



Understanding sulfide distribution in subaqueous soil systems in southern New England, USA



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A B S T R A C T

Sulfidization is an important soil forming process in estuarine and marine soils. There has been considerable work done in intertidal and upland soils regarding sulfides, as well as a body of research on sulfides in marine sediments, but there has been little published on sulfide distribution in subaqueous soils in the context of the pedologic approach to studying and classifying these materials. Our objectives were to determine the distribution of sulfides in subaqueous soils and to evaluate sulfide levels (total reducible inorganic sulfur, TRIS; acid volatile sulfides, AVS; and chromium reducible sulfur, CRS) in relation to soil properties including carbon content, CaCO₃ content, soil texture, oxidized pH, and conductivity. Sulfide analysis was completed on 52 representative samples collected from 17 pedons in three shallow coastal embayments in southern New England, USA. TRIS, calculated as AVS plus CRS, ranged from 33 to 11,592 μg g⁻¹ with CRS representing nearly 100% of the sulfides. Sand content showed a strong negative correlation ($r = -0.85$) with TRIS. Thus, sandy subaqueous soils (Psammowassents) had the lowest sulfide levels. Although oxidized pH is often used to identify sulfidic materials, we found that the proportion of the variance in oxidized pH predicted from TRIS was very low ($r = 0.19$). In contrast, the amount of salts extracted from samples after treatment with H₂O₂ (TS_{ox}) showed a strong relationship with TRIS ($R^2 = 0.70$). We found that there was generally 5 to 10 times more CaCO₃ by weight (the source of which is shell fragments) than sulfides, yet the pH often dropped below 4.0 upon moist incubation; suggesting that shell materials may not effectively neutralize acidity generated from oxidizing sulfides. Australian and World Reference Base (WRB) soil classification systems recognize both hyper (oxidized pH 4.0 or below) and hypo (contain oxidizable sulfides, but pH doesn't drop as low as 4.0) sulfidic soil materials. Soil Taxonomy, however, only recognizes materials that result in a drop in pH below 4.0 as sulfidic (hypersulfidic). The recognition of hypersulfidic and hyposulfidic materials in Soil Taxonomy should be a consideration for future changes in this soil classification system.

1. Introduction

Sulfidization, or the accumulation of sulfides, is an important soil forming process in estuarine and marine soils (Fanning et al., 2010). In these settings, sulfate, the second most common anion in seawater, is reduced to sulfide through the metabolism of sulfate-reducing bacteria in the subsurface anoxic soil (Jorgensen, 1977; Day et al., 1989). Sulfide is most often trapped in the sediment by binding with metal ions such as Fe (Jorgensen, 1977). Inorganic sulfides are commonly operationally defined based on how they are extracted from the soil sample; either as acid volatile sulfide (AVS) or chromium reducible sulfur (CRS); AVS consists primarily of Fe monosulfide (FeS) and CRS occurs in minerals such as pyrite (FeS₂) (Lasorsa and Casas, 1996; Rickard and Luther, 2007).

The ratio of AVS to CRS is dependent upon many factors including percent soil organic matter, levels of dissolved sulfides, pH, levels of available iron, and availability of O₂ (Rickard and Morse, 2005). Monosulfides are transformed to pyrite only in the absence of O₂ and in the presence of both dissolved sulfide and organic matter (Berner, 1970). If both dissolved sulfide and organic matter are abundant, the amount of reactive Fe controls the formation of pyrite. The amount of pyrite-Fe divided by the amount of pyrite-Fe plus reactive-Fe is referred to as the degree of pyritization (Berner, 1970; Boothman, 1998). In the presence of O₂, pyrite can form directly from aqueous sulfate (Fanning and Fanning, 1989; Rickard and Morse, 2005). Higher CRS levels have been found in subaqueous soils with higher organic matter contents because of inputs of carbon from eelgrass (Holmer and Nielsen, 1997) which supports previous reports that organic carbon can be a limiting

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factor in the transformation of AVS to pyrite (Westrich and Berner, 1984). Thus, in subaqueous environments, sulfide minerals may be indications of soil organic matter levels or dissolved oxygen concentrations in the soil pore water.

Sulfide content is an important consideration in many ecological, use, and management aspects of soils. For example, sulfides precipitate with a number of toxic metals, limiting the bioavailability of these metals (Griffin et al., 1989; Leonard et al., 1993). The sulfide content in subaqueous soils has been shown to have an impact on the suitability of the soil for eelgrass growth, with levels of total sulfide > 400 μM causing significant decreases in eelgrass productivity (Goodman et al., 1995; Balduff, 2007). Sulfide content of soils is also important when considering marine construction and dredging projects. If sulfide bearing subaqueous soils are disturbed or dredged allowing sulfides to oxidize, sulfuric acid can be formed, which drastically lowers soil pH and may result in acid sulfate soil formation (Fanning and Fanning, 1989; Holmer et al., 2003). If deposited near water, these active acid sulfate soils can also create leachate that is toxic to aquatic systems (Demas et al., 2004).

Potential acid sulfate soils are identified based on the presence of sulfidic materials at a shallow depth (Fanning and Fanning, 1989). Over the last 40 years the definition of sulfidic materials has changed several times. Prior to 1992, Soil Taxonomy (Soil Survey Staff, 1990) defined sulfidic materials as: “waterlogged mineral or organic soil materials that contain 0.75% or more sulfur (dry weight), mostly in the form of sulfides, and that have less than three times as much carbonate (CaCO_3 equivalent) as sulfur”. In 1992 the definition was changed to: mineral or organic soil materials with a pH value of > 3.5 which contain oxidizable sulfur compounds, and, if incubated as a layer 1 cm thick under moist aerobic conditions (field capacity) at room temperature show a drop in pH of 0.5 or more units to a pH value of 4.0 or less within eight weeks (Soil Survey Staff, 1992). In the 11th edition of Keys to Soil Taxonomy (Soil Survey Staff, 2010), the same edition in which subaqueous soils were first classified in the US system, the length of time the soils were to be incubated was increased to 16 weeks or more and the samples were to be repeatedly moistened and dried during the incubation period.

Based on studies by Fitzpatrick et al. (2009) and Sullivan et al. (2009), and in conjunction with the International Union of Soil Sciences Acid Sulfate Soil Working Group, Sullivan and others (2010) broadly defined sulfidic materials as those materials with $\geq 0.1\%$ sulfides and introduced the terms “hypersulfidic” (sulfidic materials with oxidized pH values 4.0 or less) and “hyposulfidic” (sulfidic materials that do not experience a substantial drop in pH to 4.0 or less). A substantial drop was considered a drop of at least 0.5 pH units and the incubations were completed moist (maintained at field capacity). The period of incubation was set at 8 weeks or until the pH stabilized to within < 0.1 pH unit change over at least a 14 day period, or the pH began to increase (Sullivan et al., 2010). Both the Australian and World Reference Base (WRB) soil classification systems also recognize both hyper and hypo sulfidic soil materials. Soil Taxonomy, however, only recognizes materials that result in a drop in pH below 4.0 as sulfidic.

The reasons why the definitions of sulfidic materials have changed over the years is unclear. Measurements of monosulfides and pyrite can be made in the laboratory by determining amounts of sulfide gas produced when soil is reduced with acid or chromium (Brouwer and Murphy, 1994). This method requires the researcher to have access to a laboratory with a fume hood and distillation equipment and results in chromium and zinc waste products that must be disposed of. In contrast, measuring oxidized pH can be done outside of a laboratory setting and does not require chemical additives which follows recent trends toward green and sustainable chemistry (Sheldon, 2011). In addition, oxidized pH provides a direct indication of natural formation of acidic conditions in the field (USDA-NRCS, 2007) and simply requires monitoring the change in pH over time.

In subaqueous soil mapping it would be beneficial to be able to

predict sulfide levels based on landscape unit or soil physical properties and to have relatively simple field or lab tests that could estimate the amount of the various forms of sulfide in a soil. The objectives of this study were: i) to assess the distribution of concentrations of AVS and CRS in subaqueous soils; ii) to evaluate the value of oxidized pH measurements and total salts after oxidation (TS_{ox}) as indications of sulfide concentrations; and iii) to determine if relationships exist between sulfide concentrations and various soil properties (conductivity, particle size, soil organic carbon, and CaCO_3 contents).

2. Materials and methods

Thirty-one pedons (175 horizons) were sampled within three shallow embayments in Rhode Island: Greenwich Bay (1200 ha), Wickford Harbor (160 ha), and Little Narragansett Bay (1000 ha). Greenwich Bay and Wickford Harbor are embayments within the larger Narragansett Bay. Subaerial soils adjacent to the estuaries are formed in glacial derived outwash and till with some loess influence. Each embayment has a river or stream bringing in freshwater. Average water depth ranges from 1.5 to 2 m and tidal fluctuations are approximately 1 m on average (Payne, 2007). Soil samples were collected from bay floor, cove, drowned channel, fluvio-marine bottom, spit, shoal, and depositional platform landscape units using a Macaulay peat sampler or vibracore (Stolt et al., 2017). Samples from the Macaulay were placed in plastic bags with most air removed, sealed, and put on ice until returning to the lab where they were frozen until they could be analyzed. Vibracores were capped and taped on both ends and stored in the refrigerator at 4 °C until they could be cut and sampled. Samples were immediately placed in plastic bags and frozen.

Soil samples were analyzed for oxidized pH, particle size distribution, organic carbon content, and CaCO_3 content. Particle size distribution was determined by sieving and pipette (procedure 3A1a11; Soil Survey Laboratory Staff, 2004). Oxidized pH was measured by placing approximately 10 g of bulk frozen sample into a 25 mL beaker and mixing with DI water to make a 1:1 by volume soil to water mixture. Soil pH was measured using an Accumet pH probe immediately after thawing, each day for the first 2 weeks, and then once per week. Deionized water was added when needed to keep samples moist (field capacity) during incubation (procedure 4C1a1a3; Soil Survey Laboratory Staff, 2004). Final pH measurements (oxidized pH) were defined as those made after 8 weeks of incubation or after the samples did not drop more than 0.1 unit within 2 weeks, or the pH went up (Sullivan et al., 2009; Sullivan et al., 2010). Samples were stirred periodically in order to prevent the accumulation of salts on the beaker glass.

Total organic carbon and CaCO_3 were determined sequentially by percent weight loss on ignition (LOI) of the fine earth fraction in a muffle furnace assuming organic matter combustion after 5 h at 550 °C and a soil organic carbon-organic matter ratio of 0.5 (Nelson and Sommers, 1996; Millar et al., 2015). CaCO_3 was determined by loss on ignition after 5 h at 1000 °C calculated as:

$$\text{CaCO}_3 = (\text{DW}_{550} - \text{DW}_{1000})/0.5995$$

where CaCO_3 is the weight of the CaCO_3 in the original sample, DW_{550} is the dry weight after LOI at 550 °C, DW_{1000} is the dry weight after combustion at 1000 °C, and 0.5995 represents the percent of CaCO_3 that is lost as carbon dioxide through combustion (Heiri et al., 2001).

Conductivity measurements were carried out using an Oakton WD-35607 hand-held conductivity meter (Eutech, 2004) using the saturated paste method (procedure 4.6.2.1.1.1; Soil Survey Laboratory Staff, 2004). Immediately after removal from the freezer, samples were thawed and water was added to make a saturated paste. After overnight refrigeration, water was extracted from samples by vacuuming through a glass-fiber filter and the conductivity of the extracted water was measured. The residual soil samples were treated with 30% H_2O_2 in

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