Journal of Geochemical Exploration 147 (2014) 130–138

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Use of bioassays for the assessment of areas affected by phosphate industry wastes

M.J. Martínez-Sánchez [a], C. Pérez-Sirvent [a,*], M.L. García-Lorenzo [b], S. Martínez-López [a], J. Bech [c], R. García-Tenorio [d], J.P. Bolívar [e]

[a] Department of Agricultural Chemistry, Geology and Pedology, Faculty of Chemistry, University of Murcia, Murcia, Spain
[b] Department of Petrology and Geochemistry, Faculty of Geology, University Complutense of Madrid, Madrid, Spain
[c] Department of Plant Biology, Faculty of Biology, University of Barcelona, Barcelona, Spain
[d] E. T. S. Arquitectura, Departamento de Física Aplicada II, University of Sevilla, Sevilla, Spain
[e] Department of Applied Physics, Facultad de Ciencias Experimentales, University of Huelva, Huelva, Spain

ARTICLE INFO

Article history:
Received 9 November 2013
Recieved in revised form 15 May 2014
Accepted 24 May 2014
Available online 2 June 2014

Keywords:
Bioassay
Microtox
Phytotoxicity
Ostracods
Phosphogypsum
Phosphate industry

ABSTRACT

Phosphogypsum (PG) is a waste product of the phosphoric acid production process and contains, generally, high activity concentrations of uranium series radionuclides.
This study is a contribution towards a risk assessment in areas affected by phosphate industry in SW Spain, integrating information from soil physicochemical characteristics, total and soluble potentially toxic elements (Zn, Pb, Cd, Cu, As and Fe), mineralogical composition and ecotoxicological evaluation. The applied bioassays confirmed the soil toxicity categorisation and then, it is highly recommended to complement the results from environmental chemistry with results from bioassays, in order to provide a more complete and relevant information on the bioavailability of contaminants and to characterise the risk of contaminated areas.

1. Introduction

The increasing use of phosphate fertilizers in agriculture has resulted in the development of chemical industries devoted to the production of the phosphoric acid (Dueñas et al., 2007; Pérez-López et al., 2007). Phosphate fertilizer is obtained by phosphate rock wet chemical treatment with sulphuric acid and in this process, not only the commercial phosphoric acid is produced, but also an insoluble residual calcium sulphate called phosphogypsum (PG).

Phosphogypsum is a naturally occurring radioactive material (NORM) mainly composed of a gypsum matrix ($CaSO_4 \cdot 2H_2O$) with high contents of impurities such as P_2O_5, fluorides, organic substances, potentially toxic elements (PTEs) and radionuclides. PG generally is stored in extensive piles near the factories or released to the surrounding aquatic systems (Dueñas et al., 2010). Because this by-product accumulates a fraction of the natural radionuclides originally present in the minerals treated, it can be concluded that these industries could produce a radioactive impact in their nearby environment (Bolívar et al., 1995).

In Spain, the production of phosphoric acid, and hence of phosphogypsum, was restricted to a large fertilizer industrial complex situated in the town of Huelva (SW Iberian Peninsula) (Pérez-López et al., 2007, 2010). This large complex is located at the confluence of the Tinto and Odiel rivers, an estuarine zone of salt marshes with high ecological value. Over 3 Mt of phosphogypsum wastes was produced each year and deposited in a stack occupying a large part of the salt marshes until 2010 (Periáñez et al., 2013).

The determination of the contaminant content is not enough to fully evaluate the toxic effects or to characterise contaminated sites, because the ecotoxicological danger in the environment is not reflected, and no information is provided on the effects of the chemical compounds. To estimate the environmental risk of contaminants, chemical methods need to be complemented with biological procedures. Biotests measure the bioavailability of the contaminants and the effects of the chemically not measured toxic compounds on the members of the soil community. Therefore, ecotoxicological testing may be a useful approach for assessing the toxicity as a complement to chemical analysis (García-Lorenzo et al., 2009). Any strategy for assessing properties potentially hazardous to the environment used in a classification system should include test organisms of different trophic levels representing both the terrestrial and aquatic compartments.

The aim of this study was to check the effectiveness of a battery of bioassays in the screening of environmental risks in areas affected by

* Corresponding author. Tel.: +34 868 887449; fax: +34 868884148.
E-mail address: melita@um.es (C. Pérez-Sirvent).

http://dx.doi.org/10.1016/j.gexplo.2014.05.019
0375-6742/

phosphate industry and contaminated by phosphogypsum, facilitating their zonation as a function of the toxicity. Particularly, the toxicity was evaluated by using three assays: bacteria, plants and ostracods.

2. Material and methods

2.1. Study area

The present study was carried out in the Huelva estuary, formed by the Tinto and Odiel rivers (SW, Spain). This is a scenario widely studied due to two factors (Hierro et al., 2013; Villa et al., 2011). The first one is that both rivers are strongly affected by acid mine drainage (AMD) (Nieto et al., 2007), since they drain the Iberian Pyrite Belt (IPB), one of the most important mining areas in the south of Europe (Fig. 1). Mining activity in the IPB dates from prehistoric times (Hierro et al., 2012; Pérez-López et al., 2011; Periánez et al., 2013) during two periods: the Roman Age and the last two centuries. During the last period, the pyrite mining operations upstream of the Odiel and Tinto rivers have caused the formation of sulphuric acid through the oxidation of natural sulphur deposits, the acidification of waters and the mobilisation of PTEs from the mining area to the Huelva estuary.

The second fact is related to a large chemical industrial complex located in the confluence of Odiel and Tinto rivers at the South of Huelva town (Fig. 1). This complex includes several phosphate rock processing plants devoted to the production of phosphoric acid and phosphate fertilizers from 1968 to 2010, when the production of phosphoric acid stopped (Hierro et al., 2012, 2013).

The company imported sedimentary phosphate ore (phosphate rock) from Morocco, which mainly was composed by fluorapatite ($Ca_5F(PO_4)_3$), calcite ($CaCO_3$), perovskite ($Ca(TiO_3)$), quartz (SiO_2), magnetite (Fe_3O_4), pyrite (FeS_2) and kaolinite ($Al_2Si_2O_5(OH)_4$) (Rentería-Villalobos et al., 2010).

The phosphate is treated at these plants by mixing it with sulphuric acid to produce phosphoric acid. The sulphuric acid was produced from pyrite in the same industrial plant and as a result, pyrite ashes were obtained as wastes during the roasting of pyrite ores and landfilled together with PG wastes.

Until 1998, about 20% of phosphogypsum produced annually was discharged into the sea and the remaining 80% was pumped in suspension with seawater and transported about 2 km away from the factories, to be disposed in large piles located in a salt-marsh area along the Tinto River estuary (Bolívar et al., 2000, 2009). Until 1997, the seawater used for this transportation was discharged into the estuary where the PG piles were formed. In 1998, direct discharges into the sea were banned, and all the phosphogypsum was stored in a pile in the town's surroundings. The freshwater used for its transportation had to follow a closed circuit in order to avoid any impact on the estuarine ecosystem but a small fraction of the PG produced is used in agriculture as soil amendment.

Because this by-product accumulates a significant fraction of the radioactivity contained originally in the mineral (NORM), these industries could produce an important radioactive impact on their nearby environment. From 2010, all phosphate production plants were closed and then, the phosphogypsum production was stopped.

2.2. Sampling design

For this study, a catena of sampling points was considered, with increasing distance to the contamination sources. Sampling points P1, P2, P3 and P4 were strongly affected by PG piles and P5 and P6 correspond to control points, where samples were collected upstream of contamination sources and were not influenced by PG.

The sediment, the pore-water extract, efflorescences and infiltration waters from PG piles were collected in these sampling points as follows (Fig. 2):

- Sediment samples (S1, S2, S3 and S4), collected in P1, P2, P3 and P4 respectively, were affected by PG pile and show increasing distance to the contamination source.
- Control sediments (S5 and S6) were collected in sampling points P5 and P6, located upstream of contamination sources and not influenced by PG piles.
- Water samples (Win1, Win2 and Win3) correspond to waste waters from industrial processes and were stored in PG piles. Phosphogypsum solid wastes showed high porosity and the water contained in the stacks could infiltrate until impermeable layers of the salt-marshes where they appear. In our study, these samples were collected in P1.
- Pore waters (WP1, WP2 and WP3) were collected in P1, P2 and P3 respectively.
- A water sample from the Tinto River (WT4).
- Surface efflorescences from P1, P2, P3 and P4 sampling points were collected and named from E1 to E11.
- Sediment samples PG1, PG2, PG3 and PG4 correspond to phosphogypsum pile samples.

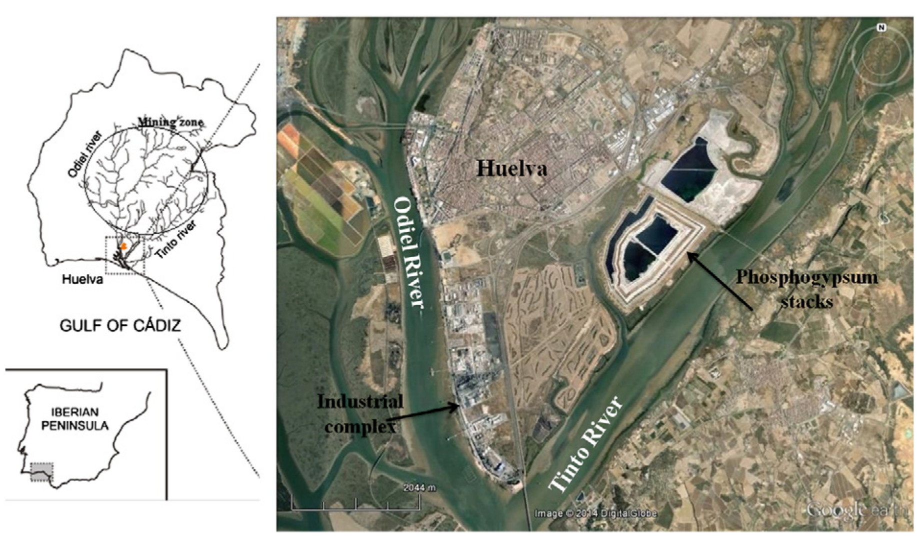

Fig. 1. Location map of the phosphogypsum pile next to Huelva town (SW Spain). Image from Google Earth software.