Inductively Coupled Plasma-Mass Spectrometry (HR-ICP-MS) as a Tool for Environment Biomonitoring

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Recebido em 12 de Março, 2003. Versão final recebida em 04 de Setembro, 2003.

High Resolution Inductively Coupled Mass Spectrometry (HR-ICP-MS) was used to determine elements in sediment, soil, forage (*Brachiaria sp)*, cattle feces and milk samples collected in a cattle breeding and agricultural zone in Curvelo city, Minas Gerais state, in Brazil. The samples were collected on the farms close to the banks of the Das Velhas River where there is periodic flood during reasonable rains. Clinic veterinary studies have shown that most animals raised in the region are affected by symptomalogic nervous diseases, still not clearly diagnosed, that suggest intoxication. The pathologies are mostly registered after floods. These nervous are due the highly concentrations of As, Cr, Co, and Fe, found in the forage samples (*Brachiaria sp)*.

A Espectrometria de Massa de Alta resolução Associada a uma fonte de Plasma Induzido (HR-ICP-MS) foi utilizada para determinar elementos em amostra de sedimentos, solos, gramineas (*Brachiaria sp)*, fezes de gado e leite. Estas amostras foram coletadas, durante o período de cheias, em fazendas da região de Curvelo - Minas Gerais - Brasil, situadas as margens do rio Das Velhas. A maioria dos animais desta região são afetados por doenças nervosas ainda não claramente diagnosticadas. Essas patologias foram observadas, na sua maioria, após o período de cheias. Estas doenças nervosas podem estar ligadas as elevadas concentrações de As, Cr, Co e Fe encontradas nas *Brachiaria sp*.

1 Introduction

Researches aiming to study environmental pollution have greatly advanced mainly because of the need for answers to various phenomena observed in natural waters, in the environment around them and in the living beings that depend on them.

According to Nriagu and Pacyna [1] millions of tons of various metals are extracted from the soil each year and then scattered all over a part of the terrestrial biosphere.

The increasing circulation of toxic metals through the soil, water and atmosphere and their ivenitable presence in men's and animals' foo chain jeopardize future generations' health up to a still unknown extent.

In the region close to the middle course and downstream the Das Velhas River basin there is a concentration of agricultural production and cattle breeding. After river overflowing and floods in the study area, both physicists and veterinarians have already registered deaths of animals whose various symptoms suggest intoxication. However it has not been possible yet to accurately determine the cause of such accidents. The clinical signs of intoxication cauded by metals are, most frequently, vomit, diarrhea, restlessness, higher cardiac and respiratory frequency, failure of motor coodination followed by depression and death.

Animal intoxication can be caused by several factors. Contamination of the soil, the sediment, the forage, industrial materials and foundry waste are some of the factors that may be related to the phenomena studies in the present experiment. The deaths of the animals raised in seasonable flooded areas, which receive several metal elements in the rainy season along the Das Velhas River.

This study is part of an ongoing investigation of inorganic elements in sediments, soils, forages, cattle feces, and milks along the middle course and downstream the Das Velhas River basin.

The proposed technique to analyze the matrices studied was the inductively coupled plasma mass spectrometry to double focusing magnetic sector (HR-ICP-MS). Advantages and drawbacks of this method are indeed dependent on nature of the material analyzed and on the elements to be determined. Therefore the ICP-MS is an adequate technique to determine the levels of trace elements due to its high sensibility and selectivity.

Other studies have already shown high levels of metals in water and sediment samples collected upstream the Das Velhas River basin. Critical sites showed high concentrations of As, Fe, Cr, Co, Au among others [2-5].

2 Materials and Methods

Environmental studies require determination of the total content of the sample and also the more soluble part. Solid samples must be dissolved prior to ICP-MS analysis, which may be the most difficult part of the analysis. Losses and contamination have to be avoided. Many methods for the total dissolution of sediments, soils and plants have been published [6].

Sediment and soil samples were collected in sterilin polystyrene tubes stored at 4°C, heated at 60° and homogenized before preparation. Forage (*(Brachiaria sp)*: forage roots and leaves were carefully collected and put in bottles previously sterilized in autoclave. On January, 2002, for each point of each matriz, six samples were collected in different sites close to the banks of the Das Velhas River, roots, leaves and stalks were dried at 40°C and then ground and homogenized. The leaves and stalks were ground and homogenized together since they are eaten together [7]. Cattle feces and milk were collected from 4 cows. The milk samples were lyophilized before prepararing.

All samples were digested in microwave in open PTFE vessels (Microdigest A301, Prolabo, Frence). Nitric acid, hydrogen peroxide and hydrofluoric acid were added successively (5 ml each). The samples were reduced to dryness, and then taken up in 3 ml nitric acid. They were again evaporated to dryness and taken up in 10 ml water. The digestion solution was poured into polyethylene flasks that had been washed with 2% nitric acid. The PTFE vessels were cleaned (boiling 1 + 1 HNO_3+H_2O) between samples. In addition to the samples studied, six aliquots of certified reference material, “Soil 7”, from the International Atomic Energy Agency - IAEA, were analyzed.

The Inductively Coupled Plasma sector type mass spectrometer (HR-ICP-MS) used to analyze all samples was a FINNIGAN ELEMENT, Service Central d’Analyses, Lyon, France. It has been designed for multi-element analysis using three fixed resolutions. Its combination of sensitivity and very low background noise makes it particularly suitable for elemental trace and ultra trace analysis. The mass range of the double focusing sector field analyzer extends from 5 to 260 Daltons. The system has a reserve a Nier-Jonson geotry i.e. the magnetid field is located in front of the toroidal electric field, in order to obtain optimum abundance sensitivity. The High-Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS) which can analyze compounds, especially trace elements, in many different matrices. It combines the effective ion generation properties of an ICP-MS and the capabilities of a mass spectrometer, i.e. the multi-element capability, the large dynamic range, the extremely low detection limits and the ability to determine isotope ratios. The instrument settings and operating conditions are shown in Table 1.

TABLE 1. HR-ICP-MS operating conditions

Instrument Accelerating Voltage Magnetic Sector	ELEMENT Finnigan MAT 8 kV Field Magnet and the Flight tube
Plasma Plasma gas	 Argon
Fonvard/Reflected power	1350 W/<2W
Nebulizer gas flow	0.861 $\min^{-1}$
Cooland gas flow	141 $\min^{-1}$
Spray chamber water-cooled	at 6°C
Mass Spectrometer Interface vacuum	 2.0 hPa
Intermediate vacuum	$< 10^{-4}$ Pa
Analyser vacuum Resolution	$< 10^{-6}$ hPa 300 - 7500
Acquisition parameters Full quantitative scan mode	
Dwell time	200ns
replicates	3
Collecting modes Analog Counting	 $10^4 - 10^{10}$ c.p.s $> 10^6$ c.p.s

TABLE 2. Results for Soil 7-IAEA (in μg.g^{-1})

Element	Concentrations measured ± standard deviation	Certified concentrations (conf limits range)
Al	66550 ± 2000	47000*(44000-5 1000)
As	14.8 ± 1.2	13.4(12.5-14.2)
Ba	138 ± 2	159*(131-196)
Cd	1.6 ± 0.2	1.3*(1.1-2.7)
Co	10.5 ± 1.0	8.9(8.4-10.1)
Cr	63 ± 2	60(49-74)
Cu	13 ± 2	11(9-13)
Fe	25000 ± 1000	25700*(25200-26300)
La	28 ± 1	28(27-29)
Mg	11900 ± 500	11300*(11000-11800)
Pb	59 ± 2	60(55-71)
Rb	53 ± 1	51(47-56)
Sb	1.6 ± 0.1	1.7(1.4-1.8)
Sc	8.7 ± 0.4	8.3(6.9-9.0)
Th	8.0 ± 0.2	8.2(6.5-8.7)

*Information values only.

3 Results and Discussion

Table 2 shows the results obtained for the elements of interest in the Certified Reference Material, Soil 7 - International Atomic Energy Agency - IAEA. The results obtained in this study were in agreement with certified values.

Table 3 shows the average concentrations of the elements detected in six samples of sediment, soil, forage, cattle feces and milk.

Sediment and soil: The results obtained in sediment and soil samples indicate a high contamination, in the samples of the Das Velhas River, in μgg^{-1}: As=390 and 650; Au$\leq$0.60; Cr=330 and 260; Fe=160000 and 115000; La=95 and 56; Sb=10; Sc=30 and 20; Th=32 and 20. This level of contamination was also shown by [7-10] because Das Velhas water river carried the waste from industries and mining companies for more than a century.

Forage (Brachiaria sp): According to [5] cattle's daily need is: 800 μgg^{-1} sodium for beef cattle, 1800 μgg^{-1} for dairy cattle; 2500 μgg^{-1} chlorine for beef and 2000 μgg^{-1} for dairy cattle. Sodium deficiency in forage is quite frequent in tropical countries. Only 14-30% was found in Brazil. During this present study around 9225 μgg^{-1} of Na and 2650 μgg^{-1} of Cl were found in forage analyzed. The sodium deficiency in cattle food was not found where samples were collected. Generally plants have a high concentration of potassium. Its content in forage depends on the plant unitary, its species, fertilizers and on the environment. Maturity is probably the main determiner of potassium content in forage. Forage usually has more K than ruminants need. Being a highly soluble element, the content found in forage may vary in the dry and rainy seasons. Potassium content found in *Brachiaria sp* forage in the present study, 112915 μgg^{-1}, is higher than those found in sediment and soil samples, respectively 34200 μgg^{-1} and 25700 μgg^{-1}. This concentration is also higher than the number determined by [11].

The concentrations of trace elements As, Co, Cr, Fe, Cu, Mn and Sc were higher than the basal values for vegetables determined by [11]. This suggests a great deal of pollutants coming from upstream Das Velhas River and possibly because of the abusive use of agricultural pollutants, [5] recommends the following contents for ruminants: 0.1 μgg^{-1} Co, 25 μgg^{-1} Mn, and 50 μgg^{-1} Fe.

Cattle feces: The results of Al and Fe concentrations in cattle feces in higher than those found in forage samples. The Aluminum is easily absorbed by the cattle and soon excreted mainly in the urine and feces.

In this study the As concentration is significant, 82 μgg^{-1}. Arsenic poisoning is an acute clinic syndrome that may kill fast. The clinical signs of acute intoxication are cramps, vomit, diarrhea, depression and death [12].

For [3] Al, Cr and Mn are poorly absorbed by the gut. Fecal results can give very useful information in suspected cases of dietary exposure.

Cattle milh: Br, Cl, K, Mn and Na concentratios found in the milk samples are the expected values for healthy animals and Fe and As concentrations are higher than the value determined by [4,5].

4 Conclusion

The results obtained in different samples of sediment, soil, forage, cattle feces suggest that there is an influence of metals that are carried by the Das Velhas River basin upstream water. The Inductively Coupled Plasma-Mass Spectrometry (HR-ICP-MS) was an adequate technique to determine the various elements in sediment, soil, forage, cattle feces and milk samples. Finally, results for soil 7, IAEA standard

TABLE 3. Results for Sediment, Soil, Forage, Cattle feces and Milk samples (in μg.g^{-1})

Element	Sediment	Soil	Forage	Cattle Feces	Cattle milk
Al	6000 ± 600	4000 ± 400	5916 ± 500 (500-4000)	28230 ± 2800	-
As	390 ± 40	650 ± 60	58.9 ± 6.0 (0.2)	82 ± 9	3.51 ± 0.3 (0.005-0.07)*
Au	0.060 ± 0.0006	-	8.3 ± 0.8	7.6 ± 0.8	-
Br	5.0 ± 0.5	4.0 ± 0.4	7.0 ± 0.7	70 ± 7	12 ± 2
Cl	–	– (60-7000)	2650 ± 260	– (900-1270)	2000 ± 100
Ba			292 ± 30 (15)	686 ± 90	10.1 ± 1.0 (10)*
Cd	-	-	1.3 ± 0.13	2.2 ± 0.3	1.0 ± 0.1
Co	28 ± 3	15 ± 2	2.1 ± 0.2 (0.5)	11 ± 1.0	–
Cr	330 ± 30	260 ± 20	44 ± 3 (0.1-0.2)	84.7 ± 9.0	0.55 ± 0.05
Cu			107 ± 10 (0.1-0.2)	231 ± 20	14 ± 1.4
Fe	160000 ± 16000	11500 ± 10000	8700 ± 850 (100-700)	25892 ± 2000	45 ± 4.0 (02-0.6)*
K	34200 ± 3400	25700 ± 2000	112915 ± 10000 (4700-25800)	53284 ± 4900	82220 ± 8000 (1130-1710)*
La	95 ± 9	56 ± 6	6.5 ± 0.6	44 ± 4.0	1.6 ± 0.16
Mg			39884 ± 3900	41992 ± 4000	6763 ± 670
Mn	1460 ± 140	1030 ± 100	987613 ± 90000	3072 ± 300	3.76 ± 0.4 (0.02)*
Na	3600 ± 160	3800 ± 160	9225 ± 90 (4700-25800)	6813 ± 500	17567 ± 1700 (450-750)*
Pb			19 ± 1.9	16 ± 1.6	10.4 ± 1.0
Rb	130 ± 20	–	436 ± 44	188 ± 18	–
Sb	10 ± 3	10 ± 3	1.8 ± 0.18	3.16 ± 0.3	1.15 ± 0.1
Sc	30 ± 3	20 ± 3	3.2 ± 0.3 (0.01)	8.6 ± 0.8	2.78 ± 0.3
Th	32 ± 3	20 ± 2	2.2 ± 0.2	11.4 ± 1.0	1.45 ± 0.15

() Expected normal values for [5] and [11];
()*Expected normal values for [4];
- No Detected; Errors $\approx$ 10%

sample, are in according with those determined by HR-ICP-MS, which validates all results including those from biological samples.

Acknowledgements

This paper has been supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq - Brazil and Universidade Estadual de Santa Cruz - UESC.

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