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Bias in determining aluminum concentrations: Comparison of digestion methods and implications on Al management

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HIGHLIGHTS

- Total recoverable Al concentration depends on digestion methods.
- USEPA method 200.7 overestimate Al concentration due to dissolution of clay.
- Total recoverable Al increases with total suspended solids.
- Dissolved Al concentration is independent of total suspended solid concentration.

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ABSTRACT

Aluminum is an important aquatic contaminant due to its ubiquity, toxicity and low regulatory discharge limits. Aluminum is mobilized in mining related, acidic drainage and is commonly a regulated pollutant. However, while aquatic toxicity studies and toxicity criteria are based on dissolved aluminum(Al_d), discharge levels are, for statutory reasons, based on total recoverable aluminum (Al_t). The rationale for using total recoverable aluminum recognizes the potential for the release of exchangeable, toxic cations or dissolution of metastable metal flocs in the event the discharge enters an acidic receiving stream. The digestion methods used in determining total recoverable metals are not meant to dissolve aluminosilicate clay particles but we found that they do, resulting in positively biased total recoverable aluminum values. This study explored the interaction between total suspended solids (TSS) and total recoverable aluminum using three digestion methods to evaluate which method introduced the least bias.

Using field collected water and sediment samples from two coal mine drainage sites in Central West Virginia, three total recoverable digestion methods (USEPA Method 200.7, M1; USGS In-Bottle method, M2; and a Modified In-Bottle method, M3) were used to determine total recoverable aluminum across a range of total suspended solids concentrations. Baseline simulation experiments were conducted at pH 2.5, 3.5, 4.5 and 5.5 at different total suspended solids concentrations. Results indicated that dissolved aluminum did not respond to increasing total suspended solids concentrations while determined total recoverable aluminum increased with total suspended solids, indicating varying degrees of clay dissolution and, thus bias in the total recoverable aluminum concentration. While all three digestion methods overestimated total recoverable aluminum, at the same total suspended solids concentration, total recoverable aluminum extracted by USEPA Method 200.7 (M1) was much higher than the other two digestion methods (M2 and M3). Total recoverable aluminum from different digestion methods indicated that amount of aluminosilicate clay is digested in decreasing order: USEPA 200.7 (M1) > USGS in-bottle (M2) > modified in-bottle (M3). At pH 2.5, positive bias using methods M1, M2 and M3 was 153–287%, 53% and 40% respectively. Positive bias was greatest at pH greater than 4.5. Methods M1, M2 and M3 yielded positive biases of 660–1060%, 120–360% and 200-320% respectively. The results suggest that USEPA method 200.7 (M1) resulted in the greatest bias. Given its application in determining regulatory compliance, this is an important issue requiring further study.

1. Introduction

Acidic mine drainage results when pyritic rock is exposed to oxidizing conditions. The process of pyrite oxidation releases

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sulfuric acid which attacks aluminosilicate minerals, liberating aluminum. Aluminum is the third most abundant element in the earth's crust (Gensemer and Playle, 1999) and it occurs primarily in aluminosilicate minerals. Suspended sediment is a source for matrix-bound constituents such as Al, Fe, and Ti (Horowitz, 2013). Al concentrations in water are primarily controlled by the solubility of $Al(OH)_3$ (Hem, 1985; Nordstrom and Ball, 1986) and pH largely controls $Al(OH)_3$ solubility. At pH levels between 6 and 8, $Al(OH)_3$ is essentially insoluble (Watzlaf et al., 2004; Sigel, 1988). $Al(OH)_3$ solubility is enhanced under acidic ($pH < 6.0$) or alkaline ($pH > 9.0$) conditions, and/or in the presence of complexing ligands, (Schecher, 1988; Gensemer and Playle, 1999; Sherreli and Ross, 1999).

The National Pollutant Discharge Elimination System (NPDES) permit program controls water pollution by regulating point sources that discharge pollutants. Responsible parties are obliged to obtain Federal Clean Water Act section 402 permits which normally involve treatment of coal mine drainage via acid neutralization and metal precipitation. The resulting permitted discharge is subject to documentation using USEPA approved methods to ensure that the discharge meets conditions of the permit. Aluminum is often an important, regulated contaminant and violation of aluminum discharge limits is subject to civil penalties. Sediment is another regulated discharge parameter. Consisting largely of clay and silt, it is measured as total suspended solids and controlled by passing discharges through sedimentation ponds prior to release. Total suspended solids is normally regulated at 35 mg L^{-1} on a monthly average and 70 mg L^{-1} daily maximum (USEPA, 2015).

Surface coal mine operators in the Central Appalachian Basin typically have numerous NPDES outlets and sediment ponds. Many are subject to discharge limits for total recoverable aluminum. In West Virginia, if the receiving stream is designated a cold water fishery, the aluminum discharge limit would be 0.14 mg L^{-1} (WVDEP, 2016). Our studies have indicated that even circumneutral discharges have difficulty meeting the permitted aluminum standard, particularly during storms when total suspended solids approaches the regulatory limit (Ziemkiewicz and O'Neil, 2012). This is puzzling since aluminum solubility is mainly controlled by pH and the pH of discharges is typically in a range where dissolved aluminum concentration is expected to be very low.

Under the NPDES, discharge criteria are based on total recoverable metal concentrations. Total metal (or total recoverable metal) is the concentration of a metal determined in an unfiltered sample after vigorous digestion by EPA method 200.7. Water samples collected for NPDES compliance are preserved by acidifying with nitric acid to a pH of less than 2 at the time of collection and the sample is not filtered prior to digestion. Digestion according to EPA method 200.7 involves the addition of HNO_3 and HCl at an elevated temperature.

The use of appropriate analytical methods is of paramount importance for risk assessment and monitoring of potentially toxic metals in environmental media. The importance of digestion methods has been recognized in earlier studies for soil and sediment extractions (Da Silva et al., 2014; Gaudino et al., 2007). EPA Method 200.7 is the default method used for regulatory compliance in determination of 23 metals (including Al) and some non-metals in potable waters and wastewaters. As noted by Horowitz (2013), this preservation procedure (e.g., nitric acid to $pH \leq 2$ for trace elements) and the USEPA method 200.7 digestion procedure at least partially quantify colloidally associated constituents along with truly dissolved constituents. The aluminum in clay minerals associated with total suspended solids is not toxic to aquatic organisms, thus should not be quantified when assessing the potential of Al toxicity in water. However, the Al in clay could be released under acidic conditions when determined by acid digestion procedures for total recoverable Al analysis (e.g., USEPA method 200.7). Dissolution of clay minerals in acidic solution has been well studied in literature and the dissolution of kaolinites, illite, montmorillonite and muscovite generally increases with decreasing pH and releases Al during the process (Knauss and Wolery, 1989; Bibi et al., 2011; Rozalen et al., 2009; Khawmee et al., 2013). Two other issues have also been recognized with USEPA method 200.7. One is related to the laboratory procedures. Use of open beakers during the digestion process may result in contamination and tend to have larger variations in data. Another issue is related to the use of hydrochloric acid in the digestion procedure. Chloride ions complex with aluminum, and keeps Al concentration artificially high in the solution. In addition, chloride ions are known to interfere with the metal analysis via ICP-MS (Garbarino and Struzeski, 1998; Garbarino and Hoffman, 1999).

To avoid the issues associated with USEPA method 200.7, USGS developed a different digestion process known as the nitric acid in-bottle digestion test (Digestion Method M2). USGS (Garbarino and Hoffman, 1999) found that the positive bias associated with USEPA 200.2 (Same procedures as USEPA Method 200.7) relative to the USGS recommended digestion method was about 75% for Al, 23% for Ni and 1% for Pb. For most elements, the USEPA digestion procedure (M1) also resulted in higher percentage yields than the USGS in-bottle procedures (M2).

This study tests the hypothesis that analytical bias inherent in digestion method (e.g. USEPA Method 200.7) is responsible for over-reported total recoverable aluminum and over-reporting of exceedances in circumneutral coal mine drainage. In many cases this positive bias may be sufficient to cause exceedance of the prevailing aluminum discharge limit. The objectives of this study are to: (1) Demonstrate whether EPA Method 200.7 results in significant false positive total recoverable aluminum values; (2) Compare and determine the bias of different digestion methods on total recoverable aluminum concentration; and (3) Test the USEPA's contention that EPA Method 200.7 accurately estimates the release of metals from coal mine drainage over the range of receiving stream conditions in the Appalachian Basin (USEPA, 2001; USEPA, 2016).

2. Experimental

2.1. Field sampling

Field sampling was conducted in a central West Virginia mine during dry and wet events at several discharge points. 500 mL of unfiltered water samples were collected and analyzed for sulfates (SO_4), total acidity, total alkalinity, and total suspended solids. In addition, a 250 mL sample was collected and preserved with 1 mL of nitric acid and analyzed for total aluminum, total iron, and total manganese. To prepare for analysis of dissolved parameters, an additional 125 mL sample was collected and filtered through a 0.45 μm pore sized mixed cellulose ester membrane filter and preserved with 1 mL of nitric acid. Field collected samples were immediately placed in a cooler and covered in ice and kept at 4 °C until transferring to the laboratory and stored in a refrigerator (4 °C) until analysis. Field measurement was conducted with an YSI 551 multi-probe meter. Flow measurements were recorded using a Marsh McBirney flow meter.

For laboratory digestion experiments, two coal mine drainage site samples were collected from upstream of two mine discharges in north central West Virginia. Sediment samples were also collected from multiple points near the receiving sediment pond exits and the discharge channels at the two sites. Six replicate water samples were collected at each location for initial characterizations, stream chemistry above the coal mine discharges is shown in Table 1. Both total recoverable aluminum and dissolved aluminum concentrations were below the discharge standard and typical of