Nuclear Application in Studies of Environmental Pollution in Brazil

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The Steel Valley region in Minas Gerais State, Brazil, receives intense waste from anthropogenic activities: industries (steel, cellulose, mining activities); untreated domestic sewage and agricultural discharges. Concentrations of several inorganic elements were determined by Neutron Activation Analysis, NAA. This work presents results obtained from a biomonitor, terrestrial epiphytic community, of air quality, in Ipatinga, Santana do Paraíso, Coronel Fabriciano, Timóteo and Marliéria cities. The samples has been collected in January (rainy) and June (dry) 2007. The results indicate high concentrations of the elements Al, Au, Co, Cr, Cu, Fe, Hg, Mn, Mg, Cr, Zn, V and Th when compared with the others papers in recent literature. The biomonitor used in this work, has showed a excellent capacity for metals retention by atmospheric contamination. Surface water, border sediment, and fish muscle, Acará (*Geophagus Brasiliensis)* has been also analysed in Piracicaba River. For the Piracicaba River, high concentrations were found in sediment and water (Cr, Fe, Co, Zn, As, Al, Mn, V) and in fish muscle (As, Cr, Hg). The Results were compared to the maximum limits for metal set by 357/2005 of the National Environmental Council (CONAMA).

Keywords: *Neutron Activation Analysis, Mining Activities, Terrestrial Epiphytic Community, Air Pollution, Surface Water, Border Sediment, Fish Muscle, Piracicaba River Pollution, Steel Valley Region; Brazil.*

1. Introduction

Intense mining activities in Minas Gerais State, Brazil, bring out tons of waste to the environment. Considerable concentrations of toxic elements penetrate the air, soil, ground waters, and rivers. This endangers the environment not only in the surrounding areas but also in ichthyofauna. The "Vale do Aço" (literally Steel Valley) represents one of Brazil's most outstanding smelting resources. The Steel Valley is located between two confluent rivers (Piracicaba and Doce), which constitute, by their tributary streams, the water supply of its half a million inhabitants. Ore smelting may well be harmful to people causing slow but chronic poisoning. This region is home to the largest steel making complex in Latin America. Three of the five largest companies in Minas Gerais state, *Companhia Siderúrgica Belgo Mineira*, *Arcelor Mittal (ACESITA)* and *USIMINAS*, are located there. Furthermore, we can find the largest open-pit mine in the world operated by the *Companhia Vale do Rio Doce*. These industrial conglomerates have an important role in Brazilian exports of iron ore, steel, and cellulose (*Cenibra*). Metal smelting is considered one of the most important anthropogenic sources of heavy metal pollution to the environment worldwide [1, 2]. This has been attributed to emissions from both smelter stacks and dispersive sources such as stockpiles and waste heaps [3]. Metal is transferred to environmental compartments, such as air; river water, sediment, and fish. It can also eventually enter

the human body through the food chain or direct ingestion, which will pose a threat to human health. Many studies have reported high levels of Al, As, Fe, Cr, Co, Hg, Zn, Cu, Sb, Th and U in environmental samples in hydrographic basins and lakes in Brazil [4, 5, 6, 7, 8].

2. Material and Method

The biomonitor, terrestrial epiphytic community samples, has been collected in the surrounding areas of the main industries in the cities of Ipatinga, Timóteo, Coronel Fabriciano , Santana do Paraíso and Marliéria, as illustrated in the figures 1. In the City of Marliéria the samples has been collected in the State Park of the Doce River, PERD, area of ambient preservation, distant of the urban centers of approximately 20 km.The Piracicaba River, Minas Gerais State, is located within the medium Doce River hydrographic basin which receives intense waste from anthropogenic activities: industries (steel, cellulose, Ore mining); untreated domestic sewage and agricultural discharges (agro toxics, fertilizers, organic materials). Sites along the river close to mining and metallurgic activities were chosen. The sampling sites are indicated in Figure 2. They are located in different cities: P_1 (Fonseca); P_2 (Rio Piracicaba); P_3 (Nova Era) and P_4 (Ipatinga).

2.1 Sampling and sample preparation

Biomonitor: terrestrial epiphytic community: The terrestrial epiphytic community samples has been collected in trees Oiti (*Licania tomentosa*) and Angico (*Piptadenia rígida*), very common in studied region. The samples were collected in 17 points and two weather season: January (rainy) and June (dry) of 2007. The samples has been removed of the trees trunks in a height of approximately 1,80 m, collected in 5,0 cm^2 using a stainless steel spatula. A surgical glove was used for to prevent contamination. After the samples has been conditioned in polystyrene bottles and stored at 4 ºC. In Laboratory they has been opened, washed with bidistilled water, dried at 40 °C, triturated and aliquot a representative one of approx. 0,30 g has been weighed for the analyses.

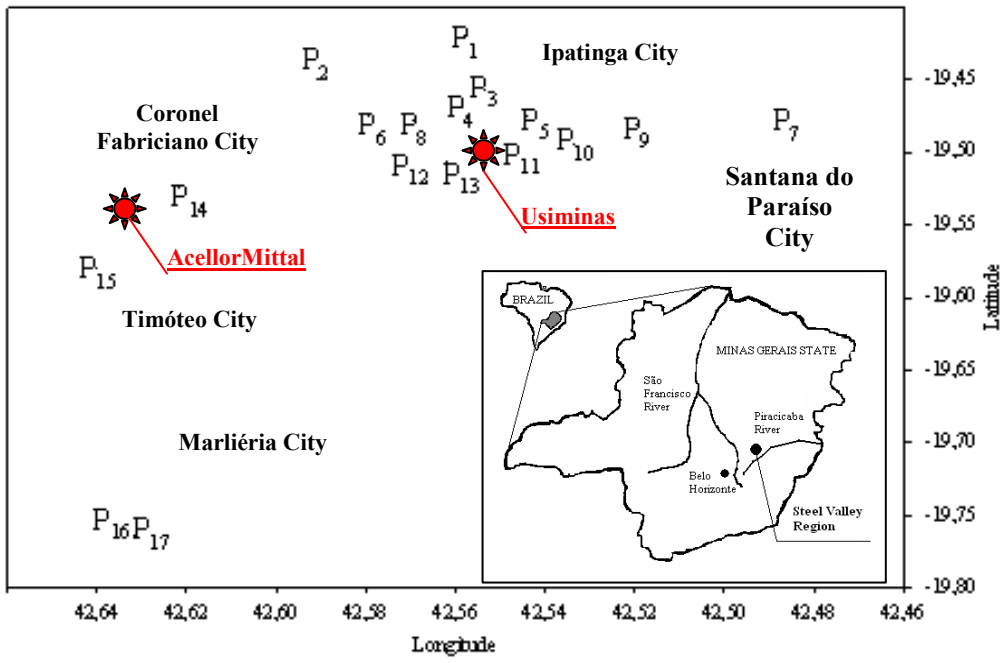

Fig. 1 Biomonitor, terrestrial epiphytic community, sampling sites.

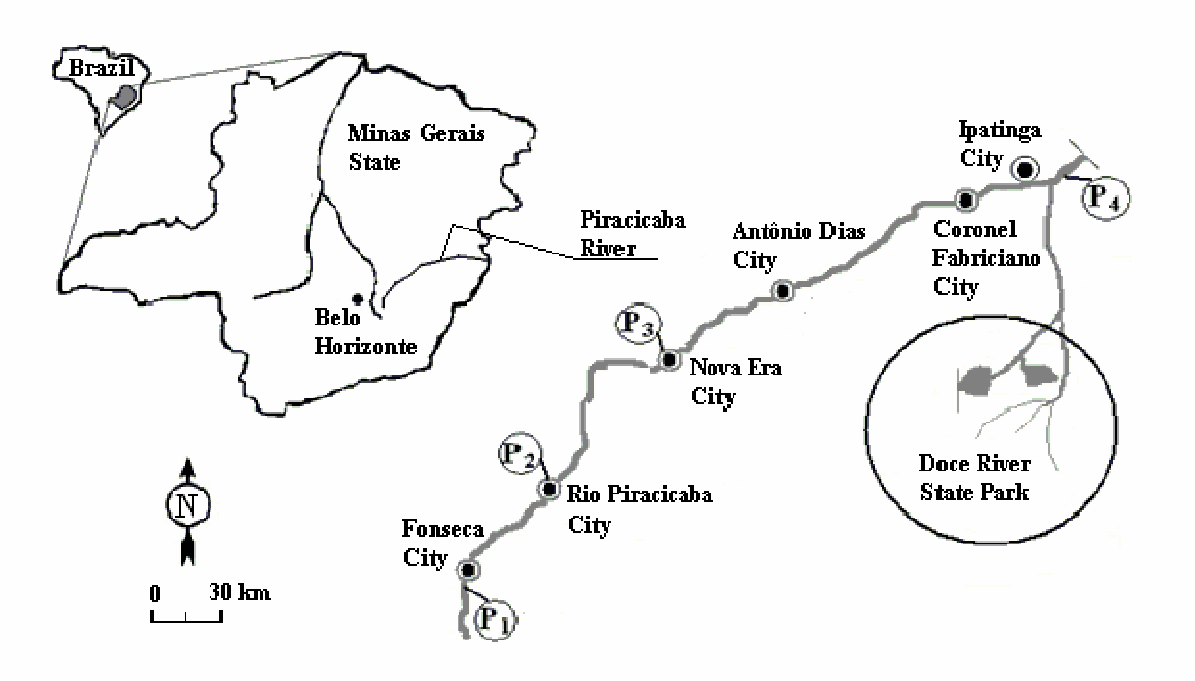

Fig. 2 Piracicaba River sampling sites.

Piracicaba River: The samples were collected in two different seasons of 2006, January (summer) and August (winter). In each sample site, three samples of surface water, border sediment and twenty samples of fish muscle (Acará – *Geophagus Brasiliensis*) were collected. The water samples were collected along the river, near the river bank at a depth of 15 cm, put into 125 ml bottles (Nalgene), acidified at the site with 5 drops of suprapur nitric acid (HNO_3, Merck). The samples were transport and stored at 4° C in a refrigerator until they were analysed. The aqueous phase was separated by centrifugation (3000 rpm for 5 min). Due to the effect of radiolysis, water samples had to be prepared in a solid form prior to irradiation for Neutron Activation Analysis, NAA. Therefore 30 ml of the water samples in aqueous phase were evaporated at 40 °C in polyethylene tubes (evaporation of 5 ml 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 five days at 40 °C prior to analysis. The 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 the sample had been reduced to 0.30 g required for analysis. The fish muscle samples of specimen Acará, *Geophagus Brasiliensis,* 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.

2.2 Neutron Activation Analysis – NAA

In this work the NAA was applied using the TRIGA MARK I IPR – R1 reactor at the Nuclear Technology Development Center of the National Council of Nuclear Energy (CDTN/CNEN), in Belo Horizonte, capital, Minas Gerais State, Brazil. At 100 kW the flux of neutrons is 6.6 10^{11} n. cm^{-2}. s^{-1}. The irradiation and measuring conditions were chosen as a function of the samples analyzed and the elements determined. Several measurements were made for each sample after increasing cooling times: Short Half Life (Al, Mn, V) 5 minutes of irradiations; 2 to 10 minutes radiation decay; counting geometry 20 cm for sediment and 10 cm for biomonitor, water and fish muscle. Medium Half Life (As, Au, Na) and Long Half Life (Co, Cr, Cs, Fe, Hg, Th, Zn): 8 hours of irradiation, 2 to 10 days to radiation decay; counting geometry 10 cm for all studied samples. Counting times from 600 to 30,000 seconds were used, based on the half-lives or activities of the radioisotopes considered. The gamma-radioactivity was measured with a 100 cm^3 coaxial ultra-pure germanium crystal coupled to a 4096 pulse-height analyzer. The "Canberra" Gennie 2000 software was used to analyse the spectra. gold

monitors were used for short irradiations and sodium monitors for long irradiations. The concentrations were calculated using K0LABSUE software, written in Turbo adapted to the conditions of both the nuclear reactor and the radiochemistry laboratory in CDTN/CNEN [9].

3. Results and Discussion

Biomonitor terrestrial epiphytic community: The average results obtained is shown in Table 1. For to compare the results obtained in this work, analyses of the terrestrial epiphytic community samples have been carried out in the *Piedade* Mountain (1751m), located in the Caeté city, at a distance of 100km. The results are also compared with recent papers [10,11].

Table 1 The average results obtained in terrestrial epiphytic community samples (σ=5%), $\mu g.g^{-1}$

	2007	Al	As	Au	Cr	Cu	Fe	Hg	Mg	Mn	Na	Th	V	Zn
P_1	rainy	37364	-	-	41	70	24224	-	2762	820	617	14	17	156
	dry	10050	0.6	0.02	15	32	8269	-	3610	343	461	3	13	97
P_2	rainy	22703	-	-	40	66	17067	-	2936	498	1587	5	19	-
	dry	13449	1.6	-	39	59	8432	-	2039	306	67	3	13	96
P_3	rainy	14444	-	-	8	-	11752	-	2183	550	803	1	10	139
	dry	58495	2.7	-	63	37	32867	-	8919	1129	738	26	30	258
P_4	rainy	9591	-	-	8	-	9021	-	3479	570	198	-	11	179
	dry	16120	1.1	0.02	42	7	16262	-	5728	530	783	5	16	-
P_5	rainy	15131	2,5	0.02	68	35	36518	-	4770	970	836	2	22	-
	dry	11204	1.8	0.01	2	23	15500	-	3539	785	487	-	15	261
P_6	rainy	23453	-	-	31	-	17359	-	3856	1300	899	4	20	-
	dry	14937	2.0	-	154	57	37759	1.5	2744	1188	979	5	26	200
P_7	rainy	18451	6,2	-	47	79	19498	-	6568	1280	1508	3	19	256
	dry	13192	5.7	-	42	61	12437	-	4303	934	1004	2	14	-
P_8	rainy	5041	-	0.01	30	14	8796	-	1440	350	378	1	8	-
	dry	8916	0.9	0.02	2	18	8000	-	2693	708	366	-	13	248
P_9	rainy	6284	-	-	10	21	12245	-	2100	520	535	1	11	208
	dried	13884	1.8	0.04	62	34	33417	-	3188	705	694	4	17	127
P_{10}	rainy	10433	1.9	0.02	12	81	23354	-	1012	640	680	-	15	198
	dry	10274	1.7	0.01	79	16	73500	0.5	1171	836	342	2	20	104
P_{11}	rainy	3712	-	0.05	21	26	11932	-	2595	732	308	-	21	249
	dry	15996	1.1	0.02	51	56	10810	-	4684	472	565	3	13	365
P_{12}	rainy	18456	-	0.14	86	106	41442	6.8	2363	2160	1751	15	31	523
	dry	13316	1.5	0.05	180	61	17154	1.4	4878	1566	1037	4	29	250
P_{13}	rainy	10770	-	0.03	-	55	20000	-	1940	360	703	-	8	-
	dry	9456	1.5	-	85	23	42747	-	1485	982	461	-	23	238
P_{14}	rainy	27815	-	-	273	-	21437	-	5791	1030	1223	2	22	226
	dry	32487	2.3	-	493	49	28519	-	8711	1264	449	8	27	168
P_{15}	rainy	28846	-	-	167	35	21651	-	4215	630	1586	4	42	164
	dry	17751	0.9	0.01	128	53	14242	-	2877	378	852	5	28	191
P_{16}	rainy	3048	-	0.39	7	-	2407	0.5	1682	740	85	-	3	-
	dry	20827	0.4	0.01	36	68	17267	1.7	1195	872	337	3	40	124
P_{17}	rainy	15010	-	0.40	56	15	13299	-	823	150	189	-	32	-
	dry	95113	1.5	0.13	58	99	36500	5.6	7875	600	946	33	71	98
*	-	1400	0.4	-	11	-	3300	0.2	590	139	56	0.2	2	85
[10]	-	394	0.15	-	0.9	-	503	0.1	-	-	-	-	1	33
[11]	-	-	-	1.9	-	32	-	-	-	-	-	-	4	25

***** *Piedade* Mountain (1751 m).

Piracicaba River: The average results obtained in surface water, border sediment and muscle fish (σ=5%) analyzed is shown in Table 2. For the water, and muscle fish samples the results were compared with the maximum limits permitted (MLP) by Brazilian Environmental Council (CONAMA) [12]. For the water samples the concentrations of Al, As, Cr, Fe, Mn, V and Zn in all sampling sites were higher than the limit values for "water class 3", according to Resolution n. 357 of 17/03/2005. The much more important result was the level of Hg in Acará fish in P_1: 1.8 μg g^{-1} (MLP: 0.50μg g^{-1}). In sediment samples the values for Cr concentration were between 126 μg g^{-1} in P_3 and 447 μg g^{-1} in P_4 MLP: 50 μg g^{-1} in non contaminated sediments according Bryan & Langston [13]. The levels of heavy metals were above the limits which can affect the animals and human health. Mercury cause damage to the brain and chromium is carcinogenic.

Table 2 The average results obtained in surface water, border sediment and muscle fish (σ=5%), $\mu g.g^{-1}$

		P_1	P_2	P_3	P_4	MLF**
Al	Sediment	*	*	*	*	-
	Water	98	189	102	269	0.2
	Fish	-	-	-	-	-
As	Sediment	35	10	6.5	3.6	
	Water	4.9	0.6	0.3	1.5	0.03
	Fish	2.8	1.3	1.8	1.9	1.00
Co	Sediment	1016	588	789	540	
	Water	-	0.8	0.3	0.4	0.2
	Fish	-	-	-	-	-
Cr	Sediment	447	202	126	173	-
	Water	0.8	0.4	0.2	1.7	0.05
	Fish	1.8	1.0	0.7	4.1	0.10
Fe	Sediment	552984	461966	81966	194987	-
	Water	478	1609	577	705	5.0
	Fish	-	-	-	-	-
Hg	Sediment	-	-	-	-	-
	Water	-	-	-	-	-
	Fish	1.8	1.0	0.7	0.8	0.50
Na	Sediment	264	599	1760	1868	
	Water	3114	2108	2764	2433	-
	Fish	-	-	-	-	-
Th	Sediment	7.9	11	11	50	
	Water	-	-	-	39	-
	Fish	-	-	-	-	-
V	Sediment	*	*	*	*	-
	Water	4.0	5.0	4.52	4.2	0.1
	Fish	-	-	-	-	-
Zn	Sediment	50	60	128	80	-
	Water	24	34	17	14	5.0
	Fish	76	55	50	43	50

*Not Analysed, ** CONAMA Resolution n. 357 of 17/03/2005 [12]

4. Conclusion

The nuclear technique, neutron activation analysis, is a very important tool to determine the levels of concentrations of several metals in mining region at Minas Gerais state, Brazil. The different samples has been studied and showed the high levels of pollution in air and river, in steel valley region.

Acknowledgements

This work was supported by CNPq – National Council for Scientific Research – Brazil. The analyses were carried out at the Center of Nuclear Technology Development – National Committee of Nuclear Energy, in Belo Horizonte city, Minas Gerais State of Brazil.

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