

## Assessing water–sediment processes for metals in rivers polluted by mining to predict environmental impacts in developing countries

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**Abstract** Water–sediment geochemical processes influencing As, Pb, Zn, Cu and Fe mobilization were investigated in a river within the historic mining area of Taxco, México. Tailings wash off and acid mine drainage have led to concentrations of metals in sediments well above the regional background. Zinc and lead associate with the carbonate fraction, followed by Fe oxyhydroxides. Arsenic and Fe concentrate in the residual fraction, followed by organic matter/sulphide and Fe oxyhydroxides. Metals are mainly transported as particulates in the water. Calcium, silicate and iron minerals are oversaturated in the river water. Limestones play a key role in the contaminant behaviour. Principal components analysis indicated that Zn, Cu and Pb may be released to the water following small changes in physico-chemical and/or hydrogeological conditions. Application of straightforward analytical techniques jointly with geochemical and statistical evaluation, is an affordable alternative to clarify the environmental impact of mining wastes in developing countries.

**Key words** mining; contamination; metals; river; sediments; Mexico; hydrogeochemistry; principal components; limestones; Taxco

### INTRODUCTION

Mining activities are one of the most important pollution sources of metals in countries with a tradition of ore extraction. Millions of tons of wastes deposited on river shores may release toxic elements to the rivers. Once in the water, metals and metalloids may be transported long distances affecting ecosystems. However, the extent of pollution depends on complex processes occurring within the river water and the bed sediments.

Ore extraction and processing has been developed in Mexico since preHispanic times. Currently, Mexico is one of the world's main producers of 20 minerals. Although recently policy makers have included laws to protect the environment from mining impact, there are still many abandoned rock wastes and tailings dispersed throughout the country. Taxco was the first place where the Spaniards started mining in America and they exploited silver at this location as early as 1522. The study area is located south of Taxco city between latitudes 18°30' and 18°35' north, and longitudes 99°32'30" and 99°40' west. The climate is warm and sub-humid with an annual

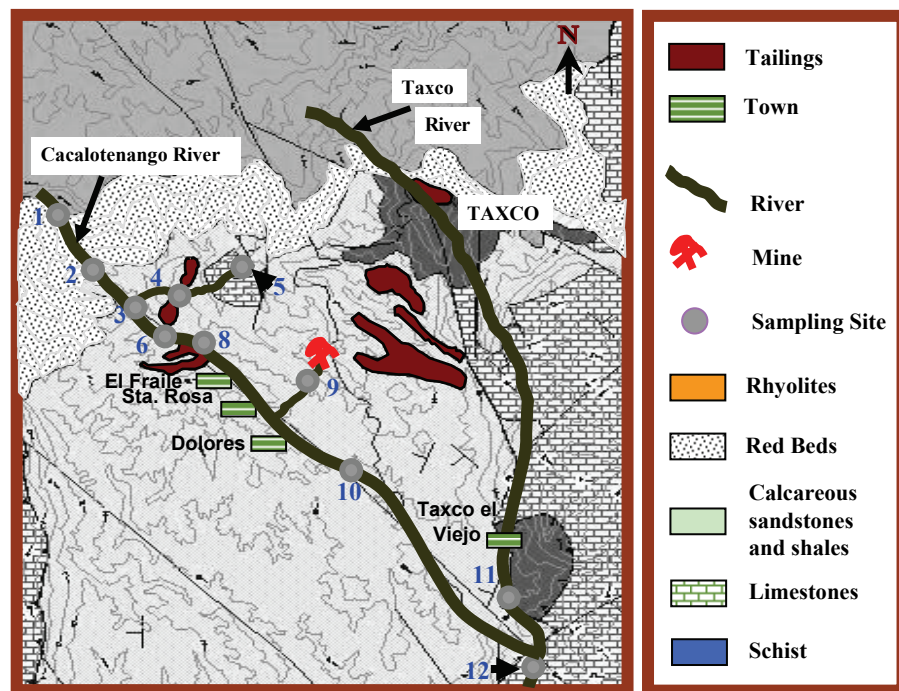


Fig. 1 Location of sampling stations.

average temperature of 26–30°C and precipitation of the order of 1000 mm (INEGI, 1998). Nevertheless, rain is concentrated in the period from June to October with maximum values of 300 mm. Local geology includes acid volcanic rocks, limestones and calcareous sandstones and shales (Fig. 1). Mineralization appears mainly in hydrothermal veins, replacement ores and stockworks hosted in limestone, shale and schist. The Cacalotenango is one of the largest rivers in the basin of the Taxco. Near its shores, old and active tailing impoundments are located and constitute sources of metal pollution. Small settlements located near the river use the water for irrigation and, occasionally, also as a potable water source.

Metals may be released from tailings as a result of erosion and sulphide oxidation producing acid mine drainage (AMD). The latter process results in low pH solutions with high concentrations of dissolved sulphate and metals (Ritcey, 1989). Metals from mining wastes may enter the rivers and be transported by the water as dissolved species and/or as particulates. Chemical reactions and changes in the river dynamics deposit metals on the river bed where they may be retained with different strengths. On the other hand, metals may also be remobilized to the water depending on their chemical speciation, type of bond with the sediments, physico-chemical and hydrogeological conditions.

Water-sediment geochemical processes influencing As, Pb, Zn, Cu and Fe mobilization were investigated in the Cacalotenango and a segment of the Taxco rivers flowing through the historic mining area of Taxco, México. Total and fractionated contents of metals in sediments, physico-chemical parameters, main ions and heavy metals in water, were determined from samples taken along the rivers. Metal processes and environmental impact were ascertained through geochemical modelling and multivariate statistics to determine the environmental impact of As, Pb, Zn and Cu.

## METHODS

Sediment and water samples were taken along the Cacalotenango River and in the Taxco River above and below its confluence with the Cacalotenango River, in February 2005 (Fig. 1). Total and fractionated contents of metals in sediments, physico-chemical parameters, main ions and heavy metals in water, were determined from samples taken along the river. Temperature, pH, Eh, and conductivity were measured in the field. Arsenic, Pb, Zn, Fe and Cu were analysed in acidified (considered total concentrations) and filtered through 0.45  $\mu\text{m}$  (considered dissolved) water samples. Zinc, Fe, and Cu were determined by flame AAS, and Pb by GFAAS using a Perkin Elmer AAnalyst 100 instrument; arsenic was measured by hydride generation with a Perkin Elmer 2380. Analyses of the main ions were undertaken following standard methods (APHA, 1995). Accuracy of major ion analyses was checked by computing the ionic balance, and for metals, through the analyses of NIST standards.

Total metal analysis in sediments was performed on the <2 mm fraction of the air-dried sediment sample (Rubio & Ure, 1993). The sample was quartered, and 200 mg of sediment were digested with 2 mL of  $\text{HNO}_3\text{:HCl}$ , 1:3 v/v and 12 mL of HF in a MARS 5 microwave oven. Analysis of Pb, Fe, Cu, Zn and Li was undertaken by flame AAS and As by HG-AAS. Quality control was assured using the reference materials of the Buffalo River sediment and Montana soil 2710 of the National Institute of Standards and Technology (NIST). A relative standard deviation of less than 10% and a mean recovery of 95% were obtained.

The technique developed by Tessier *et al.* (1979) was used to obtain metals fractionation in the sediments. Exchangeable (FX1), bound to carbonates (FX2), bound to Fe and Mn oxi-hydroxides (FX3), bound to organic matter or sulphides (FX4) and residual (FX5) fractions were obtained by sequential extraction. Metals were analysed in each fraction; analysis was performed as previously described. The relative difference between total concentrations and the sum of all fractions was less than 10%.

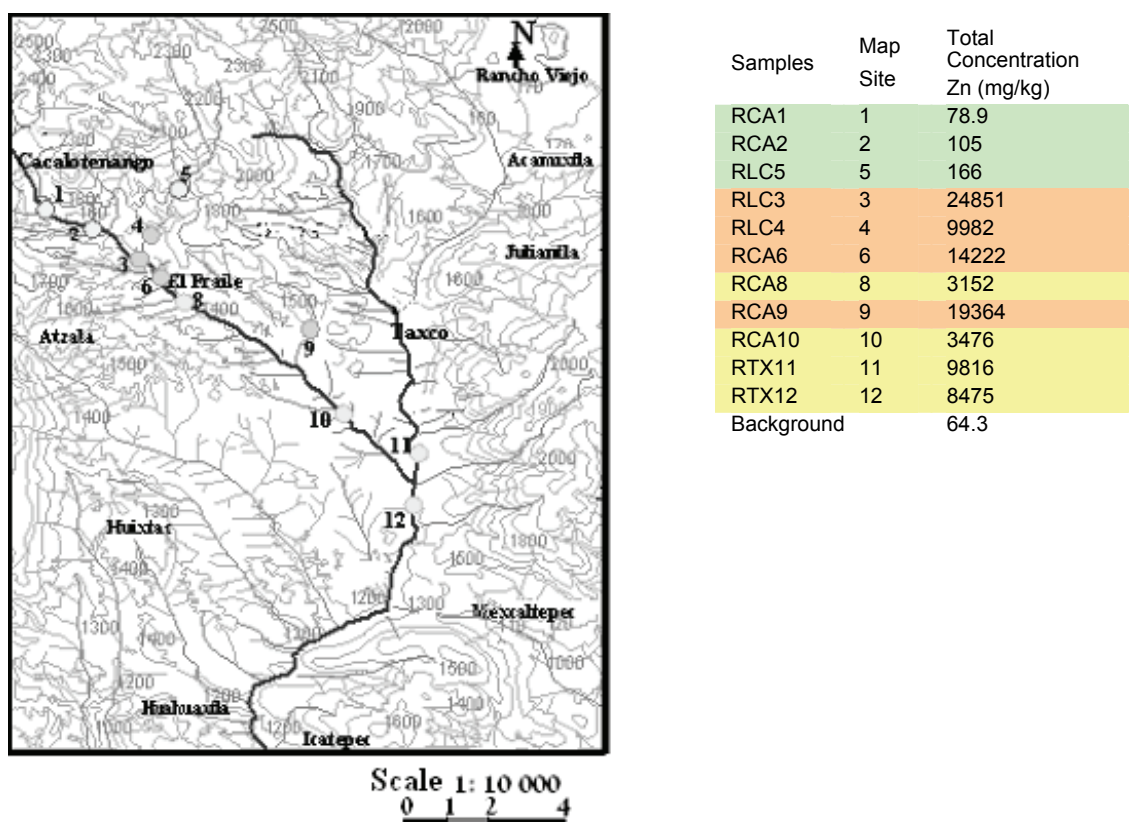
## RESULTS AND DISCUSSION

### Sediments

Iron and Zn presented the highest concentrations in sediments, followed by Pb, As and Cu (Table 1). However, all metals were above the regional background values. Total concentration of Zn at each sampling station is shown in Fig. 2. Arsenic, Pb, Zn and Cu followed the same concentration trends along the river. As expected, samples RCA1 and RCA2 located upstream of the mining wastes had the lowest metal contents. The highest concentrations were measured near El Fraile (RCA6) and La Concha (RLC3, RLC4) tailing piles, reflecting their impact on sediments. Water from a mine discharges metals above sample point RCA9 enriching the sediments at this site. The influence of the Cacalotenango River was not observed in the Taxco River for As and Pb had only a slight increase at RTX12 relative to RTX11. Moreover, a decrease in Zn content was determined in sample RTX12 relative to RTX11. Iron displayed a different tendency being more concentrated at RLC3, RCA6 and RLC5.

**Table 1** Metal concentrations in sediments (mg/kg).

Concentration range	As	Pb	Zn	Fe	Cu
River sediments	164–3648	28–11830	79–24850	2.3–7.6 %	10–466
Background <sup>a</sup>	30	26	64	2.7%	25

<sup>a</sup>Dótor, 2002.**Fig. 2** Zinc concentrations (mg/kg) along the Cacalotenango and Taxco rivers.

Geochemical fractionation gives information about the mobility of elements in a particular environment (Tessier *et al.*, 1979; Lacal *et al.*, 2003). Exchangeable metals are considered to have high mobility, whereas metals associated with iron and Mn hydroxides and organic and sulphidic phases are considered to have medium mobility that is influenced by changes in the environmental conditions. The residual fraction corresponds to the lowest metal mobility. The distribution among fractions is displayed in Table 2.

**Table 2** General distribution of As, Pb, Zn, Fe and Cu in geochemical fractions of sediments. FX1 = Exchangeable, FX2 = Bound to carbonates, FX3 = Bound to Fe and Mn oxi-hydroxides, FX4 = Bound to organic matter or sulphides, FX5 = Residual.

Element	Distribution in geochemical fractions
As	FX5 > FX4 > FX3 > FX2 > FX1
Pb	FX2 > FX4 > FX3 > FX5 > FX1
Zn	FX2 > FX3 > FX4 > FX1 > FX5
Fe	FX5 > FX4 > FX3 > FX2 > FX1
Cu	FX5 > FX4 > FX2 > FX3 > FX1

None of the metals was concentrated in the most mobile fraction. The residual and organic matter and sulphide fractions contained most of the As, Fe and Cu. Lead and Zn were mostly present in the carbonate fraction followed by the organic matter and sulphides fraction for lead, and the Fe and Mn oxi-hydroxides fraction for zinc. The predominance of Pb and Zn in the carbonate fraction reflects the influence of calcareous limestone and shale strata that underlay the majority of the river course. Sequential extraction results showed that As, Fe and Cu have the lowest environmental availability being mostly concentrated in the least mobile fractions. In contrast, Pb and Zn may be mobilized by a decrease in pH leading to carbonate dissolution. In fact, lead release from Cacalotenango River sediments at low pH has been reported in pH-controlled experiments (Arcega-Cabrera *et al.*, 2005).

### Hydrogeochemistry

All samples, except RCA1 (pH = 6.28), had basic pH values (from 7.43 to 8.17) in spite of being close to mining wastes. Calcium was the predominant cation at all sampled sites. Bicarbonate predominates over sulphate and chloride at all stations except RLC4. Relatively low conductivity (up to 345  $\mu\text{S}/\text{cm}$ ), sulphate (up to 16.3 mg/L) and calcium (up to 61 mg/L) characterize non-impacted stations (RCA1 and RCA2). Sulphate at other sites had values of up to 555 mg/L. These concentrations may result from oxidation of sulphide in tailings. Predominance of calcium along with relatively high bicarbonate concentrations (up to 488 mg/L) reflect the influence of limestones and calcareous rocks outcropping in the river basin. Water interaction with calcite also leads to the observed basic pH values. Concentration of metals at the sampled stations is shown in Table 3. Dissolved Cu, Fe and Pb were below detection levels at all sampled sites. Although the highest concentration was measured for Zn, it was still below the Mexican drinking water standard. Arsenic (total and soluble), total Pb and total Fe were above the standards at some points. Total concentrations were higher than soluble contents at all stations indicating that metals are mainly transported as particulates in the river.

**Table 3** Arsenic, Pb and Zn concentrations (mg/L) at the sampled stations; t = total, f = filtered.

Sample	As t	As f	Pb t	Cu t	Fe t	Zn t	Zn f
RCA1	0.0014	0.0010	nd	nd	0.3	nd	nd
RCA2	0.0015	0.0010	0.03	nd	nd	nd	nd
RLC3	0.0240	0.0170	0.09	nd	0.2	0.74	0.60
RLC4	0.0240	0.0009	0.25	nd	0.5	3.50	1.90
RCA6	0.0200	0.0180	nd	0.05	nd	0.06	0.04
RCA8	0.0463	0.0370	0.01	nd	0.2	0.30	0.18
RCA9	0.0330	0.0280	nd	nd	nd	0.05	nd
RTX11	0.0254	0.0200	0.08	0.05	0.6	0.29	0.04
RTX12	0.0300	0.024	0.07	0.05	0.5	0.17	nd
MDWS	0.025	0.025	0.01	2.00	0.30	5.00	5.00

nd = non detected. Detection levels: As = 0.0005 mg/L, Pb = 0.003 mg/L, Cu = 0.04 mg/L, Fe = 0.1 mg/L, Zn = 0.03 mg/L. MDWS = Mexican drinking water standard (DOF, 2000).

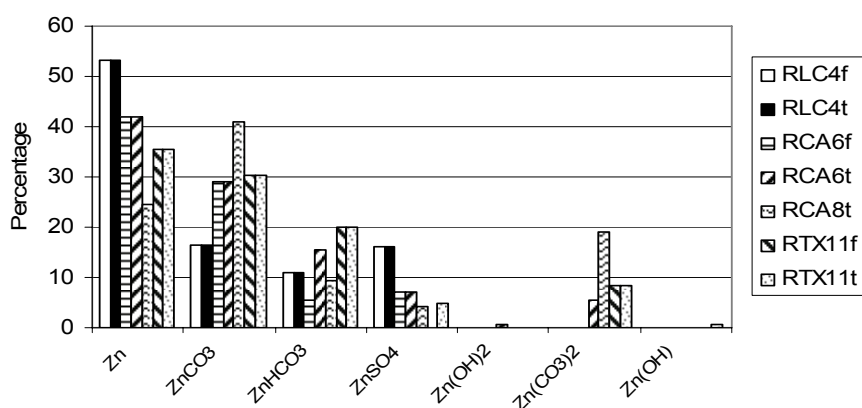


Fig. 3 Distribution of Zn species at selected stations.

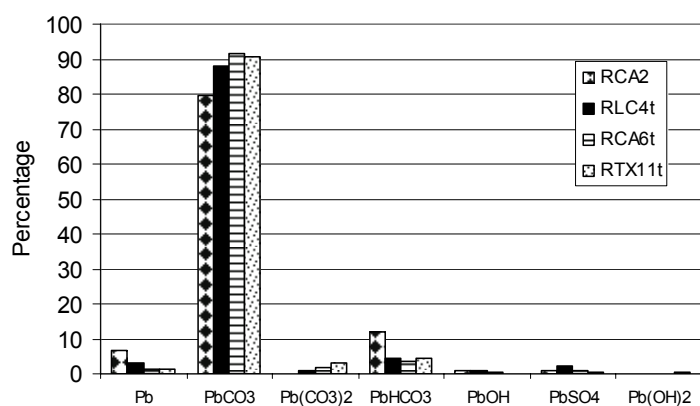


Fig. 4 Distribution of Pb species at selected stations.

Hydrogeochemical modelling of the water was undertaken using WATEQ4F (Ball & Nordstrom, 1991), version 2004, and PHREEQC (Parkhurst & Appelo, 1999) Windows version 2.10.02 computer codes. Most samples exhibited oversaturation of aragonite, calcite and silica minerals. Samples containing total iron also showed oversaturation of Fe oxides and hydroxides. The saturation index of  $\text{ZnSiO}_3$  was greater than 1.5 at stations RLC3, RLC4, RCA6, RCA8, RTX11 and RTX12. Oversaturation of jarosite at station RTX11 reflects input of tailings upstream of the confluence of the Cacalotenango River, and explains its high metal concentrations.

The distribution of species showed that zinc is mostly present in the water in ionic form, followed by carbonates and bicarbonates (Fig. 3). Lead is mainly transported as carbonate by the river water (Fig. 4). Copper is present mainly as carbonate and hydroxide, and arsenic as  $\text{H}_2\text{AsO}_4^{2-}$ .

## Statistics

Statistical analysis of the sediment data was performed by factor (Varimax normalized) analysis. Three factors explain the total variability of the studied phenomenon. Factor

1, explaining 46% of the variability, includes total metals, fractions FX2 and FX5 of Zn; FX2, FX3, and FX5 of Cu; FX3, and FX5 of Pb, and all As fractions. Grouping of total metals, together with a lack of correlation with lithium (considered as indicative of the natural source), reflects the increase of metals through anthropogenic origin at most stations. Geochemical fractions reflect possible geochemical processes for each element, i.e. FX5 and FX3 for Zn and Pb indicate that redox changes may mobilize these metals from FX5 to the Fe and Mn oxi-hydroxides fraction. Arsenic fractions, included in this factor reflect the As association with all geochemical fractions. This association may result from sorption processes, mainly on Mn and Fe oxi-hydroxides, clays and limestones, due to its presence as an ion in the water (Dzombak & Morel, 1990; Romero *et al.*, 2004). The second factor (explaining 25% of the variability) groups the more labile fractions FX1 and FX2 of Zn, FX1 of Cu and all Pb fractions except FX5. This grouping indicates that Zn, Cu and Pb may be released from sediments to the water as a result of small changes in physicochemical (mainly pH) and/or hydrogeological conditions. The third factor comprises Li, and the FX4 fraction of Zn, Cu and As. Correlation with lithium in this factor shows that Zn, Cu and As are naturally present as sulphides in sediments, which reflects the mineralization of the basin.

## CONCLUSIONS

Metals are mainly transported as particulates by the river water. Geochemical models and fractionation showed that zinc and lead form carbonate and bicarbonate complexes that enrich the sediments. Dissolved arsenic and zinc interact with Fe and Mn oxi-hydroxides and settle onto the sediment bed. Iron, As and Cu are mainly released as sulphides from the river basin and from tailings. Principal component analysis also indicated that Zn, Cu and Pb may be released to the water column following small changes in physico-chemical and/or hydrogeological conditions.

A simple filtration would produce water complying with drinking water standards at most sites. However, use of raw water for irrigation may increase metal content in crops. The presence of limestones plays a key role in the behaviour of contaminants. Application of straightforward analytical techniques, in combination with geochemical and statistical evaluation of results, may be an affordable means of clarifying the environmental impact of mining wastes in developing countries.

**Acknowledgements** The authors are grateful for financial support given by CONACyT-SEMARNAT project number C01-0017-2002.

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