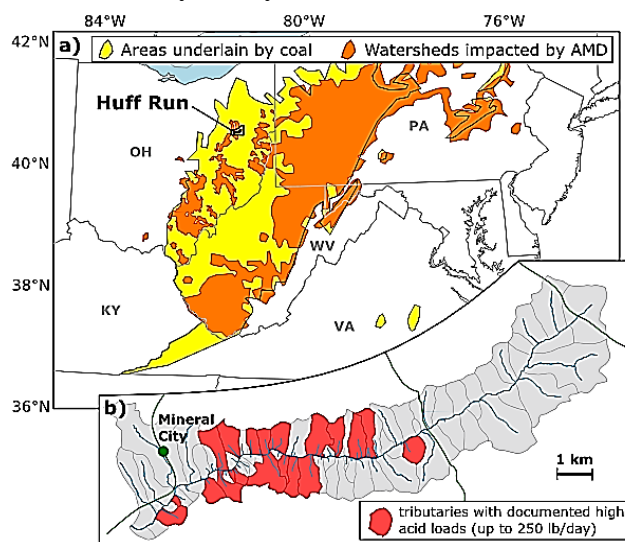


## FINAL REPORT

### *Problem and Research Objectives*

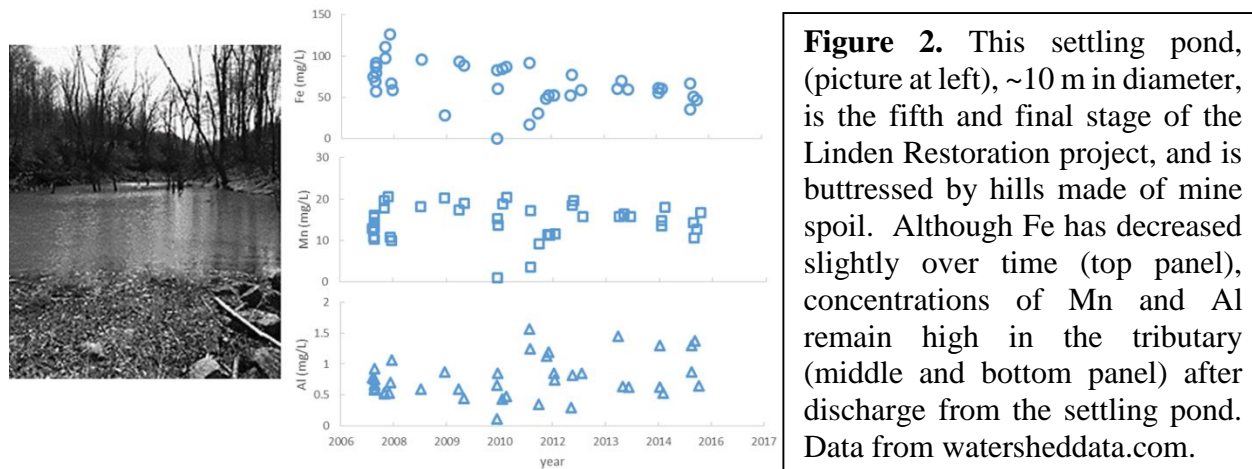
Mine spoil is an obligate waste product of coal mining and energy production. These materials are chemically similar to the parent material but are no longer economically viable to continue removing coal. Although chemically similar, the physical properties of the solid phase have changed dramatically, primarily due to a large increase in surface area and porosity. The treatment and storage of these materials is an inherent cost of coal-based energy production. The primary environmental impact of coal mine spoil is the generation of acid mine drainage (AMD). AMD is the result of the oxidation of exposed sulfide minerals in abandoned coalmines and unreclaimed coal refuse piles in circulating rain- and groundwater, generating highly acidic, metal-rich fluids that are then discharged into the local environment. AMD is estimated to impair more than 12,000 km of streams in the eastern USA (**Figure 1**).<sup>1</sup> AMD discharge has severe, long lasting impacts on water quality and stream ecology in affected watersheds. The remediation of environmental damage caused by these mines is also extremely costly. Between 2005 and 2012, monitoring and reclamation of over 300 km of streams and rivers in Ohio was done at a cost of over \$25 million dollars.<sup>2</sup> In the US, AMD and other toxins from abandoned mines have polluted 180,000 acres of reservoirs and lakes and 12,000 miles of streams and rivers.<sup>3</sup> It has been estimated that cleaning up these polluted waterways will cost US taxpayers between \$32-72 billion.<sup>4</sup> Typical AMD treatment systems include a series of passive remediation cells that remove acid or metals from the waste stream.<sup>5</sup> These system primarily target point-sources of AMD including abandoned coalmines and mine ponds. However, historic waste spoil adjacent to these point-sources acts a non-point source of AMD and can continue to contribute to the acid and metal loading of impacted waterways despite up-stream treatment.



**Figure 1.** Huff Run site map; based on surveys by the US-EPA and Ohio Department of Natural Resources. Figure courtesy C. Rowan (KSU).

Although there is extensive literature on the reclaimed and remediated coal mine tailings (for review, see <sup>5,6</sup>), few studies have addressed the fate of trace metals in historic mine tailings, which were abandoned in the early 20<sup>th</sup> century, and now blend into the surrounding landscape. These topographic highs are known to be long-term sources of slow-leaching AMD adjacent to reclamation projects that can hinder effective remediation.<sup>7,8</sup> For example, the Linden-Lindentree passive remediation project (**Figure 2**) in the Huff Run Watershed cost over \$590,000 to complete<sup>7,9</sup>. Treated-AMD from the first four stages drains into the far side of a settling pond, which then drains into the Huff Run from a culvert at the bottom right of the image. Despite up-stream remediation, the pond often has high metal loadings and low pH values due to leaching from the untreated mine tailings that make up the hillside on both sides of the pond. Mine tailing-degraded soils are anthropogenic-impacted habitats, which experience a wide-range of problems that hinder the establishment and maintenance of healthy soils.<sup>10</sup> Ultimately, if the reclamation of an AMD-impacted area is going to be successful, the leaching of metals and acid from historic

mine-tailings must be addressed. Despite the significance of long-term soil development on mine tailings, these processes are not specifically addressed and monitored during development and construction of AMD reclamation projects. Without an understanding of how critical geochemical processes which occur during soil development limit or promote metal and acid mobility, restoration will continue to be ineffective at providing an ecological benefit to the state.

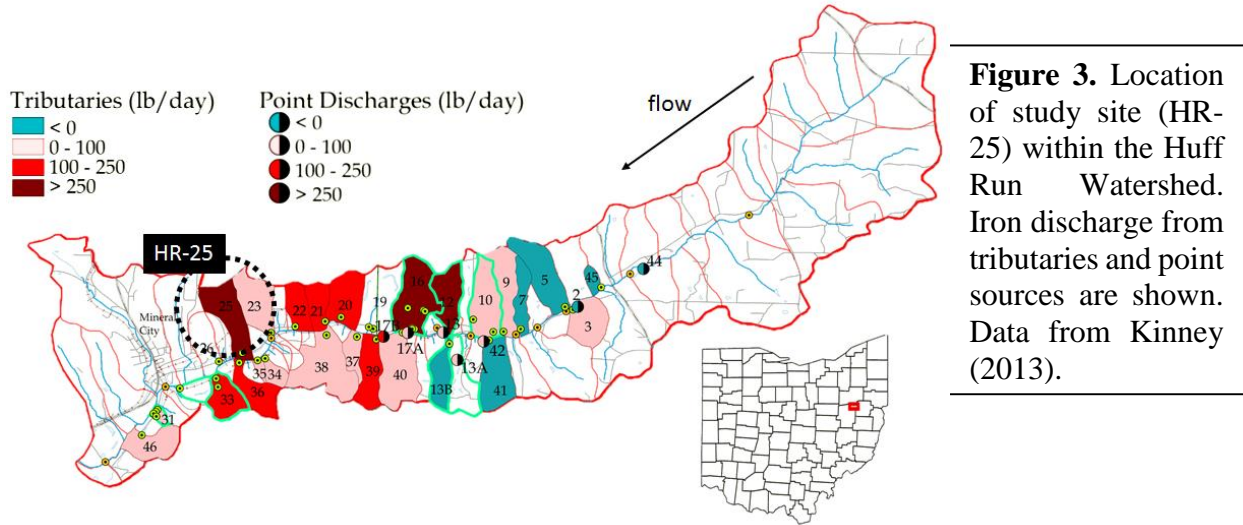


This project investigated the effects of soil development on historic coal mine tailings and the geochemical processes which control trace metal mobility over time. Specifically, we aimed to determine how do geochemically-driven mineralogical transformations in soils developing on coal mine tailings impact trace metal mobility. The main project objective was to determine mineralogical abundance and trace metal concentration in soils developing on coal mine tailings vertically through a soil profile. The work focused on the Huff Run watershed because of the magnitude of AMD challenges and efforts towards improvement in the region. To achieve the objective, measurements of spatial and temporal changes in mineralogy and trace metal mobility were performed. These measurements allowed for an integrated understanding of the geochemical processes driving these changes, and investigate their role in impacting water quality at the meter-to micron-scale.

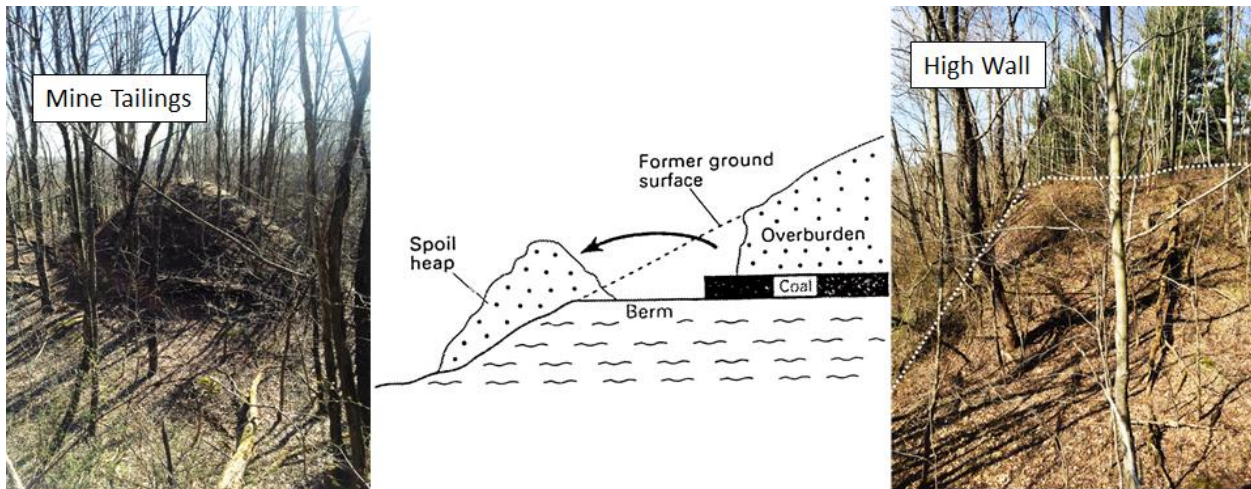
### **Methodology**

Field work was focused on the heavily AMD-impacted Huff Run watershed (**Figure 3**). The extent of groundwater contamination in the Huff Run region by AMD is currently unknown. Since 1996, 18 AMD remediation projects have been built in the watershed at a cost of over \$4.5 million.<sup>8</sup> Sites within the Huff Run have metal discharges of up to 250 lbs/day, dominated by iron and aluminum.<sup>8</sup> Restoration at sites such as Huff Run target discharge from surface and below ground mines, but typically do not target leaching from historic mine tailings. Surface mine spoil, a mixture of compacted, partly weathered fine-earth material and fragments of shale and other rock fragments account for nearly a third of the surface material in the Huff Run Watershed.<sup>11, 12</sup>

The study area is situated within the unglaciated portion of Ohio. The geology of the area is dominated by Pennsylvanian-aged bedrock with exposed strata of sandstone, shale, coal, limestone and iron ores. The watershed topography is dominated by drainages that have cut deep valleys and left narrow ridge tops.<sup>11</sup> Soils from two locations within the Huff Run (HR) Watershed were examined (**Figure 4**). The first was soils developing on historic coal mine tailings at the HR-



25 site, which has been found to have the worst water quality throughout the watershed.<sup>7</sup> Because of its downstream location, the project has not been a priority until reclamation projects upstream have been completed. The second site examinee soils developing on a shale outcrop northeast of HR-25 within the Huff Run watershed, where AMD is not detected. This provided an important comparison and baseline of trace metal mobility in undisturbed parent material.



**Figure 4.** Schematic (center) of the relationship between the highwall and mine tailings (spoil) created during mining operations<sup>13</sup>. The images show a typical conical waste pile (left) and the high wall (right) where the dashed line represents the surface.

Historical records of mine tailing emplacement are limited or non-existent within the watershed. However, the presence of Black Locust trees (*Robinia pseudoacacia*) with diameters of 0.6 m, an indication the trees are ~ 50 years old, suggests the minimum local timescale needed for tailings stabilization. This timescale is consistent with the cessation of active mining within HR-25 in the mid-20<sup>th</sup> century. Trees cores were collected (**Figure 5**) to provide a lower boundary for how long soils have been developing on these tailings.



**Figure 5.** Laura Zemanek (MS) collected soil cores (left) which were transported in drinking straws back to the lab to be dried (right). The minimum age of soil development (~50 years) for mine tailings was established by counting tree rings

### *Soil geochemical analyses*

Solid phase characterization of soils was performed on samples collected in 10 cm depth increments from the soil surface to 1.2 m depth in the soil profile. After drying, the soil samples were ground to silt size particles (10-75 micron) with a SPEX-8000M ball mill using tungsten carbide ball bearings and analyzed by: (1) bulk X-ray diffraction (XRD) to determine the dominant mineral phases present; (2) a sequential extraction procedure (discussed below) to determine the concentration of metals associated with the solid-phase as a function of depth; and (3) loss on ignition, as a proxy for organic matter content.

### *Soil water analysis*

A series of lysimeters were installed near where the soil cores are sampled at both field sites to collect pore solutions for trace metal analysis over a 6-month period (**Figure 6**). This method allows continuous sampling during any period and at several different depths of a soil profile. The installation of the suction probe is easy and the profile is only negligibly disturbed.<sup>14</sup> Lysimeters were installed at 10 cm increments, with one lysimeter per installation well. The wells were spaced at 10 cm intervals on the ground surface to minimize profile disturbances. In order to get good hydraulic contact between the suction cup at the end of the lysimeter and the soil, a slurry of the material from the soil auger was made and put back into the hole before inserting the suction probe.<sup>14</sup> Water was prevented from seeping from the surface down through the shaft as this causes hydraulic short circuits, by sinking the probe completely into the soil and using a collar around the top of the shaft. The installation of the suction probe was followed by a stabilizing phase, including simultaneous water sampling, to precondition the suction cup. Suction was put on the lysimeter using a 2005G2 Vacuum Hang Pump at a pressure of 60 kPa to create a negative pressure inside the soil water sampler. The first sample was rejected in each location. The lysimeters were sampled weekly, and filtered samples will be analyzed for cations (ICP-OES), anions (IC), and total dissolved carbon.



**Figure 6.** Lysimeter installation photos (May 2015), top left, showing (from left to right) Laura Zemanek (MS), Jonathan Mills (BS), Elizabeth Herndon (KSU assistant professor), and Mikala Coury (BS). At right, soil core samples being bagged and labeled by Laura Zemanek. The bottom left image shows the installed lysimeters from the high wall site; the dashed line represents the cliff edge.

### *Sequential Extraction*

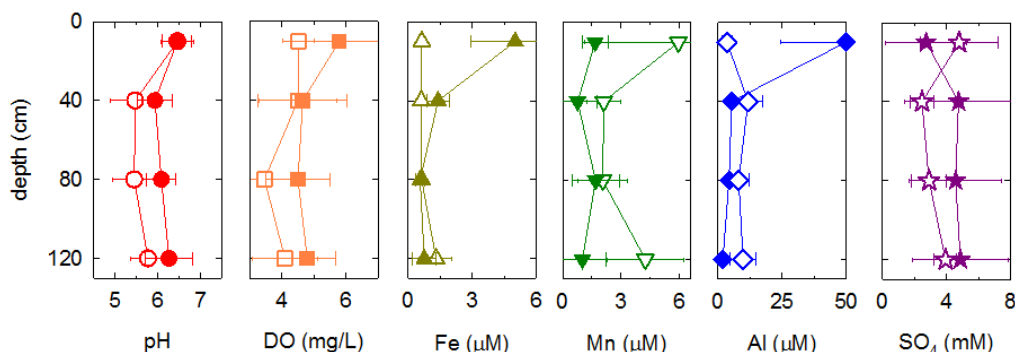
Sequential extraction modified after Tessier (1979) was performed on soil samples from all sampling depth, with triplicates performed at depths of lysimeter installation of Al, Fe, and Mn in soil fractions including exchangeable cations, oxide minerals (reducible), and organic matter/sulfides (oxidizable). Powdered soil ( $1 \pm 0.0523$  g) was agitated with four sequential solutions to remove ions from operationally defined phases. After agitation with each solution, the sample was centrifuged at 4,000 rpm for 30 minutes and decanted. 10 mL of Milli-Q water was then added and centrifuged for an additional 30 minutes to remove any remaining solution and ions before adding the next extraction solution. This rinse solution was set aside to use as a dilutant before running on the ICP-OES. The first extraction step targeted exchangeable ions; 8 mL of 2M NaCl solution at room temperature with a pH of 7, was agitated with the soil for 2 hours. The second extraction step targeted ions bound to iron and manganese oxides; a 20 mL solution of 0.3 M  $\text{Na}_2\text{S}_2\text{O}_4$  (Sodium Dithionite), 0.175 M Na-citrate, and 0.025 M H-citrate was agitated with soil for 6 hours at room temperature. The third and final extraction step targeted ions bound to organic matter; 3 mL of 0.02 M  $\text{HNO}_3$  and 5 mL 30%  $\text{H}_2\text{O}_2$ , adjusted to pH 2 by adding additional  $\text{H}_2\text{O}_2$ , was heated with the soil samples to a temperature of 85°C for 2 hours, with occasional agitation. After cooling, 5 mL of 3.2 M  $\text{NH}_4\text{OAc}$  in 20% (v/v) HOAc was added, with

Milli-Q water added to reach 20 mL if needed. The extracted solution along with the rinse solution was analyzed by ICP-OES for Fe, Mn, Al, Cu, Ni, As, and Se.

### ***Principal Findings and Significance***

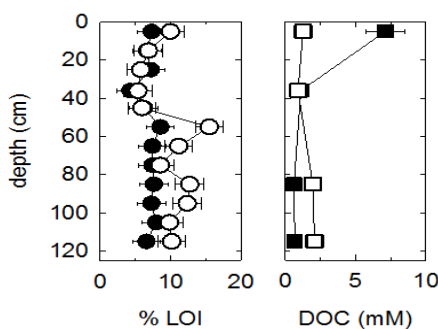
Preliminary XRD analysis of the soil core samples (data not shown) indicated the presence of typical shale weathering products; quartz, feldspars, kaolinite/illite. Crystalline Fe-bearing phases are dominated by goethite. On-going work aims to quantify the distribution of minerals in the soil cores.

Soil pore water chemistry, averaged over the field season, is shown in **Figure 7**. The pH and dissolved oxygen concentrations of pore water from the mine tailings were lower, consistent with a greater degree of coal weathering leading to AMD release. Metal solubility increases near the soil surface, but differs between sites; Fe and Al are more mobile in the highwall; Mn is more mobile in mine tailings. Interestingly, sulfate is lower in the mine tailings pore water, which was not expected as we hypothesized that greater AMD production would also result in increased sulfate concentrations. It is possible that high sulfate concentrations result in gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) precipitation which should be resolved in the on-going XRD analyses.



**Figure 7.** Soil pore water chemistry; average values from May-November 2015 for the highwall (closed symbols) and mine tailings (open symbols) lysimeters.

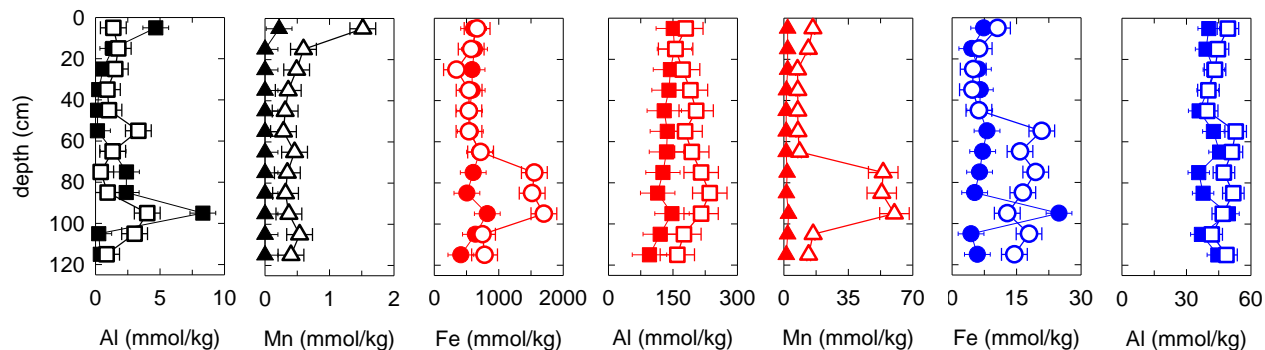
Loss-on-ignition was used as a proxy for solid phase organic matter, and coupled with DOC measurements of the soil pore water to provide an analysis of the fate of C in this system (**Figure 8**). The mine tailings contained dark, organic-rich soil at depth. Dark lenses were observed in the cores and are likely dominated by coal-bearing waste materials. DOC was high for the shallow highwall lysimeters, consistent with heavier vegetation cover and root exudates. In pore water, plant-derived organic C may mobilize Al and Fe in the undisturbed highwall soils (discussed below).



**Figure 8.** Loss-on-ignition (left) and dissolved organic carbon (right) for the highwall (closed symbols) and mine tailings (open symbols)

A sequential extraction procedure was used to quantify the distribution of Fe, Al, and Mn (**Figure 9**) and other metals (not shown). This can aid in determining what the potential is for these

soils to leach metals to surface water. In the exchangeable fraction, Fe was not detected, and the mine tailings are relatively enriched in exchangeable Mn that increases near the soil surface.



**Figure 9.** Sequential extraction data for Fe (circles), Al (squares), and Mn (triangles) from the highwall (closed symbols) and mine tailings (open symbols) soil cores. The three fractions are exchangeable (black), reducible (red), and oxidizable (blue).

An organic-rich zone (**Figure 8**) was also enriched in Fe and Mn oxides, potentially derived from pyrite oxidation. Small fractions of Fe and Al (< 3%) were observed in the oxidizable fraction; Fe (either as sulfides or organic-bound) tracks with percent loss-on-ignition. These results suggest that a pool of Fe, Mn, and Al can continue to be mobilized during weathering and impact downgradient water.

Our current conceptual framework for our results is that at depth, the mine tailings contain organic-rich zones where pyrite is weathering to form Fe and Mn-oxides. These Fe and Mn-oxide phases may compete for trace metals (e.g., As) released during weathering. Near the surface, high concentrations of labile, plant-derived DOC in highwall soils complex and mobilize Fe and Al deeper into the soils. Finally, the mine tailings are a potentially larger source of Mn to streams than previously understood.

### *Impact and Significance*

One expected outcome of this project was knowledge to guide AMD reclamation projects regarding how to address metals and acid leaching from soils developing on mine tailings, and thus improve stream quality. This research provided data that are directly transferrable to planning future AMD reclamation projects and evaluating their success. Further, this research is novel in its approach to understanding soil developing on historic coal mine tailings in Appalachian Ohio. Integration of physical and chemical data allowed us to describe how multiple processes interact, developing an important understanding that can be used by practitioners planning reclamation design. This information will allow future reclamation projects to be more effective in the long-term management of AMD to Ohio rivers and streams. Results of this project will benefit reclamation practitioners, regulators, and the scientific community through an organized plan for dissemination of the findings. Data generated from this project has been presented at state and national scientific meetings. We intend to publish our results in the journal *Applied Geochemistry*. Finally, we have continued to meet and collaborate with representatives from the Ohio Department of Natural Resources (ODNR) and from the Huff Run Watershed Restoration Partnership (HRWRP) who work with landowners in the area. The ultimate goal of the Partnership is to return Huff Run to its original, warm-water habitat. We anticipate that our findings can be employed to guide reclamation designs in Appalachian Ohio and beyond.

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