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# Environmental tracers for elucidating the weathering process in a phosphogypsum disposal site: Implications for restoration

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SUMMARY

This study provides geochemical data with the aim of identifying and tracing the weathering of phosphogypsum wastes stack-piled directly on salt-marshes of the Tinto River (Estuary of Huelva, SW Spain). With that purpose, different types of highly-polluted acid solutions were collected in the stack. Connection between these solutions and the estuarine environment was studied by geochemical tracers, such as rare earth elements (REE) and their North American Shale Composite (NASC)-normalized patterns and Cl/Br ratios. Phosphogypsum-related wastewaters include process water stored on the surface, pore-water contained in the phosphogypsum profile and edge outflow water emerging from inside the stack. Edge outflow waters are produced by waterlogging at the contact between phosphogypsum and the nearly impermeable marsh surface and discharge directly into the estuary. Process water shows geochemical characteristics typical of phosphate fertilizers, i.e. REE patterns with an evident enrichment of heavy-REE (HREE) with respect to middle-REE (MREE) and light-REE (LREE). By contrast, REE patterns of deeper pore-water and edge outflows are identical to those of Tinto River estuary waters, with a clear enrichment of MREE relative to LREE and HREE denoting influence of acid mine drainage. Cl/Br ratios of these solutions are very close to that of seawater, which also supports its estuarine origin. These findings clearly show that process water is not chemically connected with edge outflows through pore-waters, as was previously believed. Phosphogypsum weathering likely occurs by an upward flow of seawater from the marsh because of overpressure and permeability differences. Several recommendations are put forward in this study to route restoration actions, such as developing treatment systems to improve the quality of the edge outflow waters before discharging to the receiving environment.



## 1. Introduction

Some estuarine areas in Europe have undergone extensive industrialization over the past half-century due to their relatively flat surface, the nearby water availability and the proximity of the sea as a means of communication. Among these areas, a huge complex of chemical and petrochemical industries was installed in the surroundings of the Estuary of Huelva, a system formed by the confluence of the Tinto and Odiel Rivers (SW Spain). In this industrial area, several factories focus on the production of phosphoric acid for fertilizers. This manufacturing process is based on wet chemical attack of phosphate rock ore (fluorapatite, $Ca_5(PO_4)_3F$) with sulfuric acid ($H_2SO_4$) to produce phosphoric acid ($H_3PO_4$) as a commercial product and a low-value waste composed mainly by gypsum ($CaSO_4{\cdot}2H_2O$) known as phosphogypsum. The process can be summarized in the following reaction (Eq. (1)):

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

Phosphogypsum broadly contains metal(loid)s and radionuclides (Rutherford et al., 1994), also that produced by the industries located at the Estuary of Huelva (Bolívar et al., 1996; Pérez-López et al., 2007). Consequently, the market is poor for such waste and, hence, its production leads to stacking in large disposal areas close to the industrial plant, where phosphogypsum is often exposed to weathering conditions (Tayibi et al., 2009). In the Estuary of Huelva, the stack contains phosphogypsum produced for 40 years, i.e. approx. 1000 ha and 100 Mt. This dump covers the salt-marshes associated with the Tinto River estuary, less than 1 km from the city of Huelva. Phosphogypsum piles have even greater area than that of the city (approx. 1100 ha). These wastes

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are currently considered a NORM (naturally occurring radioactive material) substance and, therefore, its proximity to the urban area has awakened considerable social concern in recent years.

The mountain of waste has caused evident loss of a landscape with great ecological value and has a strong visual and landscape impact. Similar unimpacted salt-marshes on the Odiel River estuary were declared a UNESCO Biosphere Reserve in 1983 and RAMSAR-NATURA wetlands site in 1989. Fertilizer plants ceased dumping in December 2010 by decision of the Spanish National Court. However, the old stacks still remain on the salt-marshes of the Tinto River. Most of the potentially toxic impurities contained in phosphogypsum are associated with the easily mobile fraction, which is transferred to the environment in extremely acidic solutions (Pérez-López et al., 2010a). The stack base is directly in contact with the marsh soil surface. Marshes have a high content of organic matter whose oxidative decomposition leads to oxygen consumption and strongly anaerobic conditions. In the weathering profile of the phosphogypsum pile, some of the mobile metals are removed from solution by precipitation of insoluble metal sulfides in this anaerobic zone by activity of sulfate-reducing bacteria (Pérez-López et al., 2011; Castillo et al., 2012).

Pérez-López et al. (2011) clarified the redox geochemical processes occurring along the weathering profile and concretely the role of the underlying salt-marsh in the natural attenuation of contamination and, hence, in mitigating part of the phosphogypsum impact on the estuarine environment. However, several sources of highly-polluted acidic water can be recognized in the waste pile. On the one hand, surface ponds storing waters from the industrial processes, known as process waters, are directly on the pile. On the other hand, groundwater is retained above the relatively impermeable marsh surface, forcing a lateral flow through deeper saturated zones of the waste that emerges on the edge of the stack. These springs, known as edge outflow waters, drain the phosphogypsum pile and discharge directly into the Estuary of Huelva. Hence, the phosphogypsum stack is not totally watertight at present. Some of these leachates have been previously characterized from a radiological point of view (Gázquez et al., 2014), but no information has yet been published on the content of metallic impurities.

Phosphogypsum stacks are presently submitted to continuous weathering. There are some guidelines taken by the regional government for the implementation of future actions aimed at remediating the phosphogypsum disposal area (Junta de Andalucía, 2009). These already existing guidelines include, roughly, the following priority actions: (1) to remove process water from surface ponds, (2) to pump out and remove the pore-water of the piles to prevent leakages around the edges of the stack, (3) to treat ex situ the extracted wastewater in a treatment system, and (4) to cover the phosphogypsum surface by artificial-soil amendments with a drainage system to facilitate the evacuation of rainwater. This preliminary report states that the process water is the primary route of dispersion of pollutants to the aqueous environment, both by its volume and by its chemical characteristics, and thus its removal must be carried out urgently. Moreover, these guidelines also indicate that infiltration of ponded process water downward to groundwater is the direct cause of diffuse and point edge outflows toward the estuary, i.e. process water and edge outflows are linked through porous media. However, these preliminary guidelines were issued without proving the possible connection between these solutions and with an obvious lack of information on the weathering process involved in leaching and transport of contaminants from the stack to the estuarine environment. Thus, the present study aims to bridge this gap using geochemical indicators, e.g. ionic compositions and fractionation of rare earth elements (REE), as environmental tracers of the phosphogypsum weathering process. This information will be invaluable for the design and optimization of remediation actions.

## 2. Environmental setting

The Estuary of Huelva is on a mesotidal mixed-energy coast with a tidal range of 1–3 m and a tidal prism between 37 and 82 $hm^3$ during a tidal half-cycle (6 h) (Grande et al., 2000). Surprisingly, the phosphogypsum stack is located within the tidal prism of this estuary. The fertilizer plant has produced and deposited phosphogypsum with a rate of 2.5 Mt/year from 1968 to 2010. Currently, four zones are clearly recognized within the dumping area. In future plans for restoration, zones 1 and 4 (approx. 750 ha) are considered to be already restored by only covering the phosphogypsum with a layer of natural soil. Neither of these *a priori* restored zones have process water in surface ponds. In zones 2 and 3 (approx. 450 ha), the uncovered phosphogypsum is directly exposed to weathering (see in Fig. 1). The phosphogypsum management policy changed in 1997, following the OSPAR convention (OSPAR, 2002, 2007). Until then, 80% of produced phosphogypsum was transported and deposited in the four zones of the stack with seawater using an open-circuit pipe system, reaching an average height of 5 m. The water, after waste decantation, with around 20% of phosphogypsum was directly poured into the Odiel River estuary, and this was dispersed by the tidal action reaching finally the Atlantic Ocean (Martínez-Aguirre et al., 1996; Bolívar et al., 2000, 2002).

From 1997 to the end of 2010, all the phosphogypsum produced was stored in zone 2 using a closed-circuit system with freshwater as process water, forming a pyramidal pile of up to 30 m in height. Thereafter, there has been no 'direct' release to the estuary up to date (Villa et al., 2009). The closed circulation system of process waters includes the creation of the surface pond and a series of perimeter channels for collecting and incorporating acidic leachates from the phosphogypsum weathering into the closed circuit. According to the restoration guidelines of the regional government (Junta de Andalucía, 2009), these channels collect most of the infiltrating water in zone 2 and, therefore, the potential risk for the ecological receptors by 'indirect' leakage of edge outflows in this area would be presumably minimal.

In contrast, zone 3 is an abandoned area without restoration activities where no disposal of phosphogypsum has occurred since 1997. Since then, its function has been to store process water in a central pond that is part of the closed-circuit freshwater system installed after the change of management policy (Fig. 1). This process water is conducted through pipes from zone 2 of the stack. Since the cessation of phosphogypsum production in 2010, water circulation remains active and carries process water to zone 3 to be subjected to evaporation with the purpose of reducing its volume. However, zone 3 does not have any measures to prevent leached water from phosphogypsum weathering from reaching the surrounding environment. In fact, there are numerous points and diffuse sources of edge outflow that comprise a total annual flow of approx. 90,000 $m^3$ (Tragsatec, 2010). For this reason, this study focuses on the assessment of the potential contamination from this zone of the phosphogypsum stack, which may be representative of the overall disposal area.

## 3. Materials and methods

### 3.1. Sampling points

Geochemical tracers of the weathering processes in the phosphogypsum stack were studied by sampling in May 2013 (Fig. 1): (1) pore-solutions of phosphogypsum samples collected at approx. 0.5 m intervals from the stack surface to the underlying marsh surface using a soil sampling auger (bore-hole C; samples C1–C14), (2) edge outflow leachates reaching the Estuary of Huelva (samples