

# Analysis and distribution of metals in the Paraopeba and the Das Velhas Rivers, Brazil

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## Abstract

Instrumental neutron activation analysis (INAA) and inductively coupled plasma - mass spectrometry (ICP-MS) were used to analyse water and sediment samples of the Paraopeba and the Das Velhas Rivers in the state of Minas Gerais, Brazil to assess the impact of mining activities on the water environment. Elemental concentrations of Cr, Fe, Co, Ni, Cu, As, Cs, Ba, La and Ce were measured in water and sediment samples collected in different parts of the Paraopeba River, the Betim River, one of its tributaries, and in the lake near the confluence of these two rivers. Results indicate an increase in the concentration of these polluting metals in an area of industrial discharge. Elemental concentrations of Cr, Fe, Co, As and Au were also measured in water and sediment samples in the Das Velhas River. It has been clearly demonstrated that the pollution of the Das Velhas River is associated with mining exploitation. One of its tributaries, the Itabira River, carries large concentrations of Fe and Cr, and the Agua Suja tributary is highly contaminated with As from a 20-year-old deposit known as *Morro do Galo*, and Au from the waste of a 160-year-old gold mine, owned by the *Morro Velho* Company.

## Introduction

Minas Gerais is the fourth largest state of Brazil and the world's second largest producer of Fe mineral, having produced  $199 \times 10^6$  t in 1998. Brazil has the world's 6th largest reserves of this mineral containing 60.0 to 67.0% hematites and 50.0 to 60.0% itabirite. Seventy per cent of these reserves are found in Minas Gerais State (Quaresma, 1999).

Minas Gerais' freshwater sources contribute, by hydro-electric generation, nearly 20% of the electricity produced in Brazil. The Paraopeba and the Das Velhas Rivers run through an "Iron Quadrangle" region rich in Fe, Au, Mn ores, and flow into the São Francisco River which is called, "The National Integration River" because it runs through four states and is used for navigation, recreation and sources of electricity production (COMIG, 1994).

The Paraopeba River receives wastes from about 70 large industries and mining companies. One of its tributaries alone, the Betim River, receives wastes from 57 industries (FEAM, 1996a).

Intensive iron-ore mining is carried out in the Das Velhas River region, and approximately 58 companies are involved in gold-mining and precious and semi-precious stone mining (FEAM, 1996b).

While environmental management is practised by the bigger mining companies, the smaller mines release significant quantities of mineral waste in geological and aquatic environments. The accumulation and the dissolution of metal elements cause serious river pollution, a critical problem for Minas Gerais Government. Studies of freshwater ecosystems in Minas Gerais are just beginning and ecological problems have been identified in rivers, lakes and reservoirs (Coelho and Giani, 1994, Jordão et al., 1999). The Foundation for the Environment of the state of Minas Gerais (*Fundação Estadual do Meio Ambiente - FEAM*) is responsible for water quality control and monitoring the Paraopeba and the Das

Velhas Rivers. The graphite furnace atomic absorption spectrophotometry (GFAAS) has been used as a method of metal analysis in these river waters.

In this paper two other more sensitive analytical methods are proposed in water and sediment samples: Instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS). INAA is a very accurate method for the analysis of solid samples. It has also been widely used for river pollution studies (Ambulkar et al., 1992, Revel, 1999, Dupré et al., 1996). ICP-MS is a very rapid method for the analysis of liquid samples and it can analyse more than 100 samples daily. It has been recently used to determine the composition of river water and sediment for routine trace analysis (Jarvis et al., 1992, Date and Hutchison, 1987). These two methods are multi-elementary and allow high-sensitivity determination of traces of several metal elements (Vandecasteele and Block, 1993, Pinte et al., 1998).

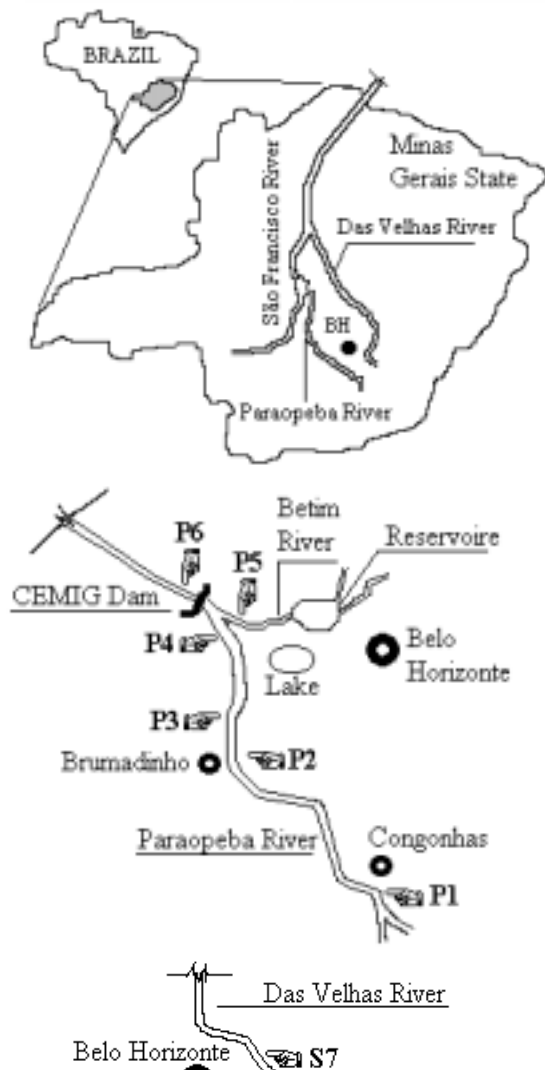
## Experimental procedures

Water and sediment samples were collected along the Paraopeba River, from the region close to the source up to a distance of 170 km. In the Das Velhas River, the same procedure was carried out within 80 km. Sampling areas are indicated in Fig. 1.

Water samples were collected near the river bank at a depth of 15 cm, put into 125 ml bottles (Nalgene) stored at 4°C. Temperature, pH and electrical conductivity were measured on site. There were no significant differences in the various samples. The average values were: temperature 25°C, pH: 7.2, electrical conductivity: 30  $\mu$ S/cm. The samples were acidified on site with 5 drops of ultrapure nitric acid (pH~2). This acidification is believed to reduce any sorption on the bottle walls (Mart, 1979). No filtration process was used in this study because it was tested and verified that filtration can be an important source of contamination (Veado et al., 1997a, Veado, 1997b). Before the analysis, all samples were centrifuged at 4 300 r-min<sup>-1</sup> for 10 min to remove all suspended materials (Bailey et al., 1981; Laxen and Harrison, 1981; Veado et al., 1997a).

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**Figure 1**  
Area of study and sample sites in the Paraopeba and the Das Velhas Rivers

Sediment samples were collected in a 20 mL polyethylene tube and also stored at a temperature of 4°C. They were dried for a day at a temperature of 80°C prior to analysis. One sediment sample was collected for each water sample at each sampling site.

#### Instrumental neutron activation analysis (INAA)

The samples were irradiated in an OSIRIS nuclear reactor, *Laboratoire Pierre Süe – Commissariat à l’Energie Atomique, Saclay, France*.

It is not possible to irradiate water in the liquid form in an

OSIRIS nuclear reactor, because of the radiolysis effect induced by neutron irradiation. Therefore, 10 mL samples were concentrated in ultrapure-quartz ampoules (Suprasil), at 80°C for 24 h and heat-sealed. The samples and the standards were irradiated with a neutron flux of  $1.4 \times 10^{14} \text{ n cm}^{-2} \text{ s}^{-1}$  for 17 h. The gamma rays emitted subsequently were measured for 8 h, with a 100 cm<sup>3</sup> coaxial high-purity germanium (HPGe) detector coupled to a 4 096 pulse height analyser after a decay time of 10 and 20 d. The computational K0 method was used to determine the concentration of the metal elements studied (Piccot et al., 1997, De Corte et al., 1986).

A representative sediment sample of each site (150 mg) was irradiated in the OSIRIS nuclear reactor for 2 h and measured for 4 h under the same conditions as the water samples.

In order to compare INAA and ICP-MS measurements, 20 mL of a 3:1 mixture of HCl and HNO<sub>3</sub> was added to the irradiated sediment samples. The mixture was evaporated at 80°C, diluted with 20 mL of 5% nitric acid and centrifuged. The liquid samples were measured for 4 h (Veado, 1997b).

#### Inductively coupled plasma spectrometry (ICP-MS)

The ICP-MS used in this study was a PlasmaQuad, PQ2+, with a Meinhard ultrasonic nebuliser, *Laboratoire Pierre Süe – Commissariat à l’Energie Atomique, Saclay, France*.

A representative sediment sample from each sampling site (250 mg) was digested with a solution of HNO<sub>3</sub>, HCl and HF under pressure at 110°C for 12 h, followed by another sequence of acid digestion, as demonstrated by Veado (1997b).

To determine major elements (concentration higher than 50 µg/L) the centrifuged river water was diluted twenty times using ultrapure water (Millipore). No dilution was made for trace element analysis.

The internal standards for water and sediment samples were 10 µg/L solution of In, Re, and Be.

#### Results and discussion

The analytical methods were used to monitor elemental losses and contamination during analysis with international reference materials. The reference materials used were Riverine Water, SLRS-3 (National Research Council of Canada) and Soils-7 (International Atomic Energy, Vienna, Austria.). The results obtained using both methods for metal elements in this study were in agreement with certified values as shown in Tables 1 and 2.

Detection limits are shown in Table 3 for water and sediment samples. INAA limits for water analysis were blank quartz-irradiated ampoules. Background measurements were the detection limits for sediment samples. ICP-MS limits were ultrapure water and acid solutions for water and sediment samples, respectively. The concentration values of acid solutions are the same as those found for ultrapure water.

More than 40 elements could be determined by the ICP-MS analytical method and 20 of them could be determined by INAA (Veado, 1997b).

All the metals studied were determined in each sample, both by INAA and ICP-MS methods, except Cu because it requires chemical separation after irradiation for analysis by INAA. However, a particular study method was routinely selected: ICP-MS for Ni, Cu, and Ba, and INAA for Cr, Fe, Co, As, Au, Cs, La, and Ce. More detailed method selection criteria are given by Veado (1997b).

#### Results for the Paraopeba River

Analytical results obtained for the Paraopeba River are shown in

<b>TABLE 1</b> <b>RESULTS OBTAINED (<math>\mu\text{g/l}</math>) BY INAA AND ICP-MS FOR RIVERINE WATER REFERENCE – SLRS 3</b>			
Element	Concentration measured $\pm$ standard deviation		Certified values $\pm$ confidence limits
	INAA (6)	ICP-MS(9)	
Cr	0.38 $\pm$ 0.04	0.38 $\pm$ 0.04	0.30 $\pm$ 0.04
Fe	110 $\pm$ 10	103 $\pm$ 20	100 $\pm$ 2
Co	0.042 $\pm$ 0.004	0.04 $\pm$ 0.03	0.027 $\pm$ 0.003
Ni	-	1.03 $\pm$ 0.06	0.83 $\pm$ 0.08
Cu	-	1.5 $\pm$ 0.1	1.35 $\pm$ 0.07
As	0.67 $\pm$ 0.07	0.67 $\pm$ 0.06	0.72 $\pm$ 0.05
Cs	0.010 $\pm$ 0.003	<0.01	-
Ba	14 $\pm$ 2	12.6 $\pm$ 0.2	13.4 $\pm$ 0.6
La	0.26 $\pm$ 0.03	0.26 $\pm$ 0.02	-
Ce	0.33 $\pm$ 0.03	0.30 $\pm$ 0.03	-

( ) Number of analyses

<b>TABLE 2</b> <b>RESULTS OBTAINED (<math>\mu\text{g/g}</math>) BY INAA AND ICP-MS FOR SOIL REFERENCE - SOIL 7</b>			
Element	Concentration measured $\pm$ standard deviation		Certified values $\pm$ confidence limits
	INAA (6)	ICP-MS(9)	
Cr	63 $\pm$ 6	63 $\pm$ 2	60
Fe	25700 $\pm$ 2000	25000 $\pm$ 1000	25700* (25200-26300)
Co	8.6 $\pm$ 0.8	10.5 $\pm$ 1.0	8.9 (8.4-10.1)
Ni	-	38 $\pm$ 8	26* (21-37)
Cu	-	13 $\pm$ 2	11 (9-13)
As	13.3 $\pm$ 1.3	14.8 $\pm$ 1.2	13.4 (12.5-14.2)
Cs	5.5 $\pm$ 0.5	5.7 $\pm$ 0.1	5.4 (4.9-6.4)
Ba	141 $\pm$ 20	138 $\pm$ 2	159* (131-196)
La	28 $\pm$ 3	28 $\pm$ 1	28 (27-29)
Ce	58 $\pm$ 6	55 $\pm$ 1	61 (50-63)

( ) Number of analyses; \* Non-certified value

Figs. 2 to 5. Sampling sites P2 to P4 were located in the "Iron Quadrangle" (Quaresma, 1999). The concentration of metal elements varies along the course of the river depending on the number of mining companies.

Sampling site P3 was a strategic point at a large mining company, which discharges its waste directly onto the river banks. The impact of this discharge is clearly shown in the high concentrations of Fe, Cu, As, Ni, Ba, Cs, La and Ce observed in the water and sediment samples of this site.

The increase in concentration of Fe, Ni, As, Ba and Cs in water samples of the Betim River, P5 tributary, is caused by several industries and the discharge of the domestic sewage from Betim, a

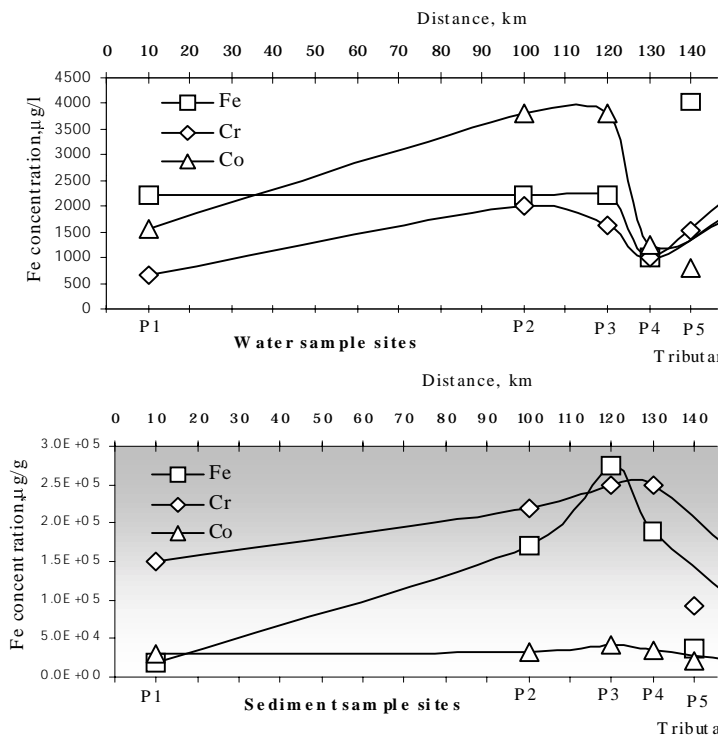
<b>TABLE 3</b> <b>DETECTION LIMITS FOR THE DETERMINATION OF METAL ELEMENTS IN WATER AND SEDIMENT SAMPLES</b>			
ICP-MS	Element	INAA	
		Water and Sediment( $\mu\text{g/l}$ )	Water ( $\mu\text{g/l}$ )
Cr	0.50	0.40	0.90
Fe	50	8.0	47
Co	0.01	0.05	0.08
Ni	0.36	2.0	17
Cu	0.15	-	-
As	0.40	0.01	0.7
Cs	0.01	0.01	0.1
Ba	0.20	2.6	20
Au	0.04	0.01	0.003
La	0.01	0.03	0.04
Ce	0.01	0.05	0.30

<b>TABLE 4</b> <b>METAL CONCENTRATIONS OF THE LAKE (7) NEAR THE CONFLUENCE OF THE PARAOPEBA AND BETIM RIVERS</b>			
Element	Water samples, $\mu\text{g/l}$		
Cr	<0.5	<0.5	<0.5
Fe	1000 $\pm$ 100	1200 $\pm$ 100	1000 $\pm$ 100
Co	0.25 $\pm$ 0.02	0.32 $\pm$ 0.03	0.24 $\pm$ 0.02
Ni	0.50 $\pm$ 0.05	0.50 $\pm$ 0.05	0.50 $\pm$ 0.05
Cu	0.46 $\pm$ 0.05	0.53 $\pm$ 0.05	0.75 $\pm$ 0.07
As	0.70 $\pm$ 0.07	0.70 $\pm$ 0.07	0.70 $\pm$ 0.07
Cs	<0.02	<0.02	<0.02
Ba	41 $\pm$ 4	54 $\pm$ 5	49 $\pm$ 5
La	0.70 $\pm$ 0.07	0.80 $\pm$ 0.08	0.70 $\pm$ 0.07
Ce	1.40 $\pm$ 0.01	1.70 $\pm$ 0.02	1.40 $\pm$ 0.01

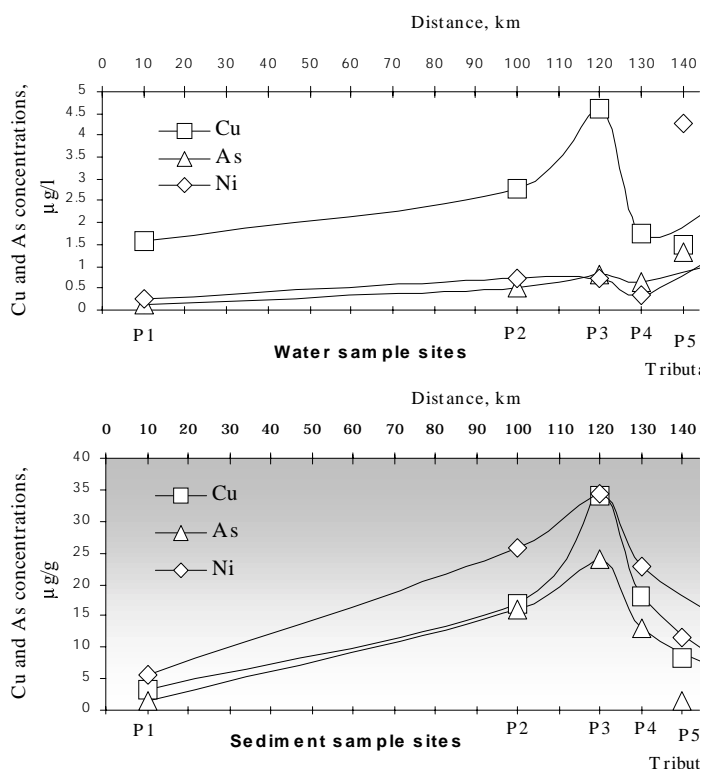
town with 100 000 inhabitants. The Betim River has a dissolved oxygen concentration of 0.2 mg/l, a value much lower than that of the Paraopeba River, with an average of 7.2 mg/l (FEAM, 1996a). Several metals are in the soluble form as a result of the formation of FeS<sub>2</sub> (Minear and Keith, 1982).

Except for the rare earth elements La and Ce, an increase in the concentration of all other elements analysed was observed in water samples from P4 and P6. This occurred despite the fact that P4 and P6 sampling points were located upstream and downstream of the *Centrais Eletricas de Minas Gerais* (CEMIG) dam providing water for a thermal power plant. This is explained by the fact that P6 receives polluted waters from the Betim River (P5). However, for sediment samples a decrease in concentration is observed for Cr, Fe, Ni, Cu, As, Cs and Ba. This could be explained by the retention of sediments by the dam.

The values of the water samples shown in Table 4 refer to a lake near the confluence of the Paraopeba and the Betim Rivers. The lake is about 2 km from their banks. Water and sediment samples were collected at three points in a triangular conformation. These values were taken as control parameters for the results obtained for



**Figure 2**  
Concentration of Fe, Cr and Co in water and sediment samples of the Paraopeba River



**Figure 3**  
Concentration of Cu, As and Ni in water and sediment samples of the Paraopeba River

the river samples because the lake is not affected by any waste. This comparison allows us to evaluate the pollution introduced by the industries along the course of these rivers. The results obtained at these three points are similar and much closer to values in a clean region. This fact reinforces the significant differences of the metal concentration values in the lake and the other polluted sample sites.

## Results of the Das Velhas River

Concentration values of Fe, Cr, Co, As and Au for water and sediment samples from the Das Velhas River and its two tributaries are shown in Fig. 6 and 7.

The increase in Fe concentration beginning in S3 confirms an industrial mining area near Itabirito City as a major pollution source. An increasing concentration of Fe, Cr and Co in water samples from the Das Velhas River, S4, S5, and S7, is caused by the large number of iron-ore mines.

The high Cr concentration in sediment samples from S1 is probably due to some clandestine leather tanning plants.

The drastic rise in As concentration of water and sediment samples from S6 is caused by an old arsenic deposit, *Morro do Galo*, situated a few kilometers from S6. A considerable level of As pollution, a well-known toxic index element (Merian, 1991) is clearly noticeable at this point. Recently, Figueiredo et al. (1999), has also found abnormal arsenic concentrations in plants and in children's urine samples collected in this area.

The abnormal concentrations of Au found in water and sediment samples at S6 are due to the intensive gold exploration and exploitation by the *Morro Velho* company. The mine has been active for the last 160 years and is a major source of water and soil pollution in the metropolitan regions of Belo Horizonte, Nova Lima and Itabirito. The government of Minas Gerais has shown a special interest in this part of the Das Velhas River because it is the main source of water for the metropolitan area.

## Conclusion

The association of multi-elementary analysis methods, INAA and ICP-MS has permitted a precise investigation of the concentrations of the elements Fe,

Cr, Co, Cu, As, Ni, Ba, Cs, La and Ce in water and sediment samples from the Paraopeba and Das Velhas Rivers, Brazil. These rivers have been receiving the wastes from industries and mining companies for more than a century. The methods are complementary and the results have evidenced the concentrations of industrial and mining pollutants.

Results indicate an increase in the concentration of polluting metals in an area of industrial discharge of the Paraopeba and Betim Rivers.

Das Velhas River water pollution is associated with mining exploration and exploitation. One of its tributaries, the Itabira River, carries large concentrations of Fe and Cr, and the Agua Suja tributary is heavily contaminated with As from a 20-year-old deposit known as *Morro do Galo*, and Au from the waste of a 160-year-old gold mine, owned by the *Morro Velho* Company.

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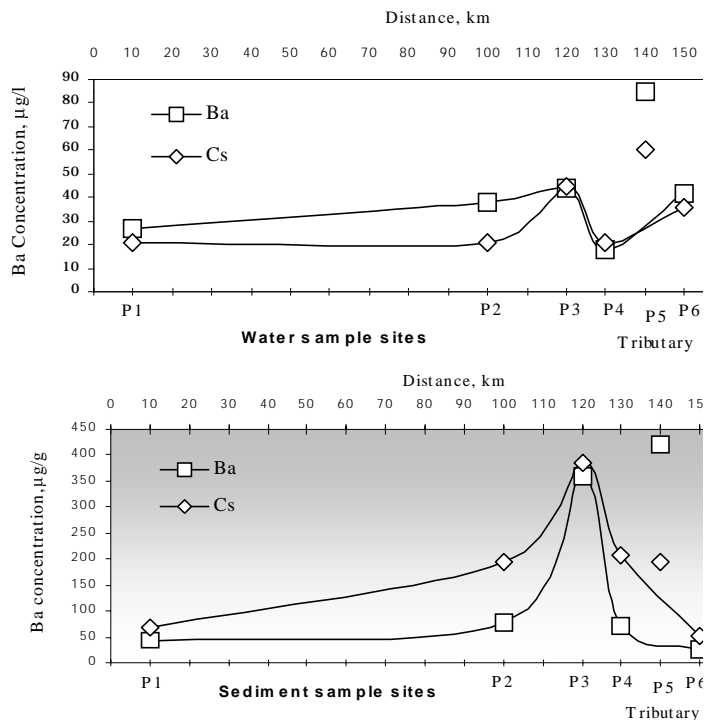
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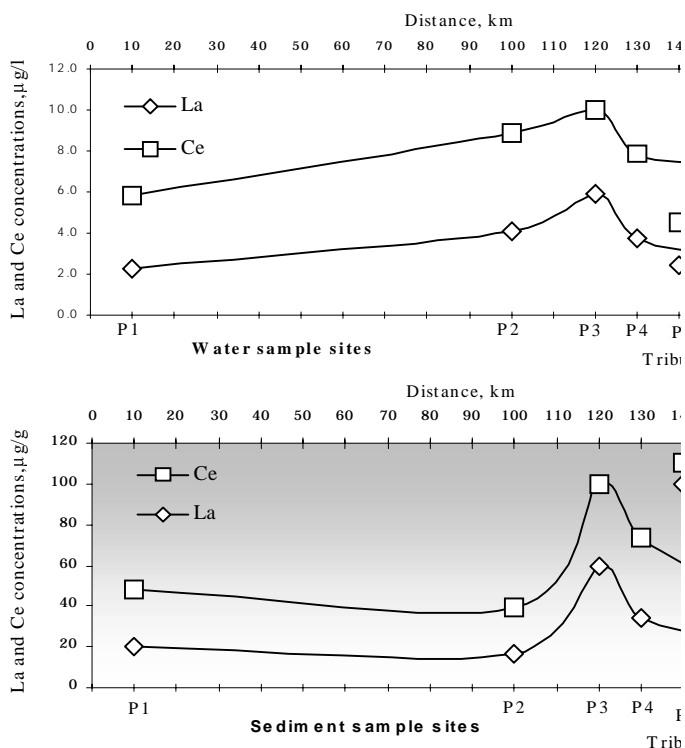
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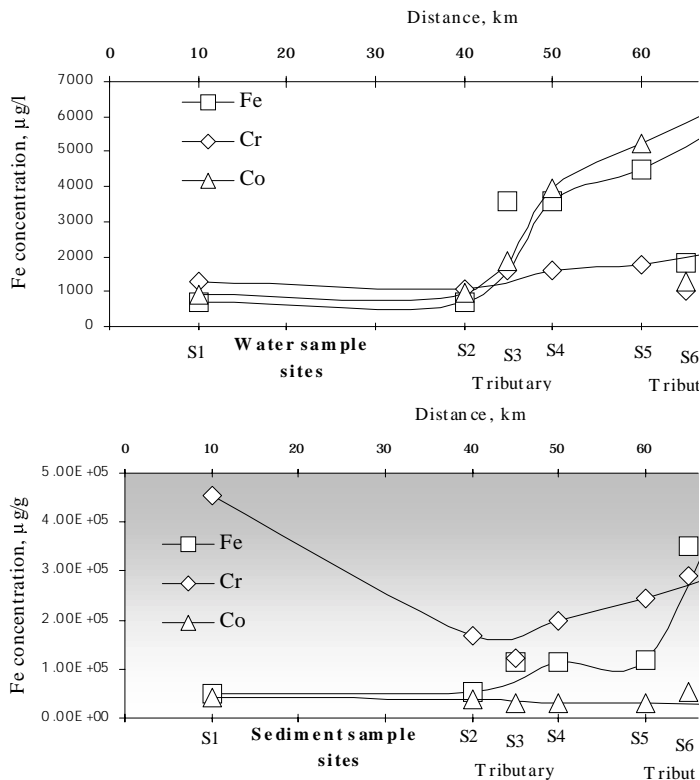
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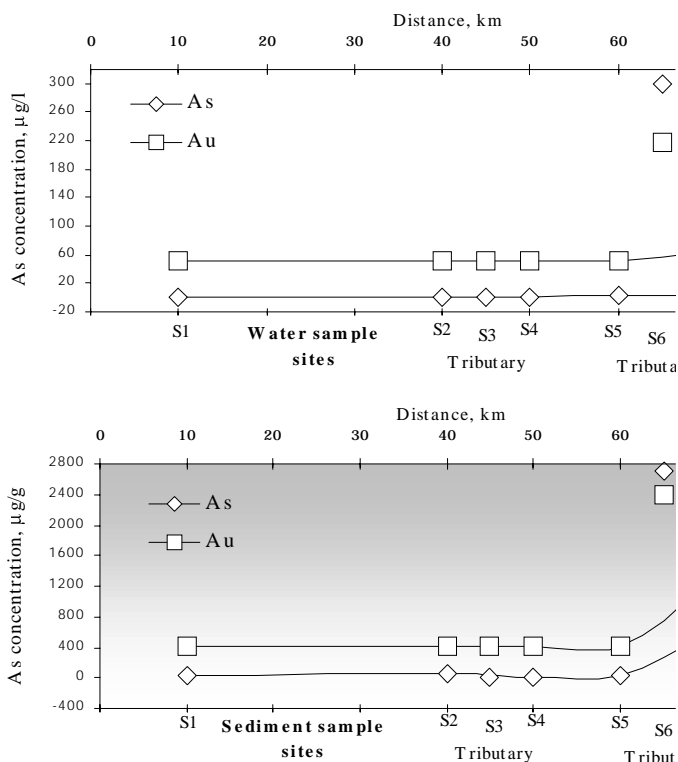
**Figure 4**  
Concentration of Ba and Cs in water and sediment samples of the Paraopeba River



**Figure 5**  
Concentration of La and Ce in water and sediment samples of the Paraopeba River



**Figure 6**  
Concentration of Fe, Cr, Co in water and sediment samples of the Das Velhas River



**Figure 7**  
Concentration of As and Au in water and sediment samples of the Das Velhas River

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