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INFLUENCE OF HEAVY METALS IN NON-ANTHROPIZED SOILS WITH HIGH LEVELS OF PRIMORDIAL RADIONUCLIDES

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ABSTRACT

High concentrations of heavy metals in the ecosystem depend naturally geological formation in each area of the planet and of anthropic activities that contribute to contamination of soil, water sources and food produced in these areas. In this context, we highlight the importance in the study of As, Cr and Ba because of the level of toxicity, availability and chemical speciation that have. The study area was chosen to present agricultural activity and milk production on a large scale. This area is located in the rugged region of the state of Pernambuco, in the town of stone, where the arable soil was monitored aiming to determine the levels of these metals. Analyses were performed by the technique of neutron activation analysis coupled with the high-resolution gamma spectrometry. Were analyzed twenty-three soil samples collected from the horizon C. The results obtained varied from values smaller that (0.2 to 6.7) $mg.kg^{-1}$ for As; (12.1 to 65.5) $mg.kg^{-1}$ for Cr and (443 a 1,497) $mg.kg^{-1}$for Ba. Comparing them with the values established by CONAMA Resolution 420/2009, it was found that the concentrations of Ba are 100% above the value of prevention, and approximately 91% of values above the intervention value. The As and Cr showed 100% of results below the value of prevention. Whereas the study area has no industrial activity, high concentrations are determined for the Ba from natural processes. For the levels found evidence of a possible contamination of water sources and food produced in this region.

1. INTRODUCTION

The term "heavy metals", as on quotations made by [1,2,3], can be applied to approximately 65 elements in the periodic table, for having a specific weight or specific density greater than 5.0 $g.cm^{-3}$, or an atomic number superior to 20, many of them have a toxic effect in microbial cells and other life forms.

Heavy metals are spread on the Earth's surface and, along with other chemical elements, compose the structure of rocks and, consequently of soil [4], where natural processes control

and modulate your downloads and interactions between all compartments of the ecosystem over time. The activities, especially from the 20th century on, have become the main source of dispersion, accumulation and, mainly, alterations in the biogeochemical cycles of many elements, including heavy metals in the terrestrial and aquatic ecosystems [5].

Some of these heavy metals, according to [2,3], are beneficial in small quantities for microorganisms, plants and animals. However, they can contaminate the environment and, because of its properties, through bioaccumulation and biomagnification in the food chain, can act causing changes in parameters physical, chemical and biological a given ecosystem, causing damage to living organisms. Plants, when exposed to the environment contaminated by heavy metals, may submit a series of physiological and nutritional disorders, among which stand out interference of the absorption, transport and functions of nutrients [3], thus offering also risks when introduced into the food chain, due to the cumulative effect.

In many regions of the world, studies referring to heavy metals present in the ecosystem indicate high concentrations of those elements in several areas close to complexes industrial urban, mining and also highly technified agricultural areas. The abnormal increase in the As, Cr and Ba concentrations, as well as other heavy metals in the soil, is associated to atmospheric deposition, weathering, application of fertilizers, correctives, agro-toxics, irrigation water, organic and inorganic residues, as well as industrial effluents thrown or deposited in the soil without treatment, in rivers or lakes, without waterproofing, protection or contention, thus becoming a grave environmental problem, with risks many times unknown to men [6].

For monitoring the potentially contaminated areas, it is necessary to know the natural contents of the metals and their soil variability, that is, their contents in soils without anthropic introduction [7].

In Brasil, the Conselho Nacional do Meio Ambiente (CONAMA) has proposed a list of values, which serve as guidelines for heavy metals in environmental prevention (Table 1) according to the 420/2009 Ruling.

Table 1 - Reference values for metals [19].

Element	V.P	V.I (APA)
	-------- mg.kg^{-1} -------	
As	15	35
Cr	75	150
Ba	150	300

V.P. – value of prevention. V.I. – value of intervention
APA – agricultural protection area.

In the "Agency Toxic Substances and Diseases Registry" (ATSDR, 2007) list - US Disease and Toxic Substance Register Agency, there is a priority order of toxic substances which potentially threaten human health. In the growing order of toxicity, the elements of this study can be found in the following positions: As (1^{st}), that is, it is in the first position since 1997, Cr (77^{th}) and Ba (109^{th}), being that last one the studied method that offers the minimum toxic risk.

According to the literature [8,9,10,11], the Neutronic Activation Analysis (NAA) is a technique used for elementary analysis, which stands out from other usual analytic methods, because it is based on reactions that occur with atomic nucleus and not orbital electrons. It is an analysis method that is non-destructive and multi-elemental, efficient in determining trace elements, allowing the characterization of over 40 elements in one sample. There is no need to analyze a write or control, because there is no usage of reagents for sample separation or digestion, and there is no possibility of contaminants after irradiation, since it is a non-destructive analysis method. It requires only reduced quantities of samples and it is quite selective, allowing the identification of an element even in the presence of others that emit signals of the same nature.

Due to the importance of the study of those heavy metals in the environment, this study aimed to quantify As, Cr and Ba in agricultural soil located in the municipality of Pedra, Pernambuco, Brazil, where the main uraniferous anomalies of this municipality are found [12].

2. MATERIAL AND METHOD

2.1 Characterization of the study area

The study area is located in the municipality of Pedra, close to latitude 08º29.817' South, longitude 36º56.450' West and altitude of 593 m, inserted in the Agreste and Vale do Ipanema Mesoregion in the State of Pernambuco, in the domains of the Ipanema River hydrographic basin [13], in the geo-environmental unit in the Plateau Borborema, being constituted by lithotypes from the Cabrobó and Belém do São Francisco complexes, from the Intrusive Leucocratic Peraluminous Suite, from Indiscriminate Granitoids and Calc-Alkaline Suites [13,14].

The study area was chosen to present radiometrically anomalous areas of uranium and thorium, high yield potential of dairy products, agriculture and livestock, as well as the lack of studies relating to heavy metals.

2.2 Collection and pre-treatment of samples

Samples were collected in an area of approximately 2 km², where granite outcrops are located and calcium-silicate amphibolitic anomalous in uranium and thorium. To accomplish the collection of soil were demarcated areas of 0.5 m² and previously cleaned, which collected about 3.0 kg of each sample to a depth of between 30 and 50 cm (C horizon), totaling 23 sampling points.

In the Mine Engineering Department at UFPE, Mineral Technology Laboratory, the soil samples were dried in a greenhouse at 60ºC, homogenized, quartered and reduced to a granulometry inferior to 63 μm, stored in polyethylene containers for later analysis.

2.3 Instrumental by neutron activation analysis (INAA) procedures

The nuclear research reactor was used in this work of the Instituto de Pesquisas Energéticas e Nucleares, IPEN / CNEN-SP, model IEA-R1. The reactor has 144 positions for irradiation in the nucleus, divided into 15 elements for radiation long and a pneumatic system for short irradiations (5 minutes). They also have nine tubes horizontal irradiation ("Beam Holes") that provide beams of neutrons used in experiments in nuclear physics, solid state physics, research in cancer therapy by boron neutron capture (BNCT) and Neutrongraphy.

The reactor core is located 6.9 meters away from the pool surface, having the shape of a rectangular solid composed by 20 standard fuel elements, 4 control fuel elements, about 25 reflectors, 7 positions for sample irradiation and lids vertically placed in an aluminum matrix plate. This plate is supported by a truss connected to a mobile platform that allows it to move along the pool [16].

The reference materials used in this work are geological patterns already sprayed that have certified concentrations. Each reference material was chosen according to the type of rock and soil to be studied. In this work we used granite GS-N (ANRT) and basalt BE-N (IWG-GIT) to be silicates and have characteristics similar to those of the elements studied.

About 100 mg of the samples were irradiated for 8 (eight) hours in flux neutron average of approximately 4.5 x 10^{12} $n.cm^{-2}.s^{-1}$. The samples were analyzed by high resolution gamma spectrometry, the first seven days after purchase, and second, fifteen days after irradiation. This was necessary for there to be radioactive decay of the activated samples, along with reference materials, thus ensuring greater efficiency in the qualification and quantification of the elements studied.

In the activity measurements for As, Cr and Ba in the soil samples, an experimental layout composed basically by a HPGe detector, manufactured by Canberra® with a 2.0 keV resolution for the 1,332 energy of ^{60}Co and a nominal efficiency of approximately 20%, attached to a MCA ("multichannel analyzer") with 8,196 channels was used. The metal measurements were realized at a geometry of 12 cm from the detector face, so that there was dead time correction. For manipulating and treating the spectrums and analyzing the data, the computer program Genie® 2000 from Canberra® was used.

3. RESULTS AND DISCUSSION

Table 2 shows the results obtained for As, Cr and Ba, relating the coordinates of each point sampled and the grades of those metals.

Table 2 - As, Cr and Ba concentrations in the soil samples with their respective deviations.

Samples	*Coordinates*		*Concentration (mg.kg^{-1})*		
	S	**W**	**As**	**Cr**	**Ba**
1	08°37.885’	36°55.573’	< DL	42.0 ± 2.0	873.0 ± 43.0
2	08°37.876’	36°55.611’	< DL	25.0 ± 1.0	730.0 ± 35.0
3	08°37.932’	36°55.396’	< DL	33.0 ± 1.0	1,212.0 ± 56.0
4	08°37.783’	36°55.570’	< DL	12.2 ± 0.5	443.0 ± 21.0
5	08°37.807’	36°55.304’	6.7 ± 0.7	12.1 ± 0.6	854.0 ± 40.0
6	08°37.693’	36°55.217’	< DL	44.0 ± 2.0	1,497.0 ± 69.5
7	08°37.650’	36°55.230’	< DL	26.0 ± 1.0	808.0 ± 38.0
8	08°37.644’	36°55.162’	< DL	39.5 ± 2.0	626.0 ± 30.0
9	08°37.535’	36°55.302’	< DL	29.0 ± 1.0	1,057.0 ± 49.0
10	08°37.512’	36°55.238’	< DL	17.5 ± 0.8	800.0 ± 37.5
11	08°37.302’	36°55.149’	< DL	37.0 ± 2.0	653.0 ± 32.0
12	08°37.449’	36°55.172’	< DL	32.5 ± 1.0	720.0 ± 36.0
13	08°37.492’	36°55.206’	< DL	39.0 ± 2.0	933.0 ± 47.5
14	08°37.335’	36°55.070’	< DL	65.5 ± 3.0	481.0 ± 25.0
15	08°37.717’	36°55.177’	0.38 ± 0.1	64.0 ± 3.0	949.0 ± 49.0
16	08°37.234’	36°55.074’	< DL	30.0 ± 1.0	1,013.0 ± 45.0
17	08°37.522’	36°55.052’	< DL	20.1 ± 0.9	1,034.0 ± 45.0
18	08°37.619’	36°55.043’	< DL	48.0 ± 2.0	751.5 ± 34.0
19	08°37.211’	36°55.058’	< DL	24.0 ± 1.0	1,035.0 ± 46.0
20	08°37.389’	36°54.988’	< DL	21.8 ± 0.9	972.0 ± 43.0
21	08°36.806’	36°54.527’	< DL	24.0 ± 1.0	964.0 ± 45.0
22	08°36.797’	36°54.462’	< DL	12.9 ± 0.6	954.0 ± 44.0
23	08°36.768’	36°54.428’	< DL	32.5 ± 1.0	495.5 ± 24.5

DL = Detection Limit

According to the methodology used, detection limits for As, Cr and Ba were estimated at 0.16 $mg.kg^{-1}$; 0.88 $mg.kg^{-1}$ and 0.34 $mg.kg^{-1}$, respectively. From the results shown on Table 2, As practically was not detected in most samples, except for samples 5 and 15, which showed values below and approximately equal to the threshold of prevention, respectively, according to CONAMA Resolution 420/2009.

Comparing the levels obtained for Cr and Ba, with the VP and VI established, it appears that the average interval and the values found in the soil were as follows: Cr, 31.81 $mg.kg^{-1}$ (12.1 - 65.5) $mg.kg^{-1}$, noting that 6% of their concentrations are higher than the VP and approximately 3% higher than for the VI and for Ba, 863.26 $mg.kg^{-1}$ (443.0 – 1,497.0) $mg.kg^{-1}$, where all samples had concentrations above the VP and approximately 91% higher than VI, featuring Ba as having a high potential contaminant in the environment, since levels of heavy metals above the VP, suggests the existence a change in soil quality and may become a potential risk to human health [17].

It is important to highlight that the contents found for the analyzed metals in the soil are not due to anthropic action, since the study area is located far away from industrial and urban areas.

A way to evaluate the distribution of these heavy metals throughout the studied area is to calculate the asymmetries, and also through the models presented in the Gauss curve for normality distribution. Figure 1 shows the relation between the concentrations of each metal and the absolute frequencies, associated to the normality test. By the graphic representation and the asymmetries results, distributions with a significant degree of heterogeneity are characterized, observed also by the mean test.

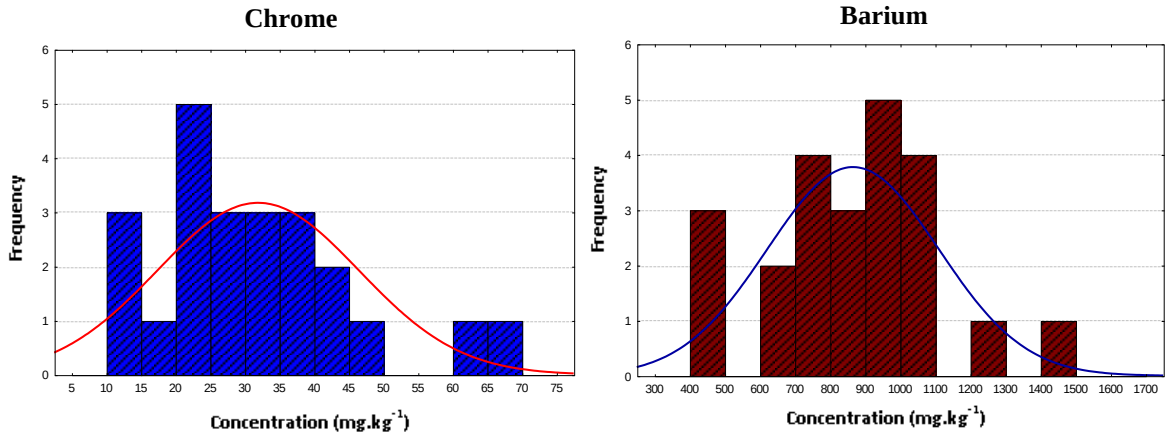

Figure 2 – Histogram for the concentrations of the elements Cr and Ba in the soil.

The Table 3 compares the results obtained in this study, with some references quoted on the literature, which relate prevention values for heavy metals in soils from different regions and countries. The analysis of such data enables us to observe that, among the studied metals, only Ba shows concentrations superior to the limits allowed in Brazil, as referenced by

CONAMA, N from England, Catalonia and NW from China, with concentration values superior to approximately 5.8; 1.8; 1.3 and 1.8, respectively. Still on this Table, we can observe that only in NE Spain Ba shows average concentration superior to the present study, characterizing a concentration factor of about 0.5.

Table 3 – Comparison between results and reference values of the heavy metals in referenced soils for different countries.

Regions	**Cr**	**Ba**
	----------mg.kg^{-1}----------	
Present study	**31.8 (12.1 - 65.5)**	**863.3 (443.0 - 1,497.0)**
Conama	75.0	150.0
NE Spain	275.0	1,762.0
N England	92.5	492.0
Catalonia	103.0	669.0
China	53.9	-
S China	13.3 – 144.0	-
USA	1,500.0	-
Poland	50.0 – 80.0	-
Austria	100.0	-
NW China	61.0	469.0
Soils	5.0 – 1,500.0	-

Sources: [17,18]

4. CONCLUSION

From the studied elements, only Ba has shown concentrations that indicate an anomaly of this metal in the environment, being able to characterize a risk to the population's health.

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REFERENCES

1. TSUTIYA, M. T. Metais Pesados: O principal fator limitante para o uso agrícola de biossólidos das estações de tratamento de esgoto – 20° Congresso Brasileiro de Engenharia Sanitária e Ambiental (1999).
2. SILVA, E. L. Desenvolvimento de metodologias analíticas para determinação de metais traços em água e em álcool combustível por FI-FAAS, com SPEUsando sílica modificada com óxido de nióbio ou 3(1-Imidazolil)Propil. Tese (Doutorado) Universidade Federal de Santa Catarina (2004).
3. ALMEIDA, E. L. Desenvolvimento de Feijão-de-Porco [*Canavalia ensiformis (L.) D.C.*] na presença de chumbo. Dissertação (Mestrado) Instituto Agronômico - IAC (2007).
4. LOUREIRO, D. D. Evolução dos aportes de metais pesados na Lagoa Rodrigo de Freitas. Dissertação (Mestrado) Universidade Federal Fluminense – UFF (2006).
5. NASCIMENTO, A. F. Determinação das concentrações dos metais pesados Pb, Cr, Zn, Cd, Cu e Ni em uma área estuarina da Região Metropolitana de Maceió (AL) através do uso do bioindicador *Callinectes Bocourti* A. Milne Edwards. Trabalho de Conclusão de Curso (Graduação) Universidade Federal Rural de Pernambuco – UFRPE (2008).
6. RAMALHO, J. F. G. P., SOBRINHO, N. M. B.A. Metais Pesados em Solos Cultivados com Cana-de-Açúcar pelo uso de Resíduos Agroindustriais. Revista Floresta e Ambiente. v. 8, n.1. p.120-129 (2001).
7. BIONDE, C. M. Teores naturais de metais pesados nos solos de referência do estado de Pernambuco, Brasil. Tese (Doutorado) Universidade Federal Rural de Pernambuco – UFRPE (2010).
8. MARTINS, P. F. F. Desenvolvimento de traçadores ativáveis para aplicação em recuperação secundária de reservatórios de petróleo. Dissertação (Mestrado) Comissão Nacional de Energia Nuclear – CNEN (2005).
9. YAMASHITA, D. M. Mobilidade de arsênio e metais pesados em solos do Vale do Ribeira, Iporanga, S.P. Dissertação (Mestrado) Universidade Estadual de Campinas (2004).
10. CRUCHO, M. R. S. M. Avaliação de micro e macroelementos, elementos tóxicos (Cd, Hg e Pb) e ácidoS graxos, em peixes disponíveis comercialmente para consumo em Cananéia e Cubatão, Estado de São Paulo. Dissertação (Mestrado) Universidade de São Paulo. Instituto de Pesquisas Energéticase Nucleares - IPEN (2009).
11. SANTOS, P. S. Avaliação dos teores de elementos essenciais no leite materno de mães de recém-nascidos prematuros e a termo e em fórmulas infantis por meio da análise por ativação com nêutrons. Dissertação (Mestrado) Universidade de São Paulo. Instituto de Pesquisas Energéticas e Nucleares – IPEN (2009).
12. SANTOS JÚNIOR., J. A.; CARDOSO, J. J. R. F.; SILVA, C. M.; SILVEIRA, S. V.; AMARAL, R. S. Determination of radionuclides in the environment using gamma-spectrometry. Journal of Radioanalytical and Nuclear Chemistry. v. 269, n. 2, p. 451-455 (2006).
13. PRODEEM - Projeto Cadastro de Fontes de Abastecimento por Água Subterrânea. http://www.cprm.gov.br (2009).
14. ZAPE – Zoneamento Agroecológico do Estado de Pernambuco. Fernando Barreto Rodrigues e Silva et al. Recife: Embrapa Solos – Unidade de Execução e Pesquisa e

Desenvolvimento – UEP Recife; Governo do Estado de Pernambuco (Secretaria de Produção Rural e Reforma Agrária) – CD-ROM (2001).
15. SANTOS JÚNIOR, J. A.; AMARAL, R.S.; SILVA, C.M.; MENEZES, R.S.C. Radium equivalent and annual effective dose from geological samples from Pedra - Pernambuco - Brazil. Radiation Measurements. p.861 – 864 (2010).
16. IPEN - Instituto de Pesquisas Energéticas e Nucleares. São Paulo. http://ww.ipen.br/sitio/?idm (2006).
17. BURAK, D. L. Geoquimicae distribuiçãoo de metais pesados em solos na região de Unai, Paracatu, Vazante, M G. Tese (Doutorado) Universidade Federal de Viçosa (2008).
18. CAIRES, S. M. Determinação dos teores naturais dos metais pesados em solos do estado de Minas Gerais como subsídios ao estabelecimento de valores de referência de qualidade. Tese (Doutorado) Universidade Federal de Viçosa (2009).
19. CONAMA- Conselho Nacional do Meio Ambiente. Resolução nº 420, de 28 de dezembro de 2009, http://www.mma.gov.br/port/conama/legiano1.cfm?codlegitipo=3&ano=2009 (2009).