Metal fluxes from the Tinto River (SW Spain) to the Atlantic Ocean: importance of flood events

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Abstract

Flood events may play a key role in the metal transport fluxes from rivers to oceans. This is especially relevant in semi-arid and arid climate regions, which alternate long drought periods and short but intense rainfall events, when most of the water discharge, dissolved contaminants, and suspended matter transport occurs. This study provides information on the metal transport from the Tinto River to the Atlantic Ocean during high resolution samplings of different flood events (2004/06 and 2017/18).

Keywords: metal transport, flood events, metal pollution, acid mine drainage

Introduction

The Tinto River drains the Iberian Pyrite Belt (IPB), one of the largest polymetallic massive sulfide regions in the world, with original reserves of the order of 1700 million tonnes. The Tinto River springs within the Riotinto Mining District (Fig. 1), the largest sulfide deposit described in the world. As a consequence of historical mining the Tinto River is strongly polluted, showing extremely low pH values and high metal concentrations up to its confluence with the Atlantic Ocean (Cánovas et al., 2007) and transport a huge load of metals into the Ocean, e.g. 5075 t/yr of Fe, 1224 t/yr of Al, 687 t/yr of Zn and 469 t/yr of Cu (Olías et al., 2006). Metal transport takes mainly place during short but intense flood events when most of the water discharge occurs. For this reason, flood rainfall events need to be studied with a high temporal sampling resolution considering the great geochemical and hydrological variability observed in these episodes. These studies should be extended to large data series in order to assess the effect of flood events on metal fluxes upon different hydrological regimes. Changes in metal transport patterns associated with climate and land use changes such as closure or reopening of mines and adoption of remediation measures in mine sites should be also addressed. In this sense, the reopening of the Riotinto mines in 2015 may have changed the metal transport pattern to the Ocean. Thus, this study provides information on the metal transport from the Tinto River to the Atlantic Ocean during high resolution samplings of flood events before (2004/06) and after (2017/18) the reopening of the mines to evaluate the effect on the metal transport to the Ocean.

Methods

A high-resolution sampling were performed during the hydrological year 2017/18 at the stream-gauge station of Gadea (Fig. 1), located approximately 41 km downstream of the Riotinto Mining District and around 20 km upstream of its entry into the Ría of Huelva estuary (Fig. 1). Results were compared to those obtained in similar samplings performed from 2004 to 2006. Sampling was performed using a Teledyne ISCO® autosampler, with a sample container holding up to 24 bottles previously washed in 10% (v/v) HNO_3. Samples were pumped by a peristaltic pump, with a schedule purge stage between samples to avoid cross-contamination. Electrical conductivity (EC), pH, and oxidation-reduction potential (ORP) were measured in situ for all samples using field with portable meters (Hanna Instruments HI 9025 and HI 9033). Samples were filtered through 0.45 µm Millipore®

Teflon filters and acidified to a pH < 2 immediately after collection, and finally stored at 4 °C until analysis. The chemical analyses were undertaken at the Central Research Services of Huelva University using inductively coupled plasma optical emission spectroscopy (ICP-AES: Jobin Yvon Ultima 2) for major elements and inductively coupled plasma mass emission spectroscopy (ICP-MS: Agilent 7700) for trace elements. Detection limits were 0.2 mg/L for major elements and 1 µg/L for trace elements. Rainfall data were obtained from different gauges distributed within the Tinto catchment and water discharge ws provided by the Environmental Andalusian Agency.

Results and Discussion

The Tinto River drainage basin is mainly composed of impermeable materials, thus this river has a fast response to rainfalls; river flow can increase up to 1000 times in a short-term scale, i.e. hours to days (Fig. 1). This fast response causes sharp changes in chemical composition of waters through the year. Figure 2 represents the evolution of some physico-chemical parameters and metal concentrations during floods monitored through the hydrological year 2017/2018. The first rainfalls after summer cause the dissolution of evaporitic sulfate salts precipitated on the river banks and mine sites, as well as the transport of accumulated weathering products of sulfide, which is especially intense during the dry period. These soluble sulfate salts may act as temporary sinks for acidity and metals in dry seasons, which are again released during rainfall events in wet seasons (e.g., Bigham and Nordstrom, 2000; Hammarstrom et al., 2005; Cánovas et al., 2008). Therefore, the first rainfalls after the dry period cause a sharp increase in EC values and the highest peak of sulfate and metal concentrations through the year; up to 11.4 mS/cm, 1529 mg/L of Fe and 115 mg/L of Cu were observed (Fig. 2). The washout of these salts also caused a slight decrease in pH values; from 2.4 to 2.1 (Fig. 2). As long as the rainy period continues a progressive depletion of metals and sulfate stored as soluble evaporitic salt minerals and concentrated pore fluids occur, and then dilution by freshwater becomes increasingly dominant. During this period hydrochemical variations are observed by Fe minerals precipitation, relative changes in the sources of AMD (e.g. mine tunnels, spoil heaps, etc.) and to differences in the rainfall distributions along the catchment (Cánovas et al. 2007). However, despite the arrival of large volumes of freshwaters, pH values in the Tinto River remain below 3 most of the time (Fig. 2) due to the buffering effect of Fe(III) precipitation,. Only when extreme rainfall episodes take place and Fe is almost depleted, pH may exceed values above 4. Then, the lowest metal concentrations of the year are observed coinciding with high flows (i.e. 60 m^3/s), i.e. down to 0.27 mg/L of Fe and 1.3 mg/L of Cu (Fig. 2).

As a consequence of such low pH values and high metal/loid concentrations, the Tinto River carries high loads of pollutants to the Ocean. Table 1 shows the metal/loid loads during the hydrological years 2004/05, 2005/06 and 2017/2018. As can be seen, metal/loid transport is strongly linked to

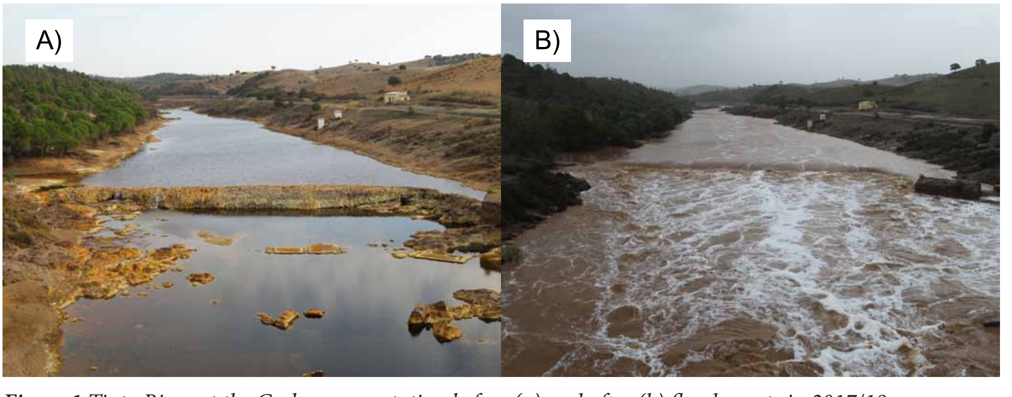

Figure 1 Tinto River at the Gadea gauge station before (a) and after (b) flood events in 2017/18

Table 1 Metal/loid transport (in tons) by the Tinto River during the hydrological years 2004/05, 2005/2006 and 2017/2018, and relative contribution to the metal/loid budget of floods events monitored

	Rainfall (mm)	Al	As	Cd	Cu	Fe	Pb	Zn
2004/05	307	485	0.87	0.51	109	869	5.8	108
% October Floods	49%	50%	57%	42%	36%	33%	90%	43%
2005/06	639	1133	2.3	1.3	240	2311	13	265
% October Floods	19%	30%	28%	39%	35%	43%	3.3%	38%
2017/18	633	2254	3.8	1.7	453	4983	16	550
% March Floods	55%	62%	27%	57%	67%	57%	97%	58%

pluviometry, with higher loads observed during the most rainy years. Thus, around 900-5000 ton of Fe, 500-2250 ton of Al, 110-550 ton of Zn, 110-450 ton of Cu and lesser amounts of Pb, As and Cd are annually transported by the Tinto River.

The most striking fact is the difference of loads transported by the river during different periods with a similar pluviometry (2005/06 and 2017/18); almost 2 times more Fe, Al, Cu and Zn were transported by the Tinto River in 2017/18 (633 mm) than in 2005/06 (639 mm). This increasing loads could be related to rainfall antecedents; when extremely long dry periods are followed by intense rainfalls events, the washout of evaporitic salts and oxidation products accumulated during this long period, leads to dramatic increases in metal/loid concentrations and loads (Cánovas et al. 2008). However, this seem not to be the reason behind such anomalous metal/loid transport. The preceeding years of October 2005 were not especially rainy, 769 and 307 mm were collected during the hydrological years 2003/04 and 2004/05, respectively. However, more intense rainfalls were recorded during the previous years to March 2018 flood event; 730 and 647mm were collected during the hydrological years 2015/16 and 2016/17. Therefore, hydrological factors seem not to be the responsible of such increasing loads, which may be instead probably related to intense mining operations after the reopening of Riotinto mines in 2015. Such mining operations also seems to have caused hydrochemical changes in the Tinto River. Figure 3 shows the Cu/Zn and Cd/Zn mass ratios during the flood events monitored in 2006, and in 2017, before and after the reopening of the mines. It can be clearly seen that Cu/Zn and Cd/Zn ratios have changed after the reopening of the mine; while Cu/Zn and Cd/Zn ratios are close to 1 and 5 before the reopening the mine, after that, noticeably lower values are observed (around 0.5 and 3; Fig. 3), except during extreme rainfall episodes, when ratios increase (especially Cu/Zn). This change in chemical composition

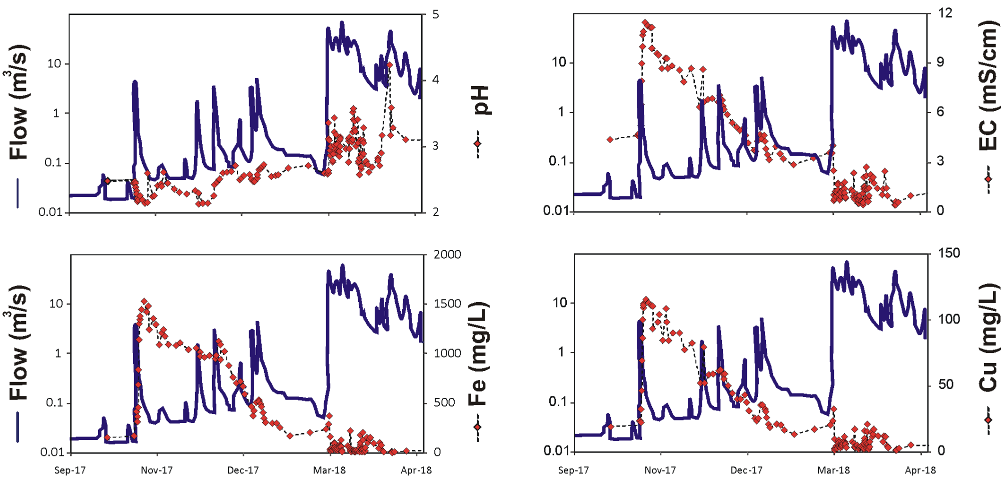

Figure 2 *Evolution of pH, electrical conductivity (EC) values and the concentration of Fe and Cu during flood events monitored in the Tinto River during 2017/18*

of the Tinto River waters may be related to change in proportion and composition of mine waters released into the river after the mine reopening. Therefore, further studies are needed to confirm this hypothesis.

Despite its short-time span (hours to days), flood events play a key role in annual metal transport in semi-arid regions affected by sulfide mining. Table 1 shows the relative contribution of monitored floods in the annual metal/loid transport in the Tinto River. These events are caused by intense rainfalls, i.e. between 19 and 55% of annual rainfalls collected in the drainage basin, and may deliver between around 30 and 70% of the annual metal/loid load to the Ocean. In the case of Pb, a metal which is mainly delivered from mine sites during extreme rainfall episodes (Cánovas et al., 2008), these events can contribute up to 98% of annual Pb carried by the river.

In order to evaluate the differences in metal loading during both periods (i.e. pre and after mine reopening) monthly metal loads are represented against the monthly precipitation. As can be seen, monthly loads of As and Fe seem to be higher after mine reopening than before in those months with a similar pluviometry. For instance, Fe loads after mine reopening double that observed before at monthly rainfalls around 50 mm. These increasing loads are even more evident for As; monthly loads are between 3 and 5 times higher for these months.

Conclusions

Flood events play a key role in annual metal transport in semi-arid regions affected by sulfide mining. This is the case of the Tinto River, probably the more AMD-affected river in the world, due to the intense mining activity in the Riotinto mine since ancient times. Changes in metal transport patterns associated with climate and closure or reopening of mines and adoption of remediation measures in mine sites can take place in these systems and therefore should be studied. This study provides information on the metal transport from the Tinto River to the Atlantic Ocean during high resolution samplings of flood events before (2004/06) and after (2017/18) the reopening of the mines.

Metal/loid transport is strongly linked to pluviometry, with higher loads observed during the most rainy years; i.e. around 900-5000 ton of Fe, 500-2250 ton of Al, 110-550 ton of Zn, 110-450 ton of Cu and lesser amounts of Pb, As and Cd are annually transported by the Tinto River. The importance of flood events in the annual flow and metal/loid fluxes to the Ocean is evidenced by the high delivery of metal/loid in such short events; between around 30 and 70% of the annual

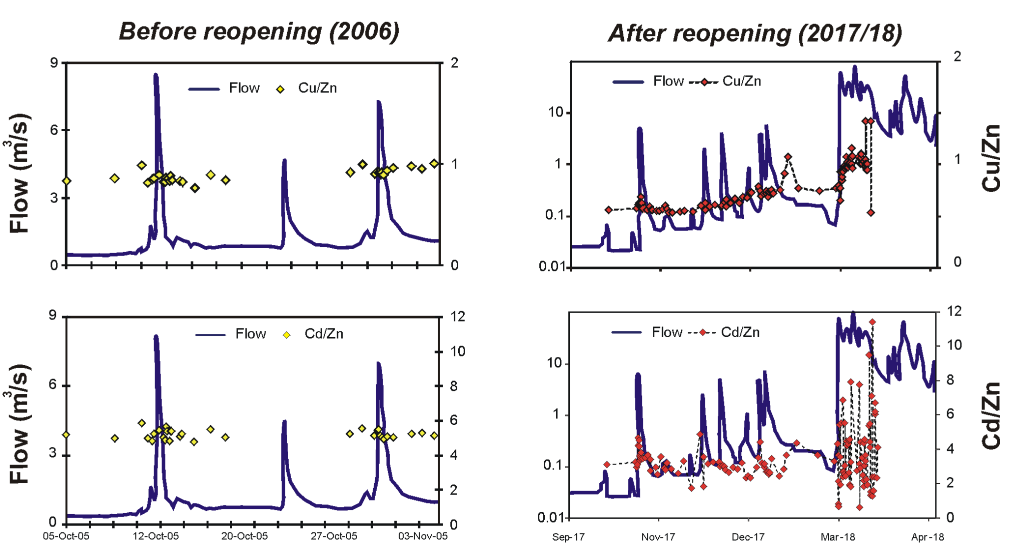

Figure 3 Tinto River at the Gadea gauge station before (a) and after (b) flood events in 2017 (Cd/Zn ratio expressed as µg/L/mg/L).

metal/loid load to the Ocean is carried by floods. In the case of Pb, these events can contribute up to 98% of total amount carried by the river.

The most striking result is the difference of loads transported by the river during periods with a similar pluviometry (2005/06 and 2017/18); almost 2 times more Fe, Al, Cu and Zn were transported by the Tinto River in 2017/18 (633 mm) than in 2005/06 (639 mm). Hydrological factors seem not to be responsible of such increasing loads, but probably related to hydrological changes induced by the reopening of Riotinto mines in 2015, which seem to have changed the geochemical signature of waters. Further studies through the time are needed to confirm this hypothesis.

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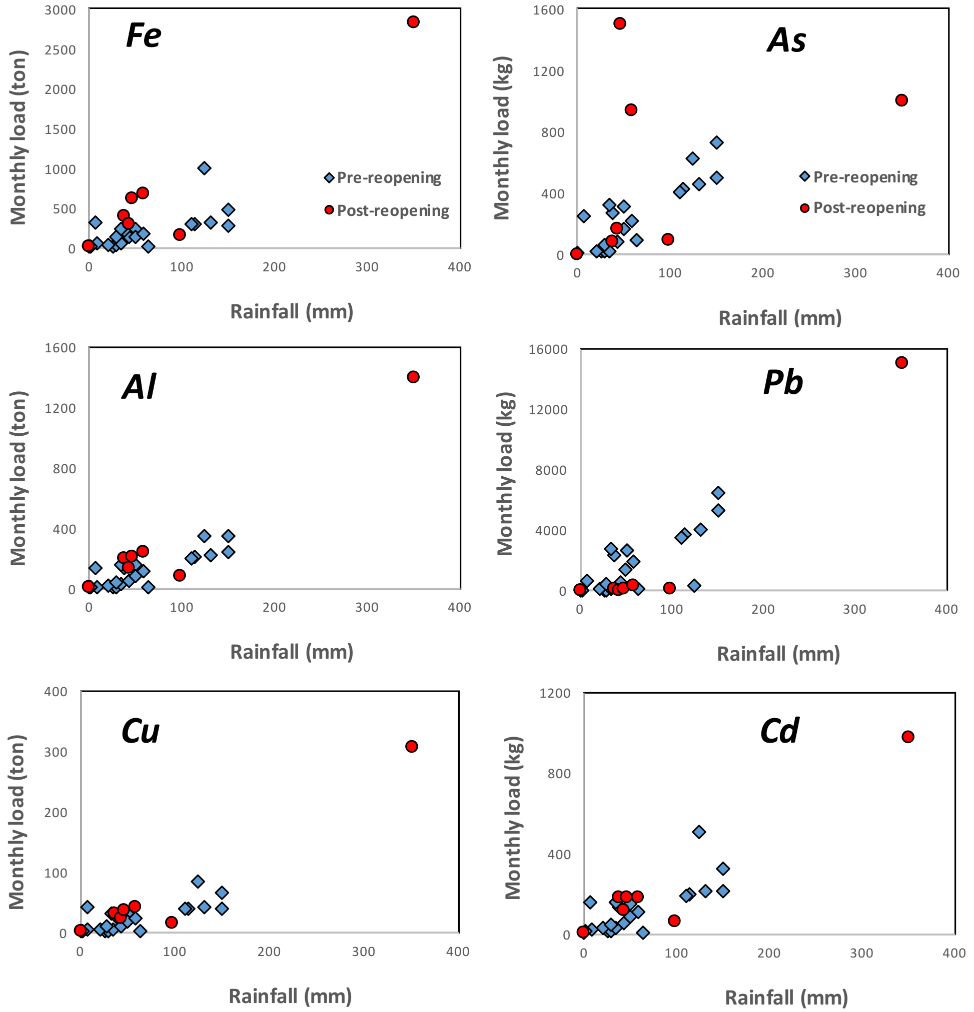

Figure 4 *Relationship between monthly metal/loid loading and precipitation before and after the reopening of the Riotinto mine.*

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