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Rare earth elements, iron and manganese in ochre-precipitates and wetland soils of a passive treatment system for acid mine drainage

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Abstract

The rare earth elements (REE) along with iron and manganese distribution in ochre-precipitates and wetland soils in a passive system for acid mine drainage treatment (Jales, Portugal) was studied. The results obtained by instrumental neutron activation analysis showed a higher incorporation of the light REE (particularly La and Ce) by the ochre-precipitates resulting from the mine water-limestone interaction. These fluffy materials influence the entrance of the first wetland where a correlation between Fe and La and Ce was found. Then Mn phases appear to play a more important role controlling REE distribution in the remaining area of the wetland soils.

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Keywords: Acid mine drainage; rare earth elements; iron and manganese; ochre-precipitates; Jales; Portugal

1. Introduction

As a consequence of sulfide oxidation in mines, dumps and tailings impoundments, acid mine drainage (AMD) often poses a long-term threat to the aquatic environment[1,2]. Passive treatment systems with wetlands have been used to remediate abandoned mining sites. The Jales mining area located near Vila Pouca de Aguiar (north of Portugal), has a passive system built to collect and treat the drainage that flows from an old adit into the Peliteira creek. The system includes a pre-treatment unit devoted to chemical processes using the water-limestone interaction and two wetlands. Previous studies of this system showed that iron, manganese and other metals are mainly controlled by iron oxyhydroxides and clay minerals among other phases[3]. Also, a depletion of REE contents in the mine water occurs at the end of the limestone channel, and the effluent of the wetlands contains significantly higher REE

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concentrations after summer, indicating their release from the fine particles to the water, when compared to the REE concentrations after the rainy season[4]. Among the phases present in the wetland soils, clay minerals with low degree of order such as mica-vermiculite mixed-layer and kaolinite, and Fe or Mn oxides and oxyhydroxides[4] may play a relevant role in sorption processes of REEs in the wetlands.

In this work REEs, Fe and Mn contents in the ochre-precipitates resulting from the mine water-limestone interaction were determined. Iron and manganese behaviors are compared with REE distribution in the fine fractions of the wetland soils in order to better understand the processes controlling the REE patterns in the fine fractions of the wetland soils, including the influence of ochre-precipitates that flow into the wetlands.

1.1. Studied area

The Jales treatment plant was part of the rehabilitation project planned to the abandoned mining site of Jales; the passive system was built to collect and treat the drainage that flows from an old adit into the nearby watercourse[5] (Fig. 1). The study site has a temperate warm climate with highest rainfall values in winter; July is the driest month; the average annual temperature and rainfall are 12.5ºC and 1214 mm, respectively.

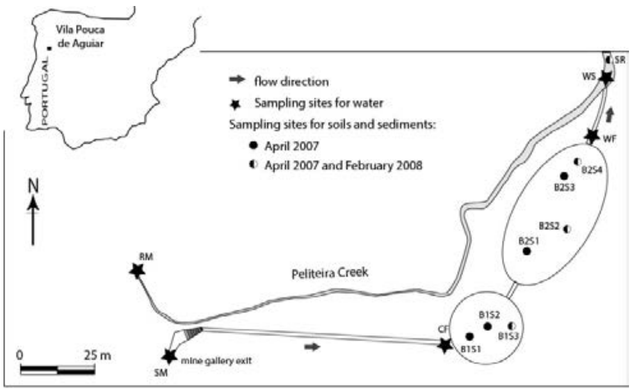

Fig. 1. Location map of the Jales mining site, including the layout of the water treatment plant. Sampling sites are indicated in the plant (reproduced by permission of Elsevier from Chemosphere, 2015, 138, 691–700).

The mine water can be generically described as an acid- (pH< 4.5) and sulphate-rich solution. After a first contact with limestone at the mouth of the mine, there follows an open limestone system devoted to neutralization and precipitation processes. This pre-treated effluent enters into a typical aerobic wetland system planted with *Typha sp*. to aid wetland performance. The whole system promotes oxygenation, pH increase, alkalinity increase and subsequent precipitation of metals as ferric hydroxide sludge (ochre-precipitates) as well as fixation of metals by plants.

2. Materials and methods

Concentrations of REEs, Fe and Mn in ochre-precipitates collected at the end of the limestone channel of the treatment system were obtained by instrumental neutron activation analysis (INAA), and compared to concentrations obtained previously for the < 20µm fraction of the wetland soils by the same method[3,4]. Two aliquots of each standard were used for internal calibration, and standard checks were performed (QA/QC). More details of this analytical method were published elsewhere[6,7].

3. Results and discussion

The ochre-precipitates collected at the end of the limestone channel of the treatment system present a high light REE (LREE)/heavy REE (HREE) ratio (La/Yb=7.9) (Table 1), when compared to the one found in the water collected underneath (La/Yb=0.67)[5] indicating the preferential incorporation of the LREEs relative to HREEs in these fluffy materials.

The results obtained for Fe, Mn and REEs in the fine fractions of the wetland soils were normalized to the "baseline" (composite sample of the soils used to construct the wetlands) to evaluate the concentration of these elements in the finer particles. The REEs are retained more in the fine fraction of soils of the first wetland, except for sample B2S3 (wetland 2) where the higher Mn value was found (Fig. 2).

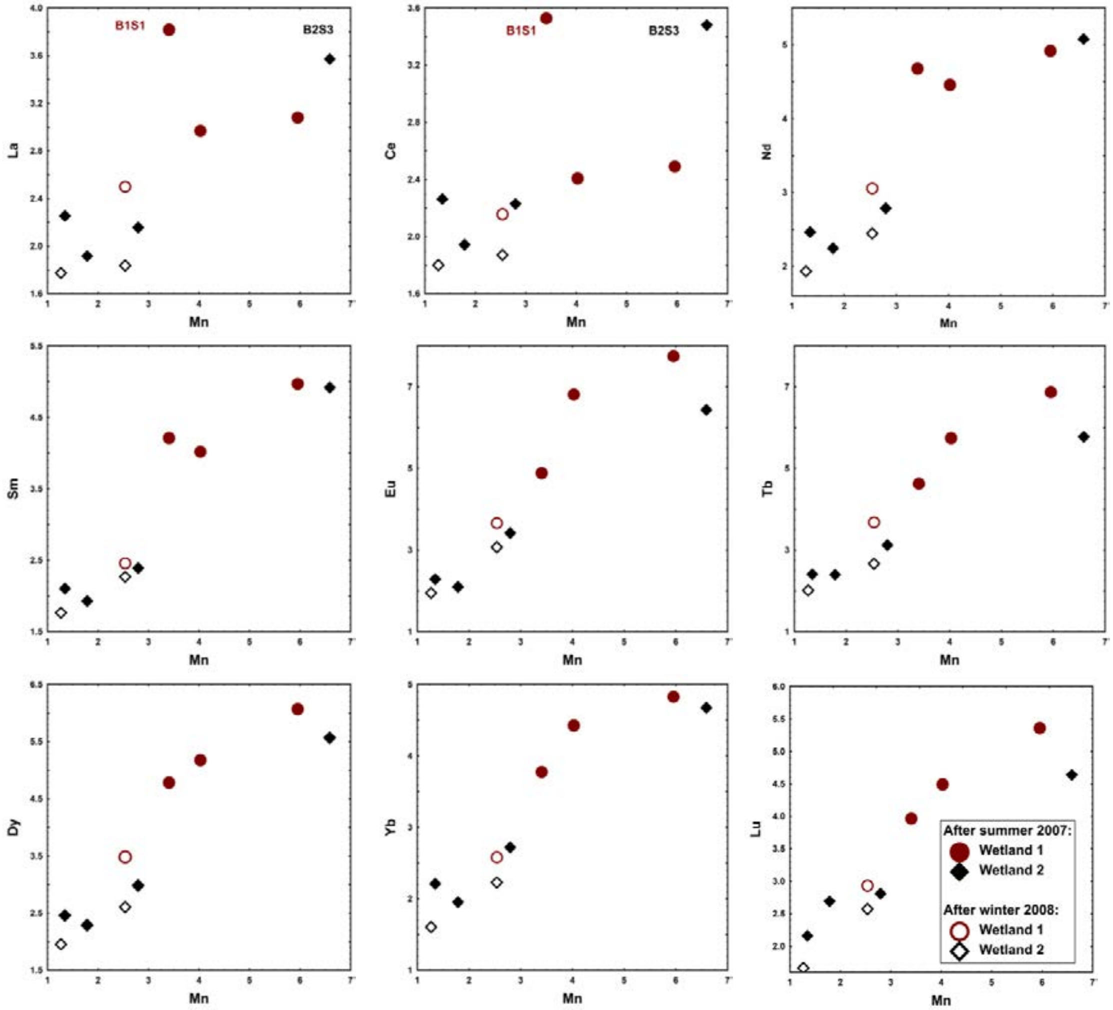

Fig. 2. Mn vs REE concentrations (mg/kg) relative to the baseline of the < 20μm of the wetland soils (Jales, Portugal).

Table 1. REE, Fe and Mn concentrations (mg/kg) obtained by INAA in the ochre-precipitates collected at the end of the limestone channel (Jales, Portugal).

Sample	La	Ce	Nd	Sm	Eu	Tb	Dy	Yb	Lu	Fe	Mn
Ochre-precipitates	16.2	19.1	37.4	2.60	1.89	1.02	5.55	2.05	0.307	456708	1146

In general REE values are correlated with manganese in both wetlands, except for La and Ce, particularly at the entrance of wetland 1 (sample B1S1). At this point of the treatment system La and Ce appear to be more correlated with iron (Fig. 3), which can be explained by the close input of ochre-precipitates where these elements are preferentially retained.

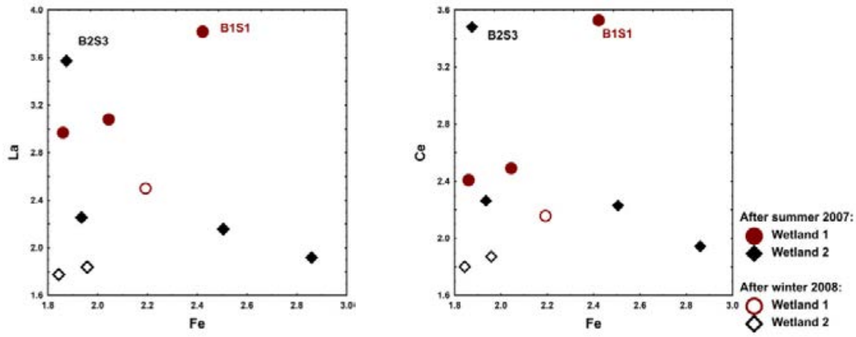

Fig. 3. Fe vs La and Ce concentrations (mg/kg) relative to the baseline of the < 20µm of the wetland soils (Jales, Portugal).

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