

# Behaviour of trace elements during evaporative salt precipitation from acid mine drainage (Agrio River, SW Spain)

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**Abstract** Polluted by acid mine drainage (AMD), the Agrio River is the major input of pollutants to the Odiel River. To study the behaviour of dissolved elements, water collected directly from the Agrio stream was subjected to infrared light to total evaporation. The physicochemical parameters, monitored daily, showed electrical conductivity increased from 15.5 to 33.1 mS/cm and pH decreased from 2.3 to 1.3. The analysed elements (major and trace elements) showed different behaviour throughout the evaporation process, concluding that evaporative salts behave as temporary sink for many elements in rivers polluted by acid mine discharges, during the dry season.

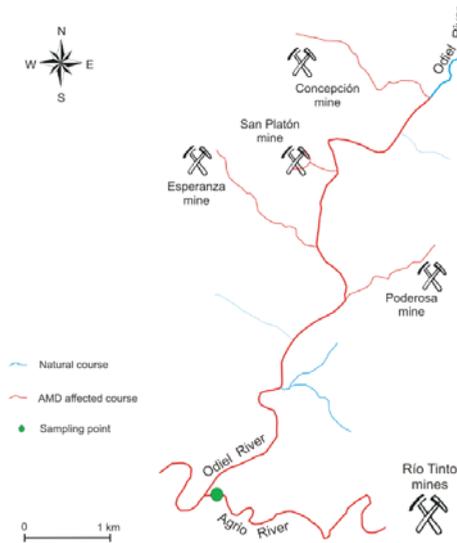
**Key words** Iberian Pyrite Belt, acid river, evaporation, rare earth elements, toxic element

## Introduction

The Iberian Pyrite Belt (IPB) is one of the largest polymetallic massive sulphide deposits in the world, which has been subjected to intense mining activity since prehistoric times (Nocete et al. 2005) but especially since the second half of the nineteenth century (Olías and Nieto 2015). Because the Tinto and Odiel river basins (SW Spain) are located over the IPB materials, their waters have undergone a deep pollution by acid mine leachates from the oxidation of sulphide-rich mining wastes. Hence, these rivers present extreme acidic conditions as well as high concentration of toxic elements (i.e. metals and metalloids) (Sáinz et al. 2002; Sarmiento et al. 2009). The acid mine drainage (AMD) in this area is a huge environmental problem not only due to the contamination of the rivers but also to the toxic metal-polluted waters that are transported continuously to the Ría of Huelva estuary and the Gulf of Cádiz (Nieto et al. 2013).

Presenting a natural stream water quality at its upper part, the Odiel River collects acidic contributions from several sulphide mining areas distributed along its watershed. Nevertheless, the main input of acid mine waters that causes its total deterioration is the Agrio River, which drain part of the Riotinto mines (Sarmiento et al. 2009). The Agrio waters present extreme contamination, with high concentrations of pollutants in solution and low pH values. Furthermore, the Mediterranean climate with almost non-existent rainfall during the dry season (from June to August) induces intense evaporation resulting in the supersaturation and the subsequent precipitation of sulphate salts (Buckby et al. 2003). These soluble minerals act as sinks for acidity and toxic metals (Fe, Al, Cd, Co, Cu, Zn, etc.), but only temporary until the arrival of the first rainfalls, in the rainy season, when they are again released by dissolution (Hammarstrom et al. 2005; Nordstrom and Alpers 1999). For this reason, the aim of this work is focused on studying the behavior of trace elements from a

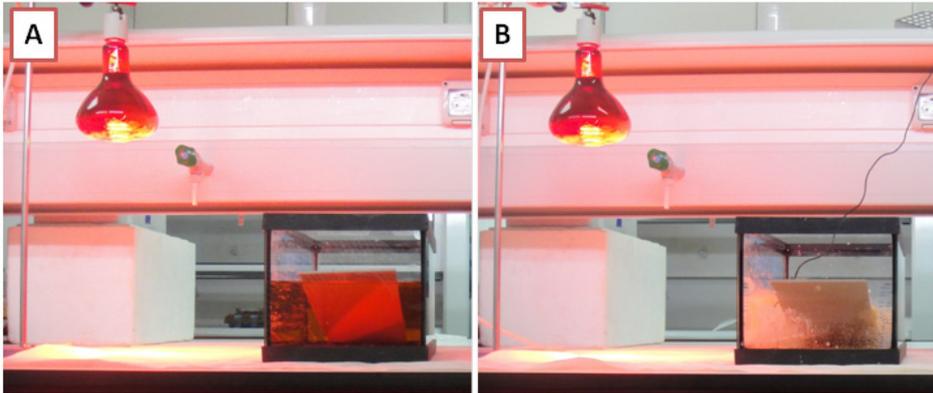
severely affected-AMD stream (Agrio creek) during evaporative salts precipitation under laboratory conditions.



**Figure 1** Location map of the sampling point in the Agrio River.

## Methods

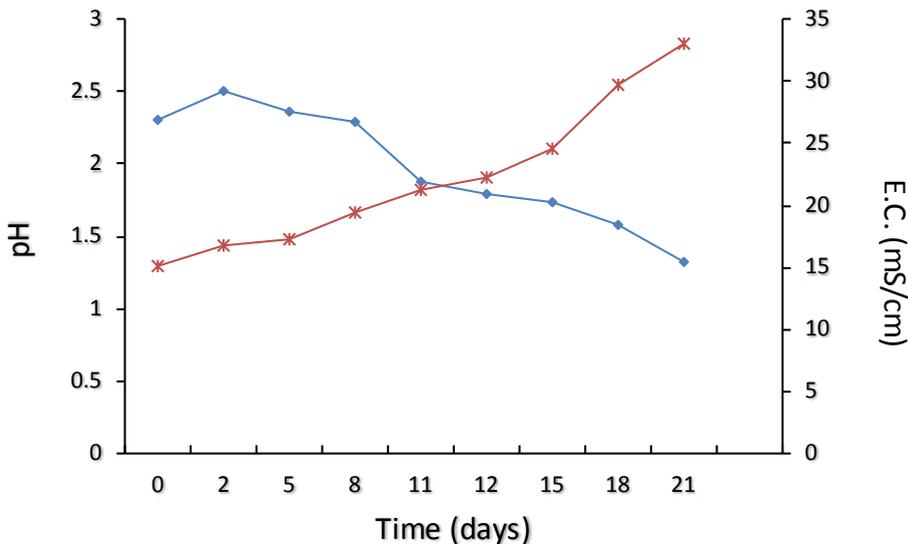
A laboratory driving-evaporation experiment was performed to study the behaviour of dissolved elements present in the Agrio River waters (fig. 1). The water from the Agrio was collected at the end of the summer in sterile polypropylene containers, transported to the laboratory, and immediately placed in the test vessel. A volume of 7 L of water was subjected for 21 days to an infrared light lamp ( $28 \pm 2$  °C) until total evaporation. The evaporation rate was calculated by measuring the loss of water volume in the experimental container. Temperature, electrical conductivity (EC), pH and oxidation-reduction potential (ORP) were measured everyday using a portable multiparameter Crison®MM40+. Water samples (20 mL) were collected daily, filtered (0.45  $\mu$ m) and acidified to pH < 1 with suprapur HNO<sub>3</sub> for trace element determination. The samples were stored at 4 °C in the dark until analysis. Concentrations of S, Na, Mg, Al, Fe, Si, Ca, Ti, Mn, Co, Ni, Cu, Zn, and other trace elements (Li, Be, Sc, Cr, Ga, Ge, Se, Sr, Cd, Th, U and rare earth elements –REE–) in the water were determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), respectively. The concentrations of SO<sub>4</sub> were obtained from the S contents. The precipitation percentage for each element was calculated based on the dissolved element concentration and the volume of evaporated water in the test vessel.



**Figure 2** Test vessel containing the Agrio water at the beginning (A), and at the end (B) of the experimental run.

### Results and Discussion

The physicochemical parameters of the Agrio River water (*in situ*) were: 18.7 °C, pH 2.3, EC 15.1 mS/cm, and ORP 453 mV. Around 330 mL of water was evaporated each day, which means 4.7% of the initial volume (fig. 2). At the end of the experiment most of the water (>90%) was evaporated. As expected, during the experimental run the pH gradually varied from 2.17 to 1.33 and the EC from 15.1 to 33.1 mS/cm (fig. 3).



**Figure 3** Temporal variation of the pH and EC along the experimental run.

The chemical analyses showed an increase of the dissolved elements concentration in line with daily evaporation to the end of the experiment, with the exception of Ca that showed a slight decrease of concentration (Table 1). Highest concentrations were found for SO<sub>4</sub>, Al,

and Mg, followed by Fe, both at the initial and last day of the experiment (A0 and A21, respectively).

**Table 1** Concentrations at the initial time of the experiment (A0) and at the end (A21) for some elements

	Al	Ca	Cu	Fe	Mg	Mn	Na	Si	SO <sub>4</sub>	Zn
<b>A0</b>	1.52	0.40	0.15	0.84	2.27	0.23	0.06	0.06	24.8	0.29
<b>A21</b>	11.7	0.32	1.28	7.18	18.7	1.71	0.54	0.46	178	2.40

	Be	Cd	Co	Cr	Ga	Ge	Li	Ni	Sc	Se	Sr	Th	Ti	U	Y
<b>A0</b>	0.09	1.39	7.09	0.13	0.07	0.07	3.03	4.26	0.24	0.23	0.81	0.07	0.05	0.17	1.46
<b>A21</b>	0.60	11.2	71.7	1.08	0.45	0.41	18.8	30.3	1.85	1.62	3.90	0.64	0.69	1.74	12.8

The concentrations of the major elements (above) are expressed as g/L; the trace elements (below) are expressed as mg/L.

Among the analysed elements, Th and U showed the highest increases in concentration in relation to their initial values (9.1 and 10.4, respectively), indicating a more conservative behaviour. On the contrary, as commented before, Ca was the element that precipitates more intensely, probably as gypsum. To a lesser extent Sr, Ge, and Ga also showed a less conservative behaviour with increases of 4.8, 5.5 and 6.6, respectively. In the case of Sr, this must be related to its coprecipitation with Ca. For Ge and Ga this pattern should be object of further research.

The precipitation percentages for selected days are plotted in fig. 4 and fig. 5. These values represent the precipitation for the elements regarding to the previous represented day. Thus, A5 includes the precipitation from the day 1 to 5, A10 the precipitation from the day 6 to 10, and so on. Some negative values for the 5 first days (A5) are due to problems in the precision of the analytical measurements because until this day the salt precipitation was very low. Among the major elements (fig. 4), Na, Zn, Si, Mn, Fe, and Cu exhibited a strong precipitation from the day 10 onwards, although some differences can be observed between them. On the contrary, Ca showed an intense precipitation between the day 6 to 10 and then a progressive decrease. This result is in concordance with the aforementioned less conservative behaviour of Ca indicating that is rapidly removed from the water. Aluminium also showed a significant precipitation from the day 6 to 10. Its seems that the comportment of Y and Cd (Fig. 5) are similar to Al. Additionally, the elements Sc, Cr, and Th (and U to a lesser extend) presented similar precipitation behaviour to the Fe. These trends will be compared by means of mineralogical analysis of the evaporitic salts currently in progress. Regarding other trace elements (fig. 5), although a similar precipitation pattern was observed, there are some differences between the elements that will be investigated in more detail.

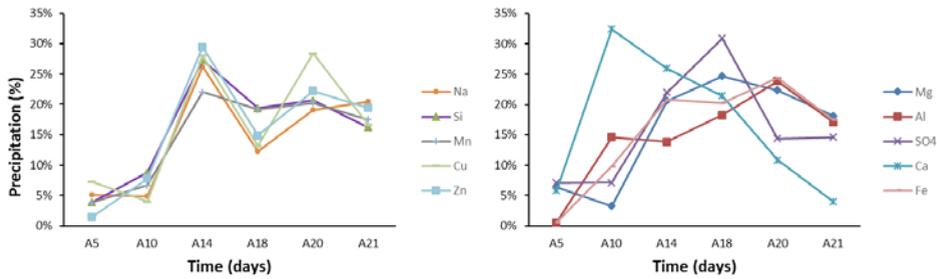


Figure 4 Precipitation percent for the major elements analysed for the days 5, 10, 14, 18, 20, and 21.

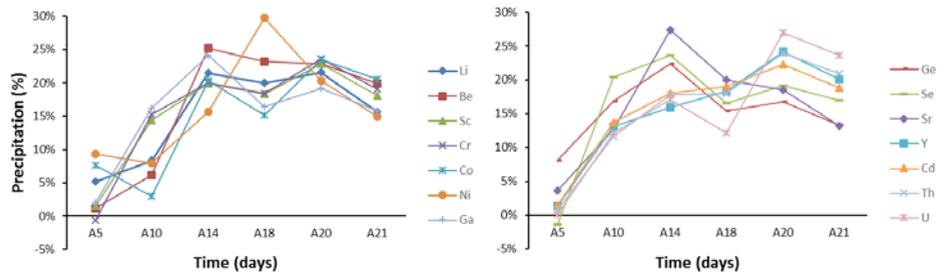


Figure 5 Precipitation percent for the trace elements analysed for the days 5, 10, 14, 18, 20, and 21.

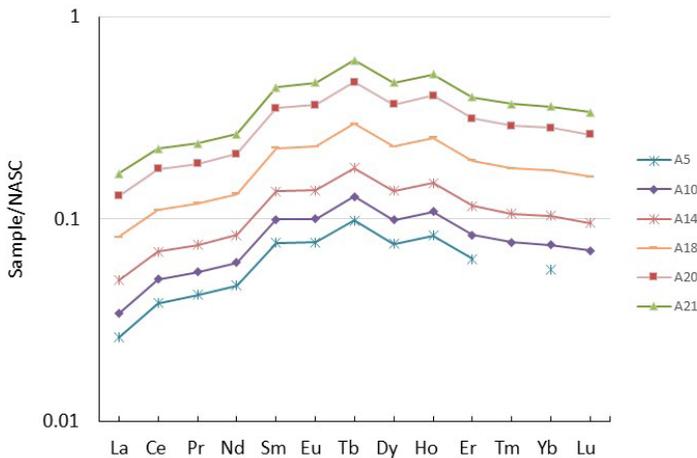
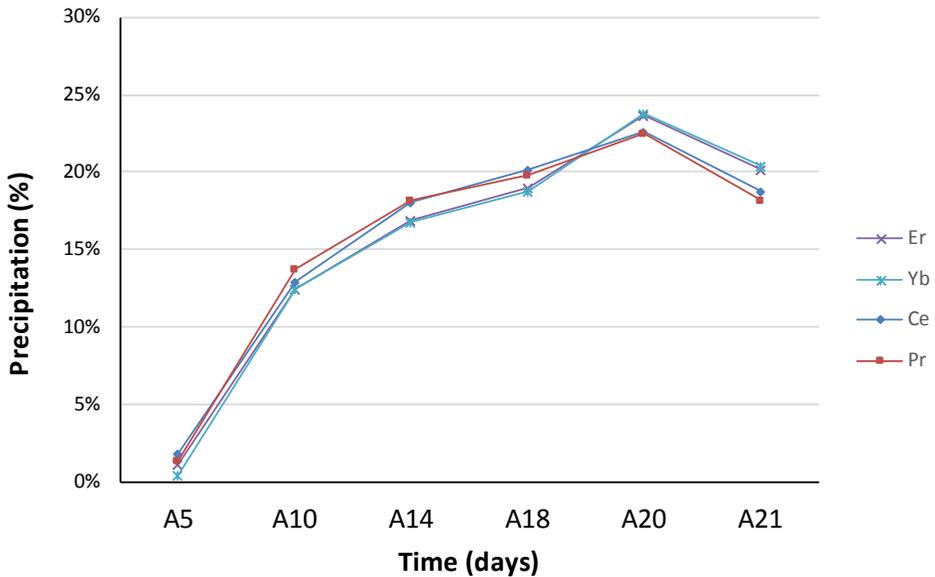


Figure 6 NASC-normalized REE concentrations values for the days 5, 10, 14, 18, 20, and 21 of the experiment.

Figure 6 exhibits the REE concentrations, normalized using the North American Shale Composite (NASC) values. Concentrations of REE ( $\Sigma$ REE) varied from about 5 mg/L, (initial concentration, A0) to approximately 45 mg/L at the end of the experiments. The NASC normalized pattern is similar for all the samples, showing the enrichment of middle REE typical of acid mine waters (Pérez-López et al. 2010).

In terms of precipitation of REE, intending to simplify the results, only four elements have been plotted (fig. 7); two representing the HREE (Er and Yb) and two for the LREE (Ce and Pr). Thus, slightly higher precipitation percentages were found for the LREE than for HREE during the first part of the experiment. But for the last days the precipitation was higher for Er and Yb, which represent the HREE behaviour. This seems to indicate slight differences between both HREE and LREE during the salt precipitation process, which agrees with the results observed in several samples taken along the Agrio River by Olías et al. (2016).



**Figure 7** Precipitation percent for some heavy-HREE (Er and Yb) and some light-REE (Ce and Pr).

## Conclusions

This study provides preliminary results on the behaviour of trace elements during salt precipitation by intense evaporation in AMD-affected systems. During the dry season, these evaporative salts play an important role as temporary sink from many elements in rivers polluted by acid mine discharges. Trace elements showed a strong removal from water due to coprecipitation processes, but some differences can be observed between them along the experimental run. The elements showing a higher precipitation were Sr, Ge and Ga while the most conservative were U and Th. A similar precipitation behaviour was observed, on one side between Sc, Cr, Th and Fe, and on the other between Y, Cd, and Al. Furthermore, the evolution of Cu and Zn presented a similar pattern. On the other hand, some slight differences between LREE and HREE seem to occur throughout the salt precipitation. The detailed behaviour of each element will be investigated in future works.

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## References

- Buckby T, Black S, Coleman ML, Hodson ME (2003) Fe-sulphate-rich evaporative mineral precipitates from the Río Tinto, southwest Spain. *Mineralogical Magazine* 67(2):263-278
- Hammarstrom JM, Seal II RR, Meier AL, Kornfeldt JM (2005) Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. *Chem. Geol.* 215(1-4):407-431
- Nieto JM, Sarmiento AM, Cánovas CR, Ollas M, Ayora C (2013) Acid mine drainage in the Iberian Pyrite Belt: 1. Hydrochemical characteristics and pollutant load of the Tinto and Odiel rivers. *Environmental Science and Pollution Research* 20(11):7509-7519
- Nocete F, Álex E, Nieto JM, Sáez R, Bayona MR (2005) An archaeological approach to regional environmental pollution in the south-western Iberian Peninsula related to Third millennium BC mining and metallurgy. *Journal of Archaeological Science* 32(10):1566-1576
- Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. In: Plumlee GS, Logson MJ, editors. *The environmental geochemistry of mine waters*. *Rev Econ Geol*; 6A: 133-160.,
- Ollas M, Nieto JM (2015) Background conditions and mining pollution throughout history in the Río Tinto (SW Spain). *Environments* 2(3):295-316
- Ollas M, Cánovas CR, Pérez-López R, Macías F, Riera J, Nieto JM (2016) REE during evaporative precipitation in a severely affected AMD-creek (SW Spain). *Proceedings IMWA 2016, Leipzig, Germany*, 1336-1338.
- Pérez-López R, Delgado J, Nieto JM, Márquez-García B (2010) Rare earth element geochemistry of sulphide weathering in the São Domingos mine area (Iberian Pyrite Belt): a proxy for fluid-rock interaction and ancient mining pollution. *Chem. Geol.* 276(1):29-40
- Sáinz A, Grande JA, de la Torre ML, Sánchez-Rodas D (2002) Characterisation of sequential leachate discharges of mining waste rock dumps in the Tinto and Odiel rivers. *J. Environ. Manage.* 64(4):345-353
- Sarmiento AM, Nieto JM, Ollas M, Cánovas CR (2009) Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel river Basin (SW Spain). *Appl. Geochem.* 24(4):697-714