

DETERMINATION OF MINING ACTIVITY OF RIVER SEDIMENTS OF THREE CHILEAN BASINS BY PARTICLE INDUCED X-RAY EMISSION (PIXE)

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(Received: March 21, 2012 - Accepted: July 4, 2012)

ABSTRACT

Mining is one of the most important industrial activities in Chile and there is growing concern on pollution by some mining and metallurgical processes. We have studied the contents of heavy metals in sediments from three river basins in Chile. Samples were collected based on hydrologic criteria in six sites along the rivers in their path from the Andes to the Pacific Ocean. Particle induced X-ray emission (PIXE), was used to determine elemental concentrations, and enrichment factors were used to evaluate the significance of anthropogenic sources. The results indicate the presence of Si, Al and Fe as major components. Cu, Cr, Mn, Pb and Zn are the main trace elements. In the Aconcagua river basin, which has less mining activity, the elemental concentrations are within the range of normal crust. Instead, samples from Choapa and Cachapoal river basins present high enrichment factors, mainly in copper. This is consistent with the fact that copper mines operate in the area. A correlation of the values obtained to copper using ICP and PIXE technique was statistically acceptable. Therefore, determination of Cu in river sediment by PIXE allows identification of areas affected by mining activities in river basins of northern Chile.

Keywords: River sediments, heavy elements, PIXE, enrichment factors.

INTRODUCTION

Pollution in rivers occurs either by the presence of compounds or elements that normally would not be there without human action, or by an increase or decrease in the normal concentration of existing substances due to human activity or by natural disasters. Some of these chemical elements are potentially toxic such as heavy metals, and/or metal trace elements, for instance: Al, Sb, As, Cd, Cu, Cr, Fe, Hg, Mn, Ni, Pb, Se, and Zn. The contribution of these metals to the water cycle comes from various sources; erosion, rain, runoff, etc. However, the largest concentrations are from antropoc origin.

The importance of the study of heavy metals in water and sediments is due to its high toxicity, high persistence and rapid accumulation by living organisms. Furthermore, toxic effects of heavy metals are not easily detected in the short term, but may have a major impact in the medium and long term. Metals are difficult to remove from the medium since the organisms themselves may incorporate them in their tissues and subsequently in their predators. The toxicity of these heavy metals is related to how easily are absorbed by living organisms; a dissolved metal in ionic form can be absorbed more easily than being in elemental form. Moreover, if the metals are found in the fine size fraction this could increase the chances of oxidation and retention by different organisms.

Sediments can behave as carriers and also as potential sources of pollution because heavy metals do not remain permanently and can be released into the water column due to changes in environmental conditions such as pH, Eh, dissolved oxygen or the presence of organic compounds¹⁻⁴. Therefore, the analysis of heavy metals in sediments could indicate contamination that eventually cannot be detected during water analysis and also provides information about critical areas in the aquatic system.⁵⁻⁹.

The selection of the most adequate analytical technique to determine trace-elements becomes a critical point, in terms of optimizing sample preparation, matrix corrections, time for each sample analysis, and non-destructive characteristics. From this point of view, several analytical methodologies for elemental analysis in agricultural applications have been explored by investigators. Certainly, each analytical technique commercially available has its own limitations. PIXE has been used successfully in agronomic applications^{10, 11} and several environmental samples such as sediments, soils, water and vegetation¹²⁻¹⁵. Moreover, in the field of soil physics, a technique which does not destroy the sample, performing accurate and fast elemental analysis with a minimum of sample preparation effort is often desired. PIXE is an analytical technique based on the ionization of the sample atoms by the incidence of a charged particle beam and the subsequent emission of its characteristic X-rays. The number of emitted X-ray photons from a given element provides information on the concentration of this element in the sample. In this study we used PIXE as analytical methodology to determine the presence of heavy

metals in river sediments from Choapa, Cachapoal and Aconcagua basins and determine influence of mining as a source of pollution.

MATERIALS AND METHODS

Study area and sampling

Samples were taken in January 2008 in the summer period which is a season characterized by low flow and an increased drought. During this period the metal concentration increases because there is no dilution as in the case of high water flow rate, which is considered a time of environmental risk¹⁶.

As shown in Figure 1, sediment samples from three selected basins were collected: Choapa, Aconcagua and Cachapoal at different points in the basin, selection was based on a hydrologic criteria *ritron* - very steep areas, therefore of high sediment transport, high-speed current, low temperatures and high concentrations of oxygen - and *potamon* - higher temperatures, lower oxygen concentration and sandy substrates, would produce sedimentation due to the decrease in slope^{17,18}. To determine the distribution of these sites six sampling points were chosen: one station without human intervention (*ritron*: E1), two in the field of *middle ritron* to characterize the sediments (E2-E3) and a third in the sector which produces *potamon* increased sedimentation (E4-E5-E6).

In the three basins site E2 could be influenced mining activities: Site E2 Choapa from Choapa basins is influenced to mining Los Pelambres, Site E2 Río Coya from Cachapoal basins is influenced to mining El Teniente, Site E2 Río Blanco is influenced from Aconcagua basins is influenced to mining Cerro Blanco.

In situ characterization of sediment samples:

In situ, three type of analysis were carried out on these samples, namely electrical conductivity (EC), pH and redox potential (Eh). Subsequently, the samples were stored in polyethylene bottles and then transported to a laboratory where they were kept at a temperature of - 4 °C.

The drying of the sediment samples was carried out in polyethylene trays at temperatures below 40 °C (dry air) and then sieved <63 microns and stored in plastic jars.

Pellets were prepared by taking about 0.5 grams of sediment to a press, where pressure ranging from 4 to 8 metric tons was applied. The applied pressure to obtain a well-compacted pellet depended on the sediment composition. Some samples were mostly sand and in these cases we used a binder (polyethylene) so that the pellet had a ratio 1:3 (sample: polyethylene). The pellets then were attached to transparent foils and mounted in the sample holder inside the PIXE chamber where the analysis was performed.

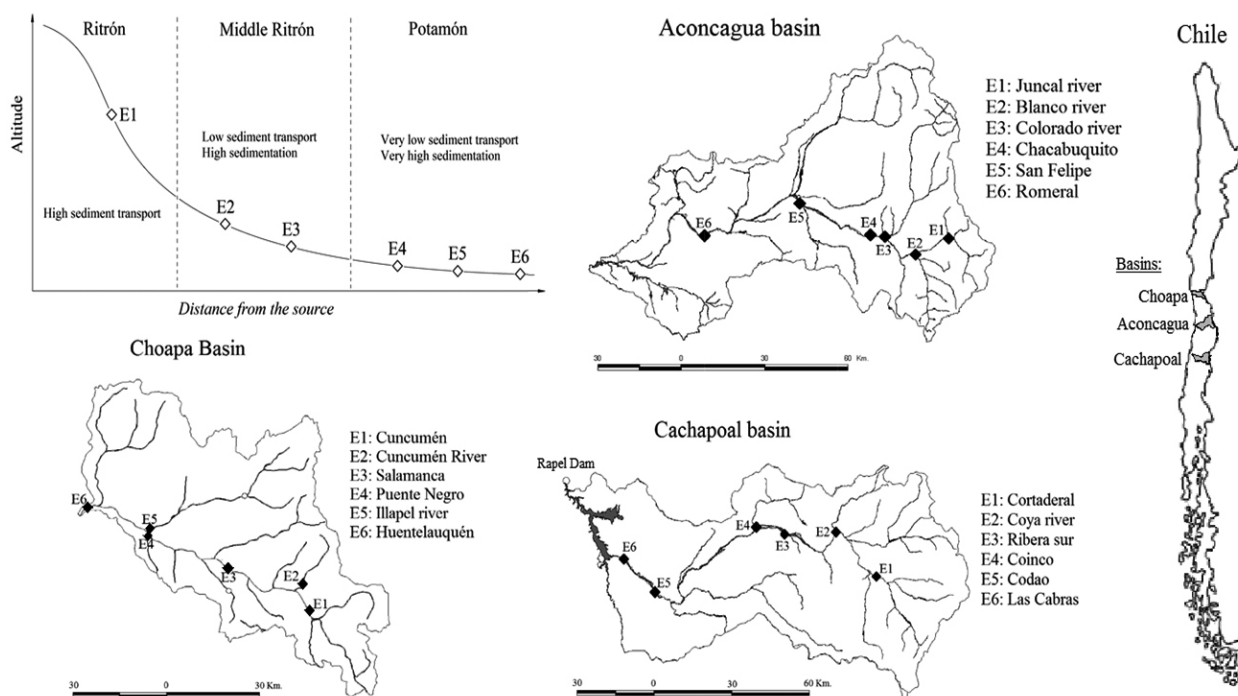


Figure 1. Sampling stations in Aconcagua, Choapa and Cachapoal basins.

PIXE technique

In the three basins site E2 could be influenced by mining activities: Site Cuncumen river from Choapa basin is influenced by mine Los Pelambres. Site Río Coya from Cachapoal basin is influenced mine by El Teniente. Site Río Blanco from Aconcagua basin is influenced by mine Cerro Blanco (see Figure 1).

Irradiation of samples was performed in a vacuum chamber adjusted in such a way that the proton beam is oriented toward a tantalum collimator of 1-2 mm thickness. The irradiation chamber has a disk which rotates and position each sample to the beam impact. The target holder may contain up to 30 samples and can be rotated from the outside without disturbing the vacuum in the chamber (10^{-5} - 10^{-6} Torr).

ICP-OES method

Optical Emission Spectroscopy in Inductively Coupled Plasma (ICP-OES) (Perkin Elmer Co, Optima-3300XI), was used to analyze copper after pretreatment extraction. In the case of the analysis of total metals in sediment, acid pseudo digestion was performed by with a mixture of HCl – HNO₃ 1:3 (concentrated acids, Merck, Suprapur) and then stirred by 16 h, at 90 ± 5 °C. This mixture can oxidize and digest sediment particles. The liquid sample is carried to the ICP to obtain the total concentration of metals in the samples. In the determinations of heavy metals by both methods in river sediments a reference material (NCS DC 78301), was used.

RESULTS AND DISCUSSION

PIXE determination

Figure 2 shows a typical spectrum, in which the most abundant elements are highlighted. Peak areas and elemental concentrations were obtained by the computer program (GUPIX).

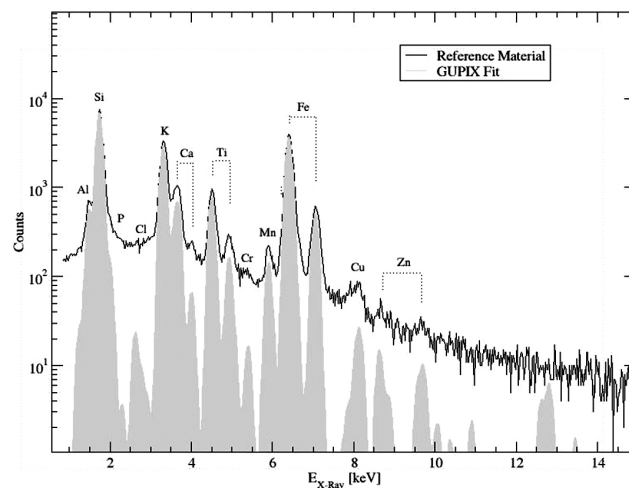


Figure 2. X-ray emission spectrum of a sample from "Coya" site in the Cachapoal basin.

The analysis of this spectrum has shown that siliceous (Si) is the most abundant element, due to the sandy nature of the sediments, reaching a concentration average of 60% in Choapa and Cachapoal rivers and 57 % in Aconcagua River.

Elemental concentration in river sediments

Concentrations determined for Al and Fe, by PIXE in river sediments in Choapa, Aconcagua and Cachapoal basins and are shown in Figure 3.

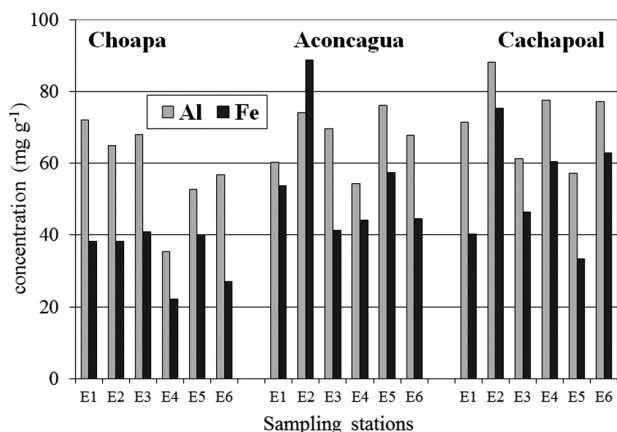


Figure 3. Concentrations of Al and Fe in sediments of Choapa, Aconcagua and Cachapoal basins.

Iron concentrations were lower than those for aluminum, except for the station E2 in Aconcagua basin. In the samples from the three basins E2 site the values for the concentrations of Al and Fe were in the range from 64.9 mgg⁻¹ (site Cuncumén River from Choapa basins) to 88.1 mgg⁻¹ (site Río Coya from Cachapoal basin) and from 32.3 mgg⁻¹ (site Cuncumén River from Choapa basin) to 88.82 mgg⁻¹ (site Río Blanco from Aconcagua basin), respectively.

In Figure 4 the concentrations determined for the minor elements in sediments of the six stations in each basin are shown.

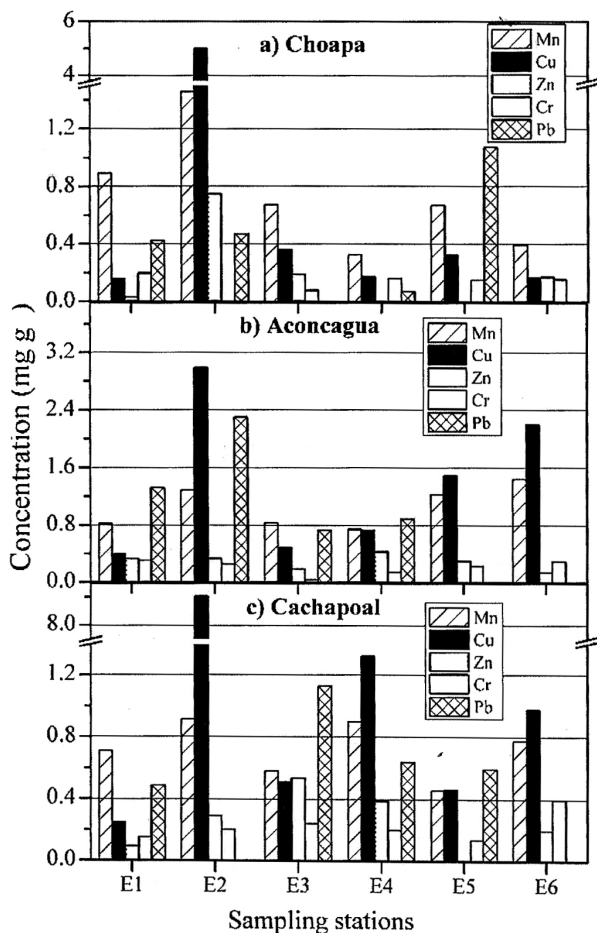


Figure 4. Minor heavy metals concentration in the three basins: d) Choapa; b) Aconcagua, c) Cachapoal.

The minor concentrations were detected for copper, chromium, manganese, lead and zinc, being copper the highest at stations E2 in all of basins, which correspond to stations receiving mining related tributaries. Mn and Zn were present in most of the stations suggesting a lithogenic origin. Lead was detected in some sites in the three basins, and its presence may be due to pollution from mines and other antropic sources, such as fossil fuel burning and industrial waste.

A comparison of the average values of each element between all stations indicates that Cachapoal basin presents the highest levels of copper and chromium, while the Aconcagua Basin has the highest levels of manganese, zinc and lead. This is expected as those watersheds are most impacted by mining and human activities.

Enrichment Factors

Enrichment factors were used to evaluate the significance of anthropogenic sources in the content of heavy metals in sediments. Sediment Enrichment Factor (SEF) was proposed by Kemp in 1979 and has been used recently to establish the degree of trace elements contamination, evaluating the enrichment factors of trace elements and their relationship with anthropogenic activities¹⁹⁻²². The SEF method involves comparing the environmental relationship between the content of some heavy metal and an element of lithogenic origin - such as Fe or Al - with respect to the relationship in the unpolluted sediment reater the enrichment factor of heavy metals in sediments, higher the level of sediments contaminated by heavy metals²³.

In this study the relationships of Fe in the Ritron Site (E1) was used as the reference value of uncontaminated sediment to compare with the relationship between the content of each metal and Fe in the other sites. E1 sites in each basin are located at high altitudes in the Andes and represent the location near the headwaters of the rivers having low human intervention and high sediment transport, so they were used as reference values for the crust in each basin according to equation (1):

$$EF_{X(E2-E6)} = (X/Fe)_{E2-E6} / (X/Fe)_{E1} \quad (1)$$

Where X represents the concentration of the element in question, Fe is the iron concentration expressed in the same units of X and E represents the sampling stations in each basin. Table 1 show the results obtained.

The analysis using the enrichment factor confirms the assumption that Cu and Zn are carried into the river by mining activities in the Choapa River Basin. In the E2 site Cachapoal basin, there is a large enrichment factor of 17.6 for Cu, which could be associated with Cu-enriched ore from a treatment plant.

Comparison with measurements by ICP-OES

In order to validate the determinations of elemental concentrations by PIXE, the same samples were analyzed by ICP-OES to determine copper. Note that the results presented for determination by ICP correspond to the total metal obtained after digestion with acids, while the values obtained by PIXE represent the total metal obtained through the irradiation of the sediment in the solid state.

Table 1. Enrichment factors calculated from equation 1. (EF > 10 in bold).

	Stations	Al	Mn	Cu	Zn	Cr	Pb
Choapa	E1	1.0	1.0	1.0	1.0	1.0	1.0
	E2	0.9	1.6	31.9	22.0	0.0	1.1
	E3	0.9	0.7	2.2	5.2	0.4	0.0
	E4	0.8	0.6	1.9	0.0	1.4	0.3
	E5	0.7	0.7	2.0	0.0	0.7	2.4
	E6	1.1	0.6	1.5	7.1	1.1	0.0
Aconcagua	E1	1.0	1.0	1.0	1.0	1.0	1.0
	E2	0.7	1.0	4.6	0.6	0.5	1.1
	E3	1.5	1.3	1.6	0.8	0.2	0.7
	E4	1.1	1.1	2.3	1.6	0.6	0.8
	E5	1.2	1.4	3.6	0.9	0.7	0.0
	E6	1.4	2.1	6.8	0.5	1.2	0.0
Cachapoal	E1	1.0	1.0	1.0	1.0	1.0	1.0
	E2	0.7	0.7	17.6	1.7	0.7	0.0
	E3	0.7	0.7	1.8	5.0	1.4	2.0
	E4	0.7	0.8	3.5	2.8	0.9	0.9
	E5	1.0	0.8	2.2	0.0	1.1	1.5
	E6	0.7	0.7	2.5	1.4	1.6	0.0

The comparison between the concentrations determined by both methods show a linear correlation of $r^2 = 0.957$ as shown in Figure 5.

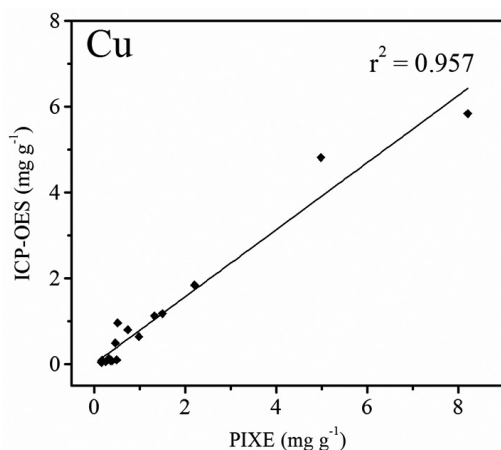


Figure 5. Correlation for Cu in all stations of three basins obtained by PIXE and ICP-OES.

Saitoh *et al.*²⁴ in 2002 performed a comparison of the values determined by PIXE, ICP-MS and ICP-AES using standard NIST urban particulate matter (SRM 1648), Buffalo River sediment (SRM 2704) and pine needle (SRM 1575) samples. They conclude that compared to ICP-MS and ICP-AES, PIXE can be used to precisely and efficiently analyze many elements, so it may become the most effective means of analysis in environmental studies in the near future. However, Lunderberg *et al.* (2008).²⁵ proposed the analysis of sediments by PIXE as a complementary technique to ICP-OES, since it has lower sensitivity for most metals and the range of elements it can analyze is more limited.

CONCLUSIONS

The PIXE technique has proved to be efficient in the elemental analysis

of river sediments samples. Results are obtained in a short analysis time and with little sample manipulation, which reduces the possibility of contamination and minimizes the error produced by the processes leading to the analysis of samples.

The analysis of sediments in the basins studied in this work indicates a high content of elements such as Cu, Zn, Al, Fe, Mn and Pb at type E2 stations. The origin of these high levels of concentration is related to acid drainage in mining operations, product wastes and tailings containing sulfide minerals or metals that leached and increase acidity of waters.

An evaluation of the correlation obtained by both techniques allows concluding that the determination of Cu by PIXE allows identification of areas frequently affected by mining activities in the basins of northern Chile.

ACKNOWLEDGEMENTS

This work has been financially by Dirección General de Aguas (DGA)-Código 300 65693-0 Chile.

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