2024 International Nuclear Atlantic Conference – INAC 2024
Escola de Guerra Naval, Rio de Janeiro, RJ, May6 - 10, 2024

Geochemical Evaluation of Radionuclides in Soil near a Dismantled Th and U Pilot Plant in São Paulo, Brazil

K.G. Oliveira[1], M.M. Redígolo[1], R.B. Ticianelli[1], M.E. Cotrim[1], P.S. Cardoso da Silva[1], and I.M.C. Camargo[1]

[1] *marcelo.redigolo@alumni.usp.br, Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP Av. Professor Lineu Prestes, 2242, Cidade Universitária, CEP 05508-000, São Paulo, SP, Brazil*

1. Introduction

Uranium is an important environmental pollutant, whose radionuclides' mobility in soil is dependent of this matrix characteristics and also climate conditions. Biogeochemical processes are responsible for transferring the radionuclides from soil to biological systems. Uranium concentrations in soil may be associated with the type of soil and their mobility to the pH [1].

Instituto de Pesquisas Energéticas e Nucleares (IPEN – CNEN/SP) has two nuclear research reactors, a radioactive waste unit, a nuclear fuel center, a radiopharmaceutical production center, a radioisotopes production center and service and research units that use radioactive and non-radioactive materials. Part of Thorium and UF_4 Production Pilot Plants and Dissolution and Uranyl Nitrate Purification Pilot Plants were dismantled in 2000-2003 [2]. The periodical environmental monitoring aims the radiological control of water and air, but the soil has not been evaluated [3].

The aim of this work is to evaluate the soil from IPEN, comparing areas free from and under radiological influence.

2. Methodology

IPEN is located within Universidade de São Paulo campus, in São Paulo municipality, and it occupies an area of 500,000 m^2, being 102,000 m^2 of constructed area [4] and 380,000 m^2 of green area (C.F.O. Mouro, personal communication, 2023). Twenty subareas (ca. 100 m^2) were sampled and divided in two groups: free from radiological influence (samples 1-3) and under radiological influence (samples 4-20). Two subareas were sampled adjacent to the restaurant and one close to the medical service department, around the thermoluminescent dosimeter from the environmental radiological monitoring program. All 17 subareas under radiological influence are adjacent to the old uranium and thorium pilot plant and the safeguard shed. Samples 4 to 11 were collected near the old U and Th pilot plant and samples 12 to 20 were adjacent to the safeguard shed, close to a thermoluminescent dosimeter, a rain gauge and two groundwater wells from the environmental radiological monitoring program. The distance between both groups (free and under radiological influence) is circa 1 km and altitude difference of 30 m, where the old pilot plant and safeguard shed are the lower terrain, with rainwater and superficial and underground water runoff. Table I presents data such as geographical coordinates and altitude of 20 sampled subareas.

Composite sampling was conducted, where circa 40-50 subsamples (20 cm deep) were collected in each subarea with the aid of a stainless-steel tubular sampler from June to November 2023. The sampled subareas ranged from 80 to 110 m^2 and sample mass from 6.5 to 11.4 kg. A larger area (450 m^2) near the restaurant was sampled (sample 2) to evaluate methodology and compare with the usual 100 m^2 area (sample 3). Samples have been pretreated (clod breaking, sieving, and quartering) and pH test was conducted as well as gamma spectroscopy to samples 1-6 (Table I). Soil pH was measured in soil:liquid suspension (1:2.5) in KCl (1 mol L^{-1}) and deionized water.

After preparing the samples to a fine powdered stage, approximately 50 g were put in cylindrical plastic containers (diameter of 5.0 cm and 1.8 cm height) and properly sealed. Plastic containers were fastened with adhesive tape to ensure they were airtight and completely sealed. The prepared samples were left to stand for at least 30 days before the measurements in order to obtain a radioactive equilibrium of ^{226}Ra decay products. Radionuclides were determined using a High Purity Germanium Detector (HPGe), from Canberra (USA), with relative efficiency of 40% resolution $\leq$ 1.8 keV FWHM at 1.33 MeV. The method was validated with three soil certified reference materials to ^{228}Ra, ^{228}Th, ^{226}Ra, ^{210}Pb, ^{40}K: IAEA-327, IAEA-375 and IAEA-Soil 6. Measured and certified values were in accordance, except for ^{228}Ra and ^{228}Th in IAEA-327.

Three undeformed soil samples were collected in volumetric cylinders (100 cm^3) with aid of a stainless steel auger in each subarea for the determination of density and humidity according to the volumetric cylinder method [5].

Table I: Description of 20 sampled subareas

Sample	Geographical coordinates		Altitude(m)	Description
1	S 23°33'57.38"	W 46°73'59.79"	781	Medical service
2	S 23°33'45.65"	W 46°44'02.53"	771	Restaurant (450 m^2)
3	S 23°33'45.57"	W 46°44'01.79"	771	Restaurant (100 m^2)
4	S 23°33`40.33"	W 46°44`24.30"	756	Old U and Th analysis laboratory
5	S 23°33`42.57”	W 46°44`25.00”	756	Old U and Th pilot plant1
6	S 23°33'41.94"	W 46°44'24.10"	756	Old U and Th pilot plant 2
7	S 23°33'41.64"	W 46°44'23.86"	756	Old U and Th pilot plant 3
8	S 23°33'40.42"	W 46°44'24.80"	756	Old U and Th pilot plant 4
9	S 23°33'39.93"	W 46°44'24.47"	756	Old U and Th pilot plant 5
10	S 23°33'39.75"	W 46°44'24.61"	756	Old U and Th pilot plant 6
11	S 23°33'39.47"	W 46°44'24.94"	756	Old U and Th pilot plant 7
12	S 23°33'40.17"	W 46°44'26.81"	756	Close to safeguard shed 1
13	S 23°33'40.14"	W 46°44'27.10"	756	Close to safeguard shed 2
14	S 23°33'40.35"	W 46°44'27.24"	756	Close to safeguard shed 3
15	S 23°33'40.19"	W 46°44'27.22"	756	Close to safeguard shed 4
16	S 23°33'40.23"	W 46°44'27.66"	756	Close to safeguard shed 5
17	S 23°33’40.04”	W 46°44’27.92”	756	Close to safeguard shed 6
18	S 23°33’40.92”	W 46°44’27.81”	756	Close to safeguard shed 7
19	S 23°33'40.18"	W 46°44'28.07"	756	Close to safeguard shed 8
20	S 23°33'40.32"	W 46°44'28.09"	756	Close to safeguard shed 9

3. Results and Discussion

Table II presents results of physical-chemical analyses. Soil density ranged from 0.97 to 1.49 g cm^{-3} in a total of 20 subareas in this work, while humidity ranged from 8.1 to 27.9%. Both soil density and humidity are key soil parameters to prepare soil columns for future study uranium mobility. Soil humidity is related to the monthly precipitation. In general, soil samples collected in the rainiest period, October and November, showed higher humidity when compared to those collected in the drier period, June to September.

Soil pH ranged from 4.08 to 7.03 in KCl solution and from 4.84 to 7.55 in deionized water, presenting acidic and neutral characteristics, depending on the collection subarea. In general, acidic soils favor heavy metal cations mobility, whereas basic soils favor anionic mobility [6].

Table II: Range of soil physical-chemical analyses results (pH, humidity, and density)

Samples	Humidity (%)	Soil density (g cm^{-3})	pH_{KCl}	pH_{H2O}
1-6	8.1-27.9	0.97-1.49	4.08-7.03	4.84-7.55
1-20			-	-

Gamma spectrometry results are presented in Table III. Activity concentrations for ^{228}Ra and ^{228}Th, decay radionuclides of the ^{232}Th series, present lower values for samples free from radiological influence (1, 2 and 3) than those adjacent to the old U and Th pilot plant (4, 5 and 6). Activity concentrations for ^{226}Ra and ^{210}Pb, decay radionuclides of the ^{238}U series, present similar values between the free subareas and those under radiological influence, except for ^{210}Pb in sample 6. This indicates that activities involving thorium in the old U and Th pilot plant contributed to an increase in activity concentration for ^{228}Ra and ^{228}Th in the sampled soil. Soil samples show variable activity concentration for ^{40}K.

Table III: Activity concentration of radionuclides (Bq kg^{-1}) in soil samples from IPEN

	1	**2**	**3**	**4**	**5**	**6**
^{228}Ra	157±40	117±29	130±33	571±143	242±61	293±73
^{228}Th	151±27	118±31	122±31	520±132	220±57	273±69
^{226}Ra	40±7	36±7	39±7	48±9	44±9	44±8
^{210}Pb	< DL	45±5	42±4	< DL	44±5	62±10
^{40}K	50±4	95±7	98±7	167±12	152±11	136±9

DL = detection limit

Results of radionuclides activity concentration were compared with soil reference values from the state of São Paulo [7], state of Rio de Janeiro [8] and worldwide [9] (Table IV). Activity concentration range for ^{40}K, ^{226}Ra and ^{210}Pb is within the range of reference values for soil and for ^{228}Ra and ^{228}Th are higher than those presented by references, but below the intervention values for ^{228}Ra in soils in the state of São Paulo for agricultural scenery, 750 Bq kg^{-1} [7]. Intervention value for ^{228}Th was not established in this reference.

Table IV: Comparison of reported activity concentration range of radionuclides (Bq kg^{-1}) in soils

Region	^{40}K	^{226}Ra	^{228}Ra	^{228}Th	^{210}Pb	Reference
IPEN-CNEN (SP)	50-167	36-48	117-571	118-520	42-62	This work
State of São Paulo (SP)	15.3-516	1.0-61.8	3.3-97.6	4.8-120	<20-121	Hiromoto *et al.*, 2010
State of Rio de Janeiro (RJ)	12.2-1,029	3.5-99.8	5.4-314	-	-	Ribeiro *et al.*, 2018

World range	140-850	17-60	11-64	-	-	UNSCEAR, 2008

4. Conclusions

The soil sampled at IPEN presented an acidic character and areas under radiological influence presented a higher activity concentration when compared to free areas, being thorium (^{228}Ra and ^{228}Th) more influential than uranium (^{226}Ra and ^{210}Pb). This is an ongoing work; therefore, more analyses are needed to draw broader conclusions. Results presented here are important to the decision-making process of soil column percolation assays.

Acknowledgements

The authors thank Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN) for the financial support (grant 2020.06.IPEN.25, and CNPq 103339/2024-8) and the infrastructure department of the Institute.

References

[1] G.V. Cardoso, N.M.B. Amaral Sobrinho, M.A.V. Wasserman, N. Mazur, "Geoquímica de radionuclídeos naturais em solos de áreas circunvizinhas a uma Unidade de Mineração e Atividade de Urânio", *Revista Brasileira de Ciência do Solo,* vol. 33, pp. 1909–1917 (2009).

[2] P. E. O. Lainetti, M. E. B. Cotrim, F.M.F. Vasques, R.J. Ferreira, M.A.F. Pires, "Reintegration of areas of the Ipen´s dismantled nuclear fuel cycle pilot plants as new laboratories of the CQMA", *Proceedings of International Nuclear Atlantic Conference – INAC*, Santos, SP, 30 Sep - 5 Oct, pp. 1-5 (2007).

[3] Instituto de Pesquisas Energéticas e Nucleares - IPEN, "Relatório de avaliação do programa de monitoração radiológica ambiental do IPEN". São Paulo, SP (RA-PMRA-2019) (2021).

[4] Instituto de Pesquisas Energéticas e Nucleares – IPEN, "Relatório de Gestão 2018",
https://www.ipen.br/portal_por/conteudo/documentos/RG_2018_ciclo_2019_v1.-(2019)

[5] P.C. Teixeira, G.K. Donagemma, A. Fontana, W.G. Teixeira, *Manual de métodos de análise de solo*, Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA), Brasília, DF (2017).

[6] B.J. Alloway, *Heavy metals in soils*, John Wiley & Sons, New York, NY (1990).

[7] G. Hiromoto, A.C. Peres, M.H. Tadei, M.R. Soares, L.R.R. Alleoni, "Radioactive Soil Characterization Of The State Of Sao Paulo, Brazil", *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*, Amherst, Massachusetts (USA), 18 – 21 Oct, vol 16, pp 1-5 (2010).

[8] F. C. A. Ribeiro, D. C. Lauria, J. I. R. Silva, E. S. A. Lima, N. M. B. A. Sobrinho, D. V. Pérez, "Baseline and Quality Reference Values for Natural Radionuclides in Soils of Rio de Janeiro State, Brazil", *Revista Brasileira de Ciência do Solo*, vol. 42, pp. 1-15 (2018).

[9] United Nations Scientific Committee on the Effects of Atomic Radiation, Sources and effects of ionizing radiation, "UNSCEAR Report", vol. I, Annex B (2008).