



Sulfate reduction processes in salt marshes affected by phosphogypsum: Geochemical influences on contaminant mobility



Rafael Pérez-López^{a,*}, Sergio Carrero^{a,b}, Pablo Cruz-Hernández^{a,c}, Maria P. Asta^d, Francisco Macías^a, Carlos R. Cánovas^a, Clara Guglieri^e, José Miguel Nieto^a

^a Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment (Natur HE), University of Huelva, Campus 'El Carmen', 21071, Huelva, Spain

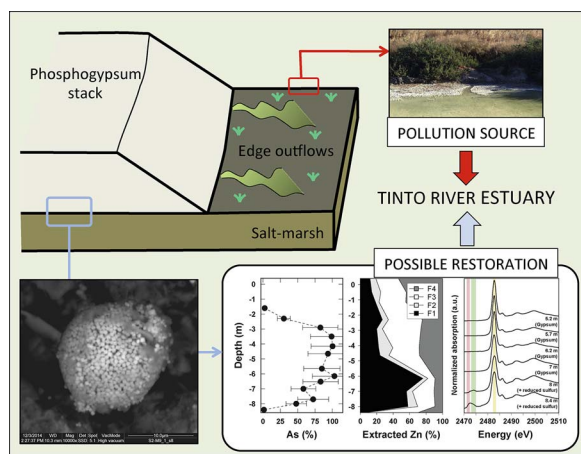
^b Department of Earth and Planetary Science, University of California Berkeley, McCone Hall, CA, 94720-4767, Berkeley, USA

^c Department of Mining Engineering, University of Chile, Av. Tupper 2069, 8370451, Santiago, Chile

^d École Polytechnique Fédérale de Lausanne, Environmental Microbiology Laboratory (EML), Station 6, CH-1015, Lausanne, Switzerland

^e Elettra-Sincrotrone Trieste, s.s. 14 km 165.3, 34149, Basovizza, Trieste, Italy

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfate reduction and its associated contaminant immobilization in marsh soils supporting a phosphogypsum stack was examined by pore-water and solid analysis, selective extractions, microscopy and sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The negative impact of this stack on estuarine environments is a concerning problem. In the weathering profile, total concentrations of most pollutants increase with depth; instead, dissolved contents in pore-waters increase to middle of the saturated zone but then decrease drastically down to reach the marsh due to sulfide precipitation. Excess of acid-volatile sulfide plus pyritic sulfur over metals bound to the oxidizable fraction indicates that sulfide precipitation is the main mechanism responsible for metal removal in the marsh. Thus, abundant pyrite occurred as framboidal grains, in addition to other minor sulfides of As, Zn and Cu as isolated particles. Moreover, high contents of elemental sulfur were found, which suggest partial sulfide oxidation, but marsh may have capacity to buffer potential release of contaminants. The importance of sulfur species was quantitatively confirmed by XANES, which also supports the accuracy of selective extraction schemes. Accordingly, managing pore-water quality through organic carbon-rich

* Corresponding author.

E-mail address: rafael.perez@dgeo.uhu.es (R. Pérez-López).

amendments over phosphogypsum stacks could lead to a decrease in contaminant loading of leakages resulting from weathering.

1. Introduction

Metal sulfide precipitation can exert a strong control on the species distribution and contaminant mobility under natural conditions in anoxic systems associated with decomposing organic matter. Activity of sulfate-reducing bacteria can be considered as the main mechanism for metal removal from pore-water through insoluble sulfide formation [1–4]. Microbially-mediated sulfate reducing processes can play a crucial role on the natural contamination attenuation in receiving media, as well as on artificial treatment systems [5,6].

Extensive anthropogenic activity and the lack of environmental regulation during the first half of the last century gave rise to many contaminated estuaries in industrialized and urbanized areas worldwide. Estuarine salt-marshes are often the sink of contaminants released from mining and industrial activity developed in the surrounding area. In these organic matter-rich environments, precipitation of sulfide minerals may sequester potentially toxic trace elements [7,8]. However, attenuation associated with these natural processes cannot be considered as a full replacement for restoration technologies, but it can sometimes help decision makers to optimize the best cost-effective and environmental friendly remediation practices [9].

Phosphogypsum is a waste from the production of phosphoric acid by phosphate fertilizer industry following wet chemical digestion of phosphate rock with sulfuric acid. This unwanted waste (mainly gypsum) is often disposed of in large stacks in coastal areas, close to the production plants, as a slurry along with leftover reactants and products from the industrial process [10]. This fact leads to the existence of highly-polluted acidic groundwaters in the waste pile containing high concentrations of metals and radionuclides [11]. Consequently, phosphogypsum stacks commonly constitute a potential source of contamination to the coastal environment [12].

The purpose of this study was to map redox zoning in the weathering profile of a phosphogypsum stack located on an estuarine marsh soil. We traced the formation and spatial distribution of reduced sulfur species in order to elucidate how sulfate-reducing processes in the marsh can control the fate of contaminants in the environment. To achieve this objective, quantitative S speciation data were obtained by combining chemical extractions with S K-edge X-ray absorption near-edge structure (XANES) spectroscopy and electron microscopic observations. Metal contents were analyzed both in pore-waters and in operationally defined selective extractants from solids for mobility discussion. As far as we know, no study has attempted to explore the sulfate-reduction processes associated with phosphogypsum waste and its impact on the environment, especially taking into account the combined use of selective extractions and synchrotron-based spectroscopic techniques. Moreover, this information will allow expanding the overall knowledge about the characteristics that regulate both the residence time and the potential release and transport of metals and metalloids from hazardous wastes to the environmental.

2. Materials and methods

2.1. Study site

The site investigated is a controversial phosphogypsum stack (100 Mt of stockpiled waste and 1200 ha of surface) located directly above salt-marshes of the Tinto River estuary (Huelva, SW Spain), less than 100 m from an urban area with similar extension (Fig. S1 of the Supporting information (SI)). The location of this phosphogypsum stack within the tidal prism makes it a potential source of pollution to the

estuarine environment. The excess of highly-polluted acidic water stored in the pore-space of this anthropogenic aquifer emerges forming springs or edge outflows reaching the estuary. Moreover, there is a clear connection between the stack and the estuary, which leads to a potential weathering by seawater intrusion from the deepest part originating these edge outflows. This fact evidences the inefficiency of the preliminary restoration actions based on the addition of an artificial topsoil cover over the bare phosphogypsum [13]. In fact, all disposal modules of the stack, two non-restored zones and other two ‘supposedly’ restored zones (Fig. S1 of the SI), act as sources of edge outflow waters to the estuary [12].

However, sulfate-reduction and sulfide precipitation processes catalyzed by bacterial activity occur naturally in the salt-marshes supporting the stack and could attenuate some contamination [14]. This deposit area is currently in a legal limbo; the company must ensure environmental restoration of the marsh although only of those areas without previous restoration actions, while social turmoil advocates total restoration or even transportation of the waste to controlled landfills. In this scenario, studying natural processes, such as sulfate reduction in the marsh soils, could allow the optimization of possible effective remediation actions not only in the case of study but also in other estuarine systems affected by industrial waste releases around the world.

2.2. Phosphogypsum coring and sample processing

Phosphogypsum core samples were collected at approx. 0.5 m intervals from stack surface to the underlying marsh soils using a soil-sampling auger (Fig. S1 of the SI). The deepest sample corresponds to the first centimeters of underlying marsh soil (8.4 m at depth). Samples were transferred to polypropylene vacuum bags and rapidly taken to the laboratory within 15 min. At the laboratory, 0.1 μm -filtered pore-waters were collected through suction cup lysimeters under $\text{N}_{2(\text{g})}$ atmosphere within a glove box. After pore-water extraction, solid samples were frozen and then lyophilized to complete dryness using a freeze-dryer.

2.3. Chemical and mineralogical analyses

For the pore-water, pH, redox potential (ORP, converted to Eh) and electrical conductivity (EC) were immediately measured after extraction. Determination of Fe(II)/(III) and H_2S concentrations was also immediately performed by spectrophotometric methods. Then, solutions were divided into two aliquots, one not acidified for anion analysis by high performance liquid chromatography (HPLC), and one acidified with HNO_3 to $\text{pH} < 1$ for analysis of major and trace elements by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), respectively. More details of the analytical procedures are described in the Section S1 of the SI.

For the solid samples, the bulk chemical composition was determined by acid digestion with *aqua regia* in Teflon vessels, and then followed by analysis with ICP-OES and ICP-MS. Sulfur speciation analyses were performed; acid-volatile sulfur (AVS, including amorphous Fe monosulfides (FeS), mackinawite, greigite as well as other HCl-soluble sulfides), pyrite-sulfur (Py-S) and elemental sulfur (ES) were differentiated by a three step sequential digestion, and their concentrations were determined using the method described by Duan et al. [15]. In order to study in detail the partitioning of metals, the following sequential extraction procedure from Rauret et al. [16] was also applied

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