

Remobilisation of Zn and Pb in a mountain stream contaminated by mining wastes during a moderate flood event (Ariège, France)

C. Brunel, M. Munoz and A. Probst

*Laboratoire de Mécanismes de Transfert en Géologie, UMR 5563 du CNRS,
38 rue des 36 Ponts, Toulouse, France*

Abstract. The Lez stream drains an orphan mining (Zn and Pb) district, whose **tailings are sources of contamination**. The evolution of the dissolved and particular Zn and Pb content was studied to evaluate the role of a moderate **flood event** on the downstream metal transfert. Although Zn and Pb behave differently, **floods appear for both elements as preferential periods for metal fluxes**.

1. INTRODUCTION

Mining districts are well-known as a source of environmental contamination. At a regional scale, they can be the main supply of trace metals (TM). The metallic ores are generally sulfides which are not stable in surface conditions. Their oxydation in mines, waste-rock dumps and tailings impoundments produces acidity and rises of the TM solubility and mobility [1-2].

In France, mining sites are numerous. In the Pyrenees and the Massif Central, several hundred metal-bearing sites have been working during the two last centuries. Today, most of these are no more exploited, but mining wastes remain in the surroundings and constitute potential sources of contamination for the downstream rivers [3-4]. The metallic contamination risk, at a medium-catchment scale, is assessed (1.) by characterizing the TM distribution between the aqueous and the solid phases (substratum, tailings, waste-rocks, river sediments, soils) – (2.) by identifying the mineralogical and geochemical processes and the hydrological conditions which control the downstream TM transfert. The influence of hydrological conditions on the TM distributions between river-associated compartments have been already described [5-7], however, their role yet remains poorly known. This study focuses on the role of a moderate flood event on the dissolved and particular fluxes of Zn and Pb downstream in a mining waste environment.

2. STUDY AREA

The mines of Bentailou are located in the upstream catchment of the Lez river (Central Pyrenees, Fig.1). In this area, the stream drains paleozoic formations, mainly composed of limestones with alternating schists. The ancient mines of Bentailou were exploited for Zn and Pb (sphalerite and galena mineralization) for one century from 1853. The galleries were located between 1650 and 2300 m asl and the treatment factory at 960 m. From this exploitation, about 1M tons of raw ore were extracted, and more than 500 000 tons of tailings produced. The tailings wastes issued from ore treatment, still contain Zn (1.6%wt) and Pb (0.8%wt), they are impounded in four dumps, on the riverbanks of the Lez. These tailings are composed of <250µm grain size material unconsolidated and submitted to erosion during floods or rainfalls.

3. MATERIAL AND METHOD

To assess the tailings impact, waters were sampled at 3 suitable sites (Fig.1). VII is above the area of influence, VIII is downstream from the two youngest tailings (flotation process) and XI at the level of the oldest ones (hydro-gravimetric process) after the confluence with a mountain creek.

The flood event was investigated at site XI. It occurred in winter, during a dry period (5 – 6/02/02). It is a moderate flood event, lasting about 15 hours. Streamwaters were collected once before and 7 times during the flood event. Waters were filtered through pre-weighted filters (0.2 μm membranes). The weight of suspended matter was determined after drying the filters at 50 C. Three filters were totally digested by a mixing of H_2O_2 , HNO_3 and HF before chemical analyses. The major ions are analysed using AAS, HPLC, titration and colorimetry, and trace elements using ICP-MS.

4. RESULTS

4.1. The dissolved phase

For all samples, the dissolved phase is typical of pyrenean rivers, draining carbonated catchments: pH is in between 7.6 and 7.8. Ca^{++} and HCO_3^- are dominant. Metal content, particularly dissolved [Zn] and [Pb], measured in 2001 and 2002, during recession flow, vary between upstream and downstream from tailings. During an autumnal low water flow, [Zn] reached 48.3 and 44.0 $\mu\text{g.l}^{-1}$ at the sites VIII and XI, respectively, while it was only of 0.1 $\mu\text{g.l}^{-1}$ at the site VII. [Pb] was 1.8 $\mu\text{g.l}^{-1}$ in VIII, while it was only of 0.1 $\mu\text{g.l}^{-1}$ in VII.

During the studied flood event, at site XI, the discharge rises from 169 l.s^{-1} (before flood) to 316 l.s^{-1} (flood peak). The dissolved [Zn] reaches to a maximum of 53.6 $\mu\text{g.l}^{-1}$ at the maximum of discharge and is significantly higher than the pre-event values (Fig.2). In few hours, the Zn content is multiplied by 1.5. However, compared to other hydrological conditions, this maximum flood-peak concentration is not abnormal (44.0 and 54.9 $\mu\text{g.l}^{-1}$, respectively for two low water flow samples). The dissolved [Pb] also strongly increases with increasing discharge, reaching its maximum value (3,83 $\mu\text{g.l}^{-1}$) at the maximum discharge. Compared to the pre-event values, the [Pb] is 24 times higher and also corresponds to maximum values relatively to other hydrological conditions (0.1 or 0.2 $\mu\text{g.l}^{-1}$ for low flow water, 0.2 $\mu\text{g.l}^{-1}$ for snowmelt). After the flood peak, [Pb] rapidly falls down to values

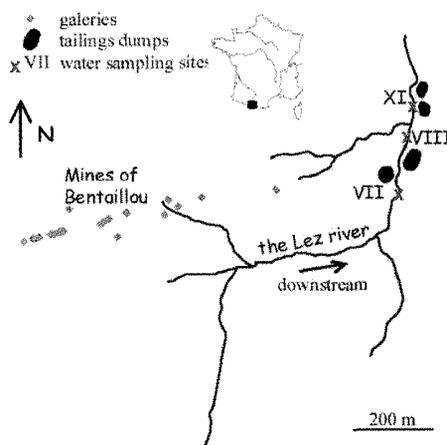


Figure 1. Schematic representation of the upstream catchment of the Lez river - Localization of the mining vestiges and of the water sampling sites.

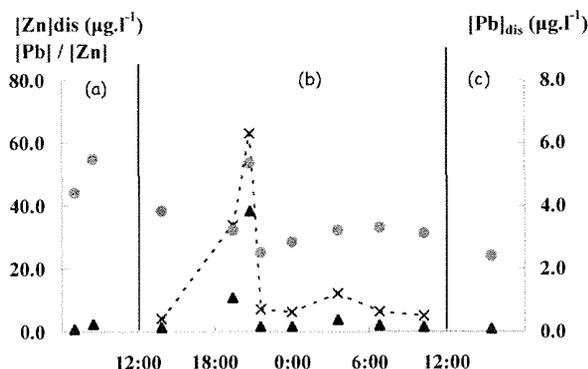


Figure 2. Evolution of dissolved concentrations of Zn (●) and Pb (▲) and of the [Pb]/[Zn] ratio (x) in stream water during a moderate flood (b). The sample collected before the rainfall event (13:35) is taken as a reference. Measurements during different hydrological conditions (a), low water flow, (c), snowmelt are also mentioned.

similar to the pre-event ones. Considering discharge, at the flood peak, the dissolved Zn and Pb fluxes are increased. They reach respectively 19355 and 1220 $\mu\text{g}\cdot\text{s}^{-1}$ at the flood peak and are 3 and 45 times higher in comparison to previous-flood fluxes. The ratio of the dissolved [Pb]/ dissolved [Zn] strongly rises with the discharge, is maximum at the flood peak and then rapidly drops.

4.2. The suspended matter, the sediments and the tailings

The Lez carries very few particles during low water flow conditions. During the flood event, the suspended load strongly rises from 0.7 $\text{mg}\cdot\text{l}^{-1}$ to 47 $\text{mg}\cdot\text{l}^{-1}$ at the flood peak ; then, the load progressively drops with decreasing discharge. Zn and Pb content of suspended matter are maximum at the flood peak and are approximatively 2 and 6 times more concentrated than those respectively sampled before and after the flood peak (Tab.1).

Preliminary results showed that tailings are very much Zn and Pb enriched (Tab.2). Like the dissolved phase, the Zn and Pb content of bottom sediments ($< 63\mu\text{m}$) largely rise between the sites VII and VIII (Tab.2).

Table 1. Suspended and dissolved [Zn] and [Pb], partitioning coefficient K ($[\text{X}]_{\text{SM}}/1000 [\text{X}]_{\text{dis}}$) at the flood peak (20:45), before (19:45) and after (21:35).

	[Pb] _{SM} $\mu\text{g}\cdot\text{g}^{-1}$	[Zn] _{SM} $\mu\text{g}\cdot\text{g}^{-1}$	Pb / Zn	[Pb] _{dis} $\mu\text{g}\cdot\text{l}^{-1}$	[Zn] _{dis} $\mu\text{g}\cdot\text{l}^{-1}$	K Pb	K Zn
19:45	5 108	12 810	0.40	1.1	32.1	4643	399
20:45 Flood peak	10 455	30 198	0.35	3.8	53.6	2751	563
21:35	1 775	4 933	0.35	0.2	25.0	8875	197

Table 2. Zn and Pb contents ($\mu\text{g}\cdot\text{g}^{-1}$) in fine fraction $< 63 \mu\text{m}$ of bottom sediments from sites VII and VIII and in tailings ($< 250\mu\text{m}$).

	[Zn]	[Pb]	Zn / Pb
VII	2 456	741	3.31
VIII	12 330	14 406	0.85
tailings	12 900	7 100	1.82

5. DISCUSSION AND CONCLUSION

Results obtained on both streamwaters and bottom sediments at sites VII and VIII show a dispersion of metallic contamination from tailings indicating that tailings are the primary source of contamination

During the studied flood event, both dissolved and suspended [Zn] and [Pb] rise and are maximum at the flood peak. Hence, this event appears as a preferential period for remobilization and transfert of these metals : downstream fluxes of dissolved and particular metals are increased. Even if flood events are time limited, they must significantly contribute to the yearly downstream metal load. During the flood event, TM are mainly transported by the suspended matter (Fig.3).

These observations lead to several questions about the origin of the remobilized particles in the suspended matter and about the [Zn] and [Pb] variations during the flood event.

Several sources of Zn and Pb can be involved. Tailings are the primary metal source and can be runned-off by rain. Contaminated bottom sediments are a secondary source that can be resuspended. Between sites VIII and XI, the Pb/Zn ratio in suspended matter differs from that of sediments and tailings. On one hand, it does not argue for no one of both origins. However, the difference could be induced by a mixing with the sediments supply by the mountain creek, and/or by considering the suspended particles size. Only the fraction $< 63\mu\text{m}$ of bottom sediments was analysed. Observations on filters show that suspended particles are mainly silts but some are fine sands. Analyses are being realised on the $< 250\mu\text{m}$ fraction of sediments from the Lez stream (sites XI, VIII, VII) and from the tributary to check their metal content.

Several hypotheses can be drawn to explain the concentration variations in the particular phase. First, it has been showed that TM are mainly transported by clays and silts [4]. During the flood event, the suspended [Zn] and [Pb] are maximum at the flood peak, when coarse particles are in suspension. However, although it is involved, the suspended particle size cannot be the only determining factor.

Second, the particles origin can vary with time. The metal content of remobilized particles from bottom sediments depends on the brook (the Lez stream or its tributary) and on the burial depth. The superficial layer is certainly the first remobilized. Bottom sediments secondly remobilized might be under more reducing conditions than the superficial ones. Such different redox conditions could induce differences in particles metal content. Particles from tailings must also be remobilized and reach the Lez stream by running-off. Their variable input and their specific metal content can contribute significantly to the metal content variations in the suspended matter.

Third, exchange processes can occur between the particular and the dissolved phases. During the flood event, Zn and Pb contents rise and are maximum at the flood peak in the two phases, suggesting exchange processes between both. The Pb/Zn ratios and the partitioning coefficient show that the two metals behave differently. Pb is probably associated with colloids and fine particles in such a carbonated environment [9]. During the flood event, with the increasing discharge, the dissolved phase is enriched relatively to the suspended particle.

Desorption processes, from the suspended matter to the dissolved phase, could explain these partition changes. The Zn partition changes are opposite. Adsorption processes of Zn can occur during the flood event, but exchange processes do not seem to control the Zn content evolution. To check these hypotheses, leaching-tests and sequential chemical extraction will be performed.

Other processes can be involved to explain the increasing dissolved metal content with the discharge. The rainwater runs-off tailings and soils and could generate a flushing of draining-waters. Exchange processes and dissolution of efflorescent minerals formed during the dry season would also contribute to metal release in surface waters which reach the Lez river.

A chemical and mineralogical study of different contamination sources (tailings, sediments, suspended matter) will be carried out to identify the processes controlling the Pb and Zn behaviors.

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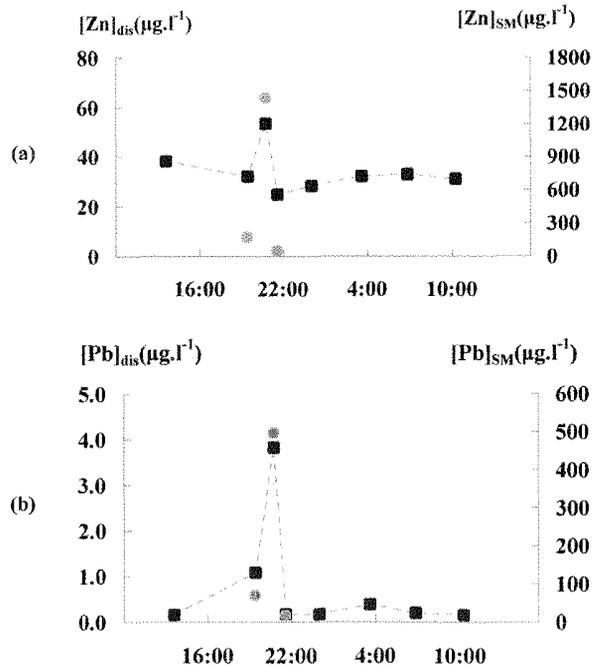


Figure 3. Comparison of evolutions of dissolved and particular [Zn] (a) and [Pb] (b) per streamwater liter over times during the pluvial flood event of the 5 and 6 February 2002 (■, dissolved phase ; ●, particular phase).