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Appalachian coal mine spoil elemental release patterns and depletion

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ABSTRACT

Elevated total dissolved solids (TDS) in Appalachian coal mining-influenced streams result from the interaction of oxygen and rainwater with fractured mine rocks. The weathering of common minerals in sedimentary coal-bearing strata such as silicates (quartz, feldspars, muscovite and chlorite), sulfides (pyrite), and carbonates (including siderite) releases soluble ions to streams. In this study, we determined mine spoil bulk composition and elemental depletion via column leaching, applied models to leaching patterns, compared model results among individual elements, and interpreted results to infer geochemical controls of soluble element release from mine spoils. Temporal release patterns of 15 elements from 26 mine spoils were determined via column leaching. Two five-parameter segmented models, one an exponential decay function combined with linear function and the second a growth function combined with a linear function, were applied to the elemental leaching patterns. Of the elements analyzed, Al (60,711 mg kg^{-1}) and K (19,157 mg kg^{-1}) had the largest concentrations on average in the bulk spoil samples. Leaching patterns for major elements (Ca, Mg, S, Ca, Na, K) differed from the release of Al, Fe, and Mn, and from trace elements (As, Cu, Ni, Se). Major elements tended to require more leaches to decay and transition to a stabilized state relative to Al, Fe, Mn and trace elements. Sulfur, Ca and Se were most depleted during the leaching period. Overall, results indicated that certain ions (Ca, Mg and HCO_3^-) were released to counter-balance the acid-production of S oxidation, whereas other elements, such as those released by feldspar hydrolysis (K, Na) were less associated with S oxidation but still contributed to overall TDS release from the mine spoils.

1. Introduction

The release of total dissolved solids (TDS) to streams by areas mined for coal in Appalachia has been the focus of many studies in recent times (e.g. Evans et al., 2014; Sena et al., 2014; Cook et al., 2015; Timpano et al., 2018a, 2018b). Predominant components of TDS in Appalachian streams influenced by surface coal mining are generally SO_4^{2-}, Ca^{2+}, Mg^{2+}, and HCO_3^-, but other major and trace elements are also present in mining-influenced streams (Pond et al., 2008; Lindberg et al., 2011). Appalachian surface coal mining entails fracturing and removing rock strata overlying coal seams; those rocks (termed mine spoils) are used after coal extraction to reconstruct landforms and the land surface, which exposes mine spoils to rapid geochemical weathering. Movement of infiltrated waters through the materials causes release of soluble elements to streams (Agouridis et al., 2012; Griffith et al., 2012).

The release of soluble elements from mine spoils affects freshwater streams, as altered aquatic macroinvertebrate community structure and aquatic taxa losses are commonly found in waters with elevated specific conductance (SC, measured as a proxy for TDS) (Pond et al., 2008; Cormier et al., 2013; Timpano et al., 2018a). In Appalachia's unmined reference streams, SC is typically < 200 μS cm^{-1} and often < 100 μS cm^{-1} (Pond et al., 2008, 2014; Timpano et al., 2018a). Waters with SCs > 300 μS cm^{-1} have been associated with the extirpation of 5% of aquatic genera in Appalachian streams (Cormier et al., 2013) and waters with SCs ≥ 500 μS cm^{-1} have been associated with altered assemblages of aquatic organisms and losses of taxonomic groups (Pond et al., 2008, 2014).

Prior research has demonstrated patterns of SC and major ion release from Appalachian mine spoils in both laboratory and field experimental settings (Sena et al., 2014; Orndorff et al., 2015; Daniels et al., 2016; Clark et al., 2017). In a study of 15 mine spoils placed in leaching columns intended to simulate field leaching conditions, Orndorff et al. (2015) showed that S, Ca, Mg, K and Na concentrations in leachates tended to decline over the leaching period, whereas the HCO_3^- ion concentrations tended to increase during early phases of

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leaching and then stabilized as leaching continued. Sena et al. (2014) demonstrated declines of SC and S in waters leached from field lysimeters on a Kentucky coal mine over a period of nine years.

Although general patterns of major element release from Appalachian mine spoils have been documented, quantitative analyses of leaching patterns have not been performed. Furthermore, general release patterns of trace elements have not been documented nor quantitatively analyzed. Trace elements of ecotoxicological concern released from mine spoils and potentially found in mining-influenced waters at elevated concentrations or in exceedance of United States Environmental Protection Agency aquatic thresholds include As, Cd, Cu, Ni, Pb, Se, and Zn (Bryant et al., 2002; Hartman et al., 2005; Cravotta, 2008; Pond et al., 2008, 2014). Quantitative models of elemental release patterns can improve understanding of the leaching behaviors of elements. By enabling comparisons of individual element release patterns, quantitative elemental release models can also improve the understanding of mine spoil weathering, mineral sources, and associated geochemical controls on elemental release.

The chemistry of mining-influenced waters is ultimately influenced by the mine rock mineralogy, the weathering reactions that result in elemental leaching, and the pre-mining weathering extent of the mine rocks. Typical central Appalachian mine rocks are sedimentary in origin and include Pennsylvanian-aged sandstones, siltstones, mudstones, and shales (Daniels et al., 2016). Prior studies have indicated that silicate minerals including quartz (SiO_2), feldspars ($(Na,Ca)AlSi_3O_8$; $KAlSi_3O_8$), micas ($KAl_2(AlSi_3O_8)(OH)_2$-muscovite) and other clays, sulfide minerals such as pyrite (FeS_2), carbonate minerals including calcite ($CaCO_3$) and siderite ($FeCO_3$), and oxyhydroxides such as goethite ($FeO(OH)$) are sources for solutes in drainages from central Appalachian mine rocks (Cravotta, 2008; Clark et al., 2018). The weathering of these minerals directly influences mine spoil elemental leaching patterns and, by extension, the chemistry of waters discharged from mine spoils.

The objectives of this study were to: (1) determine the bulk chemical composition of central Appalachian mine spoils of varying rock types and weathering extents; (2) examine individual mine spoil elemental release patterns via unsaturated leaching conditions in laboratory columns, and model and compare those patterns; (3) determine the degree of elemental depletion after leaching, and (4) infer the geochemical factors influencing elemental release from mine spoils. Overall, results were intended to improve scientific understanding of the processes influencing the release of the specific chemical constituents that comprise elevated TDS releases from Appalachian mine spoils.

2. Methods

Twenty-six spoil samples were collected from active surface coal mines in Virginia, West Virginia, and Kentucky (Fig. 1). Spoil samples were collected from identifiable rock strata that had been freshly fractured and included samples collected from multiple strata and of different weathering extents. West Virginia samples ($n = 11$) sourced from the Kanawha and Allegheny Formations, Kentucky samples ($n = 10$) sourced from the Princess and Four Corners Formations, and Virginia samples ($n = 5$) sourced from the Norton, Four Corners, and Middle and Lower Wise Formations (Daniels et al., 2016). These 26 samples were selected from the larger dataset described by Daniels et al. (2016) because of the availability of complete datasets for all 15 elements of focus in this study.

Initial characterization of the mine spoil samples included spoil classification by rock type. Rock types included mudstones ($n = 7$), mixed rocks ($n = 6$), and sandstones ($n = 13$). The term “mixed rocks” describes a spoil that had ≤ 80% of a single rock type (mudstone or sandstone). Samples were also classified by the following weathering extents: unweathered ($n = 17$), mixed weathering ($n = 6$) and weathered ($n = 3$); weathering status was inferred from initial physical and chemical properties such as Fe-oxide stains on the sample, and the pH and SC of the sample measured in a water – paste solution.

2.1. Geochemical properties of the mine spoil samples

A prior study on a sixteen sample subset of the spoils analyzed in this study detailed the mine spoil mineralogical composition using thin section analysis (Clark et al., 2018). Common framework minerals included quartz, feldspars, lithic metamorphic fragments, muscovite, chlorite, and goethite that were cemented together by quartz, kaolinite, and siderite. Rare pyrite and little to no calcium or magnesium carbonates were evident (Clark et al., 2018). These spoil samples' acid-base-accounting parameters have also been reported in prior studies (Daniels

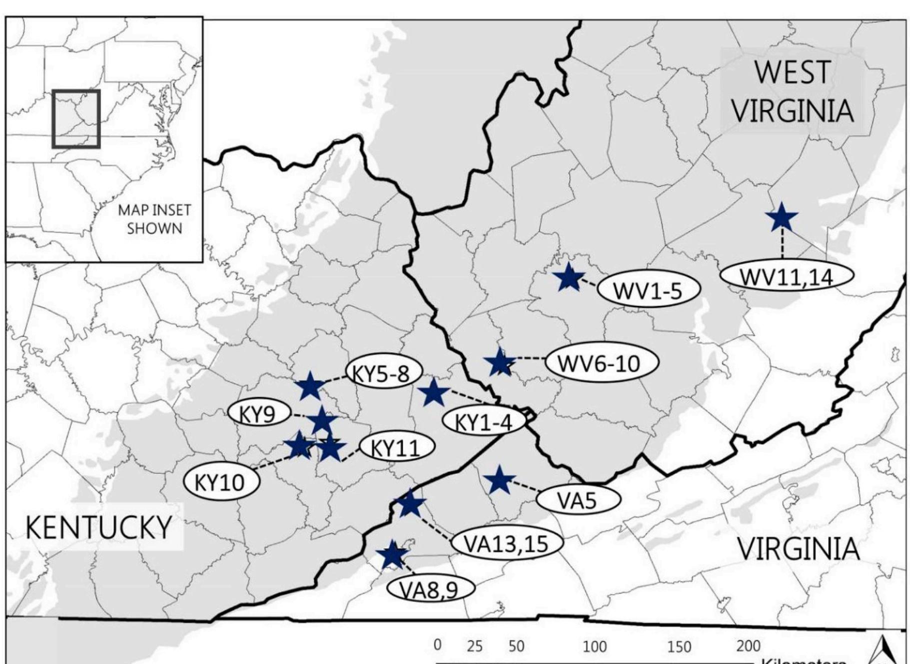

Fig. 1. Location map of the 26 collected mine spoils. The Appalachian coalfields are indicated by gray coloration.