

## Kinetic Study of the Release of Lead in a Mine-Impacted Tropical River

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Mining in Mexico produces large quantities of solid and liquid wastes that constitute a potential source of pollution (Armienta et al., 2003). In mining areas, the main source of potential pollution is the formation of acid mine drainage (AMD) that plays an important role on the solubilization, transport and release of metals to the environment. AMD can also promote pH decrease of water bodies and alterations of Eh (Oxidation-Reduction potential) and conductivity (Sangupta, 1993; Ritcey, 1989).

One way to evaluate the potential pollution of rivers by metals from mining wastes is through kinetic studies (Coker, 1995; Förstner *et al.*, 1989; Rendell *et al.*, 1980; Sholkowitz, 1978; Clevenger and Samir, 1997; Wilkins, 1991; Rashid, 1973). After investigating the effect of changes in the variables that control the sorption and solubility of metals, it was concluded that laboratory results can be used to predict metal behaviour in natural systems. These results will in turn be useful to prevent possible threats to the environment and human populations.

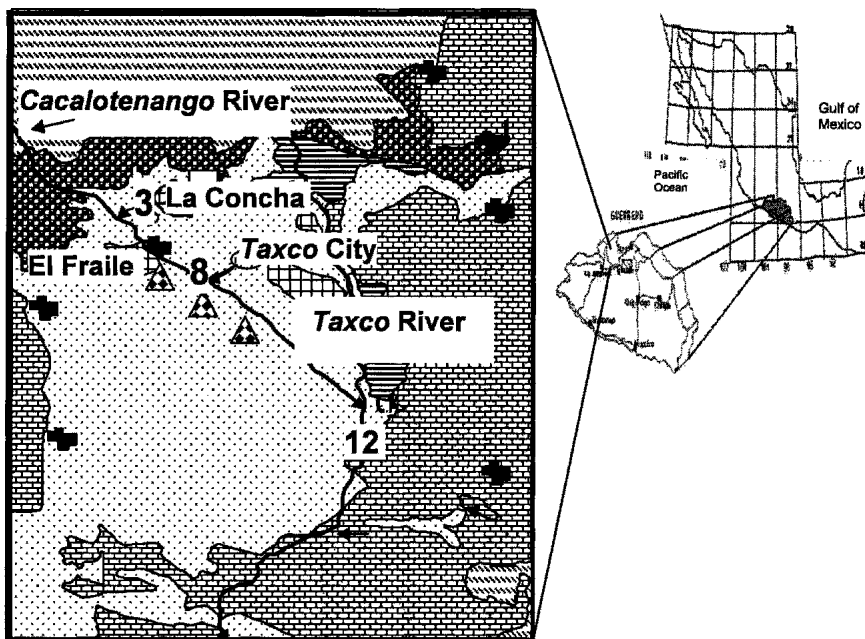
Here we present a kinetic study of lead release from sediments to the water column under controlled conditions (T, pH). The range of pH values for dry, rainy and post rainy-seasons of the Cacalotenango and Taxco rivers were reproduced in the experiments.

The study area (Fig. 1) is located in the north of the state of Guerrero, Mexico, 10 Km SW from the city of Taxco de Alarcón. It is located between the 18° 30' and 18° 33' North latitude and 99° 36' and 99° 40' West longitude. The hydrological basin has two main rivers, Cacalotenango and Taxco, that receive mine and urban wastes. The towns of Dolores, Santa Rosa, El Fraile and Cacalotenango are within the study area, as well as two tailings (El Fraile and La Concha), one closed mine (Jesús), and one active mine (La Concha).

### MATERIALS AND METHODS

Water and sediment samples were collected at stations 3 (S3), 8 (S8) and 12 (S12) (Fig. 1) during the post-rainy season using the methods proposed by Rubio and Ure (1993) and Loring and Rantala (1992).

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**Figure 1** Study area showing the location of the sampling sites (3, 8 and 12) and the main features of importance for the study. Geological formations (SECOFI, 1999):

■ Quaternary    ▨ Tilzapotla, ▩ Balsas, ▧ Mexcala, ▦ Morelos and  
 ▤ Taxco Verde Viejo    □ Rockwaste Dump, ▲ Towns, ⊕ Tailings,  
 ⊗ Jesus Mine and ➔ Rivers

Four samples were collected at each station, placed in plastic containers and transported to the laboratory (transportation time <2 h).

Air was bubbled through the samples to maintain water circulation and oxygen levels similar to field conditions. Temperature was kept constant and similar to field conditions.

Four experiments were carried out for each station, in which pH was fixed and kept constant as follows: 6.0, 7.0, 8.0 and field pH. Aliquots (5mL) of overlaying water were sampled at 0, 0.5, 1, 2, 3, 4 and 6 hours and 0.5 mL of concentrated  $\text{HNO}_3$  (J. T. Baker, ACS reagent) were added to avoid adsorption to the containers. Sediments collected were analyzed for carbonates and organic matter content (Loring and Rantala, 1992).

The pH, temperature (T) and conductivity were measured using a Conductronic PC18 potentiometer/conductivity meter calibrated with pH=4 (J. T. Baker, potassium acid ftalate buffer, NIST as RS), pH=7 (J. T. Baker, phosphates buffer, NIST as RS) and pH=10 (J. T. Baker, borate buffer, NIST as RS) buffers, and

with a solution of 1000 mg L<sup>-1</sup> of KCl (J. T. Baker, ACS) corresponding to a conductivity value of 1990  $\mu\text{S cm}^{-1}$ .

For measuring Eh an Instrulab ORP Meter was used and was calibrated with a Zobell solution (potassium ferrocyanide, and potassium ferricyanide, J. T. Baker, ACS) prepared as indicated by APHA (1992).

These parameters were constantly monitored to assure the constant conditions of the experiment.

The dissolved Pb present in the acidified water aliquots and in the sediment was measured using an AAS flame/graphite furnace depending on the concentrations, and using the technique established by Loring and Rantala (1992). Detection limit was 0.3  $\mu\text{g L}^{-1}$  (flameless) and 0.3 mg L<sup>-1</sup> (flame). The accuracy of the technique was tested against the standard reference material NIST 1640 with a mean recovery of 94.6%.

In order to gain insight into the processes governing the sorption/release of lead, laboratory results were analyzed by factor analysis.

## RESULTS AND DISCUSSION

Field conditions at each station for pH, Eh, conductivity, organic matter content and carbonates content are shown in table 1.

**Table 1.** Field Conditions (FC) at stations 3 (S3), 8 (S8) and 12 (S12).

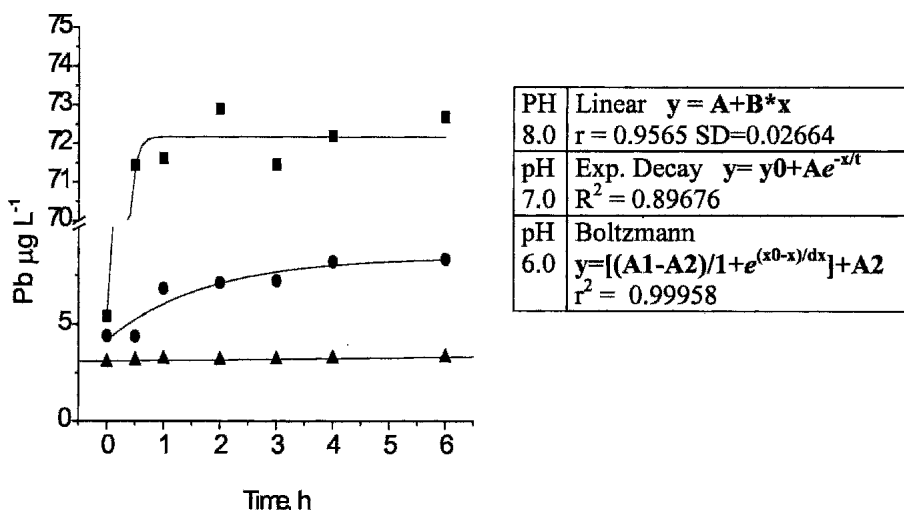
	pH	Conductivity ( $\mu\text{S}$ )	Eh ORP (mV)	OM (%)	Carbonates (%)
FC S3	7.38	463	312	3.22	22
FC S8	6.78	323	239	2.08	14.7
FC S12	8.27	630	215	4.4	9.0

Lead concentrations as a function of time for each sampled station are presented in Fig. 2, 3 and 4.

The *in situ* pH results for S3, S8 and S12 show that the concentration variation as function of time does not exceed the 0.18 pH units, that is a non significant variation ( $p=0.5$ ) that can be explained in terms of the standard deviation of the technique. The concentration of these samples can be considered constant as a function of time under the conditions of the experiment.

Significant changes in dissolved lead concentration were observed among samples and experimental pH values.

In station 3 (S3) an increment of the release velocity with pH can be observed on the fitted curves (Fig. 2) as they go from a linear to a sigmoideal curve (Steinfeld et al., 1989; Espenson, 1981). This is probably due to the large percentage of carbonates (22%) found in the sediments of this area.



**Figure 2.** Dissolved Lead Concentrations in station 3 as a function of time for pH ▲8.0, ●7.0 and ■6.0.

It is possible that lead is mainly sorbed on the carbonates, and it may easily be desorbed to the water column when pH decreases below 6.4 ( $pK_a$   $H_2CO_3/HCO_3^-$  6.4) (Shu et al., 2001; Clevenger and Samir, 1997; Rendell, P., G. Batley y A. Cameron, 1980).

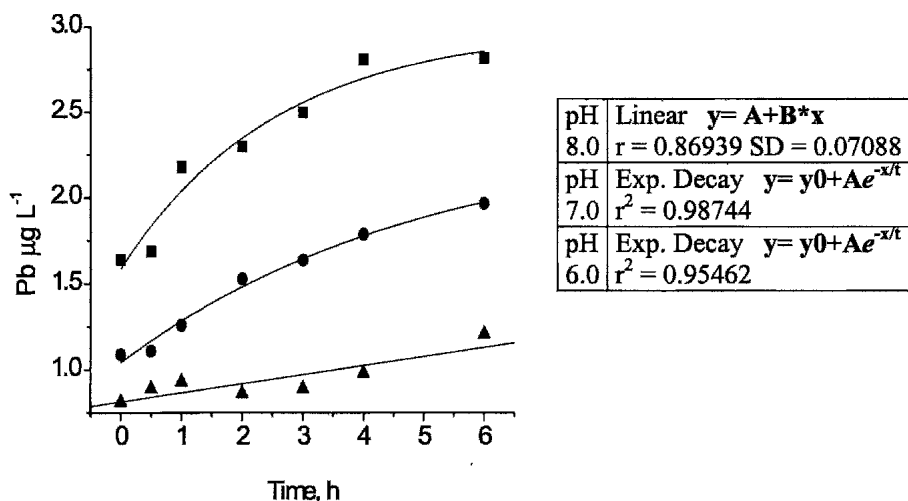
Dissolved lead concentrations in station 3, that is close to La Concha tailing, at pH 8, 7 and 6 are above the EPA Freshwater Chronic Criterion ( $3.2 \mu g L^{-1}$ ) (Irwin et al., 1997).

A similar behaviour was observed for station 8 (S8) (Fig. 3) but the release velocity was lower than that of S3. In these sediments lead may be sorbed to the organic matter as well as to carbonates, since the amount of carbonates (14.7%) is lower than in S3.

In station 12 (S12) (Fig. 4) lead concentration decreased with time at pH 6.0 and 8.0, and increased slightly at pH 7.0. This was probably due to the settlement of the particulate matter that in this station was significantly higher ( $0.2 g L^{-1}$ ) than in S3 ( $0.02 g L^{-1}$ ) and in S8 ( $0.04 g L^{-1}$ ).

We think that the amount and pressure of the provided air was not enough to emulate the flux of the Taxco River. The amount of lead released from sediments also depends on the flux conditions of the experiment, which should be close to those found in the natural system. The release process of lead in this sample might require a longer time than the period used for the experiment or/and a larger change in pH value.

In S12 the fitted curve changes from linear to sigmoideal. However, the velocity



**Figure 3.** Dissolved Lead Concentrations in station 8 as a function of time for pH ▲8.0, ●7.0 and ■6.0

of the change is even slower than that for S3 or S8.

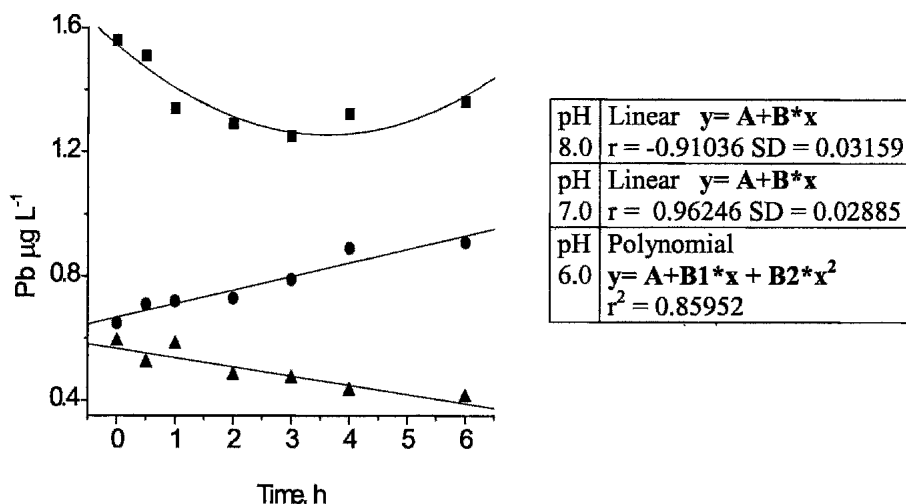
This can be explained by the significant higher organic matter content (4.4%) in these sediments, providing another substrate for lead. Release of lead from organic matter would require a longer time and a lower pH.

In conclusion lead released to the water column in the Cacalotenango-Taxco river system has an inverse correlation with pH and varies as a function of the percentage of carbonates and organic matter present in sediments.

A decrease in the natural pH level in the Cacalotenango-Taxco river system would then promote the release of significant concentrations of lead sorbed to the sediments.

Factor Analysis corroborates the results previously discussed. The variability of lead concentration was explained in 91% by pH, conductivity and Eh in S3. Conductivity correlates positively whereas pH correlates negatively with dissolved lead. Decrease of pH results in the dissolution of carbonates that in turn releases lead and increases conductivity (release from sediments of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-/\text{CO}_3^{2-}$ ). The percentage of organic matter in sediments of this station did not show a correlation with dissolved lead. This supports the hypothesis that lead is mainly sorbed to carbonates.

The variability of lead concentration was explained in 94% by pH, conductivity, Eh and organic matter percentage in sediments in S8. An inverse correlation of dissolved lead with pH and Eh, and a direct correlation with organic matter percentage in sediments was found. This supports the hypothesis that lead is sorbed to carbonates and also to organic matter.



**Figure 4.** Dissolved Lead Concentrations in S12 as a function of time for pH ▲ 8.0, ● 7.0 and ■ 6.0.

In S12 the factor analysis for the experiment at pH 7.0 showed that 92% of the variability was explained by pH, conductivity, Eh, and organic matter content in the sediments and in the water column.

A direct correlation with conductivity and an inverse correlation of dissolved lead with pH and Eh were found, showing that some of the lead present in these sediments is sorbed to carbonates. A significant direct correlation with particulate suspended matter and organic matter percentage in the sediments and in the water column was found. This indicates that lead present in this station is mainly sorbed to the organic matter.

These results along with the kinetic study show that sediments are a potential pollution source for the river water used by the residents of the area.

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