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Pollutant flows from a phosphogypsum disposal area to an estuarine environment: An insight from geochemical signatures

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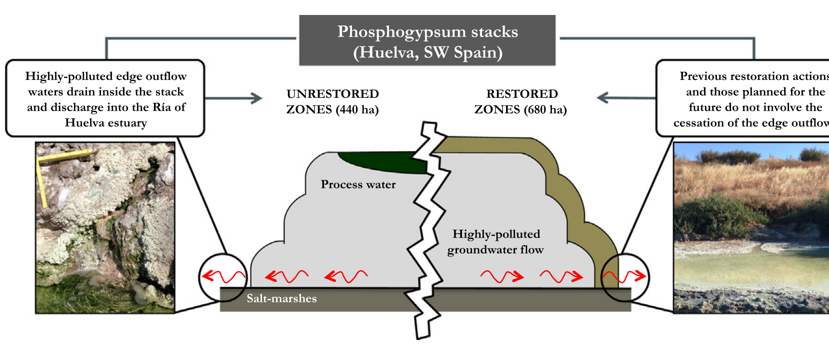
HIGHLIGHTS

- Acidity and contaminants from phosphogypsum leaching are released to an estuary.
- Already-restored zones act as a pollution source just as unrestored zones.
- Cl/Br ratios and REE patterns were suitable to assess the restoration inefficiency.
- Changes in the remediation strategies of the phosphogypsum stack are hence necessary.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphogypsum wastes from phosphate fertilizer industries are stockpiled in stacks with high contamination potential. An assessment of the environmental impact, including the use of geochemical tracers such as rare earth elements (REE) and Cl/Br ratios, was carried out in the phosphogypsum stack located at the Estuary of Huelva (SW Spain). Inside the pile, highly polluted acid pore-waters flows up to the edge of the stack, emerging as small fluvial courses, known as edge outflows, which discharge directly into the estuary. The disposal area is divided into four zones; two unrestored zones with surface ponds of industrial process water and two a priori already-restored zones. However, an extensive sampling of edge outflows conducted in the perimeter of the four zones demonstrates the high potential of contamination of the whole stack, including those zones that were supposedly restored. These solutions are characterized by a pH of 1.9 and concentrations of 6100 mg/L for P, 1970 mg/L for S, 600 mg/L for F, 200 mg/L for NH_4^+, 100 mg/L for Fe, 10–30 mg/L for Zn, As and U, and 1–10 mg/L for Cr, Cu and Cd. Preliminary restoration actions and those planned for the future prioritize removal of ponded process water and cover of the phosphogypsum with artificial topsoil. These actions presuppose that the ponded process water percolates through the porous medium towards the edge up to reach the estuary. However, geochemical tracers rule out this connection and point to an estuarine origin for these leachates, suggesting a possible tidal-induced leaching of the waste pile in depth. These findings would explain the ineffectiveness of preliminary restoration measures and should be considered for the development of new action plans.

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1. Introduction

The production of phosphoric acid (H_3PO_4) by fertilizer industry following the wet chemical digestion of phosphate rock (fluorapatite, $Ca_5(PO_4)_3F$) with sulfuric acid (H_2SO_4) generates huge amounts of a waste known as phosphogypsum (gypsum, $CaSO_4 \cdot 2H_2O$). The overall reaction is (Eq. (1)):

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF + Heat. \quad (1)$$

The phosphate rock is commonly concentrated by flotation prior to phosphoric acid manufacturing. The flotation process is enhanced by the addition of chemical reagents such as ammonium hydroxide or amine. The final phosphogypsum is soaked with the chemical reactants used and the products obtained in the industrial process, which leads to the existence of interstitial acidic solutions containing high concentrations of mainly phosphate, but also of sulfate, fluoride and often ammonium (Lottermoser, 2010). Phosphate corresponds to the fraction of residual phosphoric acid obtained as product that cannot be effectively separated in the industrial process for sale. On the other hand, phosphate rocks also contain metal and radionuclides as impurities that are released during the industrial process and finally concentrated in the reaction products (Rutherford et al., 1994). Most of toxic elements, including U and Th, are transferred from the phosphate rock to the phosphoric acid (Bolívar et al., 2009; Pérez-López et al., 2010). Thus, the residual phosphoric acid trapped in the interstices of phosphogypsum particles explains the acidic nature and the high contaminant release potential under leaching conditions of this waste. Moreover, these impurities limit the commercial use of the phosphogypsum.

Phosphogypsum is transported and dumped as an aqueous slurry in huge, aboveground stockpiles, without any prior treatment, known as stacks. These stacks are often vulnerable to weathering, and contaminant leaching can occur and cause serious environmental damage (see review in Tayibi et al., 2009). Moreover, contaminants in phosphogypsum-affected environments can be transferred finally to living beings (Boryło et al., 2013). Most of dumping areas are located in coastal regions close to phosphoric acid production plants. Some examples of potential leaching from phosphogypsum stacks to coastal environments are described in detail in the Santos-Cubatão estuarine system (Brazil; Sanders et al., 2013), in the Lebanese coast (El Samad et al., 2014) and in the Gulf of Gabes (Tunisia; El Zrelli et al., 2016), among many others.

Of particular interest is the case of the phosphogypsum stack located at the estuary formed by the confluence of the Tinto and Odiel Rivers, the so-called Ría of Huelva estuary (SW Spain). Since the beginning of the fertilizer production, phosphogypsum was transported and deposited over the Tinto River salt-marshes in several decantation zones. In this environment, phosphogypsum deposition may be influenced by physical and geochemical processes associated with estuarine systems (Sanders et al., 2013). The presence of the residual phosphoric acid trapped in the interstices of the gypsum particles makes the piles behave as an unconfined aquifer, clearly distinguishing an unsaturated zone and a saturated zone with contaminated groundwater flow (Pérez-López et al., 2011). The piles are directly settled on bare marshland soils without any type of isolation, which act as an impermeable barrier that withholds groundwater in depth and forces the water to flow laterally. When the groundwater reaches the edge of the stack, polluted water emerges forming superficial drainages, known as edge outflows, which release high load of contaminants into the estuary. Therefore, the leakages from the phosphogypsum stacks pose a potential risk to the ecological receptors (Bolívar et al., 2002; Borrego et al., 2013). Nevertheless, the Ría of Huelva also receives huge amounts of contaminants through the Tinto and Odiel Rivers. Both rivers are intensively affected by acid mine drainage from sulfide oxidation in the more than one hundred abandoned mines in the Iberian Pyrite Belt (Olías et al., 2006).

Preliminary restoration actions were carried out for some disposal modules of the phosphogypsum stack by following guidelines included in a report from the regional government (Junta de Andalucía, 2009). The same restoration guidelines are planned to be performed in unrestored zones. As far as we know, most studies characterizing the contamination from edge outflows focus mainly on one of the unrestored zone of the phosphogypsum stack (e.g. Gázquez et al., 2014; Martínez-Sánchez et al., 2014; Pérez-López et al., 2015). The research reported here expands the preliminary studies to the rest of the unrestored stack and to those zones that have already been supposedly restored. Thus, the main objective of this study is to assess the efficiency of the previous restoration measures since it is of paramount importance to optimize future restoration criteria for the whole phosphogypsum stack. The obtained results will provide useful information for managers to use in assessing other environmental systems globally threatened by leakages from phosphogypsum stacks, particularly in coastal regions.

2. Material and methods

2.1. Study area

Phosphogypsum was produced by several phosphate fertilizer plants and deposited over Tinto River salt-marshes from 1968 to 2010, when the dumping ceased under a decision of the Spanish National Court. These fertilizer facilities commonly imported phosphate ore from Morocco to manufacture the phosphoric acid. The total amount of stockpiled phosphogypsum is around 100 Mt (approx. 1200 ha of surface) at <300 m of the Huelva city (Fig. 1). The stack lies within the tidal prism of the Ría of Huelva, which ranges from 37 to 82 hm^3 during a tidal half-cycle (6 h) (Grande et al., 2000). The climate of the area is Mediterranean with annual average precipitation of 490 mm, mainly during autumn and winter, and temperature of 19.2 °C (1990–2010; from National Meteorology Institute). From 1968 to 1997, phosphogypsum was transported using seawater to several decantation zones that reached up to 10 m in height on average. After decantation, seawater used for transport along with the remaining 20% of phosphogypsum was directly released to the estuary without any treatment despite showing high acidity and pollutant concentrations. The enforcement of more strict environmental regulations in 1997 compelled the factory to avoid any direct discharge to the estuary according to the OSPAR convention (OSPAR, 2002; 2007). The new waste management plan proposed two main measures to fulfill this goal; on the one hand, the deposit of phosphogypsum in a large pyramidal pile over a single, previously-used zone; and on the other hand, the implementation of a closed-circuit system for transport and settling of phosphogypsum using freshwater instead of seawater. The closed-circuit system, also known as process water circuit, included the existence of ponds to store water in the central part of the stacks and different perimeter channels collecting all lixiviates from the piles and returning them to the closed-loop. Presently, the successive changes in environmental regulations have led to the existence of four different zones or modules within the stack (Fig. 1):

- Zone 1 (35 Mt; 400 ha and 2–3 m in height) was closed and restored in 1992 by adding a 25 cm layer of natural soil and vegetation over the bare phosphogypsum. Phosphogypsum is not visually observed and there are not perimeter channels or process water ponded on the top part.
- Zone 2 (25 Mt; 240 ha and up to 30 m in height) is the large pyramidal pile of phosphogypsum deposited after 1997 with the new waste management plan. This zone has been active until discharge stopped in 2010. Restoration measures have not been adopted and, hence, this module is currently exposed to weathering. Ponds with process