

## METAL POLLUTION IN THE ENVIRONMENT OF MINAS GERAIS STATE – BRAZIL

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(Received 25 March 2004; accepted 6 June 2005)

**Abstract.** Intense mining activities in Minas Gerais State – Brazil brings out tons of waste to the environment. Considerable concentrations of toxic elements penetrate the soil, ground waters and rivers. This endangers the environment quality not only in the surrounding areas but also in ichthyofauna and in more distant areas of cattle raising and agricultural activities. After seasonal floods, veterinary clinic studies have shown that most animals raised in this region are affected by symptomatologic nervous diseases, still not clearly diagnosed, which suggests intoxication. These pathologies are mostly noted after floods. Instrumental Neutron Activation Analysis was applied to determine Al, As, Au, Ba, Br, Ca, Cl, Co, Cr, Cs, Cu, Fe, Hg, K, La, Mg, Mn, Na, Nd, Rb, Sb, Sc, Sm, Th and Zn in environmental samples. The obtained results show that the water and sediment contaminated with heavy metals and toxic elements from the Das Velhas River upstream basin, the mining region, carry contamination to the ichthyofauna and farming region within a distance of approximately 400 km.

**Keywords:** fish, forage, INAA, mining environment, sediment, trace elements, water

### 1. Introduction

Researches to study environmental pollution widely advanced mainly because of need for answers to various phenomena observed in natural waters and in the living beings that depend on them. Instrumental Neutron Activation Analysis has been widely employed for the determination of multielemental concentrations in the environment (Batley, 1989; Gunn and Host, 1980; Silva *et al.*, 2002; Stoppler and Marian, 1981). The diversity and abundance study of aquatic fauna species in control and mining affected areas, correlated with the physical and chemical factors of water and sediment, will serve as another environmental indicator of water quality resources in the Candiota region, Brazil, which receives important metallic loads originated from point (industrial and domestic effluents) and diffuse sources (coal mines and mining waste and ash disposal areas) and constitute the area of potential influence for investigation (Ortiz *et al.*, 1999).

Industrial waste from mining, chemical industries and metal processing is the major source of soil pollution because it contains a large variety of heavy metals. The environment is being contaminated with several metals from mine waste, agricultural materials in fertilizers (Cd, Zn, V), pesticides (As, Pb, Zn) and wood preservatives (As); metal corrosion (Zn, Cd), metallurgical industries (Ni, Si, Mn, Ag, As, Sb, etc.) and from other sources such as pigments and paint, additives, lubricants and medicines (Lepard, 1983).

The Iron Quadrangle, the central region of Minas Gerais State – Brazil, has important mineral reserves of Fe (the World's second largest iron ore producer), Mn, Cu, Sb, As, Au, Al, and U (Comig, 1974). The intense mining activities in Minas Gerais State throw out tons of waste in the open air, water, sediment and soil. The considerable accumulated concentrations of heavy metals and toxic elements penetrate the soil, underground waters and rivers, jeopardizing the environmental quality (Veado *et al.*, 2002). Other more distant regions of farming activities – crop production and cattle raising – are being affected by contaminated water and sediments due to the Das Velhas River frequent floods. This river originates in the mining region and flows throughout Minas Gerais State and into the São Francisco River (Veado, 1997; Veado *et al.*, 1997, 2000a, b).

## 2. Experimental Procedures

The Instrumental Neutron Activation Analysis – INAA was applied to determine concentrations of Al, As, Au, Ba, Br, Ca, Cl, Co, Cr, Cs, Cu, Fe, Hg, K, La, Mg, Mn, Na, Nd, Rb, Sb, Sc, Sm, Th and Zn in unpolluted areas and in the mining and farming region of the Das Velhas River basin. The samples analyzed were water, sediment, forage (root and stem+leaf) and fish (live and dead). Figure 1 shows the

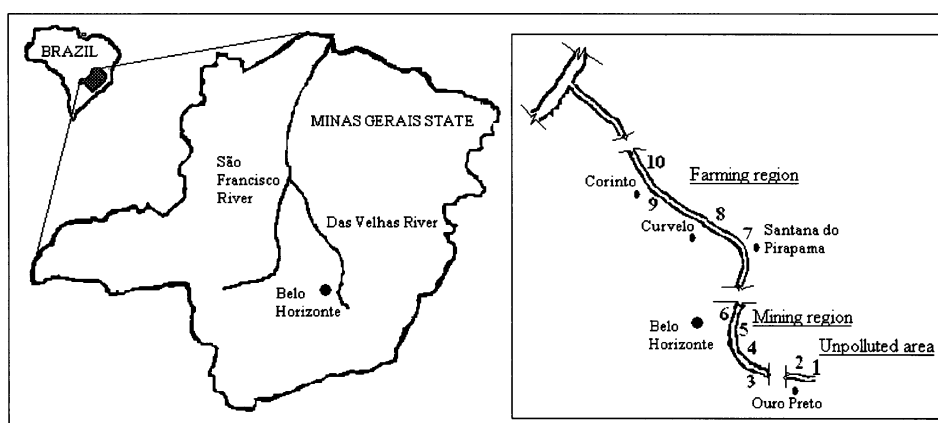


Figure 1. Location of study area and sample sites in the Das Velhas River.

location of the study area and sample sites. The sampling protocols are based on “Environmental Analytical Chemistry” by Fifield and Haines (1995).

The samples sites are located at points (see Figure 1):

1. Unpolluted areas (Das Velhas River Source): 1–2;
2. Mining Region: 3–6;
3. Farming Region (in the farms close to the banks of this river, periodically flooded): 7–10.

At each sample site, two samples of water and sediment were collected. Three fish and five forage samples were collected at sites in the farming region. Three replicates of all studied samples were analysed.

In addition, certified reference materials were analysed six times: Soil 7, Rye-Flour and Fish Tissue-407 from the International Atomic Energy Agency – IAEA and riverine water SLRS-3 from National Research Council of Canada, to confirm the data obtained in this paper.

The water samples were collected along the river, near to the river bank at a depth of 15 cm, put into 125 ml bottles (Nalgene) and stored at 4 °C. Temperature, pH and electrical conductivity were measured at the studied site. The average values were: temperature 25 °C, pH 7.2, electrical conductivity 30  $\mu$ S/cm. The water samples were acidified at the site with 5 drops of ultrapure nitric acid (pH ~ 2). Due to the effect of radiolysis, water samples had to be prepared in a solid form prior to irradiation for INAA and 30 ml samples were evaporated in polyethylene tubes for irradiation (evaporation of 1 ml for a day).

The sediment samples were collected in 20 ml polyethylene tubes, which represent a quantity of approximately 150 g and stored at a temperature of 4 °C. They were dried for a day at 60 °C prior to analysis. According to Dobbs and Grant (Dobbs and Grant, 1978) there is no problem for As volatilization at 60 °C. They also state that 13–27, 22–44, and 70–77% of arsenic is volatilized at temperatures of 400, 800, and 1000 °C, respectively. The temperature for Sb volatilization process is between 550 and 600 °C according to W.C. Butterman and J.F. Carlin (Butterman and Carlin, 2004). The sediment sample was poured into a cone shaped heap, divided into four equal parts. Two opposite quarters were combined and re-coned. The process was repeated until the amount of sample had been reduced to 0.30 g that required for analysis.

The fish muscle samples, *Pseudoplatystoma coruscans* (*surubim*); *Prochilodus* ssp. (*curimatá*) and *Salminus brasiliensis* (*dourados*), were frozen at –70 °C in an external freezer for 12 h, and lyophilized in freeze dried (Labconco® Benchtop Freeze Dry System). Aliquots of around 0.30 g were analysed. To calculate the results for the natural fish muscle the level values found for dry weight samples were multiplied by 0.25 (conversion factor of lost humidity).

The forage samples, *brachiaria* sp, were collected in farming activity areas with crop production and cattle raising affected by contaminated water and sediment

caused by the Das Velhas River frequent floods. Roots, stem+leaf were carefully collected and put into previously autoclave-sterilized bottles. The forage samples were carefully washed with distillate acetone and deionised water and then dried at 40 °C. Aliquots of around 0.50 g from each root, stem+leaf samples were weighed, homogenized and packed in polyethylene tubes for irradiation.

### 3. Analytical Method

Instrumental Neutron Activation Analysis – INAA is based on a simultaneous irradiation comparison between standard and studied samples in a nuclear reactor. The irradiation characteristics are chosen to determine the isotopes under the best conditions. In this work the INAA was applied using the TRIGA MARK I IPR – R1 reactor at the Nuclear Technology Development Center of the National Committee of Nuclear Energy (CDTN/CNEN), in Belo Horizonte city, Minas Gerais State, Brazil. At 100 kW of potency the flux of neutrons is  $6.6 \times 10^{11} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ . After the necessary decay time for the interfering radioisotopes, the gamma spectrometry was applied in the high-purity germanium (HPGe) detector “Canberra”, coupled to a 4096 high pulse analyser. The “Canberra” Gennie 2000 software was used to analyse the spectra. The isotopes nuclear characteristics in INAA, half-time, type of emission and gamma ray energies are well known (de Corte, 1986) and the “ $k_0$  parametric neutron activation analysis” ( $k_0$ PNA) was a complementary method used to determine multi-elements in a given sample (De Corte, 1986; Miguel, 2003).

### 4. Results and Discussion

The obtained results for the international reference material to validate the achieved results in this work were in quite a good agreement with the certified values as shown in Tables I, II, III and IV.

The average results obtained in water and sediment analyzed are shown in Table V. Figures 2–7 indicate the behavior of the studied element concentration along the course of the Das Velhas River: unpolluted area; mining region and farming region.

The average values ( $\sigma = 10\%$ ) for the analysed forage (dry weight) are shown in Table VI. Figure 2 indicates the average values of forage samples (root and stem+leaf).

The average values ( $\sigma = 10\%$ ) for live and dead fish are shown in Table VII. Figure 3 indicates the comparison of results between live and dead fish for the detected elements.

TABLE I  
Results obtained ( $\mu\text{g/g}$ ) by INAA soil reference Soil 7 (International Atomic Energy Agency, Vienna, Austria)

Element	Concentration measured $\pm$ standard deviation	Certified values (significance level: 0.05)
Al	$52000 \pm 800$	47000 <sup>a</sup> (44000–51000)
As	$13.3 \pm 1.3$	13.4 (12.5–14.2)
Ba	$141 \pm 20$	159 <sup>a</sup> (131–196)
Ce	$58 \pm 6$	61 (50–63)
Co	$8.6 \pm 0.8$	8.9 (8.4–10.1)
Cr	$63 \pm 6$	60 (49–74)
Cs	$5.5 \pm 0.5$	5.4 (4.9–6.4)
Cu	$10 \pm 2$	11 (9–13)
Fe	$25700 \pm 2000$	25700 <sup>a</sup> (25200–26300)
La	$28 \pm 3$	28 (27–29)
Mn	$680 \pm 60$	(631–660)
Na	$2300 \pm 20$	–
Rb	$61 \pm 6$	51 (47–56)
Sb	$1.9 \pm 0.2$	1.7 (1.4–1.8)
Sc	$9.4 \pm 0.9$	8.3 (6.9–9.0)
Zn	$108 \pm 10$	104 (101–113)
Th	$8.1 \pm 0.8$	8.2 (6.5–8.7)

<sup>a</sup>Non-certified value.

TABLE II  
Results obtained ( $\mu\text{g/g}$ ) by INAA vegetation reference RYE FLOUR (International Atomic Energy Agency, Vienna, Austria)

Element	Concentration measured $\pm$ standard deviation	Certified values $\pm$ confid. limits
Al	$3.8 \pm 0.4$	2.6 (1.1–4.1)
Ca	$150 \pm 10$	149 (139–159)
Co	$0.0030 \pm 0.0003$	0.0023 (0.0014–0.0032)
Cu	$0.98 \pm 0.05$	0.95 (0.76–1.14)
Fe	$4.2 \pm 0.6$	4.1 (3.4–4.8)
K	$1820 \pm 200$	1925 (1790–2060)
Mn	$2.10 \pm 0.03$	2.06 (1.94–2.18)
Sb	$0.0024 \pm 0.0010$	0.0026 (0.0006–0.0046)
Zn	$2.65 \pm 0.20$	2.53 (2.20–2.86)
Ca	$154 \pm 10$	149 (139–159)

TABLE III  
Results obtained ( $\mu\text{g/g}$ ) by INAA riverine water reference, SLRS-3 (National Research Council of Canada)

Element	Concentration measured $\pm$ standard deviation	Certified values $\pm$ confid. limits
Al	$29 \pm 1$	$29 \pm 1$
As	$0.67 \pm 0.07$	$0.72 \pm 0.05$
Ba	$14 \pm 2$	$13.4 \pm 0.6$
Ce	$0.33 \pm 0.03$	–
Co	$0.042 \pm 0.8$	$0.027 \pm 0.003$
Cr	$0.38 \pm 0.30$	$0.30 \pm 0.04$
Cs	$0.010 \pm 0.003$	–
Cu	$1.5 \pm 0.1$	$1.35 \pm 0.07$
Fe	$110 \pm 10$	$100 \pm 10$
La	$0.26 \pm 0.03$	–
Na	$2450 \pm 250$	$2300 \pm 200$
Rb	$1.75 \pm 0.18$	–
Sb	$0.17 \pm 0.02$	$0.12 \pm 0.01$
Sc	$0.0060 \pm 0.001$	–
Zn	$2.7 \pm 0.3$	$1.04 \pm 0.09$
Th	$0.017 \pm 0.002$	–

TABLE IV  
Results obtained ( $\mu\text{g/g}$ ) by INAA fish reference, Fish Tissue-407 (International Atomic Energy Agency, Vienna, Austria)

Element	Concentration measured $\pm$ standard deviation	Certified values $\pm$ confid. limits
Al	$12.0 \pm 1.0$	13.8 (12.4–15.2)
As	$12.5 \pm 0.4$	12.6 (12.3–12.9)
Co	$0.08 \pm 0.01$	0.10 (0.09–0.11)
Cr	$0.75 \pm 0.04$	0.73 (0.67–0.79)
Cu	$3.26 \pm 0.10$	3.28 (3.20–3.36)
Fe	$142 \pm 10$	146 (143–149)
Hg	$0.20 \pm 0.02$	0.222 (0.216–0.228)
K	$12.0 \pm 1.4$	13.1 (12.2–14.0)
Mg	$2.60 \pm 0.20$	2.72 (2.58–2.86)
Na	$13.2 \pm 0.1$	13.1 (12.4–13.8)
Zn	$67.4 \pm 0.6$	67.1 (66.3–67.9)

TABLE V  
Results obtained in water and sediment samples, in  $\mu\text{g/g}$

Element	Samples	Unpolluted area (1, 2)	Mining region (3, 4, 5, 6)	Farming region (7, 8, 9, 10)
Al	Water	$207 \pm 20$	$12100 \pm 1500$	$10200 \pm 1000$
	Sediment	$52000 \pm 5200$	$70000 \pm 6000$	$4000 \pm 400$
As	Water	$0.30 \pm 0.03$	$2.3 \pm 0.2$	$1.4 \pm 0.2$
	Sediment	$56 \pm 6$	$560 \pm 40$	$650 \pm 60$
Au	Water	<0.01	$0.05 \pm 0, 01$	n.d.
	Sediment	<0.01	$0.06 \pm 0, 01$	n.d.
Co	Water	$0.10 \pm 0.01$	$63 \pm 7$	$52 \pm 7$
	Sediment	$23 \pm 2$	$28 \pm 3$	$15 \pm 2$
Cr	Water	$2.1 \pm 0.4$	$15 \pm 2$	$10 \pm 2$
	Sediment	$63 \pm 6$	$330 \pm 30$	$260 \pm 20$
Cs	Water	$0.06 \pm 0.01$	$0.30 \pm 0.03$	$0.20 \pm 0.03$
	Sediment	<1.0	$0.40 \pm 0.04$	$0.40 \pm 0.04$
Cu	Water	$1.4 \pm 0.3$	$37 \pm 3$	$26 \pm 3$
	Sediment	$47 \pm 5$	$58 \pm 6$	$60 \pm 6$
Fe	Water	$640 \pm 60$	$5900 \pm 600$	$4300 \pm 400$
	Sediment	$55000 \pm 5000$	$160000 \pm 16000$	$115000 \pm 10000$
K	Water	$2000 \pm 200$	$3200 \pm 300$	$3000 \pm 300$
	Sediment	$30000 \pm 300$	$34200 \pm 3400$	$25700 \pm 2000$
La	Water	$1.0 \pm 0.1$	$58 \pm 6$	$45 \pm 6$
	Sediment	$45 \pm 5$	$95 \pm 9$	$56 \pm 6$
Mn	Water	$620 \pm 60$	$860 \pm 80$	$640 \pm 80$
	Sediment	$960 \pm 60$	$1460 \pm 140$	$1030 \pm 100$
Na	Water	$1500 \pm 500$	$1680 \pm 200$	$1500 \pm 200$
	Sediment	$2000 \pm 200$	$3600 \pm 160$	$3800 \pm 160$
Rb	Water	$2.3 \pm 0.3$	$7 \pm 1$	$5 \pm 1$
	Sediment	$92 \pm 9$	$130 \pm 20$	$116 \pm 35$
Sb	Water	$0.05 \pm 0.02$	$0.06 \pm 0.02$	$0.10 \pm 0.01$
	Sediment	$2.6 \pm 0.8$	$10 \pm 3$	$10 \pm 3$
Sc	Water	$2.2 \pm 0.2$	$3.4 \pm 0.4$	$3.2 \pm 0.4$
	Sediment	$15 \pm 2$	$30 \pm 3$	$20 \pm 3$
Th	Water	$0.08 \pm 0.01$	$1.4 \pm 0.3$	$0.50 \pm 0.04$
	Sediment	$16 \pm 2$	$32 \pm 3$	$20 \pm 2$

() Samples site.

#### 4.1. WATER AND SEDIMENT

Changing water pH can modify the physicochemical behavior of many elements. Thus, the concentrations of all transition metal elements are considerably higher in acid waters (Veado, 1997). The river waters in this particular region of Brazil known as the “Iron Quadrangle” are subject to perturbations of pH (7-2), induced by sulphide minerals, such as pyrite pyrrhonite and arsenopyrite affected by mining

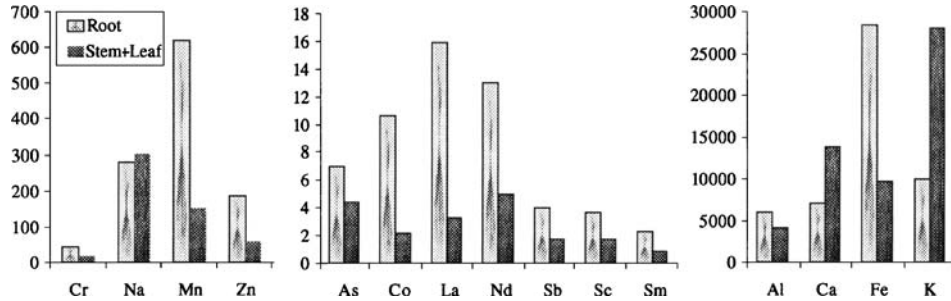


Figure 2. Comparison results between root and stem+leaf for the detected elements, in forage samples ( $\mu\text{g/g}$ ).

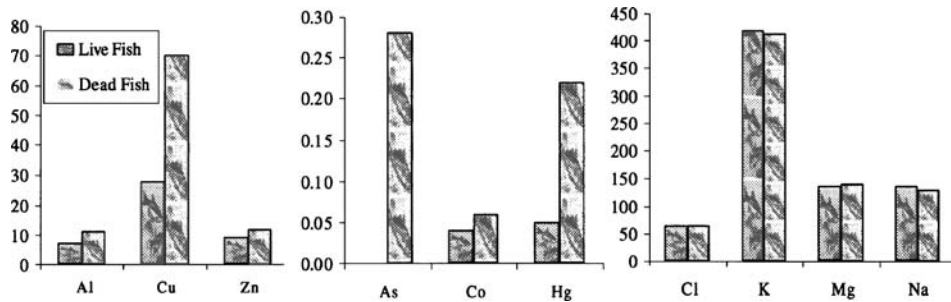


Figure 3. Comparison results between live and dead fish for the detected elements ( $\mu\text{g/g}$ ).

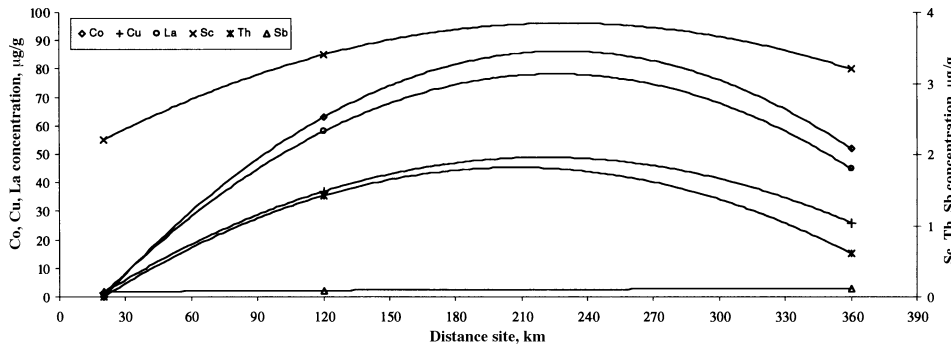


Figure 4. Tendency curve of concentration of Co, Cu, La, Sc, Th and Sb in water samples in unpolluted area, mining and farming region.

wastes and gold mines (Veado *et al.*, 2000a). The obtained results for the Das Velhas River water and sediment samples – mining companies region – show a high level ( $\mu\text{g/g}$ ) of contamination with the analyzed elements, mainly in the sediment samples. Other studies have already shown high levels of metals in water and sediment samples collected in the Das Velhas River upstream basin (Veado,



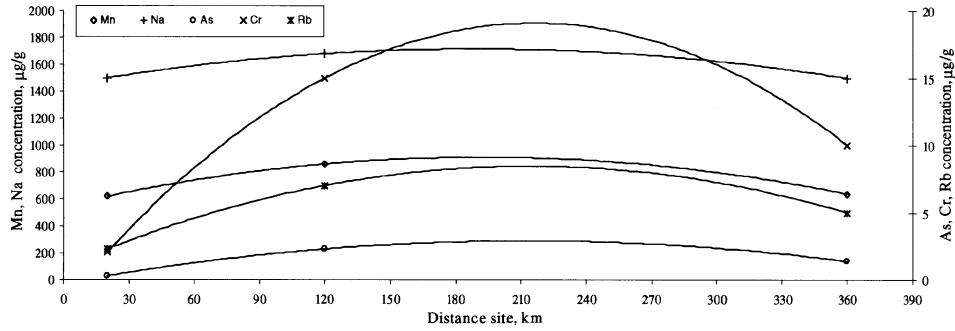


Figure 5. Tendency curve of concentration of Mn, Na, As, Cr and Rb in water samples in unpolluted area, mining and farming region.

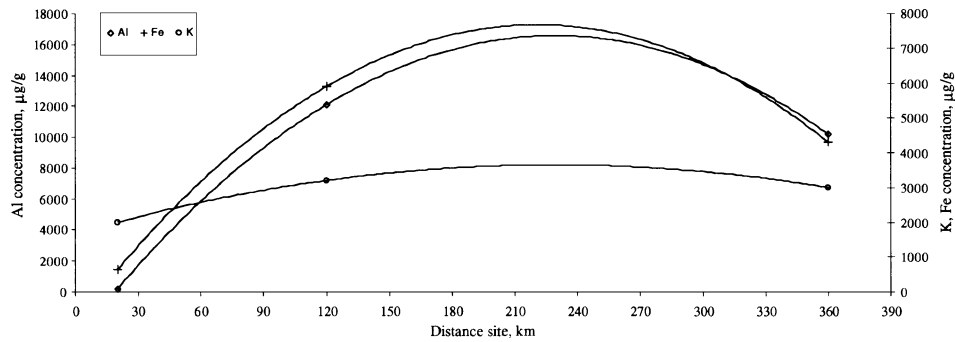


Figure 6. Tendency curve of concentration of Al, Fe and K in water samples in unpolluted area, mining and farming region.

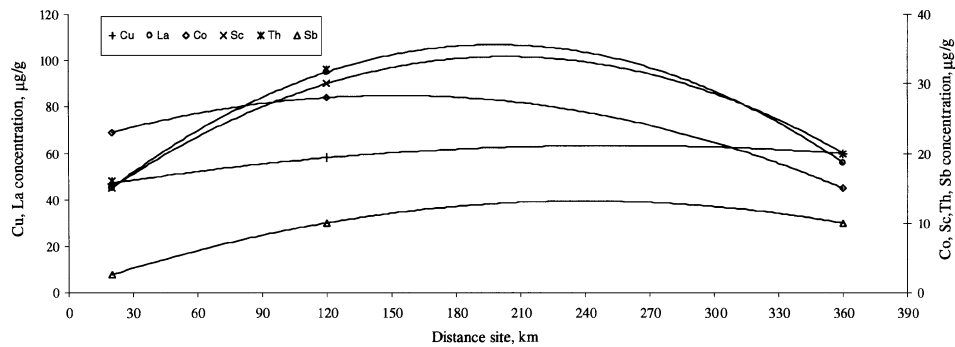


Figure 7. Tendency curve of concentration of Co, Cu, La, Sc, Th and Sb in sediment samples in unpolluted area, mining and farming region.

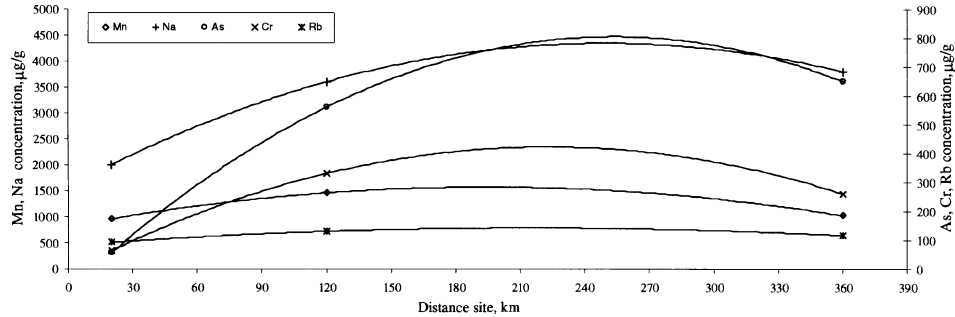


Figure 8. Tendency curve of concentration of Mn, Na, As, Cr and Rb in sediment samples in unpolluted area, mining and farming region.

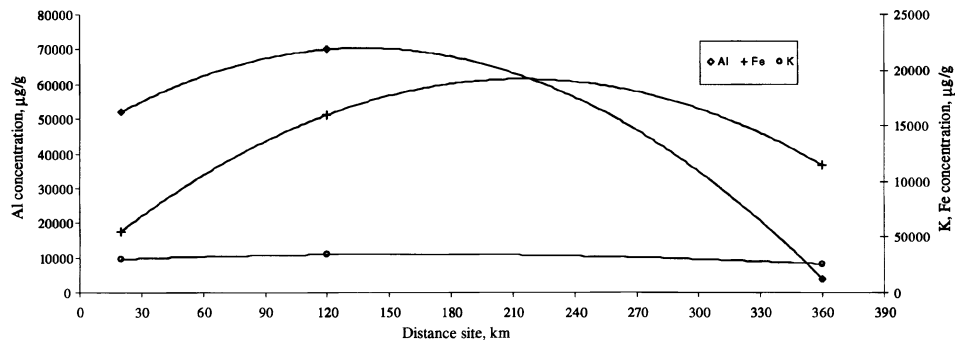


Figure 9. Tendency curve of concentration of Al, Fe and K in sediment samples in unpolluted area, mining and farming region.

1997; Veado *et al.*, 1997, 2000a, b). Figures 2–7 show the effect of the mining rejects on the more distant farming regions. As and Sb are present in abnormally high concentrations in water and sediment and are considered toxic elements, according to Förstner and Wittman. (Förstner and Wittmann, 1981). Antimony can be reduced and methylated by microorganisms in the aquatic environment, similar to arsenic, and become mobilized (Andreae *et al.*, 1983; Austin and Millward, 1988). This reaction is most likely to occur in reducing environments, such as in bed sediment. In the case of arsenic, this reaction may be mediated by fungi and bacteria (Beijer and Jernelov, 1986), but it is not known whether this is the case with antimony. Although Antimony is non-essential for life, it is found in biological specimens who have been exposed to industrial sources of the metal or who are being treated with drugs containing it. Antimony is used by industry as a bearing metal, which is added to tin as an alloy and to lead for batteries. Levels in the unexposed population are usually below  $0.005 \mu\text{g/g}$  (McKenzie and Smythe, 1988).

TABLE VI  
Results obtained in forage samples (roots and stem+leaf), in  $\mu\text{g/g}$ ,  $\sigma = 10\%$

Element	Sample	Normal value	Paper data
Al	Roots		6000
	Stem+Leaf	200 <sup>a</sup>	4200
As	Roots		7
	Stem+Leaf	0.2 <sup>b,c</sup>	4.4
Ca	Roots		7070
	Stem+Leaf	5000–24000 <sup>d</sup>	13750
Co	Roots		10.6
	Stem+Leaf	0.5 <sup>b,c</sup>	2.2
Cr	Roots		43
	Stem+Leaf	0.2 <sup>b,c</sup>	20
Cu	Roots		n.d.
	Stem+Leaf	5 <sup>a</sup>	n.d.
Fe	Roots		28400
	Stem+Leaf	100–700 <sup>b,c</sup>	9735
K	Roots		10000
	Stem+Leaf	14000 <sup>e</sup>	28000
La	Roots		15.9
	Stem+Leaf	0.085 <sup>e</sup>	3.3
Na	Roots		280
	Stem+Leaf	1200 <sup>e</sup>	302
Nd	Roots		13
	Stem+Leaf	–	5
Mn	Roots		620
	Stem+Leaf	630 <sup>b,c</sup>	153
Sb	Roots		4
	Stem+Leaf	0, 06 <sup>e</sup>	1.8
Sc	Roots		3.7
	Stem+Leaf	0.01 <sup>b,c</sup>	1.8
Sm	Roots		2.3
	Stem+Leaf	–	0.9
Zn	Roots		186
	Stem+Leaf	17–60 <sup>f</sup>	59

<sup>a</sup>Bowen, 1979; <sup>b</sup>Siegel, 1974; <sup>c</sup>Chappuis, 1981; <sup>d</sup>Jones *et al.*, 1970; <sup>e</sup>WHO <http://www.who.int/en/>; <sup>f</sup>McDowell, 1992.

#### 4.2. FORAGE

The chemical composition of plants is generally related to the elemental content of nutrient solutions. Absorption processes are very complex; the pathway of trace elements to plants is via the roots. The high level of Fe, found in the forage, indicates there was a great adsorption of this element that abounds in the water and sediment

TABLE VII  
Results obtained in natural fish muscle samples (live and dead fish) in  $\mu\text{g/g}$ ,  $\sigma = 10\%$

Element	Sample	Normal value <sup>a</sup>	Paper data
Al	Live fish	0.007–4.8	7.3
	Dead fish		10.9
As	Live fish	0.11–0.18	n.d.
	Dead fish		0.28
Cl	Live fish	–	65
	Dead fish		65
Cu	Live fish	0.12–0.28	2.8
	Dead fish		7
Co	Live fish		0.04
	Dead fish		0.06
Hg	Live fish	0.001–0.03	0.05
	Dead fish		0.22
K	Live fish	–	419
	Dead fish		412
Mg	Live fish	–	137
	Dead fish		141
Na	Live fish	–	137
	Dead fish		131
Zn	Live fish	4.8–12	9.3
	Dead fish		11.9

<sup>a</sup>Chemical safety information from intergovernmental organizations – <http://www.inchem.org/documents/ehc/ehc/ehc224.html>.

during the periodic floods. The Fe level in forage can be greatly affected by soil contamination (McDowell, 1992). According to Sousa *et al.*, several forage samples collected in Brazil show Fe concentrations of  $263 \mu\text{g/g}$  (Sousa *et al.*, 1981). It can also be noticed that the Fe concentration levels in the forage meet the minimum necessary requirement of  $50 \mu\text{g/g}$  of dry substance in cattle diet. Consequently there is no need to add Fe to the cattle diet. On the other hand, the obtained value is above the maximum tolerable concentration of  $1000 \mu\text{g/g}$  of dry matter (National Research Council; 1989). The average achieved results for the elements As, Co, Cr, Fe, Mn, and Sc are much higher than the ones indicated by Siegel (1974) and Chappuis (1991). Brazil's Ministry of Agriculture Standards (*Ministério da Agricultura e do Abastecimento*, 2000) concerning the necessary minerals for cattle are (in:  $\mu\text{g/g}$ ): K = 6000; Fe = 30; Mn = 20; Co = 0.25 and Zn = 40. The obtained results in forage samples show that the contaminated water and sediment with heavy metals and toxic elements from the Das Velhas River upstream basin, mining companies region, carry contamination to the farming region at a distance of approximately 400 km. After seasonable floods, clinic veterinary studies have

shown that symptomatologic nervous diseases, still not clearly diagnosed, which suggest intoxication, affect most animals raised in this region. These pathologies are mostly recorded after floods. In other studies the obtained results in different samples of cattle urine and feces, also suggest an influence of metals that are carried by the Das Velhas River basin upstream water (Veado *et al.*, 2002). Cobalt is a dietary essential for ruminants; rumen microorganisms incorporate Co into vitamin B12. A direct requirement for Co is found only in certain bacteria and algae; vitamin B12 is produced only by these microorganisms and not by higher plants or by animals. Cobalt concentration in soils and plants are highly variable, with plant Co concentration affected by many factors including soil Co concentration, fertilization plant species, plant growth, and soil factors. It has been reported that forage in healthy areas contains around  $0.1 \mu\text{g/g}$  of Co or more, on the average, as compared with  $0.004\text{--}0.007 \mu\text{g/g}$  for deficient areas. The maximum dietary tolerable level of Co for common livestock species is  $10 \mu\text{g/g}$  (McDowell, 1992). In this work the Cobalt results were  $10.6 \mu\text{g/g}$  (root) and  $2.2 \mu\text{g/g}$  (stem+leaf). The obtained Calcium results were within between normal values. Calcium is generally deficient in grains and abundant in most forage stacks. Calcium deficiencies are influenced by the availability of different sources and interrelationships with additional mineral elements or nutrients. Calcium in plants tissue may be rendered unavailable by forming insoluble salts with oxalic acid. The relatively low calcium levels in tropical forage and the high level of oxalic acid found in some tropical species suggest that calcium availability may limit forage quality (Jones *et al.*, 1970). Zinc values for forage range between  $17$  and  $60 \mu\text{g/g}$ . Zinc requirements for dairy cattle are  $30\text{--}40 \mu\text{g/g}$  (McDowell, 1992). The Zn results obtained in this work are in agreement with these normal value. The content of Cr in food product, flora and forage given by Schoroeder (1971) were lower than  $0.01 \mu\text{g/g}$ . The Cr results were highly exceeding this value. Chronic exposure to chromate dust has been correlated with the increase of lung cancer, and oral administration of  $50 \mu\text{g/g}$  of Cr has been associated with growth decrease and liver and kidney damage in experimental animals (Anderson, 1987). Chromium exposure is a common skin sensitizer in allergic eczema (Norseth, 1981). Food Products contain less than  $0.5 \mu\text{g/g}$  of As and rarely exceed  $1 \mu\text{g/g}$  on a fresh basis. Arsenic is not readily absorbed by plants from soils, even when the levels in the soils have been raised by continued use of arsenicals, but surface contamination of fodder with spray residues can increase arsenic concentration (Underwood, 1973).

#### 4.3. FISH

In this work the dead fish samples had higher concentration levels of Al, Cu, Zn, As, Co and Hg compared with the live fish samples. The effects of heavy metals on fish behaviour like, locomotion, breathing, learning, reproduction, and feeding and predator avoidance were discussed in a recent comprehensive review. One obvious defensive reaction against elevated metal concentrations is to move away and try

to find uncontaminated water nearby. There are several reports of this behavior in the literature in response to concentrations as low as  $0.0001 \mu\text{g/g}$  of Cu and  $0.0056 \mu\text{g/g}$  of Zn. Atchison *et al.* (1987) have studied the effects of Cu toxicity in the metabolic state of the fish. The experiment was carried out with fed and starved fish. After seven-day exposure to  $0.08 \mu\text{g/g}$  of Cu both fed and starved specimens had accumulated Cu in the gills, but only the starved fish accumulated the metal in the liver. If the fish were fed again after 7 days of starvation and contamination there was a decrease in the concentration of Cu in the liver but if starvation continued the Cu was retained. Ezoe *et al.* (2001) have determined the concentration of Al in fish tissues by ICP-MS. The amounts of some elements in particular tissues of *C. asiatica* living in acid environments were larger than those in fish living in neutral environments. The concentration of Al in fish liver was the most appropriate indicator of acidification. Metals, especially aluminum, are suspected to pollute the ecosystem and inhibit the metabolism of living things like fish. It can be said that gill, intestine, muscle, bone and skin are affected by the high concentration of trace metals in fish (Ezoe *et al.*, 2001). Freshwater fish and crustaceans generally contain much less As than their seawater counterparts (Underwood, 1977). The protection of freshwater and seawater aquatic life requires that the total recoverable trivalent inorganic arsenic should not exceed  $0.44$  and  $0.58 \mu\text{g/g}$ . To protect human health, the preferable level should be zero but the WHO – World Health Organization – and many national agencies have set admissible arsenic level of  $0.05 \mu\text{g/g}$  in drinking water (McKenzie and Smythe, 1988; Underwood, 1977). In this study the average values in live and dead fish samples for Na, Mg, Cl and K are about the same. The concentrations of Mg did not show remarkable differences with respect to the fish that live in the acid and neutral environments (Ezoe *et al.*, 2001). Many trace element contaminants entering the aquatic environment may have dramatic effects on the bioavailability and toxicity of the biological process. For example, Hg and As undergo biomethylation in the water-sediment interface, resulting in the production of more toxic species which are concentrated in fish (Fifield and Haines, 1995).

## 5. Conclusion

The multi-elemental analysis technique INAA was applied to determine the major as well as the trace elements concentrations and to show the contamination by heavy metals in water, sediments, forage and fish samples from mining and farming regions.

This pollution is credited to the tons of waste poured without treatment into the river from several mining companies and other clandestine human activities, such as gold-diggers, in the Iron Quadrangle region in Minas Gerais State, Brazil. Part of the waste has been accumulated in the water, sediment and bottom of the river and spread and caused serious environmental problems. During the period of floods, in farming regions hundreds of kilometers away, contamination is found in fish and

forage, reaching and harming both people and animals that live in the marginal region.

### Acknowledgments

This work was supported by CNPq – Conselho Nacional de Pesquisa Científica (National Council for Scientific Research) – Brazil, Profix-540861/01-4. The analyses were carried out at the Center of Nuclear Technology Development – National Committee of Nuclear Energy, in Belo Horizonte, Minas Gerais State of Brazil.

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