



# Identification of sulfidic materials in the Rhode River subestuary of Chesapeake Bay



B.M. Wessel\*, M.C. Rabenhorst

Department of Environmental Science and Technology, University of Maryland, College Park, MD 20740, USA

## ABSTRACT

Sulfide-containing soil materials can undergo a process known as sulfurization if disturbed, triggering the production of sulfuric acid through the oxidation of Fe sulfides and causing environmental degradation. Several systems exist to classify these types of materials based on the level of environmental hazard that they may pose. Hypersulfidic materials undergo extreme acidification, hyposulfidic materials may undergo acidification to a lesser extent or not at all, and monosulfidic materials contain a more reactive form of Fe sulfide. The definitions for these terms vary, so a brief review of how these materials are described and classified both globally and in the Rhode River region is provided. Testing for these materials is costly and time consuming, with current methods sometimes taking 16 weeks or longer to identify these materials. In subaqueous environments, where dredging and other marine construction activities may be delayed by requirements to obtain this information, better methods for the field identification of these materials would be of use to subaqueous soil surveyors. In this study, subaqueous soil materials from the Rhode River estuary were sampled, described, and divided into six categories based on morphologic properties: fluid muds, unconsolidated Holocene sandy materials, organic materials, buried A horizons, Tertiary materials with Fe oxide concentrations, and Tertiary materials without Fe oxide concentrations. These materials were then evaluated and classified as different types of sulfide-containing materials using current methods. Buried A horizons, organic materials, and Tertiary materials without Fe oxide concentrations are the most likely to be hypersulfidic materials, and therefore of the greatest environmental concern. Fluid muds, unconsolidated Holocene sandy materials, and Tertiary materials with Fe oxide concentrations are less likely to consist of hypersulfidic materials, but may still be of environmental concern as hyposulfidic materials or monosulfidic materials. Subaqueous soil surveyors can use these findings to help understand the relative environmental hazards posed by similar subaqueous soil materials in similar settings.

## 1. Introduction

Acid sulfate (AS) soils are problematic soils that are able to undergo extreme acidification if disturbed (Fanning and Fanning, 1989); this kills plants or stunts their growth (Muhrizal et al., 2003), leaches heavy metals (Roos and Åström, 2006), degrades infrastructure (Breitenbucher et al., 2009; Salmon et al., 2014), and contaminates waterways (Åström and Björklund, 1995). These soils contain reduced sulfur compounds, often as pyrite but sometimes also as metastable Fe sulfides (e.g. mackinawite and greigite). If these soils are disturbed these minerals can oxidize and produce sulfuric acid in a process known as sulfurization, which is the root cause of the severe problems associated with these soils (Boman et al., 2008; Rickard, 2012). They have long been recognized and understood as environmental hazards (Pons, 1973), with early references to the problems associated with their disturbance extending back to the 1700s (Dent and Pons, 1995). The

identification and classification of these soils is therefore important so that disturbance, and the subsequent problems that it entails, can be avoided or appropriately planned for.

This is a particularly pressing issue in the case of subaqueous soils (SAS). Shallow marine and freshwater sediments have only been recognized and mapped as SAS in the United States since 1999 (Rabenhorst and Stolt, 2012; Soil Survey Staff, 1999). Despite identifying pedogenesis in the subaqueous environment (Demas and Rabenhorst, 1999; Demas et al., 1996) and outlining the factors of SAS formation (Demas and Rabenhorst, 2001), the classification of these soils is still a matter of some controversy (Fanning and Rabenhorst, 2008; Rabenhorst et al., 2016b; Wessel et al., 2016; Wessel et al., 2015), and the most appropriate analytical tests and technical terms to use for these soils and soil materials have yet to be agreed upon by the international community working in these environments (Kristensen and Rabenhorst, 2015). Several recent SAS studies have been conducted in

\* Corresponding author.

E-mail address: [bwessel@terpmail.umd.edu](mailto:bwessel@terpmail.umd.edu) (B.M. Wessel).

the United States (Balduff, 2007; Erich and Drohan, 2012; Millar et al., 2015; Still and Stolt, 2015; Stolt et al., 2011; Wessel and Rabenhorst, 2016), Australia (Creepers et al., 2015), and Italy (Antisari et al., 2016; Ferronato et al., 2016), and it has become clear that the international community can benefit from adopting standardized terms for describing the soil materials found in these environments in terms of their properties as AS soil materials. In addition to the hazards associated with upland AS soils, some subaqueous AS soils can consume water column oxygen if disturbed, devastating populations of aquatic organisms (Holmer et al., 2003); additionally, understanding the environmental hazards of different SAS materials is also important in preventing dredged materials from producing acid drainage (Demas et al., 2004; Fanning and Burch, 2000; Koropchak et al., 2016). Unfortunately, despite several decades of research and development, there is no universally accepted method of identification or system of classification for “potential AS soil materials” (i.e. the bulk materials from different horizons in AS soils that are able to undergo acidification as a result of sulfur oxidation) (Wessel et al., 2016).

The goal of this study is to identify SAS materials in the Rhode River subestuary of Chesapeake Bay that are easily discerned from one another in the field (defined primarily by their field morphological properties using common field and laboratory tests) and to establish if these morphologies exhibit strong relationships to three classes of sulfide-containing materials. By classifying these common SAS materials as different types of sulfide-containing materials (i.e. hypersulfidic, hyposulfidic, and monosulfidic materials) the relative hazards associated with disturbing these types of materials can be understood. This will enable SAS surveyors in the field to better predict the environmental hazards that may be posed by disturbing these types of materials in similar settings. Further, because AS soils are handled differently in several different soil classification systems (and because these definitions have changed over time), a brief review will be provided on identifying and classifying AS soil materials globally and in the Rhode River region.

### 1.1. Identification and classification of potential AS soil materials

The first classification for these materials was adopted in the United States in 1975 and contains the single category “sulfidic materials.” These materials were defined as containing “0.75 percent or more sulfur (dry weight), mostly in the form of sulfides and that have less than three times as much carbonate ( $\text{CaCO}_3$  equivalent) as sulfur.” Alternatively, these can be identified by repeatedly moistening and air-drying a sample of material in the shade for about 2 months, and monitoring the pH drop. Sulfidic materials were those that became “extremely acid” under these conditions. As a field test, a sample could be boiled in concentrated  $\text{H}_2\text{O}_2$  to hasten the oxidation and pH change (Soil Survey Staff, 1975), a method no longer widely used in the United States due to interference from some clays (Fanning and Fanning, 1989). Definitions and methods have improved considerably since then, but United States *Soil Taxonomy* still only recognizes one type of sulfidic material (Soil Survey Staff, 2014). In contrast, the *World reference base for soil resources* (WRB) recognizes “hypersulfidic materials” and “hyposulfidic materials” (Food and Agriculture Organization of the United Nations, 2015), and the *Australian Soil Classification* recognizes both of these as well as “monosulfidic materials” (Isbell and National Committee on Soil and Terrain, 2016).

Although the specific definitions of each of these types of materials varies by type and by classification system, all three of these soil classification systems recognize the importance of the “moist aerobic incubation” test for oxidized pH. In this test, enough field-moist soil is added to a sample container to cover the bottom to a depth of approximately 1 cm. Following the procedure of the 12th Edition of the *Keys to Soil Taxonomy*, this is moistened to a paste and the pH is recorded before allowing the sample to air-dry over the following week. The sample is then moistened to a paste again and the pH recorded, and

this process is repeated for up to 16 weeks, or longer if the pH is still dropping (Soil Survey Staff, 2014). The process fosters the growth of aerobic bacteria, including sulfur oxidizing bacteria that oxidize pyrite and other Fe sulfide minerals, producing sulfuric acid in the process (Arkesteyn, 1980; Fanning and Fanning, 1989). The process used in the WRB and the *Australian Soil Classification* is similar to that outlined in *Soil Taxonomy* but the sample moisture is maintained at field capacity and samples are not allowed to become air-dry, sample thickness is 2–10 mm, and the duration is at least 8 weeks. A similar yet simplified method of “chip-tray” incubation is increasingly being used in Australia because it offers time and space savings, allowing samples to be collected, incubated, and archived in one container (Creepers et al., 2012), though the method has yet to be adopted in the *Australian Soil Classification*. Soil materials can be classified as hypersulfidic materials or hyposulfidic materials based on the degree to which they acidify during moist aerobic incubation. The use of concentrated  $\text{H}_2\text{O}_2$  to force oxidation of sulfides and the associated pH change in a short amount of time (e.g. hours) is still in use in Australia (Ahern et al., 2004), but does not always correlate with the results from moist aerobic incubation (Fanning and Fanning, 1989).

In addition to acidification as a result of moist aerobic incubation, several definitions of the types of potential AS soil materials depend on measurements of soil S (as sulfide, which produces sulfuric acid upon oxidation) and measurements of the ability of a soil sample to neutralize or buffer acidity that may be produced in the soil. The WRB and *Australian Soil Classification* relate these measurements through an “acid-base accounting” method that attempts to predict, based on stoichiometric relationships, whether a soil sample will produce excess acid or have the capacity to neutralize acid (Ahern et al., 2004). There are many methods available to make these measurements and to make an accounting of them (Ahern et al., 2004), but of particular relevance to this study are methods to measure acid volatile sulfide (AVS) and Cr reducible sulfur (CRS). These S fractions are measured sequentially in a distillation apparatus that produces  $\text{H}_2\text{S}$  gas from the S species in a sample, captures this gas as a precipitate in a gas trap, and subsequently measures the S concentration in the trap. Different fractions can be produced by heating or cooling the apparatus (cold Cr reducible sulfide, CCRS and hot Cr reducible sulfur, HCRS) (Boman et al., 2008), but the simplest fractionation is between AVS and CRS (this implies HCRS, bypassing and including the CCRS fraction). Diluted HCl (6 M) is added to samples to measure AVS and represents the metastable Fe sulfide fraction, probably a mixture of greigite and mackinawite, but also aqueous FeS and porewater bisulfide ( $\text{HS}^-$ ) (Rickard and Morse, 2005). The CRS fraction is resistant to acid treatment and requires 1 M  $\text{CrCl}_2$  to evolve  $\text{H}_2\text{S}$ . It is thought to represent pyrite and elemental S, with CCRS representing only pyrite while HCRS also represents elemental S (Boman et al., 2008).

Several field methods are also in use to better describe sulfide-containing soil materials. A “whiff” test can be done to rank the concentration of  $\text{H}_2\text{S}$  present in a soil on a scale from zero to three, with zero indicating no odor and three indicating that the “rotten egg” smell of  $\text{H}_2\text{S}$  can be smelled simply by walking through a site. This rating does correlate with total S content (Darmody et al., 1977). The odor indicates ongoing sulfidization in the soil—sulfate reduction and the potential formation of metastable Fe sulfides and pyrite (Fanning and Fanning, 1989). In subaqueous settings, a whiff test result of one or greater is often taken as evidence that no Fe oxides remain in the soil material being examined. This is because  $\text{H}_2\text{S}$  will react with Fe oxides to form metastable Fe sulfides in a matter of minutes (Rabenhorst, 1990; Rabenhorst et al., 2010). The reaction is reliable enough and quick enough that porewater sulfide concentrations can be estimated based on the degree to which Fe oxides are transformed to Fe sulfides when they are inserted into the soil (Rabenhorst et al., 2016a; Rabenhorst et al., 2010). This is consistent with observations of sulfide-containing shallow marine sediments, which generally contain no reactive Fe oxides below the top few centimeters (Kristensen et al., 2003;

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