $\mu\text{S}/\text{cm}$  during the largest storms (Figure 2). In all cases, SC values recovered rapidly to pre-event levels. With the exception of storms, there was little seasonal variation in SC for the small mined watershed, with SC near  $\sim 1500$   $\mu\text{S}/\text{cm}$  for all of the year. In contrast, SC varied seasonally in the larger mined watershed, shifting from dormant season values of  $\sim 1000$   $\mu\text{S}/\text{cm}$  SC to highs near 1500  $\mu\text{S}/\text{cm}$  for the majority of the growing season (Figure 2).

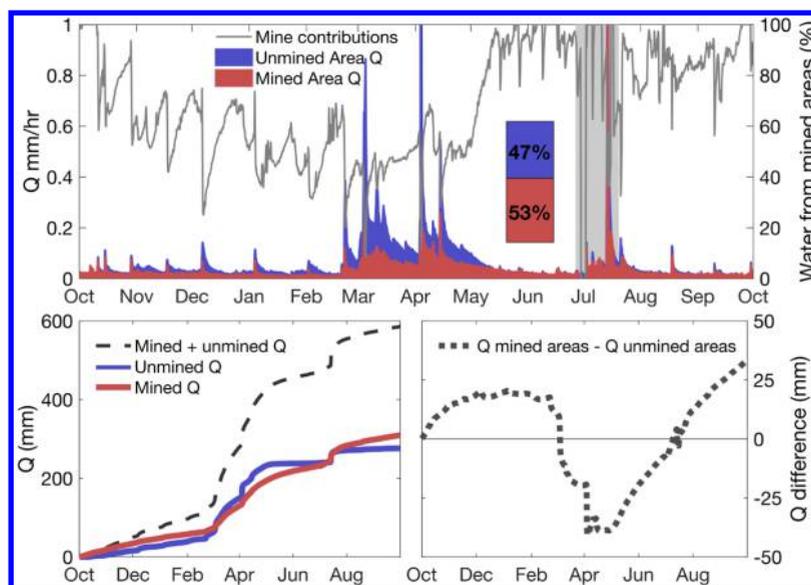
This seasonal variation in specific conductance in the fourth order Mud River is caused by a shift in the relative contribution of mined and unmined portions of the watershed over the water year. Hydrograph separations were used to determine that mined areas contributed slightly more water to the overall annual runoff than unmined areas (53% vs 47%, respectively, Figure 5, top panel), despite making up a smaller proportion of the watershed (46% of the MR watershed is in MTMVF). In

addition to having a higher water yield, the mined areas of MR exported more water during the drier growing season and the unmined portions exported more water during the dormant season (Figure 5, bottom panels). During baseflow periods, 64% of runoff originated from mined areas, but that percentage decreased to just 44% during stormflow periods, indicating a shift in contributions from mining-dominated baseflow periods to stormflow periods dominated by runoff from the unmined portions (Figure 6). During the most extended baseflow periods (e.g., 05/12/2015–06/27/2015) contributions from the mined areas increased to 94% of total flow as unmined headwaters ran dry. Only during the wettest portion of the year (e.g., 02/21/2015–04/17/2015) did contributions from the mined areas fall to levels (46% of total flow) that were equivalent to their areal extent. At the peak of stormflows, contributions from the mined areas frequently dropped below 30% and fell to the annual minimum of 8% during the year's largest storm (Figure 5, top panel).

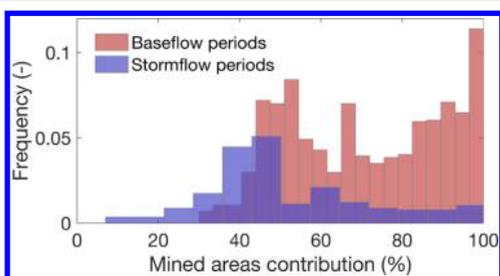
## DISCUSSION

In our study, we found that watersheds affected by mountain-top removal coal mining with valley fills (MTMVF) had reduced stormflows and enhanced baseflows relative to reference watersheds. In these MTMVF impacted watersheds, both baseflows and stormflows export large quantities of total dissolved solids derived from strong acid weathering of carbonate bedrock. Because of their elevated baseflow, MTMVF watersheds contribute disproportionately to the flow of downstream rivers during low flow periods. These significant alterations of both watershed hydrology and water chemistry are likely to lead to both more perennial and saltier streamflows throughout Appalachia where at least 7% of the ecoregion has been converted to MTMVF mines.<sup>24</sup>

**Baseflow/Stormflow Ratios.** Our paired watershed analysis documented significant reductions in stormflow and



**Figure 5.** Hydrograph separation for the partially mined MR watershed. Portions of the hydrograph originating from unmined areas are denoted in blue; mined area contributions are denoted in red. The gray shading marks the time when the mining company actively pumped water out of the small sedimentation pond above the LB instrumentation (top panel). Cumulative flux from mined and unmined areas of MR (bottom left panel). Runoff differences between mined area runoff and unmined area runoff in MR (bottom right panel).



**Figure 6.** Frequency distributions of mined area contributions during baseflow (red) and eventflow (blue) periods.

enhanced baseflow as a result of MTMVF activities. These findings were robust, with similar proportional changes in baseflow/stormflow ratios in the first-order and fourth-order watershed pairs. These results support the suggestion that valley fills lead to massive increases in porosity and water holding capacity<sup>26,68</sup> and that as a result valley fills have much greater impacts on downstream hydrology than surface compaction during mine reclamation.

The effect of MTMVF streamflow was almost equally strong for both the first- and fourth-order watersheds, despite the difference in watershed size and the fraction of the watershed impacted by mining. For both sets of watersheds, stormwater runoff was substantially lower for the mined watershed and high baseflow contributions from the MTMVF watersheds suggest increased infiltration into deep valley fill storage, from which the water then slowly drains. Our findings that MTMVF increases baseflow in both of these watersheds are consistent with earlier studies in the region reporting increased runoff ratios<sup>30</sup> and higher baseflows<sup>31</sup> from mined watersheds elsewhere in West Virginia. The current study improves upon these earlier studies by performing comparisons and hydrograph separations on paired watersheds in which the only mining impacts are MTMVF, thus greatly enhancing our ability to connect MTM to observed changes in hydrology and biogeochemistry. Our observations that mining reduces storm-

flows contrast with prior work in which Negley and Eshleman<sup>33</sup> documented increased stormflows from several surface coal mines in western Maryland. The difference between the Maryland study and our study watersheds is easy to explain, as Negley and Eshleman<sup>33</sup> watersheds did not include valley fills. Negley and Eshleman<sup>33</sup> attributed the hydrologic alteration in their study to increased overland runoff resulting from surface compaction during mine reclamation. While to some extent this mechanism may be acting in our WV mines, both their hydrology and chemistry suggest increased infiltration into deep valley fill storage, from which the water then slowly drains.

A notable attribute of mountaintop mined landscapes is the emergence of flat areas<sup>69</sup> that are rare in the steep Appalachian mountains. These newly created flat areas favor enhanced infiltration due to low slope gradients, at least partially offsetting the influence of surface compaction. Therefore, instead of increasing stormflow because of surface compaction, the valley fills increase the baseflow portion of total streamflow. Additionally, preferential flowpaths along the spoil-bedrock interface could enhance infiltration into the VF.<sup>70</sup> Unfortunately, little published research provides insight on the internal structure of valley fills and how settlement or sorting of material may affect hydrologic flowpathways.<sup>68,70,71</sup> Greer et al.,<sup>72</sup> for example, demonstrated high subsurface heterogeneity in a valley fill in Virginia using electrical resistivity imaging. It is reasonable to assume that the physical characteristics of the VFs affect how much water can be stored in the VFs and how the stored water is subsequently released to sustain streamflow. Ross et al.<sup>26</sup> determined large variability in VF area, depth, and volume among >1500 VFs in Central Appalachia. While we reference the increased storage in the VFs as reason for the baseflow increases, it is unfortunately not possible at this point to make quantitative assessments on how different VF characteristics would influence the hydrologic response of mined watersheds. However, while this may be important for individual small headwater-watersheds, over larger areas responses of individual VFs of different sizes would likely be

obscured by the combined response of all VFs present in the watershed.

**Impacts of MTMVF on Watershed Water Balances.** MTMVF watersheds have lower plant biomass and reduced topographic relief relative to unmined watersheds in the region. Both the loss of evapotranspiration by vegetation and the change in runoff and infiltration associated with landscape flattening are expected to exert strong influence on the annual water budget.

Differences in  $Q$  between mined and reference watersheds are commonly attributed to the lack of vegetation on mined areas and the associated elimination/reduction of the transpiration component. Clearcutting vegetation typically results in decreased ET and subsequent increases in  $Q$ .<sup>73–75</sup> The same response might be expected on mined areas due to deforestation, especially on younger valley fills. Yet the differences in annual water export between the mined and reference watersheds in our study (first-order: 68 mm; fourth-order: 40 mm) were smaller than differences measured between forested and clear-cut watersheds in other parts of the Appalachians, e.g., 130 mm reduction after 85% clearcutting in Fernow, WV,<sup>76</sup> or 150–400 mm after 100% clear-cutting at Coweeta, NC.<sup>77</sup> While it is near certain that the rates of evapotranspiration must be lower from recently mined and deforested landscapes, the relatively small change in annual water yield suggests that the loss of ET may be compensated for by other components of MTMVF affecting the water balance.

Reductions in watershed slope may be counterbalancing this reduction in ET by increasing infiltration and water residence times. Ross, McGlynn and Bernhardt<sup>26</sup> determined that across southern West Virginia premining landscapes had a modal slope of  $\sim 28^\circ$ , while postmining landscapes exhibited bimodal slope distributions of  $\sim 2^\circ$  and  $\sim 20^\circ$ . Annual runoff ratios are typically positively correlated with watershed slope,<sup>78,79</sup> while decreased slopes are typically associated with greater infiltration into the subsurface and longer water residence times.<sup>79,80</sup> In vegetated watersheds, these longer water residence times should increase the potential for water uptake by vegetation and subsequent losses through evapotranspiration.<sup>78</sup> We suspect that the lower topographic relief coupled with reduced evapotranspiration in MTMVF watersheds is changing the flowpaths and the residence time of water in mined watersheds without fundamentally altering the total water yield.

**Contributions to Streamflow from Mined and Unmined Areas.** The spatial configuration of our study watersheds allowed for separation of MR streamflow into contributions from mined and unmined areas, using the first-order mined and reference watersheds as end members. The constantly high base SC values in LB, even during the wet dormant season, suggest that baseflow in the mined watershed—or rather VF—is generated from a deeper water source within the VF that is largely unaffected by incoming precipitation. Dilution occurred during runoff events, but even then, the SC values in LB remained above  $650 \mu\text{S}/\text{cm}$ . These sustained high SC values suggest limited overland flow on mine soil, which is contrary to previous conclusions about the role of overland flow in surface mining environments without VFs.<sup>33,81</sup> The runoff from mined areas that contributed to streamflow could be displaced water with varying concentrations from within the valley fill that has not reached maximum SC values, similar to differences often observed between groundwater and soil water in undisturbed sys-

tems<sup>82,83</sup> or precipitation that infiltrated into the VF and dissolved readily available solutes while moving rapidly via preferential flowpathways.

In the partially mined fourth-order MR watershed, runoff from the mined areas was 53% of annual runoff, which is slightly greater than the fraction of the watershed that was mined ( $\sim 46\%$ ). This is consistent with our finding that the mined watersheds exhibited greater runoff than the reference watersheds, but less than would be expected if the mined areas had simply been clear-cut (see the discussion point on water balance comparisons). The hydrograph separation in the partially mined watershed (MR) corroborates that reference watersheds export more water during the wetter dormant season (64%  $Q$  from unmined areas), with peak contributions from unmined areas exceeding 80% of total streamflow. The brief rise in SC immediately coincident with streamflow increases (Figure 5, top panel) is likely caused by the spatial arrangement of mined and unmined areas, with the mined areas being closer located to the watershed outlet (Figure 1a). Because of this—and especially during the wetter periods—the stream received brief inputs of mined water only (which is itself diluted but still higher in SC than the MR streamwater) until the runoff from the unmined areas further upstream travels to the watershed outlet.

During baseflow periods the majority of MR streamflow originated from mined areas (64%  $Q$  from mined areas). High contributions during long baseflow periods (up to 94%) suggest that the unmined areas in MR contribute little water to streamflow during the growing season, similar to the reference sites LB and LF that frequently fall dry during the growing season after longer periods without precipitation. This highlights the strong effect that MTMVF runoff can exert on water quality and quantity, especially during low-flow periods when it can be the dominant source of streamflow downstream.

**Implications.** This study highlights and further demonstrates the cascading effects that mountaintop mining has on the immediate location of the disturbance (i.e., the disturbed areas themselves) as well as the surrounding ecosystems (in this case downstream areas). The changes to the hydrologic responses to rainfall and the seasonality of streamflow are indicators of this massive critical zone disturbance. While the hydrologic impacts of most disturbances are rather easily identified and often predictable, assessing the balance of the opposing effects associated with MTMVF can be challenging. For example, deforestation (through insect infestations, wildfires, clear-cutting, etc.) typically lead to increases in annual  $Q$  through reduced evapotranspiration<sup>77</sup> and urbanization or decreased infiltration rates typically results in flashier hydrographs and an increase in stormflow and associated reduction in baseflow.<sup>84</sup> The effect of other forms of surface mining without valley fills often resemble the effects of urbanization.<sup>36,85</sup> In contrast, the effect of MTMVF with valley fills on simple hydrologic response is perhaps more comparable to the effect of dams on riverine systems, since dams typically are designed or managed to reduce high flows and increase low flows.<sup>9,86–88</sup> However, the effect on hydrologic response is achieved via completely different mechanisms. While damming impacts hydrology by placing a structure within the river network and directly regulating the stream/river, MTMVF can alter the critical zone of entire landscapes hundreds of meters deep. This deep impact thereby dramatically changes the runoff generation processes themselves, i.e. how water moves through the system once it reaches the ground surface. The consequences are both

an altered hydrologic regime as well as degradation of streamwater quality through the export of weathering products.

Increased baseflow portion in mined watersheds and high streamwater specific conductance indicate that rainfall spends more time in the subsurface, especially in the VFs. This has implications for two key issues: First, the water draining mined watersheds has been in contact with VF material, with greatly enhanced weatherable surfaces,<sup>26</sup> for extended periods of time. This results in increased concentrations of weathering products that contribute to downstream alkaline mine drainage and thus impair aquatic ecosystems. This degradation in streamwater quality following MTMVF and its effect on stream biota—even decades after mine reclamation—has been documented across Central Appalachia.<sup>39,41,42,44,45,89,90</sup> Recent research on mine reclamation techniques, especially reforestation both on current as well as former mines,<sup>91</sup> promises faster regrowth of native vegetation on unconsolidated spoil material. While the positive effect on tree growth has been demonstrated,<sup>92</sup> the effects on hydrologic response are not as clear. Agouridis et al.<sup>93</sup> for example measured sharply declining electrical conductivities in several reforested plots on a mine in Kentucky over a three-year period after plot establishment. However, the mine spoil plots were only 2.5 m deep<sup>94</sup> and may not be representative of valley fill spoils >100 m deep.

Second, enhanced baseflow itself, even in large partially mined watersheds, can contribute to stream-impairment. Our hydrograph separations in the partially mined MR watershed (Figure 5) demonstrate that the water quality influence from mined areas was most dominant during low flow periods. Similar runoff rates and patterns between mined and reference streams during the dormant season (Figures 4 and 5) indicate that the downstream impact of mining was less dramatic during the winter high-flow period. During the summer baseflow period, the majority of streamwater originated from VF outflow in the fully mined and 46% mined study watersheds. Because of the disproportionate influence of mined areas on stream baseflow, the effect of MTMVF on downstream systems would extend further than a simple area-mixing model<sup>40</sup> would predict, especially during baseflow periods that constitute ~80% of the year.

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### Notes

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## REFERENCES

- (1) Broushaki, F.; Thomas, M. G.; Link, V.; López, S.; van Dorp, L.; Kirsanow, K.; Hofmanová, Z.; Diekmann, Y.; Cassidy, L. M.; Diez-del-Molino, D.; Kousathanas, A.; Sell, C.; Robson, H. K.; Martiniano, R.; Blöcher, J.; Scheu, A.; Kreutzer, S.; Bollongino, R.; Bobo, D.; Davudi, H.; Munoz, O.; Currat, M.; Abdi, K.; Biglari, F.; Craig, O. E.; Bradley, D. G.; Shennan, S.; Veeramah, K. R.; Mashkour, M.; Wegmann, D.; Hellenthal, G.; Burger, J. Early Neolithic genomes from the eastern Fertile Crescent. *Science* **2016**, *353*, 1–15.
- (2) Riehl, S.; Zeidi, M.; Conard, N. J. Emergence of Agriculture in the Foothills of the Zagros Mountains of Iran. *Science* **2013**, *341* (6141), 65–67.
- (3) Achard, F.; Eva, H. D.; Stibig, H.-J.; Mayaux, P.; Gallego, J.; Richards, T.; Malingreau, J.-P. Determination of Deforestation Rates of the World's Humid Tropical Forests. *Science* **2002**, *297* (5583), 999–1002.
- (4) Pongratz, J.; Reick, C.; Raddatz, T.; Claussen, M. A reconstruction of global agricultural areas and land cover for the last millennium. *Global Biogeochemical Cycles* **2008**, DOI: [10.1029/2007GB003153](https://doi.org/10.1029/2007GB003153).
- (5) Townsend, P. A.; Helmers, D. P.; Kingdon, C. C.; McNeil, B. E.; de Beurs, K. M.; Eshleman, K. N. Changes in the extent of surface mining and reclamation in the Central Appalachians detected using a 1976–2006 Landsat time series. *Remote Sensing of Environment* **2009**, *113* (1), 62–72.
- (6) Dudka, S.; Adriano, D. C. Environmental impacts of metal ore mining and processing: A review. *Journal of Environmental Quality* **1997**, *26* (3), 590–602.
- (7) Schindler, D. Tar sands need solid science. *Nature* **2010**, *468* (7323), 499–501.
- (8) Vörösmarty, C. J.; Meybeck, M.; Fekete, B.; Sharma, K.; Green, P.; Syvitski, J. P. M. Anthropogenic sediment retention: major global impact from registered river impoundments. *Global and Planetary Change* **2003**, *39* (1–2), 169–190.
- (9) Graf, W. L. Downstream hydrologic and geomorphic effects of large dams on American rivers. *Geomorphology* **2006**, *79* (3–4), 336–360.
- (10) Meyer, W. B.; Turner, B. L. Human-Population Growth And Global Land-Use Cover Change. *Annu. Rev. Ecol. Syst.* **1992**, *23*, 39–61.
- (11) Hesse, R. Geomorphological traces of conflict in high-resolution elevation models. *Applied Geography* **2014**, *46*, 11–20.
- (12) Hupy, J. P.; Schaetzl, R. J. Soil development on the WWI battlefield of Verdun, France. *Geoderma* **2008**, *145* (1–2), 37–49.
- (13) Brantley, S. L.; Goldhaber, M. B.; Ragnarsdottir, K. V. Crossing disciplines and scales to understand the Critical Zone. *Elements* **2007**, *3* (5), 307–314.
- (14) Foley, J. A.; DeFries, R.; Asner, G. P.; Barford, C.; Bonan, G.; Carpenter, S. R.; Chapin, F. S.; Coe, M. T.; Daily, G. C.; Gibbs, H. K.; Helkowski, J. H.; Holloway, T.; Howard, E. A.; Kucharik, C. J.; Monfreda, C.; Patz, J. A.; Prentice, I. C.; Ramankutty, N.; Snyder, P. K. Global Consequences of Land Use. *Science* **2005**, *309* (5734), 570–574.
- (15) Peterson, B. J.; Wollheim, W. M.; Mulholland, P. J.; Webster, J. R.; Meyer, J. L.; Tank, J. L.; Marti, E.; Bowden, W. B.; Valett, H. M.; Hershey, A. E.; McDowell, W. H.; Dodds, W. K.; Hamilton, S. K.; Gregory, S.; Morrall, D. D. Control of Nitrogen Export from Watersheds by Headwater Streams. *Science* **2001**, *292* (5514), 86–90.
- (16) McGlynn, B. L.; McDonnell, J. J. Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resour. Res.* **2003**, *39* (4), SWC 3-1–SWC 3-18.
- (17) Konar, M.; Todd, M. J.; Muneeppeerakul, R.; Rinaldo, A.; Rodriguez-Iturbe, I. Hydrology as a driver of biodiversity: Controls on carrying capacity, niche formation, and dispersal. *Adv. Water Resour.* **2013**, *51*, 317–325.
- (18) Bunn, S. E.; Arthington, A. H. Basic principles and ecological consequences of altered flow regimes for aquatic biodiversity. *Environ. Manage.* **2002**, *30* (4), 492–507.
- (19) Gaffield, S. J.; Goo, R. L.; Richards, L. A.; Jackson, R. J. Public health effects of inadequately managed stormwater runoff. *Am. J. Public Health* **2003**, *93* (9), 1527–1533.

- (20) Wellen, C. C.; Shatilla, N. J.; Carey, S. K. Regional scale selenium loading associated with surface coal mining, Elk Valley, British Columbia, Canada. *Sci. Total Environ.* **2015**, *532*, 791–802.
- (21) Yang, X. J.; Lin, A.; Li, X.-L.; Wu, Y.; Zhou, W.; Chen, Z. China's ion-adsorption rare earth resources, mining consequences and preservation. *Environmental Development* **2013**, *8*, 131–136.
- (22) Slonecker, E. T.; Bengler, M. J. Remote sensing and mountaintop mining. *Remote Sensing Reviews* **2001**, *20* (4), 293–322.
- (23) DEP. *Standards and Specifications for Erosion and Sediment Control Excess Spoil Disposal Haulageways*; Department of Environmental Protection Division of Mining and Reclamation: 1993.
- (24) U.S. EPA. *The Effects of Mountaintop Mines and Valley Fills on Aquatic Ecosystems of the Central Appalachian Coalfields*; United States Environmental Protection Agency: Washington, DC, 2011.
- (25) Ebel, B. A.; Mirus, B. B. Disturbance hydrology: challenges and opportunities. *Hydrological Processes* **2014**, *28* (19), 5140–5148.
- (26) Ross, M. R. V.; McGlynn, B. L.; Bernhardt, E. S. Deep Impact: Effects of Mountaintop Mining on Surface Topography, Bedrock Structure, and Downstream Waters. *Environ. Sci. Technol.* **2016**, *50* (4), 2064–2074.
- (27) Miller, A. J.; Zegre, N. P. Mountaintop Removal Mining and Catchment Hydrology. *Water* **2014**, *6* (3), 472–499.
- (28) Zegre, N. P.; Maxwell, A.; Lamont, S. Characterizing streamflow response of a mountaintop-mined watershed to changing land use. *Applied Geography* **2013**, *39*, 5–15.
- (29) Messinger, T. Comparison of Storm Response of Streams in Small, Unmined and Valley-Filled Watersheds, 1999–2001, Ballard Fork, West Virginia. *Water-Resources Investigations Report 02-4303*; U.S. Geological Survey: Charleston, WV, 2003.
- (30) Messinger, T.; Paybins, K. S. *Relations Between Precipitation and Daily and Monthly Mean Flows in Gaged, Unmined and Valley-Filled Watersheds, Ballard Fork, West Virginia, 1999–2001*; U.S. Department of the Interior; U.S. Geological Survey: Charleston, WV, 2003.
- (31) Zegre, N. P.; Miller, A. J.; Maxwell, A.; Lamont, S. J. Multiscale Analysis Of Hydrology In A Mountaintop Mine-Impacted Watershed. *J. Am. Water Resour. Assoc.* **2014**, *50* (5), 1257–1272.
- (32) Evans, D. M.; Zipper, C. E.; Hester, E. T.; Schoenholtz, S. H. Hydrologic Effects of Surface Coal Mining in Appalachia (US). *J. Am. Water Resour. Assoc.* **2015**, *51* (5), 1436–1452.
- (33) Negley, T. L.; Eshleman, K. N. Comparison of stormflow responses of surface-mined and forested watersheds in the Appalachian Mountains, USA. *Hydrol. Processes* **2006**, *20* (16), 3467–3483.
- (34) Simmons, J. A.; Currie, W. S.; Eshleman, K. N.; Kuers, K.; Monteleone, S.; Negley, T. L.; Pohlad, B. R.; Thomas, C. L. Forest to reclaimed mine land use change leads to altered ecosystem structure and function. *Ecological Applications* **2008**, *18* (1), 104–118.
- (35) McCormick, B. C.; Eshleman, K. N.; Griffith, J. L.; Townsend, P. A. Detection of flooding responses at the river basin scale enhanced by land use change. *Water Resour. Res.* **2009**, *45*, 1–15.
- (36) Ferrari, J. R.; Lookingbill, T. R.; McCormick, B.; Townsend, P. A.; Eshleman, K. N., Surface mining and reclamation effects on flood response of watersheds in the central Appalachian Plateau region. *Water Resour. Res.* **2009**, *45*.[10.1029/2008WR007109](https://doi.org/10.1029/2008WR007109)
- (37) Miller, A. J.; Zegre, N. P. Landscape-Scale Disturbance: Insights into the Complexity of Catchment Hydrology in the Mountaintop Removal Mining Region of the Eastern United States. *Land* **2016**, *5* (3), 22.
- (38) Griffith, M. B.; Norton, S. B.; Alexander, L. C.; Pollard, A. I.; LeDuc, S. D. The effects of mountaintop mines and valley fills on the physicochemical quality of stream ecosystems in the central Appalachians: A review. *Sci. Total Environ.* **2012**, *417*, 1–12.
- (39) Lindberg, T. T.; Bernhardt, E. S.; Bier, R.; Helton, A. M.; Merola, R. B.; Vengosh, A.; Di Giulio, R. T. Cumulative impacts of mountaintop mining on an Appalachian watershed. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108* (52), 20929–20934.
- (40) Bernhardt, E. S.; Lutz, B. D.; King, R. S.; Fay, J. P.; Carter, C. E.; Helton, A. M.; Campagna, D.; Amos, J. How Many Mountains Can We Mine? Assessing the Regional Degradation of Central Appalachian Rivers by Surface Coal Mining. *Environ. Sci. Technol.* **2012**, *46* (15), 8115–8122.
- (41) Palmer, M. A.; Bernhardt, E. S.; Schlesinger, W. H.; Eshleman, K. N.; Foufoula-Georgiou, E.; Hendryx, M. S.; Lemly, A. D.; Likens, G. E.; Loucks, O. L.; Power, M. E.; White, P. S.; Wilcock, P. R. Mountaintop Mining Consequences. *Science* **2010**, *327* (5962), 148–149.
- (42) Pond, G. J.; Passmore, M. E.; Borsuk, F. A.; Reynolds, L.; Rose, C. J. Downstream effects of mountaintop coal mining: comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. *Journal of the North American Benthological Society* **2008**, *27* (3), 717–737.
- (43) Timpano, A. J.; Schoenholtz, S. H.; Soucek, D. J.; Zipper, C. E. Salinity As A Limiting Factor For Biological Condition In Mining-Influenced Central Appalachian Headwater Streams. *J. Am. Water Resour. Assoc.* **2015**, *51* (1), 240–250.
- (44) Bier, R. L.; Voss, K. A.; Bernhardt, E. S. Bacterial community responses to a gradient of alkaline mountaintop mine drainage in Central Appalachian streams. *ISME J.* **2015**, *9* (6), 1378–1390.
- (45) Voss, K. A.; King, R. S.; Bernhardt, E. S. From a line in the sand to a landscape of decisions: a hierarchical diversity decision framework for estimating and communicating biodiversity loss along anthropogenic gradients. *Methods in Ecology and Evolution* **2015**, *6* (7), 795–805.
- (46) Murphy, J. C.; Hornberger, G. M.; Liddle, R. G. Concentration-discharge relationships in the coalmined region of the New River basin and Indian Fork sub-basin, Tennessee, USA. *Hydrological Processes* **2014**, *28* (3), 718–728.
- (47) NRCS. *Soil Survey of Lincoln County, West Virginia*; United States Department of Agriculture; Natural Resources Conservation Service in cooperation with the West Virginia Agricultural and Forestry Experiment Station and West Virginia Conservation Agency, 2007.
- (48) NRCS. *Soil Survey Geographic Database (SSURGO 2.2)*; Natural Resources Conservation Service, U.S. Department of Agriculture, 2015.
- (49) Nicholson, S. W.; Dicken, C. L.; Horton, J. D.; Labay, K. A.; Foose, M. P.; Mueller, J. A. L., *Preliminary integrated geologic map databases for the United States: Kentucky, Ohio, Tennessee, and West Virginia*; US Geological Survey: 2005.
- (50) Braun, E. L. *Deciduous forests of eastern North America*; Free Press: New York, 1974.
- (51) PRISM. *PRISM Gridded Climate Data*; OSU PRISM Climate Group, 2016.
- (52) Adams, M.; Kochenderfer, J.; Edwards, P. The Fernow Watershed Acidification Study: Ecosystem Acidification, Nitrogen Saturation and Base Cation Leaching. *Water, Air, Soil Pollut.: Focus* **2007**, *7* (1–3), 267–273.
- (53) Searcy, J. K.; Hardison, C. H. Double Mass Curves. *Geological Survey Water-Supply Paper 1541-B*; United States Government Printing Office: 1960.
- (54) Manning, R.; Griffith, J. P.; Pigot, T.; Vernon-Harcourt, L. F. *On the flow of water in open channels and pipes*; Dublin, 1890.
- (55) Hewlett, J. D.; Hibbert, A. R. Factors affecting the response of small watersheds to precipitation in humid areas. *Forest Hydrology* **1966**, 275–291.
- (56) Wolock, D. M., *Base-flow index grid for the conterminous United States, 03-263 ed.*; U.S. Geological Survey: Reston, VA, 2003.
- (57) Pettyjohn, W. A.; Henning, R. *Preliminary Estimate of Ground-Water Recharge Rates, Related Streamflow and Water Quality in Ohio*; Water Resources Center, The Ohio State University: Columbus, 1979.
- (58) Blume, T.; Zehe, E.; Bronstert, A. Rainfall-runoff response, event-based runoff coefficients and hydrograph separation. *Hydrol. Sci. J.* **2007**, *52* (5), 843–862.
- (59) Pinder, G. F.; Jones, J. F. Determination of the ground-water component of peak discharge from the chemistry of total runoff. *Water Resour. Res.* **1969**, *5* (2), 438–445.

- (60) Sklash, M. G.; Farvolden, R. N.; Fritz, P. A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer. *Can. J. Earth Sci.* **1976**, *13*, 271–283.
- (61) Buttle, J. M. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. *Progress in Physical Geography* **1994**, *18* (1), 16–41.
- (62) McGlynn, B. L.; McDonnell, J. J.; Seibert, J.; Kendall, C. Scale effects on headwater catchment runoff timing, flow sources, and groundwater-streamflow relations. *Water Resour. Res.* **2004**, *40* (7), 1–14.
- (63) Caissie, D.; Pollock, T. L.; Cunjak, R. A. Variation in stream water chemistry and hydrograph separation in a small drainage basin. *J. Hydrol.* **1996**, *178* (1–4), 137–157.
- (64) Jencso, K. G.; McGlynn, B. L.; Gooseff, M. N.; Bencala, K. E.; Wondzell, S. M. Hillslope hydrologic connectivity controls riparian groundwater turnover: Implications of catchment structure for riparian buffering and stream water sources. *Water Resour. Res.* **2010**, *46*, 1–18.
- (65) Laudon, H.; Slaymaker, O. Hydrograph separation using stable isotopes, silica and electrical conductivity: an alpine example. *J. Hydrol.* **1997**, *201* (1–4), 82–101.
- (66) Pellerin, B. A.; Wollheim, W. M.; Feng, X.; Vorosmarty, C. J. The application of electrical conductivity as a tracer for hydrograph separation in urban catchments. *Hydrol. Processes* **2008**, *22* (12), 1810–1818.
- (67) Kobayashi, D. Separation of a snowmelt hydrograph by specific conductance. *J. Hydrol.* **1986**, *84* (1–2), 157–165.
- (68) Wunsch, D. R.; Dinger, J. S.; Graham, C. D. R. Predicting ground-water movement in large mine spoil areas in the Appalachian Plateau. *Int. J. Coal Geol.* **1999**, *41* (1–2), 73–106.
- (69) Maxwell, A.; Strager, M. Assessing landform alterations induced by mountaintop mining. *Nat. Sci.* **2013**, *5*, 229–237.
- (70) Dinger, J. S.; Wunsch, D. R.; Kemp, J. E. *Occurrence of Groundwater in Mine Spoil, a Renewable Resource: Star Fire Tract, Eastern Kentucky, Mining and Reclamation Conference and Exhibition*, Charleston, WV, 1990; Charleston, WV, 1990.
- (71) Wunsch, D. R.; Dinger, J. S.; Taylor, P. B.; Carey, D. I.; Graham, C. D. R. *Hydrogeology, Hydrogeochemistry, and Spoil Settlement at a Large Mine-Spoil Area In Eastern Kentucky: Star Fire Tract*; Kentucky Geological Survey, University of Kentucky, Lexington, 1996.
- (72) Greer, B. M.; Burbey, T. J.; Zipper, C. E.; Hester, E. T. Electrical resistivity imaging of hydrologic flow through surface coal mine valley fills with comparison to other landforms. *Hydrological Processes* **2017**, *31* (12), 2244–2260.
- (73) Hewlett, J. D.; Helvey, J. D. Effects of Forest Clear-Felling on Storm Hydrograph. *Water Resour. Res.* **1970**, *6* (3), 768–782.
- (74) Moore, R. D.; Wondzell, S. M. Physical hydrology and the effects of forest harvesting in the Pacific Northwest: A review. *J. Am. Water Resour. Assoc.* **2005**, *41* (4), 763–784.
- (75) Bosch, J. M.; Hewlett, J. D. A review of catchment experiments to determine the effect of vegetation changes on water yield and evapotranspiration. *J. Hydrol.* **1982**, *55* (1–4), 3–23.
- (76) Reinhart, K. G.; Eschner, A. R.; Trimble, G. R., Jr. *Effect On Streamflow Of Four Forest Practices In The Mountains Of West Virginia*; Northeast Forest Experiment Station: Upper Darby, PA, 1963.
- (77) Hewlett, J. D.; Hibbert, A. R. Increases In Water Yield After Several Types Of Forest Cutting. *International Association of Scientific Hydrology. Bulletin* **1961**, *6* (3), 5–17.
- (78) Nippgen, F.; McGlynn, B. L.; Emanuel, R. E.; Vose, J. M. Watershed memory at the Coweeta Hydrologic Laboratory: The effect of past precipitation and storage on hydrologic response. *Water Resour. Res.* **2016**, *52* (3), 1673–1695.
- (79) Nippgen, F.; McGlynn, B. L.; Marshall, L. A.; Emanuel, R. E. Landscape structure and climate influences on hydrologic response. *Water Resour. Res.* **2011**, *47*, 1–17.
- (80) McGuire, K. J.; McDonnell, J. J.; Weiler, M.; Kendall, C.; McGlynn, B. L.; Welker, J. M.; Seibert, J. The role of topography on catchment-scale water residence time. *Water Resour. Res.* **2005**, *41* (5), 1–14.
- (81) Ritter, J. B.; Gardner, T. W. Hydrologic Evolution Of Drainage Basins Disturbed By Surface Mining, Central Pennsylvania. *Geol. Soc. Am. Bull.* **1993**, *105* (1), 101–115.
- (82) Hendershot, W. H.; Savoie, S.; Courchesne, F. Simulation Of Stream-Water Chemistry With Soil Solution And Groundwater-Flow Contributions. *J. Hydrol.* **1992**, *136* (1–4), 237–252.
- (83) Scanlon, T. M.; Raffensperger, J. P.; Hornberger, G. M. Modeling transport of dissolved silica in a forested headwater catchment: Implications for defining the hydrochemical response of observed flow pathways. *Water Resour. Res.* **2001**, *37* (4), 1071–1082.
- (84) Dunne, T. *Water in environmental planning*. W. H. Freeman: San Francisco, 1978.
- (85) McCormick, B. C.; Eshleman, K. N. Assessing Hydrologic Change in Surface-Mined Watersheds Using the Curve Number Method. *Journal of Hydrologic Engineering* **2011**, *16* (7), 575–584.
- (86) Magilligan, F. J.; Nislow, K. H. Changes in hydrologic regime by dams. *Geomorphology* **2005**, *71* (1–2), 61–78.
- (87) Singer, M. B. The influence of major dams on hydrology through the drainage network of the Sacramento River basin, California. *River Research and Applications* **2007**, *23* (1), 55–72.
- (88) Poff, N. L.; Olden, J. D.; Merritt, D. M.; Pepin, D. M. Homogenization of regional river dynamics by dams and global biodiversity implications. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104* (14), 5732–5737.
- (89) Bernhardt, E. S.; Palmer, M. A., The environmental costs of mountaintop mining valley fill operations for aquatic ecosystems of the Central Appalachians. In *Year in Ecology and Conservation Biology*, Ostfeld, R. S., Schlesinger, W. H., Eds.; Wiley, 2011; Vol. 1223, pp 39–57.
- (90) Pond, G. J.; Passmore, M. E.; Pointon, N. D.; Felbinger, J. K.; Walker, C. A.; Krock, K. J. G.; Fulton, J. B.; Nash, W. L. Long-Term Impacts on Macroinvertebrates Downstream of Reclaimed Mountaintop Mining Valley Fills in Central Appalachia. *Environ. Manage.* **2014**, *54* (4), 919–933.
- (91) Burger, J.; Graves, D.; Angel, P.; Davis, V.; Zipper, C. *The Forestry Reclamation Approach; The Appalachian Regional Reforestation Initiative (ARRI)*, 2005.
- (92) Angel, P. N.; Burger, J. A.; Davis, V. M.; Barton, C. D.; Bower, M.; Eggerud, S. D.; Rothman, P., The Forestry Reclamation Approach And The Measure Of Its Success In Appalachia. In *National Meeting of the American Society of Mining and Reclamation*; Barnhisel, R. I., Ed.; ASMR: Lexington, 2009.
- (93) Agouridis, C. T.; Angel, P. N.; Taylor, T. J.; Barton, C. D.; Warner, R. C.; Yu, X.; Wood, C. Water Quality Characteristics of Discharge from Reforested Loose-Dumped Mine Spoil in Eastern Kentucky. *Journal of Environmental Quality* **2012**, *41* (2), 454–468.
- (94) Taylor, T. J.; Agouridis, C. T.; Warner, R. C.; Barton, C. D.; Angel, P. N. Hydrologic characteristics of Appalachian loose-dumped spoil in the Cumberland Plateau of eastern Kentucky. *Hydrol. Processes* **2009**, *23* (23), 3372–3381.