Environmental Science & Technology

Article

pubs.acs.org/est

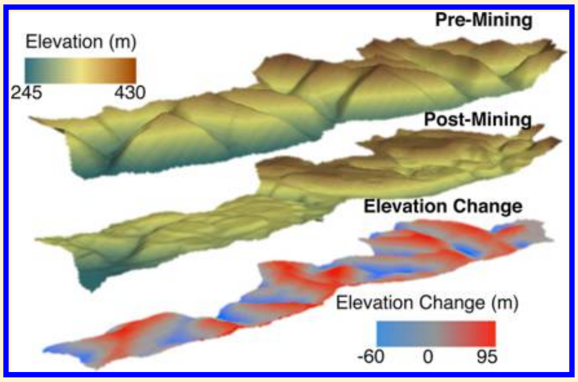
Deep Impact: Effects of Mountaintop Mining on Surface Topography, Bedrock Structure, and Downstream Waters

Matthew R. V. Ross,*,† Brian L. McGlynn,‡ and Emily S. Bernhardt†

†Department of Biology, Duke University, Durham, North Carolina 27708, United States

‡Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

Supporting Information



ABSTRACT: Land use impacts are commonly quantified and compared using 2D maps, limiting the scale of their reported impacts to surface area estimates. Yet, nearly all land use involves disturbances below the land surface. Incorporating this third dimension into our estimates of land use impact is especially important when examining the impacts of mining. Mountaintop mining is the most common form of coal mining in the Central Appalachian ecoregion. Previous estimates suggest that active, reclaimed, or abandoned mountaintop mines cover ~7% of Central Appalachia. While this is double the areal extent of development in the ecoregion (estimated to occupy <3% of the land area), the impacts are far more extensive than areal estimates alone can convey as the impacts of mines extend 10s to 100s of meters below the current land surface. Here, we provide the first estimates for the total volumetric and topographic disturbance associated with mining in an 11 500 km^2 region of southern West Virginia. We find that the cutting of ridges and filling of valleys has lowered the median slope of mined landscapes in the region by nearly 10 degrees while increasing their average elevation by 3 m as a result of expansive valley filling. We estimate that in southern West Virginia, more than 6.4km^3 of bedrock has been broken apart and deposited into 1544 headwater valley fills. We used NPDES monitoring datatsets available for 91 of these valley fills to explore whether fill characteristics could explain variation in the pH or selenium concentrations reported for streams draining these fills. We found that the volume of overburden in individual valley fills correlates with stream pH and selenium concentration, and suggest that a three-dimensional assessment of mountaintop mining impacts is necessary to predict both the severity and the longevity of the resulting environmental impacts.

INTRODUCTION

Humans directly alter more than 50% of the earth's surface,[1] with land use change causing substantial impacts to biodiversity,[2,3] climate warming,[4] water quality,[5] and river flow.[6,7] The impacts of deforestation, agriculture, urbanization, and other land use impacts are typically quantified and compared on an areal basis, and it is assumed that the extent of degradation scales with the spatial footprint of the land use.[8] Assessing all land use change in this two-dimensional framework may limit our understanding of deep disturbances, like surface mining.

Surface mining activities are the dominant form of land use in some regions[9−11] and penetrate far more deeply below the earth surface than other forms of land use change. Mountaintop mining, a form of surface mining used in steep landscapes, is now the dominant form of coal extraction[12,13] and land cover change in the Central Appalachian ecoregion of the United States,[9,11] an area that includes parts of Kentucky, Virginia, Tennessee, and West Virginia.[14] Mining activities generate some environmental impacts that are common to all types of land use change like habitat loss and water quality degradation;[15−17] but also generate unique impacts such as altering landform shape and structure,[18] burying headwater streams,[19] and creating constructed stream channels and settling ponds.[20]

Mountaintop mining activities start by logging forests, and then using explosives and heavy machinery to access shallow ~1m-thick coal seams[21] located within 100−300m of the soil surface.[11,22] This process generates tremendous quantities of waste rock (called spoil or overburden), which is deposited into headwater valleys or used to partially reconstruct ridges on reclaimed mines. Such anthropogenic valley fills have buried more than 1000 km of headwater streams within the region.[19]

In 2011, the U.S. Environmental Protection Agency reported that abandoned, reclaimed, and active surface coal mines covered ~7% of the 48 000 km^2 area in the Central Appalachian ecoregion. Since 1970, more than ~2 billion

Received: September 16, 2015
Revised: January 20, 2016
Accepted: January 22, 2016

tons of coal have been extracted from this landscape,[12,13,21] with 0.87 m^2 of land disturbed per short ton of coal recovered.[21] However, because each square meter of mining can extend 10−100s of meters into the underlying bedrock, this areal impact is likely to have a far greater impact on ecosystem properties than an equivalent square meter of deforested or agricultural land.

One way to conceptualize how different these physical impacts are from surficial disturbances is in the context of Hans Jenny's soil forming factors.[23] Jenny proposed that soils and ecosystems evolve as a result of five key factors: regional climate, potential biota, relief, parent material, and time.[23] The most common forms of land use change (agriculture, low density development, and forestry) only directly alter the potential biota (by removing most species while intentionally inserting others) and may reduce the reliance on parent material as a source of nutrients through the addition of fertilizers and soil amendments. In contrast, mountaintop mining alters all five of Jenny's factors. Climate is altered because surface mines have higher albedo and insolation and highly reduced rates of evapotranspiration compared to unmined portions of the landscape.[24] Native plants are removed during mining operations and, because native trees rarely establish in the thin, alkaline soils of reclaimed mines,[25,26] they are typically replaced by hydroseeded grasses and non-native tree species.[26,27] The topographic relief of landscapes helps determine the rates of soil erosion and water movement. Mountaintop mining completely reshapes topography by flattening the landscape.[18,24,28] These operations also alter parent material, as coal is removed and carbonate and shale residues are both exposed at the landscape surface and fragmented so that the effective reactive surface area of bedrock is greatly increased.[29] Such fundamental changes in postmining landscapes reset the soil and evolutionary evolutionary clock, by disrupting the relationships between landforms and biota that coevolved over millennia.[30]

These dramatic changes to the land lead to significant changes in element cycling within mined watersheds. Mining exposes coal and shale residues to air and water, leading to the dissolution of pyrite and the production of sulfuric acid.[31] Pyrite dissolution is responsible for the production of strongly acidic mine drainage in many mines throughout the world.[32−35] In the mountaintop mines of Appalachia, mining companies intentionally mix acid generating spoil materials with carbonate rock overburden to ensure that the acidity generated from pyrite oxidation is consumed in weathering reactions.[36,37] Although acidity (H^+) is consumed, the resulting high rates of weathering generate alkaline mine drainage (AlkMD) characterized by elevated pH and specific conductance (a proxy measure of salinity) generated by high concentrations of sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) ions, and elevated concentrations of Selenium (Se) and many trace metals.[16,17,38−41] This AlkMD leaches from valley fills into downstream ecosystems, where the resulting high streamwater conductivity and high Se have been linked to declines in macroinvertebrate diversity,[41,42] fish abundance and biomass,[43] and rates of organic matter decomposition.[44] These impacts can extend well downstream of mined landscapes.[40]

To better understand mountaintop mining and the generation and longevity of AlkMD impacts, our study objective was to quantify the areal, topographic, and volumetric impact of mountaintop mining in southern West Virginia. Second, we explored if these 3D physical characteristics of disturbance could explain a significant fraction of the variation in AlkMD signals in receiving streams. We are particularly interested in considering how the volume and age of fill material may alter the chemical signal of AlkMD in receiving streams. There is some disagreement in the literature on this issue. Prior work has documented a strong correlation between the cumulative areal extent of mining in a watershed and downstream declines in surface water quality that is not dependent upon mine age[38,40] a correlation which has been used to suggest that AlkMD generation will perisist for many decades. In contrast, field studies using soil column experiments and/or space-for-time substitution approaches—where relatively few individual valley fills have datasets longer than a decade—have suggested that the production of AlkMD associated ions[45] and selenium from valley fill material both decline over a ∼25-year period.[46,47] To date, no study has quantified the amount of overburden created within individual valley fills and examined how variation in overburden volumes relates to water quality downstream.

MATERIALS AND METHODS

Study Area. Our study area is a ∼11 500 km^2 section of the southern coalfields of West Virginia (Figure 1). The area is

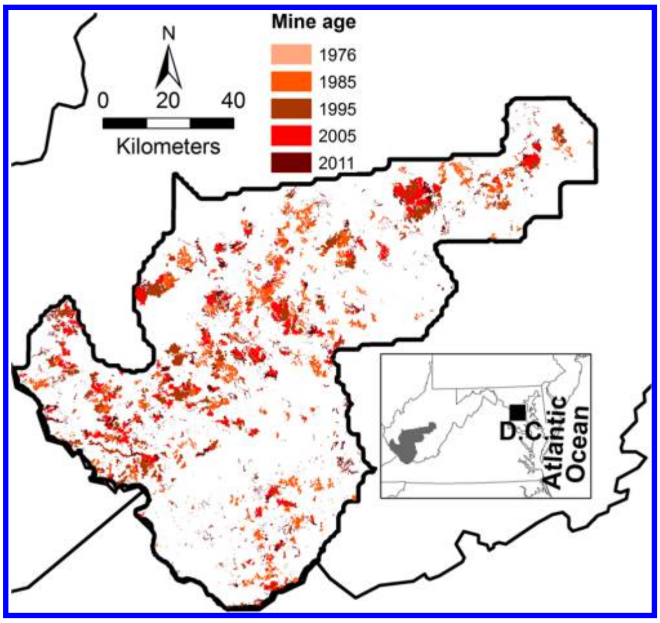


Figure 1. Study area in southwestern West Virgnia. Colored polygons show areal estimates of mining impact in years 1976, 1985, 1995, 2005, 2011. Data from refs 40 and 54.

entirely inside of the Central Appalachian ecoregion, which is characterized by steep slopes, dissected topography, shallow soils, mixed shale and sandstone bedrock, and mixed mesophytic forest.[14] The southwest corner of WV produces the majority of the state's mountaintop mined coal[12,21] and has a long history of both deep mining and other forms of surface mining (contour mining or highwall mining). Since the passage of the 1977 Surface Mining Control and Reclamation Act, many of these historic surface mining practices have been broadly defined and regulated as mountaintop mines.[48] In the early 1970s mountaintop mining began to rapidly expand in use and it has become the dominant form of both land use[9,11] and coal production.[12,13,21] The area studied was chosen due to publicly available elevation data from LiDAR flights flown in

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

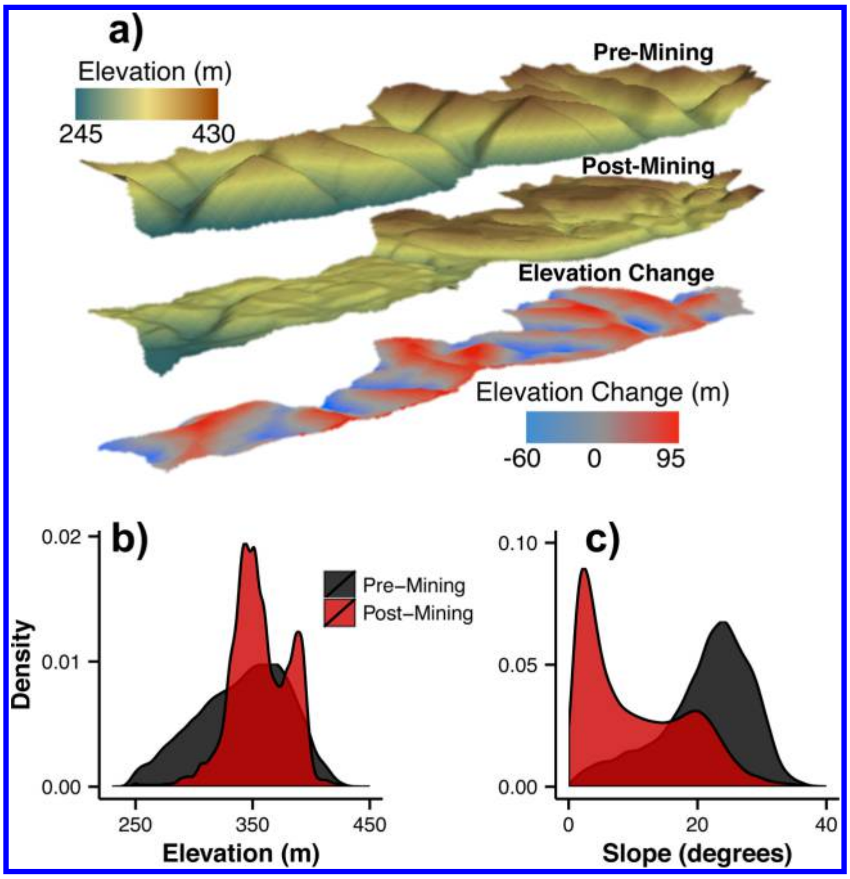


Figure 2. Change in watershed shape from mining at a single valley fill, Connelly Branch in the Hobet Mine Complex, WV. (a) 3-D surfaces highlighting areas with significant elevation change (valley filling in red, ridge cutting in blue). (b) and (c) show probability density functions for elevation and slope for preand postmining watershed configuration.

2010 (http://tagis.dep.wv.gov/home/?q=node/6), and readily available digitized historic elevation maps from the West Virginia Department of Environmental Protection (WVDEP). LiDAR, a portmanteau of light and radar, is a technique employed to yield high-resolution elevation data using aircraft, onboard GPS, and laser bursts that return elevation information at subcm vertical (z) and horizontal (x,y) accuracy.

Approach. We confined our analysis of elevation change to areas of southern West Virginia for which mountaintop mining has been detected via areal imagery delineation.[40] This initial analysis by Bernhardt and others[40] mapped cumulative area under active, abandoned, and reclaimed mines on a decadal time scale since 1976. We updated this map by adding areas of mining detected in a more recent analysis of mining extent from 2011.[28] This final data set of mining extent includes cumulative estimates of areas mined for the years 1976, 1985, 1995, 2005, 2011. In some cases underground mines occur deep below mountaintop mines. However, the geomorphic impact from deep mines on the surface is much more localized[49] and relatively small compared to the magnitude of impact from surface mines.

In order to examine changes in both topography and valley fill volumes, we compared a historic premining digital elevation model (DEM) to a postmining DEM generated in 2010 (approach illustrated in Figure 2a). The premining DEM was generated by the WVDEP using USGS 7.5 min quadrangles and ARCGIS's TOPOGRID conversion algorithm (ESRI, Redlands, CA) to produce a 10m resolution premining DEM[50,51] with most data generated before 1970. We generated the 10m postmining DEM from LiDAR flown in 2010 using the LiDAR to raster tool in ARCGIS 10.1, with coordinates matching the premining DEM extent.

Because the two DEMs were generated using different techniques, we assessed potential background measurement error between DEMs by generating more than 300 000 random points in areas with no current, historic, or permitted mining or other forms of land use, other than forestry.[28,40] At each of these points we subtracted the 2010 DEM from the historic DEM, attributing any difference in elevation to differences in elevation caused by the two different DEM-generation techniques (Topogrid vs LiDAR). LiDAR elevation data were generated in 2010, so for our analysis of mined landscapes, we only used areas that were mined as of 2005, to avoid misclassifying areas that were not mined in 2010, but were in 2011.

Historic elevation estimates were tightly correlated with the 2010 elevation values with a slope of 0.998 and an R^2 of 0.999 (Supporting Information (SI) Figure 1), but there are some differences between the two DEMs. The error distribution is normally distributed with a median, mean, and standard deviation of 0.22 m, 0.36 m, and 6 m, respectively (SI Figure 2). These values reflect that overall, the historic elevation data set consistently under-predicts the 2010 LiDAR elevations by an average of 36 cm, potentially because LiDAR has been shown to overestimate elevation in densely forested areas of southern West Virginia.[50] As with elevation, we also assessed background differences between the LiDAR and historic DEM in terms of slope. Median, mean, and standard deviation slope differences in unmined landscapes were 1.09°, 1.14°, and 0.09°,

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

respectively, with LiDAR sourced DEMs generating steeper slope estimates. This difference in unmined landscapes likely reflects the finer resolution data from LiDAR being able to detect steeper slopes.[52]

Determining Changes in Topography. Changes in topography were evaluated by aggregating data at the regional scale and at the smallest watershed size catalogued by the USGS (Hydrologic Unit Code HUC-12, SI Table 1). These watersheds range in size between 50 and 150 km^2 and were clipped to areas with available data. After removing watersheds with <1% mining, we had 90 HUC 12-digit watersheds remaining in our study area. For each watershed, we assessed changes in topography by comparing pre- and postmining elevation and slope distributions (Figure 2). With these data, we estimated how both the entire watershed and the mined portions of each watershed changed in terms of altered slope and elevation distributions.

Identifying Valley Fills and Calculating Valley Fill Volumes. With the pre- and postmining elevation data sets, we detected valley fills by subtracting the premining DEM from the postmining DEM. To generate a database of valley fills, we set a threshold for real elevation increases attributable to mining at the point where 96% of background error could be excluded (SI Figure 2). This corresponded to 11.4 m. We then subtracted the mean error (0.36 m) from this threshold to ensure a conservative valley fill delineation threshold. Thus, any elevation gains greater than 11m could be classified as a valley fill. The 96% threshold was used because it mapped valley fills that most clearly overlapped with the database of valley fills generated by the WVDEP.[50,51] For each identified valley fill, we estimated the mean and maximum depth of the fill and the total areal extent. From this we calculated the volume of overburden. We matched our valley fill database to the WVDEP's database, which was generated using similar DEM differencing approaches and mining permits.[50,51] Both the WVDEP database and our own analysis detected valley fills that were not associated with permits, but we restricted our analysis to only fills identified in both analyses.[50,51] One advantage to merging these databases is that the WVDEP database has approximate age estimates for valley fill completion era. These are pre-1984, 1985−1990, 1991−1996, 1997−2003, and 2004−2009. The WVDEP data set contains a total of 1,765 permitted valley fills in our study area. Our DEM differencing approach detected 1,544 of these fills, with smaller fills being missed due to our conservative minimum threshold of 11m of elevation change.

Collection and Analysis of Valley Fill Chemistry Data. To understand how the physical changes from mining impact water quality, we examined water chemistry data collected on a bimonthly basis for the National Pollution Discharge Elimination System (NPDES). Ideally, we would look at trends in the dominant ions associated with AlkMD (SO_4^{2-}, Ca^{2+}, Mg^{2+}, HCO_3^-). However, NPDES monitoring data only consistently report pH, iron (Fe), and manganese (Mn) (critical indicators of acid mine drainage) and a subset reported selenium (Se) in some more recent cases. Of these only pH and Se have been identified as indicators of AlkMD so we focused our analyses on these constituents.[16] Se is one of the key pollutants associated with mountaintop mining and has an EPA water quality standard of 5 parts per billion, due to its negative impacts on birds and fish.[19] To examine changes over time within individual valley fills, we restricted our analysis to sites with more than three years of data.

We linked individual NPDES monitoring points with valley fills from our database using ESRI ARCGIS (Redlands, CA) network analysis tool. We verified the spatial colocation of monitoring sites and valley fill locations using Google Earth. In the end we were able to amass data for 91 valley fills where biweekly pH data was reported for more than 3 years, and 31 valley fills for which biweekly Se data was reported for more than 3 years. This analysis generated a data set that linked valley fill characteristics (age, overburden depth, area, and volume) together with bimonthly stream chemistry.

Multiple linear regression models were used to test how geology (primary and secondary bedrock type), valley fill characteristics (mean depth, area, overburden volume), watershed characteristics (slope, elevation, % mining), and mine age influenced pH and Se concentration, using mean concentrations for each NPDES site. Within each NPDES site, we tested for changes in Se concentration and pH over time by running simple linear regression with annually averaged values. All statistical analyses and figurs were done using R statistical software and ggplot2.[53]

RESULTS

By combining data from Bernhardt and others[40] and Maxwell et al.[54] we estimate that from 2005 to 2011 mining has expanded from 938 km^2 to 1165 km^2, with active, reclaimed and abandoned surface coal mines now covering more than 10% of the study area (Figure 1). Because mining occupies such a large portion of the landscape we report landscape change results for the entire 11 500 km^2 study area as well as for the mined fraction independently.

Mining Impacts on Topography. Mountaintop mining has dramatic and sometimes counterintuitive impacts on landscape topography which are easier to describe for an individual mine. We illustrate the topographic impact using a single large fill, Connelly Branch, (6.4 km^2, Figure 2). In the Connelly Branch watershed mining operations raised the minimum elevation of the valley by 36m (1% quantile) as a result of filling the valleys with waste rock. This rock was generated by mining ridges within the watershed, lowering them by a mean of 11 m (99% quantile). Together this ridge cutting and valley filling increased the mean elevation of the Connelly Branch watershed by 14.5 m, decreased the standard deviation of elevation by 14m, and decreased the mean watershed slope by 11° (Figure 2). The majority of slopes in the watershed are now found at two distinct peaks (2° and 21°), that are each distinct from the premining slope distribution peak of 28°(Figure 2).

The results at Connelly Branch capture general trends for topographic changes observed throughout our study area. Elevation changes detected in our analysis show that valley fills can be buried as deep as 200m and ridge cuts as deep as 200m, values in the range of previous work.[11,22] Pre vs post mining 3D map comparisons and topographic descriptors are available for all watersheds at www.minedwatersheds.com. Over mined areas, we measured slope decreases in all 90 HUC-12 watersheds with 84 watersheds having decreases greater than 1.14°, a detection threshold from background error estimates between the two source DEMs. For elevation change this threshold is 36 cm, and we found 74 watersheds with significant increases in elevation and only nine with significant decreases. For the nine watersheds with decreases in elevation, this may occur because overburden material has been moved across watershed boundaries and deposited into an adjacent water-

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

shed, or relatively slight subsidence induced from deep mines may lower surface elevations.[55]

Prior to mining, watersheds in the region had a distinct unimodal slope distribution with peak frequencies ∼28° (Figure 3). Mining activities have altered the slope distributions, so that now there are two characteristic peak frequencies occurring at slopes of ∼2° and ∼20°. Such bimodal slope distributions are rarely observed in watersheds of this size in the absence of mining.[56] This change to mined landscapes has created a secondary slope peak for the entire 11 500 km^2 region (Figure 3). In mined locations, there has been a 30% increase in areas with slopes lower than 25°, reflecting newly created flat ridges and gentle hillslopes, once rare in Central Appalachia.[18,24,57] In many areas, mining also creates flat plateaus,[18,24] a sharp contrast to the observed pattern of steepening topography in the Appalachians caused by differential erosion rates.[57,58]

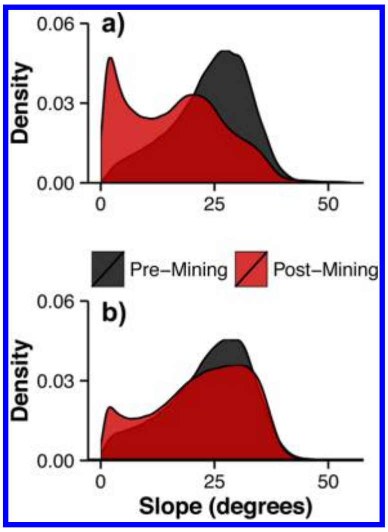


Figure 3.) Changes in slope distributions over (a) mined regions exclusively, and (b) regional slope distribution by creating large tracts of land with slopes near 0−2°.

Mining alters topography both in terms of slope and elevation. Postmining landscapes have been raised an average of 3m in elevation, despite the removal of coal seams estimated to be 1−1.5 m thick.[21] This counterintuitive result can only be explained by significant increases in the volume of pore space within the-now-crushed valley fill material, where porosity has been estimated to range from 20 to 57%.[59,60]

There are two important implications of this increased pore space and flattened topography. First, some proportion of this pore space is capable of storing water, which likely alters flowpaths and creates enhanced water storage capacity within individual mined watersheds and throughout the region.[22,61] Second, this increased porosity should act in concert with reduced slopes to increase the residence time of water within mined watersheds, a prediction confirmed empirically for some watersheds.[62−64] In addition to altering the relationship between patterns of rainfall and runoff this increased water residence time promotes the extraction of soluble constituent elements from coal and shale residues within the fill material, a process that is likely generating the AlkMD signal seen in so many previous studies.[16,38−40]

Identification and Characterization of Valley Fills. Valley fills within the study area vary widely in size, depth, and volume (Figure 4), with typical median dimensions (area, mean depth, max depth, volume) all increasing over time (SI Figure 4) such that median valley fill volumes have been increasing by an average of 75 000 m^3 per year for 25 years (Figure 4A). Since the early 1970s, there has been a linear increase in the total volume of waste rock deposited in central Appalachian valleys (Figure 4d). The largest valley fill identified is 2.9 km^2 in area with a maximum depth of 184 m, and a mean depth of 70 m. This single fill holds more than 200 million m^3 of rock overburden, a volume equal to the volume of material deposited from the 1980 Mt. St. Helens eruption.[65] Cumulatively, the 1544 valley fills in the study area contain more than 6.4 billion m^3 (6.4 km^3) of rock overburden (Figure 4d), a volume roughly equivalent to the volume of ejecta from the 1991 Mount Pinatubo eruption.[66] While large, this is a substantial underestimate of the total volume of displaced rock. Mining operations deposit much of the overburden generated during mining operations into valley fills, but not all. Some unknown portion of unconsolidated bedrock is also used to rebuild the ridges and plateaus typical of the postmining landscape. Because our estimates only detect the volume of overburden stored in valley fills, they represent a highly conservative estimate of the total overburden volume deposited in the postmining landscape.

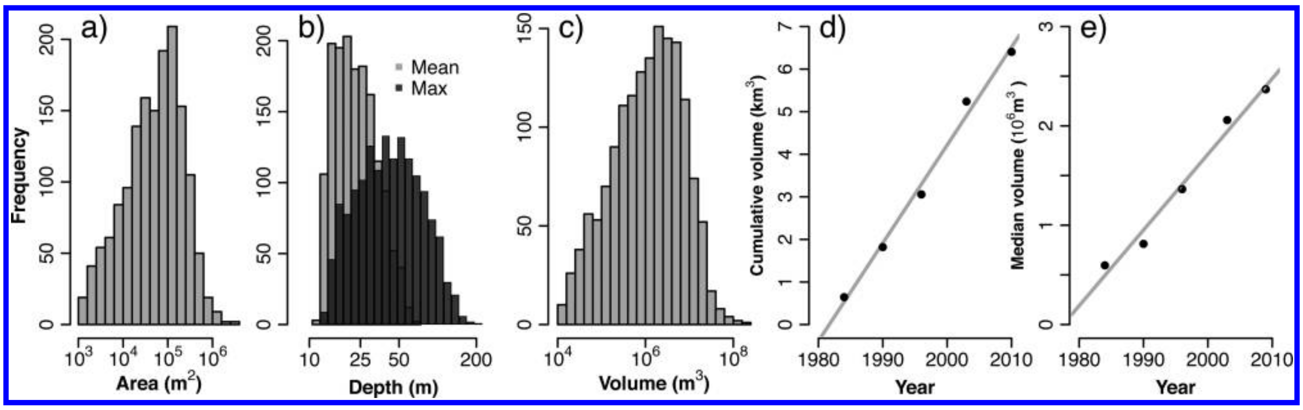


Figure 4. Valley fill attributes for 1544 valley fills detected in our analyses from 1984 to 2009. (a) Histogram of valley fill areas. (b) Histogram of both mean (in light gray) and max (in dark gray) depth of valley fills while (c) the volume of valley fills. (d) The constant, increasing cumulative volume of overburden deposited into headwater valleys. (e) Shows the constantly increasing median volume of valley fills through time.

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

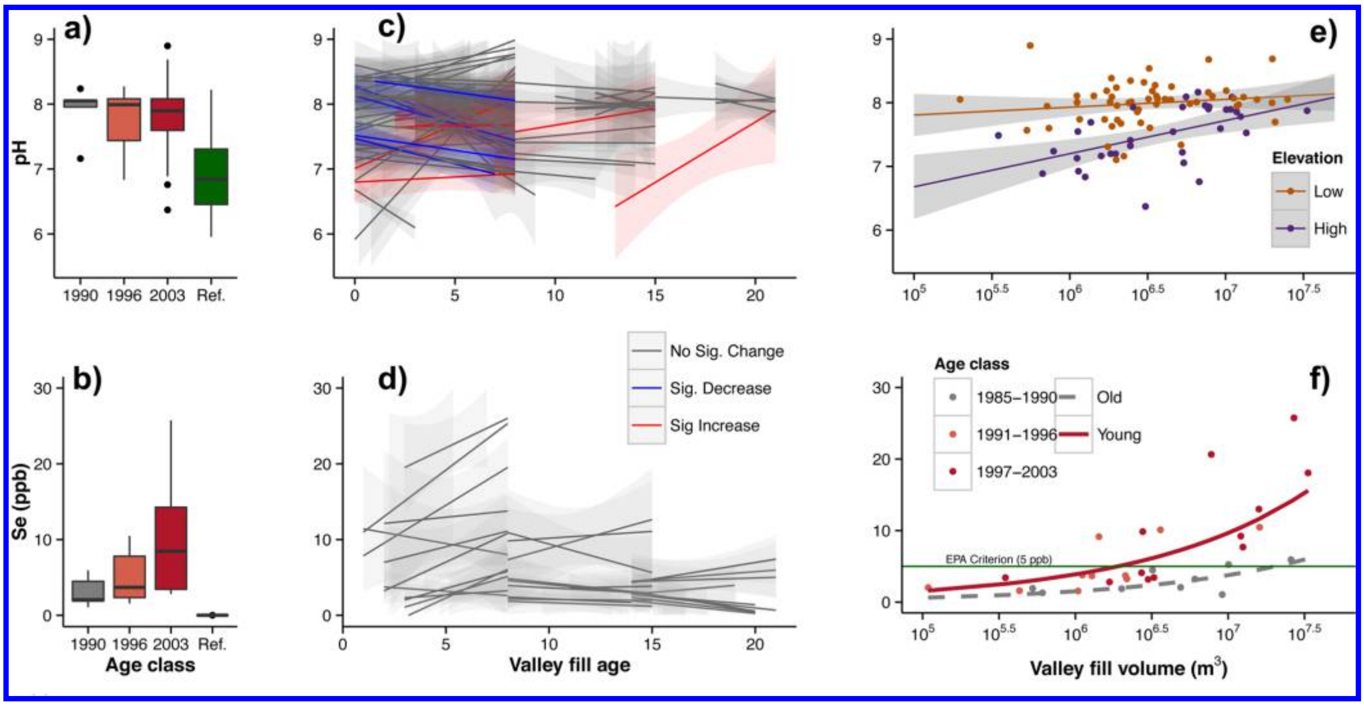


Figure 5. Boxplots for average stream concentration of (a) pH and (b) Se for mines of different ages, shows mean (black bar), 25−75% quanties (box), range (whisker lines), and outliers (black dots). (c) and (d) show regression lines for annual mean stream concentration of (c) pH and (d) Se within individual valley fills. Gray lines indicate no significant trend, whereas red shows significant increases, and blue shows significant declines over time; Se (d) had no trends over time for any valley fills. Relationship between valley fill volume and (e) pH and (f) Se. For pH Valley fill volume is a strong predictor of pH only at high elevation sites ($p < 0.001$ $r^2 = 0.30$) with elevation and volume explaining 37% of the variation in pH ($p < 0.001$). For Se valley fill volume and valley fill age class combine to explain 63% of variance in Se trends between sites, both old (gray), and young (red) sites have the same slope in log−log space, but the *y*-axis shown here is not in log space. There is an order of magnitude increase in valley fill volume showing a 2.6 ppb increase in mean Se concentration.

There are reasons to expect that larger volumes of overburden will induce larger effects on downstream hydrology and biogeochemistry. Valley fills have large potential to store water, where in the matrix of unweathered pyritic bedrock, water, and air generate alkaline mine drainage. Previous studies estimate actual volumetric water content of waste rock to be from 20 to 40%[37,59] and total porosity, or potential water storage, to be from 20 to 57%.[59,60] Some portion of this pore space can fill with water, and conservatively scaling from this lower bound of 20%,[37,59,60] we estimate that valley fills in the study area have a theoretical capacity to store more than 1.3 km^3 of water or 7 m spread over all 180 km^2 of valley fills in southwestern West Virginia. This water volume is approximately equivalent to 1 year's worth of rainfall for the region(http://www.prism.oregonstate.edu/normals/). For comparison, unmined hillslope catchments in southern West Virginia have very shallow soils (typically <2 m)[67] and fractured[68,69] but low porosity bedrock.[69] Using the highest estimate of water holding capacity for clay/loam soils of 40%[70] times a max soil depth of 2m, unmined catchments could hold a maximum of 0.8 m of water. Even using these conservative estimates, mining could increase the water holding capacity of the region by 10×. While it is possible that water that reaches valley fills is quickly routed through large macro-pores and underground channels, the large storage volume coupled with observed increases in baseflow in some mined watersheds,[62,64] generally support the idea that valley fills can store and retain large volumes of water.

Linking Valley Fills with Water Chemistry Impacts. Streams draining valley fills have significantly higher pH and Se concentrations than reference streams in the region (Figure 5a,b). For the 91 valley fills reporting pH data, average effluent pH had a mean pH of 7.8 (7.7−7.9, 95% CI), whereas reference streams have an average pH almost an order of magnitude lower than mined sites at 6.9 (6.6−7.1, 95% CI, Figure 5a). Selenium was reported for many fewer valley fills ($n = 31$), but was consistently higher in valley fill effluent, averaging 6.4 and ranging from 1.4 to 19.3 ppb (95% quantiles), while Se is nearly always below detection (0.01 ppb) in reference streams (Figure 5b). Within the full data set of Selenium, 12 valley fills reported mean Se concentrations that were above the EPA criterion of 5 ppb, and all 31 of the valley fills reported Se concentrations greater than 5 ppb on at least one sampling occasion.

With such common exceedances, we—and previous researchers—have worked to understand what drives observed differences between different streams impacted by mountaintop mining. One strong trend evident in this research is with more mining, measured as percent cover, there is a cumulative impact on stream chemistry with increasing concentrations of AlkMD constituents.[16,38,40] However, there is still large variation in valley fill effluent chemistry when percent mining is equally high between watersheds,[38] suggesting that there are strong drivers of stream chemistry beyond percent area mined.

One possible explanation for this variation is that older mines and valley fills have lower concentrations of AlkMD constituents. Studies of acid- and deep-mine pollution evolution shows that mining-associated pollutant concentration generally declines over time in Scotland,[32,71] Wales,[32] England,[32] Pennsylvania,[35] Germany,[33] and Utah.[72] The timescale of these declines range from 25 years[35] to more than a

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

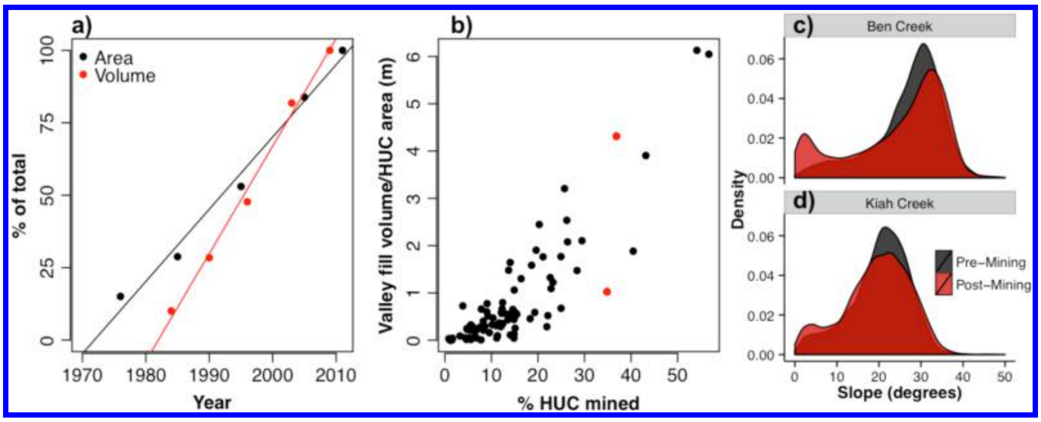


Figure 6. Two vs three-dimensional assessment of mining impacts. (a) Shows that the rate of increase in cumulative valley fill volume (shown as a percentage of current total, in red) is growing faster than the rate of areal expansion of mining (in black). (b) Shows how variation in % watershed mined and cumulative volume, highlighting two particularly divergent watersheds of similar % area mined (~35%, in red) but 5× difference in cumulative valley fill volume. (c) and (d) Again show how watersheds with similar % area mined can have very different impacts on topography with Ben Creek (c) showing a much higher reduction in slope than Kiah Creek (d).

century.[33] In mountaintop mining overburden spoil piles, similar time-scales (~25 years) of declining pollution have been estimated for selenium[46,47] and salinity.[45] However, since few individual mines have been monitored for more than a decade after construction, these estimates of the longevity of mountaintop mining are based on a space-for-time substitution approach or future projections of water quality.[45,46] These approaches suggest a sharp decline in specific conductance[45] (a proxy for many AlkMD associated ions) and selenium[46] over a ~25 year period. It is important to note that to this approach implicitly assumes that mining impacts have not changed over time or vary across space. As our analysis clearly shows, this assumption is violated. There have been significant increases in median depth, area and volume of valley fills over the last three decades with significant spatial variation between mines.

Using our database of valley fill characteristics we were able to examine how variation in physical features of these fills could explain variation in effluent pH and Se. For selenium, we were able to acquire data for 31 sites with between 4 and 9 years of sampling data at each site. There were no significant declines in annual mean selenium concentration over time for any of these fills (Figure 5d), even in the intermediate and older valley fills, where previous estimates would suggest that selenium generation should be declining.[46] We were able to obtain pH data for 90 sites with between 3 and 8 years of sampling data (Figure 5c). Reductions in alkaline mine drainage generation should be associated with declines in pH toward reference conditions, yet we only observed a significant decline in pH in seven out of the 90 streams draining valley fills (Figure 5c). A similar number of streams (n = 9) documented additional increases in pH over the monitoring period. For the majority of fills (n = 75) pH remained elevated and there were no detectable trends over time. These results are inconsistent with the conclusions of prior studies,[45,46] which have indicated that AlkMD production declines over relatively short time scales. Our results suggest instead that older fills are generating less Se than modern fills, but the lack of any directional change in individual fills supports the hypothesis that this difference arises from changes in mining practice over time (e.g changes in the type or number of coal seams and shale overburden layers accessed) rather than a predictable decline of Se generation over time.

Further supporting this alternate hypothesis, we found that average pH and Se concentration were positively correlated with valley fill volume. For pH, the positive relationship between fill volume and increasing pH was detectable at higher elevation sites (>415m, Figure 5e). At these sites, valley fill volume explained 30% of the variation in effluent pH; the slope of this relationship suggests that for every order of magnitude increase in fill volume (e.g., from 10^6 to 10^7 m^3) there is a 0.54 unit increase in effluent pH (Figure 5e). No relationship between pH and valley fill volume was seen for lower elevation sites, where pH is consistently elevated by mining activities regardless of fill volume (Figure 5e). The combined linear model with both elevation as a factor (high and low elevation sites) and volume, explains 37% of the variation in pH (p < 0.001). One possible explanation for the difference between low and high elevation sites is that the chemical composition of coal seams or bedrock may vary with elevation in subtle ways not represented by coarse regional maps of geology.[73] This may affect pyrite:calcareous bedrock mixing ratios which help determine valley fill effluent pH.[74]

Together valley fill volume and fill age explained 63% of the variation in Se concentrations (P < 0.001, Figure 5). The slope of the relationships relating stream Se and valley fill volume was the same for both old and young fills, suggesting that for every order of magnitude increase in valley fill volume mean Se concentration increases by 2.6 ppb (Figure 5f). The difference between the two valley fill age classes was in the intercept, which was 2.4 ppb higher for younger valley fills. The divergent intercepts between age classes is consistent with the hypothesis that more recent mines may be accessing coal and shale layers with a higher Se content than their earlier counterparts.

While valley fill volumes are correlated with Selenium concentration and pH, we cannot isolate a clear mechanistic link between fill volume and AlkMD generation. There are several possible explanations for this correlation. First, it is likely that larger volume fills are associated with mines that are larger and deeper and thus accessing a larger number and greater diversity of acid generating and Se bearing deposits. It is nearly certain that larger valley fill volumes represent larger stores (in mass) of both pyritic material and carbonate bedrock which generate stronger signals of AlkMD as shown by Wellen and others.[75] Another possibility is that larger valley fills have more hydrologic flux through spoil piles. Prior research on

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

deep[35] and surface mines[72] has shown that, at least early in mine-spoil chemical evolution, higher hydrologic fluxes increased mine pollutant concentration. Even as a proxy metric, these results, where volume of valley fill is strongly correlated with stream chemistry, highlight the importance of accounting for the scale of geomorphic change (especially overburden volume) when attempting to understand long-term impacts of mining on downstream chemistry,[45,47] though see ref 75.

Implications. While both the total area mined and the volume of overburden have grown linearly over the last 25+ years, the rate of increase in overburden volume is increasing faster than total area mined (Figure 6a). This suggests that, per area mined, mining operations were generating progressively more overburden through the 2010s, with important implications for continued impairment of downstream ecosystems. Additionally, these results highlight how poorly areal estimates of mining reflect the scale of disturbance in any given watershed. At the hydrologic unit code or HUC-12 scale, percent watershed mined does correlate strongly with estimates of overburden volume per unit area, or overburden depth if it were spread across entire watershed, (Figure 6b). However, there are orders of magnitude of variation around this relationship (Figure 6b), where the three-dimensional physical impacts to the landscape are more accurately captured in terms of overburden volume (Figure 6c), or total slope change (www.minedwatersheds.com).

With the volume of valley fills growing faster than the area of land disturbed, one key finding in this study is that valley fill volume correlates more strongly with stream chemistry than areal metrics (like percent area disturbed). This result is consistent with previous studies where the mass (or volume) of overburden is the single best predictor of stream chemistry for streams emerging from valley fills.[75] Mining expansion rates, as detected by areal analysis of satellite imagery as in[40] do not provide sufficient data to understand and predict current and future water quality impacts from mining activities. Furthermore, studies attempting to understand the long-term water quality trends downstream of mines must account for variation in valley fill and overburden volume.

The volume of change in bedrock—or in Jenny's soil formation terms,[23] parent material—is only one aspect of mountaintop mining disturbance. Mining also effects relief, climate, biotic communities, and time, or time for ecosystem to coevolve with other state factors. The large reduction in local and regional relief can have several cascading impacts, including increasing insolation by reducing hillslope shading as Wickham and others found,[24] slowing the delivery of stormwater from hillslopes to streams,[62,64] and increasing the residence times for water stored in overburden piles.[64]

Contrastingly, reclaimed mines have been shown to have areas with high surface soil compaction,[60,76] with evidence that some mines can act to increase stormflow.[77,78] This apparent contradiction where mines can both decrease[64] and increase stormflow[77,78] may be explained by different mine reclamation techniques with varying degrees of soil compaction,[76] or regional variation,[79] or threshold type responses.[80] For smaller or less intense rainstorms, it is possible that reclaimed mine areas are able to effectively store incoming water, while for the largest or most-intense storms, areas of the mine with compacted soils reach excess infiltration quickly and generate a strong storm response.[61] These ideas are speculative and the potential for threshold responses in the hydrology of mined sites requires further study.[45,64,81]

The biogeochemical and hydrologic cycles are further impacted by the reduced interaction between plants and the water table. In the premined environment, soils are typically shallow, at most 2 m deep.[67,68] Tree roots can access water throughout the shallow soil profile, exerting a strong control on patterns of transpiration and total water yield from forested watersheds.[82] In the postmined environment, overburden depths can exceed 200 m (the maximum valley fill depth in our data set is ~250 m) and most mined sites have little or no forest recovery following mining.[26] Instead mines are covered in grasses and shrubs.[26] Together these deep overburden depths and plant species with shallower rooting systems[83] are likely to greatly reduce the influence of plants on hydrologic and biogeochemical cycling in postmined landscapes. Along with reduced slopes and increased storage potential, this reduction in transpiration may help explain increases in baseflow in mined sites[61,64] and stronger signals of alkaline mine drainage (higher specific conductance, pH and ion concentrations) during low-flow periods, when deep flow-paths most dominate the stream network.[61] Further, these changes in relief and hydrogeochemistry in the mined environment may provide feedbacks that discourage the recovery of native vegetation,[26] which evolved in steep landscapes with dilute, shallow flow systems.[61]

■ CONCLUSIONS

Our analysis demonstrates that the scale of mining impacts penetrate deep into bedrock and persist over longer time scales than traditional two-dimensional assessments of land use would suggest. Mountaintop mining has little physically in common with deforestation, where the dominant effects from disturbance are mediated through ecological factors, and ecosystems return to similar predisturbance hydrologic and biogeochemical regimes over decadal time scales.[84] The physical effects from mountaintop mining are much more similar to volcanic eruptions, where the entire landscape is fractured, deepened, and decoupled from prior landscape evolution trajectories, effectively resetting the clock on landscape and ecosystem coevolution.

For disturbances deep enough to reset not only short-term ecological community structure, but also geology and geomorphologic evolution, it is vital that we account for the full three-dimensional scale of environmental impact. Maps of environmental change can create false equivalencies between quantitative and qualitatively different impacts. The need for a three-dimensional analysis of change is clear for mountaintop mining,[75] but will also improve our assessments of land use change with substantial earth-moving activities[85] like building cities,[86,87] creating agricultural land and suburbs,[87] and mining other hydrocarbons.[10] In the case of mountaintop mining, quantifying the physical dimensions of landscape impact provides demonstrable improvements in prediction of water quality trends over time, and potentially, other valuable insights like changes to stream and river flooding[61,64,79] and baseflow[62,64] in mined catchments.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04532.

Table showing all USGS watersheds is in SI Table 1. Figures showing correlation (SI 1) and background error distribution (SI 2) in unmined sites between historic DEM and 2010 DEM. The difference in slope distributions in unmined landscape, where there should be little geomorphic change is shown in SI Figure 3. Finally, the changing median characteristics of valley fills is shown in SI Figure 4 (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: matt.ross@duke.edu.

Author Contributions

The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the West Virginia Department of Environmental Protection for providing the data used in this study, as well as helpful reviews from Bill Schlesinger, Greg Hancock, and Fabian Nippgen. Several anonymous reviewers also helped improve this work. We gratefully acknowledge financial support from the Foundation for the Carolinas to the Nicholas School of the Environment, Duke University and to the Wireless Intelligent Sensor Network IGERT (grant DGE-1068871) and NSF Graduate Research Fellowship Program and NSF EAR (grant 1417405).

REFERENCES

(1) Hooke, R.; Martín-Duque, J.; Pedraza, J. Land transformation by humans: A review. *GSA Today* **2012**, *22*, 4−10.
(2) Foley, J.; DeFries, R.; Asner, G.; Barford, C. Global consequences of land use. *Science* **2005**, *309*, 570−574.
(3) Cardinale, B. J.; Duffy, J. E.; Gonzalez, A.; Hooper, D. U.; Perrings, C.; Venail, P.; Narwani, A.; Mace, G. M.; Tilman, D.; A.Wardle, D.; et al. Biodiversity loss and its impact on humanity. *Nature* **2012**, *489*, 326−326.
(4) Kalnay, E.; Cai, M. Impact of urbanization and land-use change on climate. *Nature* **2003**, *423*, 528−531.
(5) Broussard, W.; Turner, R. E. A century of changing land-use and water-quality relationships in the continental US. *Front. Ecol. Environ.* **2009**, *7*, 302−307.
(6) Vörösmarty, C. J.; Pahl-Wostl, C.; Bunn, S. E.; Lawford, R. Global water, the anthropocene and the transformation of a science. *Curr. Opin. Environ. Sustain.* **2013**, *5*, 539−550.
(7) Vörösmarty, C.; Sahagian, D. Anthropogenic disturbance of the terrestrial water cycle. *BioScience* **2000**, *50*, 753−765.
(8) Green, K.; Kempka, D.; Lackey, L. Using remote sensing to detect and monitor land-cover and land-use change. *Photogramm. Eng. Remote Sensing* **1994**, *60*, 331−337.
(9) Drummond, M. A.; Loveland, T. R. Land-use pressure and a transition to forest-cover loss in the eastern United States. *BioScience* **2010**, *60*, 286−298.
(10) Latifovic, R.; Fytas, K.; Chen, J.; Paraszczak, J. Assessing land cover change resulting from large surface mining development. *ITC J.* **2005**, *7*, 29−48.
(11) 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 Sens. Environ.* **2009**, *113*, 62−72.
(12) WVGES. *Coal Summary Statistics*; 2010.
(13) KGS. *Coal Production Database*; 2015.
(14) Omernik, J. M.; Griffith, G. E. Ecoregions of the conterminous United States: evolution of a hierarchical spatial framework. *Environ. Manage.* **2014**, *54*, 1249−1266.
(15) Bernhardt, E. S.; Palmer, M. a. The environmental costs of mountaintop mining valley fill operations for aquatic ecosystems of the Central Appalachians. *Ann. N. Y. Acad. Sci.* **2011**, *1223*, 39−57.
(16) 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*−*418*, 1−12.
(17) Palmer, M. A.; Bernhardt, E. S.; Schlesinger, W. H.; Eshleman, K. N.; Fougoula-Georgiou, E.; Hendryx, M. S.; Lemly, A. D.; Likens, G. E.; Loucks, O. L.; Power, M. E.; et al. Mountaintop mining consequences. *Science* **2010**, *327*, 148−149.
(18) Maxwell, A. E.; Strager, M. P. Assessing landform alterations induced by mountaintop mining. *Nat. Sci.* **2013**, *05*, 229−237.
(19) U. S. EPA. *The Effects of Mountaintop Mines and Valley Fills on Aquatic Ecosystems of the Central Appalachian Coalfields*; Washington, DC, 2011.
(20) Palmer, M. A.; Hondula, K. L. Restoration as mitigation: analysis of stream mitigation for coal mining impacts in Southern Appalachia. *Environ. Sci. Technol.* **2014**, *48*, 105520−110560.
(21) Lutz, B. D.; Bernhardt, E. S.; Schlesinger, W. H. The environmental price tag on a ton of mountaintop removal coal. *PLoS One* **2013**, *8*, 1−5.
(22) Miller, A.; Zégre, N. Mountaintop removal mining and catchment hydrology. *Water* **2014**, *6*, 472−499.
(23) Jenny, H. *Factors of Soil Formation: A System of Quantitative Pedology*; McGraw-Hill: New York, NY, 1994.
(24) Wickham, J.; Wood, P. B.; Nicholson, M. C.; Jenkins, W.; Druckenbrod, D.; Suter, G. W.; Strager, M. P.; Mazzarella, C.; Amos, J. The Overlooked Terrestrial Impacts of Mountaintop Mining. *BioScience* **2013**, *63*, 335−348.
(25) Angel, P.; Davis, V.; BurgerJ. The Appalachian regional reforestation initiative*For. Reclam.* **2005**
(26) Zipper, C. E.; Burger, J. a; Skousen, J. G.; Angel, P. N.; Barton, C. D.; Davis, V.; Franklin, J. a. Restoring forests and associated ecosystem services on appalachian coal surface mines. *Environ. Manage.* **2011**, *47*, 751−765.
(27) Rodrigue, J. A.; Burger, J. A.; Oderwald, R. G. Forest productivity and commercial value of pre-law reclaimed mined land in the eastern United States. *North. J. Appl. For.* **2002**, *19*, 106−114.
(28) Maxwell, A. E.; Warner, T. a. Differentiating mine-reclaimed grasslands from spectrally similar land cover using terrain variables and object-based machine learning classification. *Int. J. Remote Sens.* **2015**, *36*, 4384−4410.
(29) Bendfeldt, E. S.; Burger, J. a.; Daniels, W. L. Quality of Amended Mine Soils After Sixteen Years. *Soil Sci. Soc. Am. J.* **2001**, *65*, 1736.
(30) Corenblit, D.; Baas, A. C. W.; Bornette, G.; Darrozes, J.; Delmotte, S.; Francis, R. a.; Gurnell, A. M.; Julien, F.; Naiman, R. J.; Steiger, J. Feedbacks between geomorphology and biota controlling Earth surface processes and landforms: A review of foundation concepts and current understandings. *Earth-Sci. Rev.* **2011**, *106*, 307−331.
(31) Silverman, M. P.; Ehrlich, H. L. Microbial formation and degradation of minerals. *Adv. Appl. Microbiol.* **1964**, 6.15310.1016/S0065-2164(08)70626-9
(32) Younger, P. L. The longevity of minewater pollution: A basis for decision-making. *Sci. Total Environ.* **1997**, *194*−*195*, 457−466.
(33) Gerke, H. H.; Molson, J. W.; Frind, E. O. Modelling the effect of chemical heterogeneity on acidification and solute leaching in overburden mine spoils. *J. Hydrol.* **1998**, *209*, 166−185.
(34) Banks, D.; Younger, P. L.; Arnesen, R. T.; Iversen, E. R.; Banks, S. B. Mine-water chemistry: The good, the bad and the ugly. *Environ. Geol.* **1997**, *32*, 157−174.
(35) Lambert, D. C.; McDonough, K. M.; Dzombak, D. A. Long-term changes in quality of discharge water from abandoned

underground coal mines in Uniontown Syncline, Fayette County, PA, USA. *Water Res.* **2004**, *38*, 277−288.
(36) Evangelou, V. P. (Bill); Zhang, Y. L. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Crit. Rev. Environ. Sci. Technol.* **1995**, *25*, 141−199.
(37) Hawkins, J. W. Predictability of Surface Mine Spoil Hydrologic Properties in the Appalachian Plateau. *Groundwater* **2004**, *42*, 119−125.
(38) 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*, 20929−20934.
(39) Vengosh, A.; Lindberg, T. T.; Merola, B. R.; Ruhl, L.; Warner, N. R.; White, A.; Dwyer, G. S.; Di Giulio, R. T. Isotopic imprints of mountaintop mining contaminants. *Environ. Sci. Technol.* **2013**, *47*, 10041−10048.
(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*, 8115−8122.
(41) 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. *J. North Am. Benthol. Soc.* **2008**, *27*, 717−737.
(42) 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*, 919.
(43) Hitt, N. P.; Chambers, D. B. Temporal changes in taxonomic and functional diversity of fish assemblages downstream from mountaintop mining. *Freshw. Sci.* **2014**, *33*, 915−926.
(44) Fritz, K. M.; Fulton, S.; Johnson, B. R.; Barton, C. D.; Jack, J. D.; Word, D. a.; Burke, R. a. Structural and functional characteristics of natural and constructed channels draining a reclaimed mountaintop removal and valley fill coal mine. *J. North Am. Benthol. Soc.* **2010**, *29*, 673−689.
(45) Evans, D. M.; Zipper, C. E.; Donovan, P. F.; Daniels, W. L. Long-term trends of specific conductance in waters discharged by coal-mine valley fills in central appalachia, USA. *J. Am. Water Resour. Assoc.* **2014**, *24061*, 1−12.
(46) Ziemkiewicz, P. F.; Lovett, R. J. Natural Selenium Attenuation at the Lab, Outlet, and Watershed Scales. In *West Virginia Mine Drainage Task Force Symposium*; West Virginia Water Research Institute, West Virginia University, 2012; pp 8−20.
(47) Ziemkiewicz, P. F.; O'Neal, M.; Lovett, R. J. Selenium leaching kinetics and In situ control. *Mine Water Environ.* **2011**, *30*, 141−150.
(48) Copeland, C. *Mountaintop Mining: Background on Current Controversies*, 2014.
(49) Doerr, A.; Guernsey, L. Man as a geomorphological agent: the example of coal mining. *Ann. Assoc. Am. Geogr.* **1956**, *46*, 197−210.
(50) Shank, M. Development of a mining fill inventory from multi-date elevation data. In *the Advanced Integration of Geospatial Technologies and Integration Conference*; 2004; p 1:9.
(51) Shank, M. Trends in Mining Fills and Associated Stream Loss in West Virginia 1984−2009. *Environ. Prot.* **2010**, 1−15.
(52) Chow, T. E.; Hodgson, M. E. Effects of lidar post-spacing and DEM resolution to mean slope estimation. *Int. J. Geogr. Inf. Sci.* **2009**, *23*, 1277−1295.
(53) Wickham, H. ggplot2. *Wiley Interdiscip. Rev. Comput. Stat.* **2011**, *3*, 180−185.
(54) Maxwell, A. E.; Strager, M. P.; Yuill, C. B.; Petty, J. T. Modeling critical forest habitat in the southern coal fields of West Virginia. *Int. J. Ecol.* **2012**, *2012*.110.1155/2012/182683
(55) Gray, R. E.; Bruhn, R. W. Coal mine subsidence−eastern United States. *Rev. Eng. Geol.* **1984**, *6*, 123−150.
(56) Wolinsky, M. A.; Pratson, L. F. Constraints on landscape evolution from slope histograms. *Geology* **2005**, *33*, 477.
(57) Gallen, S.; Wegmann, K.; Bohnenstiehl, D. Miocene rejuvenation of topographic relief in the southern Appalachians. *GSA Today* **2013**, *23*, 4−10.
(58) Liu, L. Rejuvenation of Appalachian topography caused by subsidence-induced differential erosion. *Nat. Geosci.* **2014**, *7*, 518.
(59) Diodato, D. M.; Parizek, R. R. Unsaturated Hydrogeologic Properties of Reclaimed Coal Strip Mines. *Groundwater* **1994**, *32*, 108−118.
(60) 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*, 73−106.
(61) Evans, D. M.; Zipper, C. E.; Hester, E. T.; Schoenholtz, S. H. Hydrologic effects of surface coal mining in Appalachia (U.S.). *J. Am. Water Resour. Assoc.* **2015**, *24061*, 1436, DOI: 10.1111/1752-1688.12322
(62) Messinger, T.; Paybins, K. *Relations between Precipitation and Daily and Monthly Mean Flows in Gaged, Unmined, And Valley-Filled Watersheds, Ballard Fork, West Virginia, 1999−2001*; Charleston, WV, 2003.
(63) Paybins, K. S.; Messinger, T.; Eychaner, J. H.; Chamgers, D. B.; Kozar, M. D. *Water Quality in the Kanawha-New River Basin: West Virginia, Virginia, and North Carolina, 1996−98.*, 2000.
(64) 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*, 1257−1272.
(65) United States Geological Survey. *Mount St. Helens—From the 1980 Eruption to 2000*, 2000.
(66) Koyaguchi, T. Vol. estimation of tephra-fall deposits from the June 15, 1991, eruption of Mount Pinatubo by theoretical and geological Methods. In *Fire and Mud: Eruption and Lahars of Mount Pinatubo, Philippines*; Newhall, C. G.; Punongbayan, R. S., Eds.; University of Washington Press: Seattle, 1996; pp 584−600.
(67) Sucre, E.; Tuttle, J.; Fox, T. The use of ground-penetrating radar to accurately estimate soil depth in rocky forest soils. *For. Sci.* **2011**, *57*, 59−66.
(68) Everett, A. G. Secondary permeability as a possible factor in the origin of debris avalanches associated with heavy rainfall. *J. Hydrol.* **1979**, *43*, 347−354.
(69) Kozar, M. D.; Brown, D. P. *Location and Site Characteristics of the Ambient Ground-Water-Quality-Monitoring Network in West Viriginia*; 1995.
(70) Saxton, K. E.; Rawls, W. J.; Romberger, J. S.; Papendick, R. I. Estimating Generalized Soil-water Characteristics from Texture. *Soil Sci. Soc. Am. J.* **1986**, *50*, 1031−1036.
(71) Younger, P. L. Mine water pollution in Scotland: Nature, extent and preventative strategies. *Sci. Total Environ.* **2001**, *265*, 309−326.
(72) Mayo, a. L.; Petersen, E. C.; Kravits, C. Chemical evolution of coal mine drainage in a non-acid producing environment, Wasatch Plateau, Utah, USA. *J. Hydrol.* **2000**, *236*, 1−16.
(73) WVGES. Coal Bed Mapping Project.
(74) Skousen, J.; Simmons, J.; McDonald, L. M.; Ziemkiewicz, P. Acid-base accounting to predict post-mining drainage quality on surface mines. *J. Environ. Qual.* **2002**, *31*, 2034−2044.
(75) 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.
(76) Taylor, T. J.; Agouridis, C. T.; Warner, R. C.; Barton, C. D.; Angel, P. N. *Hydrol. Processes* **2009**, *3381*, 3372−3381.
(77) 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*, 3467−3483.
(78) 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*, 1−11.
(79) 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.

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

(80) Tromp-Van Meerveld, H. J.; McDonnell, J. J. Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. *Water Resour. Res.* **2006**, *42*, 1−11.
(81) Zégre, N. P.; Maxwell, A.; Lamont, S. Characterizing streamflow response of a mountaintop-mined watershed to changing land use. *Appl. Geogr.* **2013**, *39*, 5−15.
(82) Hornbeck, J. W.; Adams, M. B.; Corbett, E. S.; Verry, E. S.; Lynch, J. A. A summary of water yield experiments on hardwood forested watersheds in northeastern United States. In *10th Central Hardwood Forest Conference*; 1995; pp 282−295.
(83) Canadell, J.; Jackson, R. B.; Ehleringer, J. B.; Mooney, H. a.; Sala, O. E.; Schulze, E.-D. Maximum rooting depth of vegetation types at the global scale. *Oecologia* **1996**, *108*, 583−595.
(84) Brown, A. E.; Zhang, L.; McMahon, T. a.; Western, A. W.; Vertessy, R. a. A review of paired catchment studies for determining changes in water yield resulting from alterations in vegetation. *J. Hydrol.* **2005**, *310*, 28−61.
(85) Wilkinson, B. H. Humans as geologic agents: A deep-time perspective. *Geology* **2005**, *33*, 161−164.
(86) Jones, D. K.; Baker, M. E.; Miller, A. J.; Jarnagin, S. T.; Hogan, D. M. Tracking geomorphic signatures of watershed suburbanization with multitemporal LiDAR. *Geomorphology* **2014**, *219*, 42−52.
(87) Li, P.; Qian, H.; Wu, J. Environment: Accelerate research on land creation. *Nature* **2014**, *510*, 29−31.

DOI: 10.1021/acs.est.5b04532
Environ. Sci. Technol. XXXX, XXX, XXX−XXX