Soil-color changes by sulfuricization induced from a pyritic surface sediment

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ABSTRACT

Colors are widely used to describe hydroxysulfate minerals and acid sulfate soils but seldom to study an active sulfuricization process. Our research was designed to measure the spectrophotometric colors of a soil sulfuricized by pyritic sediment over 15 years (8 profiles, 75 samples) and to determine whether color could be employed to identify the new soil materials. The Munsell *value* of gray sulfidic materials deposited on the soil surface changed over time from 3.0 to 5.6 ($R^2 = 0.97$) because of Fe leaching and the formation of whitish sulfates. The underlying native soil was first pigmented yellowish brown by illuvial precipitates appearing in SEM as "bubble wrap" coating soil particles and having the EDX peaks of Fe, S and O, and the XRD peaks at 0.255 and 0.166 nm. Between pH values 3 and 4 its spectral character in the second-derivative Kulbelka–Munk function registered a maximum at 440 nm and a minimum at 480 nm, both drastically attenuated after oxalate Fe-extraction. Therefore, we attributed most of precipitates to schwertmannite phases. Their subsequent progressive transformation to jarosite in parallel to a pH decline was colorimetrically detected by a displacement of the spectral maximum to 450 nm, its intensity reduction with increasing jarosite content, and yellowing of aggregates and ground-soil samples from 8.5YR to 0.2Y. Finally, the dominance of jarosite below pH 2.4 resulted in soil materials with a spectral minimum at 440 nm and Munsell *hue* between 1.3Y and 5.3Y. Because sulfidic, schwertmannitic, and jarositic materials, as well as their compositional changes, were unambiguously identified, soil sulfuricization could be determined by colorimetry.

1. Introduction

Sulfuricization is a soil-formation process whereby sulfide-bearing materials are oxidized, minerals are weathered by the sulfuric acid produced, and sulfate minerals are formed from the dissolution products (Fanning and Fanning, 1989; Jacobs et al., 2014; Lowery and Wagner, 2012; Schaetzl and Anderson, 2005). Ferrous sulfates are formed first and then rapidly oxidized to ferric sulfates, which in turn may be partially or totally hydrolyzed to form hydroxysulfates and/or Fe oxides (Fanning et al., 2002). The neoformed mineral depends largely upon the pH and solution sulfate activity in which the reaction occurs. The biogeochemical models of Bigham and Murad (1997) and Murad and Rojik (2004) estimated a pH range of 1.5–3 and [SO₄] > 3000 mg/l for jarosite ($MFe_3(OH)_6(SO_4)_2$), pH ≈ 3–4 and [SO₄] ≈ 1000–3000 mg/l for schwertmannite ($Fe_8O_8(OH)_6SO_4$), and pH < 6 and [SO₄] < 1000 mg/l for goethite (α-FeOOH). Less acidic conditions (pH > 5) are required for ferrihydrite. When CaCO₃ minerals are present in a material being sulfuricized, gypsum also forms (Fanning et al., 2002; Moon et al., 2013). Eventually, a sulfuric horizon with an ultra-acid pH and high amount of sulfate minerals (Soil Survey Staff, 2014) characterizes these soils broadly called acid sulfate soils.

Acid sulfate soils have been documented from consolidated sediments, tidal marshes, dredged materials, and landfill caps containing iron sulfide minerals. Their oxidation occurs when they are exposed on the surface by geologic uplift, erosion, earth-moving activities, alteration of water tables, or surface disposal (Fanning et al., 2002, 2010; Fitzpatrick, 2003; Rabenhorst and Valladarez, 2005; Johnston et al., 2011; Creeper et al., 2015, and references cited therein). All these research articles have addressed the soil properties, mineralogy, genesis, and environmental hazards (including toxicity and damages to infrastructures) caused by the release of large amounts of acidity and other contaminants such as Fe, Al, Pb, and As. Most studies have also mentioned the striking yellow to reddish-brown colors of these soils caused by the minerals formed in the course of pedogenesis.

The color of minerals that are common in acid sulfate soils has been separately studied in detail. Schwertmann (1993) described the specific Munsell color of Fe oxides, hydroxides, oxyhydroxides, and hydroxysulfates, stressing their usefulness as field indicators of pedogenetic environments. The spectral color of several minerals was also characterized by Bishop and Murad (1996) and Scheinost et al. (1998). These latter authors used second-derivative diffuse reflectance spectroscopy, which derives the position and intensity of the light-

absorption bands produced by crystal-field transitions of Fe^{3+} in an octahedral ligand field (Sherman and Waite, 1985). Subsequently, a thorough colorimetric study of Fe oxides and hydroxysulfates was performed by Scheinost and Schwertmann (1999) using the color systems CIE, CIELAB, and Munsell. In particular, considering natural and synthetic specimens, including acidic mine-water precipitates (Murad and Rojik, 2003, 2004), jarosites were found to be straw-yellow with a Munsell *hue* between 2.5Y and 5Y and high lightness (7–8 in *value*). For goethites, the *hue* went from 7.3YR to 1.6Y, whereas schwertmannites and ferrihydrites were deemed to be, respectively, orange (8.0YR to 2.5Y) and reddish-brown (2.8YR to 9.2YR) in color. The authors explained these colors by subtle differences in absorption bands assigned to the two single-electron transitions $(^4E; ^4A_1) \leftarrow ^6A_1$ near 400 nm and $^4T_2 \leftarrow ^6A_1$ around 700 nm, and the electron-pair transition $(^4T_1 + ^4T_1) \leftarrow (^6A_1 + ^6A_1)$ close to 500 nm.

Much less is known about the color of acid sulfate soils having Fe oxides and hydroxysulfates. Soil Taxonomy (Soil Survey Staff, 1990) and the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006) even used mineral color rather than soil color to define, respectively, sulfuric and thionic horizons. However, pedogenic species as well as their mixture with other soil materials may differ in color with respect to pure minerals; this is probably why there are currently no taxonomically specified color criteria (IUSS Working Group WRB, 2014; Soil Survey Staff, 2014). In addition, the color significance to infer other valuable soil information remains scarce and controversial. Scheinost et al. (1998) and Scheinost and Schwertmann (1999) doubted its reliability for identifying pedogenic Fe minerals because the color of several isolated pure species overlapped each other. On the contrary, Fanning et al. (1993) asserted that color could be useful in determining soil evolution as visual evidence of each stage in the sulfuricization process. Virtually achromatic colors in the preactive stage because of materials enriched in pyrite (sulfidic materials) turned yellowish during the active oxidation stage with hydroxysulfates, whereas whitish colors of gypsum and barite or reddish colors of Fe oxides indicated a postactive stage. Williams et al. (2002), Murad and Rojik (2003), and Moon et al. (2013) also used color as an indicator of the acidity and oxidation conditions in sulfate environments.

The present study arose from the color changes perceived in a soil covered with pyritic sludge accidentally spilt from a holding pond of a pyrite mine (Aznalcóllar, SW Spain). Soil surveys for monitoring pollution revealed the appearance of striking colors only two months after the spill (Dorronsoro et al., 2002). The nature of sludge and its exposure to the atmosphere suggested that the underlying soil could be affected by a particular sulfuricization process. Accordingly, our first objective was to design a soil-sampling plan in order to investigate the coloring process and quantify the soil-color changes over time. Secondly, our study seeks to determine whether spectrophotometric measurements of soil color could unambiguously identify acid sulfate soil materials.

2. Materials and methods

2.1. Setting

The study site is located in the middle reaches of the Guadiamar River (SW Spain). Its Holocene alluvial floodplain, roughly 40 km long and 400 m wide, was accidentally inundated on 25 April 1998 by five million cubic meters of pyritic sludge (80% water and 20% solid tailings), resulting in a surface layer of sediment between 2–10 cm thick (López-Pamo et al., 1999). Although the area was quickly restored, several plots of about 25 × 25 m with the sediment layer were reserved without any remediation. We studied the soil of one plot (6% slope) located in the so-called Vado del Quema (UTM 29S 4125330N 742630E), where the pyritic sediment has been oxidizing and interacting with the underlying soil under natural conditions (Martín et al., 2008). The climate is typically Mediterranean with mean annual rainfall of 700 mm, a mean annual temperature of 18 °C, and a potential evapotranspiration of 975 mm.

2.2. Soil sampling

The soil of Vado del Quema was sampled eight times from 1998 to 2013 in locations close together covering 625 m², the first two in May and June 1998 (sampling references Q98M and Q98J) at 30 and 60 days after the pyritic spill, subsequently in the summers of 1999 (Q99), 2002 (Q02), 2005 (Q05), 2007 (Q07), 2011 (Q11), and finally 2013 (Q13), 15 years after the spill. A pit exposing a vertical surface of approximately 50 cm was dug each time, taking bulked samples from horizons or layers with different visual colors, including the overlying sediment, according to a discrete depth sampling (Fig. 1). In total, 75 bulk soil samples were collected, air dried, and divided into halves. While in one the natural unaltered aggregates were preserved, in the other the aggregates were broken with a wooden rolling pin to pass through a 2-mm sieve (fine earth). We also prepared ground-soil samples by grinding 10 g of fine earth in an automatic agate mortar over 10 min.

2.3. Soil analysis

Following standard procedures (Klute, 1986; Page et al., 1982), we analyzed the particle-size distribution in the fine-earth fraction by sieving (sand) and the pipette method (silt and clay) after removal of organic matter and iron forms with H_2O_2 and citrate/bicarbonate/dithionite, respectively, and dispersion with sodium hexametaphosphate. The pH was potentiometrically measured in a 1:2.5 soil–water suspension and the content of $CaCO_3$ equivalent with a Bernard calcimeter. Also, we determined the organic carbon content by the difference between total carbon, measured by dry combustion with a LECO TruSpec CNHS instrument (LECO, Michigan, USA), and inorganic carbon from $CaCO_3$ equivalent. In addition, in the pyritic sediment samples, pH measurements 1:1 in water were repeatedly performed after successive wetting and drying phases on a weekly basis, until the pH reached a nearly constant value (Soil Survey Staff, 2014).

In ground-soil samples (<0.05 mm), we measured by atomic absorption spectrophotometry the amount of citrate/bicarbonate/dithionite-extractable iron (Fe_d) (Mehra and Jackson, 1960) and ammonium oxalate-extractable iron (Fe_o) (McKeague and Day, 1966). Total iron (Fe_t) was analyzed by XRF in a NITON XLt 792 instrument (Niton, Billerica, USA). Finally, X-ray diffraction patterns of most these powdered samples, before and after iron extraction, were also made with a Philips PW-1700 instrument, using $CuK\alpha$ radiation ($\lambda = 0.15406$) at 35 kV and 15 mA, angular range 2°–65° at 0.04° steps, and 2 s counting time per step. Minerals were identified and quantified using XPowder software (J. Daniel Martín®, Spain).

From the natural unaltered aggregates, we selected small peds and soil pieces with coatings separated from coarse aggregates with the help of tweezers and a cutter. These samples between 2 and 5 mm in size, once fixed to a holder with colloidal silver and metallized with carbon in two orientations diverging 20–30°, were analyzed by scanning electron microscopy (SEM). We used a Zeiss SUPRA40VP apparatus (ZEISS Co., Germany) with an acceleration voltage of 30 kV and nanometric resolution, in conventional mode of secondary electrons and backscattered electrons. For the elemental microanalysis of mineral particles, an energy-dispersive X-ray (EDX) spectrometer was connected to the SEM, model AZTEC 2.4 (Oxford instruments, UK), in pinpoint mode (diameter 1 μm), resolution of 10 eV/ch, and a spectrum reaching time of 100 s.

2.4. Color measurement and analysis

We performed spectral reflectance measurements using a Konica Minolta CM-2600d spectrophotometer (Minolta Co. Tokyo). This instrument has an illuminating/viewing geometry d/8 and two Xenon lamps as the light source, recording the light reflected by a soil sample with the specular component excluded between 360 and 740 nm at 10 nm intervals. As usual in laboratory studies (Torrent and Barrón, 1993),