Contamination load in a river affected by AMD discharges: Odiel River (Huelva, Spain)

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Abstract

In the Odiel River can be observed how a clean river at its source, starts to decay as a consequence of various water mine discharges. The high concentrations of metals like iron, aluminum, copper or zinc provokes the acid mine drainage (AMD) contamination in the river. This work presents a theoretical contamination load estimate from the mixes river-mine discharges and it is compared with the observe contamination load obtained from a sampling campaign. In this way, there has been calculated the total and dissolve metals transported by the river and the behavior of each one has been analyzed. As long as the river keep the pH around 7, elevate portion of iron, copper and aluminum precipitate while cobalt and zinc remain mostly dissolved. When the pH falls down to 4, all metals turn to be conservative excepting iron.

Key words: AMD, Contamination Load, Odiel River

Introduction

The Odiel River is situated in the Iberian Pyrite Belt (SW Iberian Peninsula) and is heavily affected by acid mine drainage (AMD). The presence of many polymetallic massive sulfide deposits has generated intense mining activity in the past. The impact of AMD processes in the Odiel river basin have been thoroughly studied. For instance, Olias et al. (2006) determine that both the Odiel and Tinto rivers transport annually 7922 t of Fe, 5781 t of Al, 1721 t of Cu and 3475 t of Zn.

The Odiel headwaters show a good quality status, however the confluence of several mining discharges (i.e. Concepción, San Platón, Esperanza and Poderosa; Fig. 1) along a 7 km-long reach cause a water quality worsening. The deterioration of the Odiel river waters become irreversible with the confluence of the Agrio River, which drains the AMD highly contaminated from the Riotinto mines (Sanchez-España et al., 2006; Nieto et al., 2013). The aim of this work is to analyze the evolution of the dissolved metal load along the first AMD contaminated reach as well as to determine the different metal transport patterns.

Methods

A sampling was carried out in 14 points of this reach in February 2015 (Figure 1), when the river had average flow rates (1140 L/s). Water samples were taken in each AMD discharge and along the Odiel River. The samples were filtered and acidified to pH<2 in order to determine the dissolved concentration. The pH, oxidation-reduction potential (ORP), temperature and electric conductivity were measured in situ using an equipment CRISON model MM40+. Water samples were analyzed by ICP-OES and ICP-MS for major elements and trace elements respectively. The flow rate was measured in each AMD discharge by means of an electromagnetic flowmeter. On the other hand, the flow rate at the beginning of the studied reach was measured by a tracer injection test.

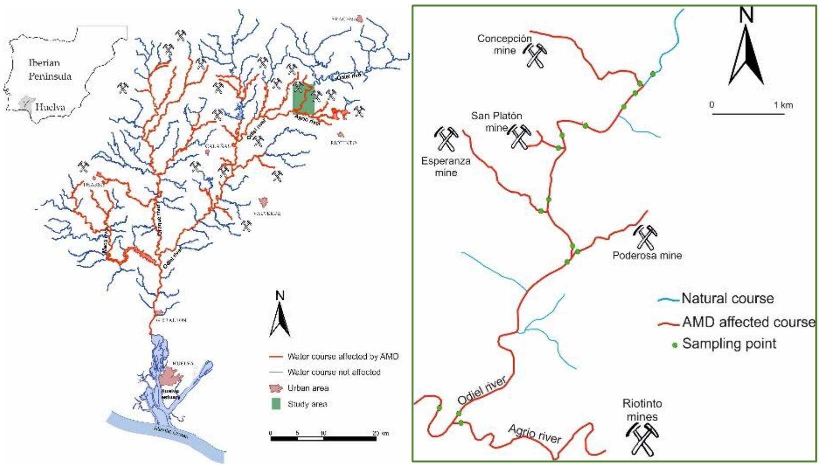

***Figure 1** Site and sampling points situation.*

Results and discussion

The observed contaminant load (OCL) was calculated from the flow rates and the analyzed concentrations. By far, the Agrio River constitutes the major metal contributor with up to 2292 kg/day of Fe, 4724 kg/day of Al, 643 kg/day of Zn, 579 kg/day of Mn, 279 kg/day of Cu and lesser amounts of Co, Ni or Pb. (Table 1). Concerning the rest of AMD discharges, Concepción transported between 4 and 16 times higher discharge than the others drainages, however only carried greater loads of Al, Mn, Co and Ni (Table 1). Especially lower loads were carried by Esperanza due to the implementation in December 2014 of a treatment plant that partially neutralizes AMD discharges. It is also striking the greater As contribution from San Platón (including the Agrio River) considering the low flow rate of this source. In spite of the confluence of these AMD discharges the pH in the Odiel River was close to 7.7 up to junction of the Agrio River when the alkalinity may be totally consumed and the pH dropped to 3.9.

***Table 1** Flow rate (L/s), pH values and observed contamination load (OCL) (kg/day) in the AMD discharges studied.*

Mine discharge	pH	Flow rate	Fe	Al	As	Pb	Cu	Zn	Mn	Co	Ni
Concepción	2.9	20	77	41	0.003	0.011	2.4	3.7	3.33	0.28	0.023
San Platón	2.8	1.2	146	23	0.078	0.003	1.4	12	0.92	0.068	0.008
Esperanza	3.5	2.0	7.0	4.7	0.0001	0.002	0.4	0.54	0.46	0.014	0.005
Poderosa	2.6	4.8	78	20	0.10	0.017	4.7	3.8	0.88	0.066	0.013
Agrio River	2.7	132	2292	4724	0.063	0.095	279	643	534	16	7.2

The theoretical contaminant load (TCL) along the reach was calculated considering conservative mixing of the Odiel River (Q_0, C_0) and the AMD discharges (Q_i, C_i). Before San Platón mines an increase in sulfates (600 kg/day), Zn (8 kg/day), Co (0.3 kg/day), Mn (2.6 kg/day) etc. was detected, related to diffuse discharges into the river, which were also considered for calculating the TCL:

$$TCL = Q_0 \cdot C_0 + \sum Q_i \cdot C_i$$

Figure 2 compares OCL and TCL for some selected metals in the Odiel River upstream the Agrio confluence. Differences between both dissolved loads may indicate a deviation from a conservative behavior and thus, a quantification of the precipitated mass which is deposited in the riverbed. It can be seen that most of the Fe and Cu dissolved may precipitate (300 kg/day of Fe and 8 kg/day of Cu) during mixing processes. In the same way, As, Al and Pb (not shown in Fig. 2) were present in all discharges (see Table 1), but were not detected in the river due to precipitation processes.

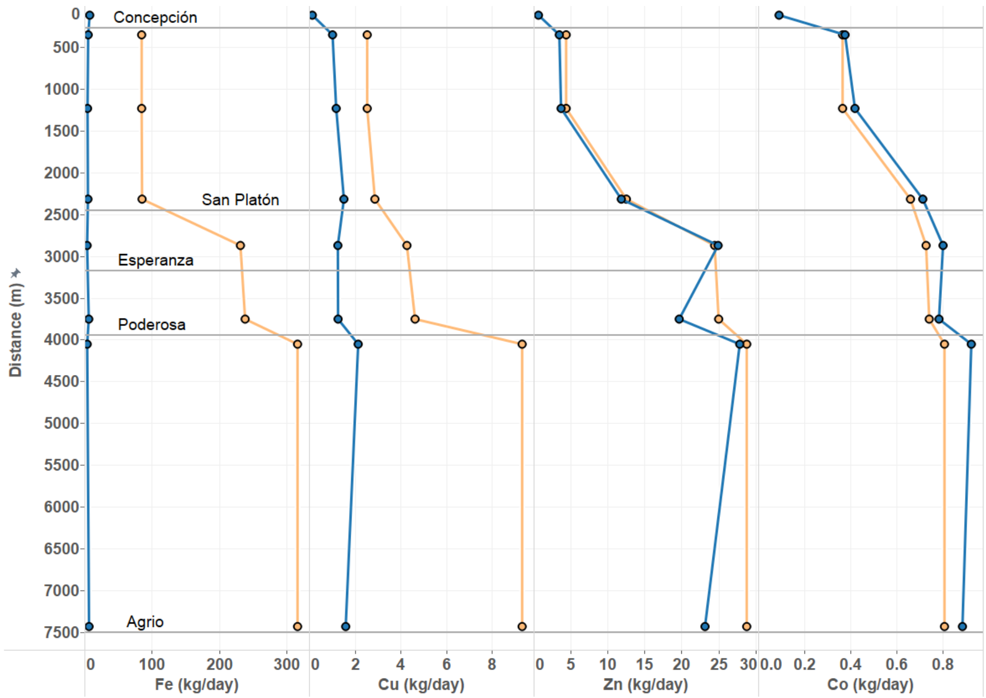

Figure 2 *Evolution of observed contamination load (OCL) vs theoretical contaminant load (TCL) along the Odiel River, upstream of the Agrio River confluence.*

Zn seems to behave initially almost conservatively, although after the Esperanza and Poderosa discharges precipitation along the river may occur (Fig. 1). The behaviour of dissolved Co and Mn (the last not shown in Fig. 2) also seem to be conservative. The small differences observed between OCL and TCL for Co must be due to the analytical uncertainty.

The metal transport pattern in the Odiel River change drastically after the Agrio confluence. The river pH decreases to 3.9 and Al become a conservative element increasing its dissolved load up to 5000 kg/day. In addition Co, Cu, Zn and Mn remain mostly in the aqueous phase during the rest of the Odiel course (18 kg/day, 376 kg/day, 843 kg/day and 630 kg/day of dissolved metal load, respectively). Most of Fe transported by the Agrio River (2292 kg/day) precipitates during mixing processes with the Odiel waters (pH 7.7), although a significant increase in Fe transport is observed after the confluence of the Agrio River (from 6 to 90 kg/day).

One important issue that emerges from these observations is that most of the precipitates remains in the river in form of poorly crystallized minerals (Fe and Al oxyhydroxysulfates). This was previously highlighted by Sánchez-España et al. (2006) and produces a relevant secondary contamination of the Odiel River due to high contents of particulate matter which accumulate in the sediments

Conclusions

The dissolved metal/loid load transported by the Odiel River along its first AMD contaminated reach has been quantified. The confluence of these mine discharges provokes the progressive deterioration of the river quality, causing the precipitation of some non-conservative elements (Fe, Al, Cu, As or Pb) while the most mobile elements (Mn, Co, Ni and Zn) remain in solution. The Agrio confluence produces an inflection point in the Odiel river water quality; the dissolved metal load increases significantly and the river become acidic (pH drop under 4) enhancing the solubility of Al which was entirely precipitated upstream. At this point, the Odiel River transports up to 5000 kg/day of Al, 843 kg/day of Zn and 376 kg/day of Cu.

Acknowledgements

This work was financed by the Spanish Ministry of Economy and Competitiveness through the project EMPATIA (Ref. CGL2013-48460-C2-1-R) and the grant associated BES-2014-068354.

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