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Inorganic chemical characterization of the soil from the springs at RPPN Fazenda Renópolis

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1. Introduction

In recent years, monitoring both climatic variations and anthropogenic activities and their consequences for nature and human health has emerged as a primary concern within the scientific community. Numerous studies have been conducted across diverse environmental areas to investigate these concerns [1].

To conduct such studies, various environmental ecosystems, including water, living organisms, suspended particulate matter, sediment, and soil, are utilized [2]. The Brazilian Soil Classification System defines soil as a conglomerate of natural formations, three-dimensional and dynamic, encompassing solid, liquid, and gaseous components [3].

The study of soil constitutes a valuable tool for understanding the geochemical and geophysical aspects of aquatic ecosystems [4]. Geochemical data can be subdivided into four main categories: major elements, trace elements (such as Rare Earth Elements (REE)), radiogenic and stable isotopes [2].

The Environmental Radiometry Laboratory (LRA) at the Institute of Energetic and Nuclear Research (in Portuguese IPEN) conducts the analysis of water, sediment, and soil samples from various regions within the “Circuito das Águas de Minas Gerais” and the “Circuito das Águas Paulista”. These mineral water circuits are situated in the Serra da Mantiqueira, which is characterized by numerous water sources, rivers, and water springs [5-7].

The objective of this study was to perform the inorganic chemical characterization of the soil from seven water springs located in the Private Reserve of the National Heritage Fazenda Renópolis (“RPPN” Fazenda Renópolis) also situated in the Serra da Mantiqueira. Instrumental Neutron Activation Analysis (INAA) was employed for determination of trace and major elements, including As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zn. The concentration values obtained for these elements were compared to the reference values of the Upper Continental Crust (UCC) and United States Department of Agriculture – Natural Resources Conservation Service (USDA-NRCS) [2].

2. Methodology

The RPPN Fazenda Renópolis (22°48’22.10”S 45°37’31.80”W) is situated in the city of Santo Antônio do Pinhal, within the Paraíba Valley, in the Southeast region of the State of São Paulo. The area is part of the “Circuito das Águas Paulista” in the Serra da Mantiqueira, known for its mineral water sources, with some of them being classified as radioactive mineral water [8].

In this study, 500g of soil samples were collected from seven springs located in RPPN Fazenda Renópolis. After collection, the samples were air-dried at room temperature. Following the drying process, all samples underwent sieving with a 2mm mesh and were stored in polyethylene containers for the analyses.

INAA is a non-destructive analytical method that enables the identification of up to 40 chemical elements in a single sample. The precision and accuracy of this approach differ for each individual element [9]. Neutron activation analysis serves as a technique for both the qualitative and quantitative assessment of elements. It relies on the detection of distinctive radiation emitted by radionuclides generated through the irradiation of materials with neutrons [10].

Particle size analysis is a parameter used to describe the dimensions of soil particles. The particle sizes were classified according to NBR 6502/95 as follows: Sand (diameter between 2mm and 0.06mm), Silt (diameter between 0.06mm and 2μm), and Clay (diameters less than 2μm) [9]. The quantity of organic matter is a crucial parameter for environmental analyses, as it influences the bioavailability, toxicity, transportation, and accumulation of metallic elements in the environment [11]. The determination of organic matter was conducted using the gravimetric method of Loss on Ignition (LOI) [12]. Another important parameter in inorganic chemical characterization is soil porosity. This is a measure that allows the identification of how water and pollutants are transported through the soil profile [11]. Real and apparent density are parameters that allow the estimation of total soil porosity and were determined based on the Soil Analysis Manual [13].

3. Results and Discussion

Table I presents the sample codes, geographic coordinates, particle size analysis (%), the LOI results (%), the real (d_{real}) and apparent densities (d_{ap}), both in g cm^{-3}, and total porosity (P_T).

Table I: Sample codes, geographic coordinates, particle size analysis (%), LOI (%), d_{ap} (g cm^{-3}), d_{real} (g cm^{-3}) and (P_T) (%).

Sample codes	Coordinates	Grain size distr. (%) wt.			(% LOI)	d_{ap} (g cm^{-3})	d_{real} (g cm^{-3})	P_T (%)
		Sand	Silt	Clay				
NASO1	22°48’22” S 45°37’28” W	41.74	14.39	43.88	31.3	0.95	2.29	58.67
NASO2	22°48’23” S 45°37’30” W	37.6	9.9	52.5	38.3	0.89	2.37	62.42
NASO3	22°48’25” S 45°37’28” W	72	13	15	33	0.70	1.87	62.5
NASO4	22°48’22” S 45°37’30” W	65.7	17.4	16.9	22.3	0.82	2.45	66.42
NASO5	22°48’21” S 45°37’14” W	62.9	21.2	15.9	21.5	0.77	2.39	67.55
NASO6	22°48’28” S 45°37’05” W	59.7	19.1	21.2	30.1	0.73	2.13	65.54
NASO7	22°48’15” S 45°37’32” W	44.7	23.4	31.9	21.4	0.80	2.31	65.13

The particle size distribution varied significantly for each spring, with a predominant percentage of sand; this granulometric variation can be explained by different weathering conditions. Except for samples NASO1 and NASO2, which showed the highest percentages of clay, the soil samples are predominantly composed of sand.

Using the soil classification system of the USDA-NRCS, the soils of the springs NASO1, NASO6, and NASO7 are classified as Sandy Clay Loam. In the case of samples NASO3, NASO4, and NASO5, the classification is Sandy Loam; only NASO2 was classified as Sandy Clay.

The mean percentage of organic matter obtained by the LOI method was 28.3%. The highest observed value was for sample NASO2 (38.3%), while the lowest obtained value was 21.4% for NASO7.

Regarding the calculated total porosity percentage, the lowest value was obtained in NASO1, where it can be observed that it was also the sample with the most balanced distribution of grain sizes. All other samples exhibited total porosity values exceeding 62%.

Table II presents the mean, minimum and maximum concentration values in mg kg^{-1} of the inorganic chemical elements and the UCC reference values [2]. The elements determined by INAA are often analysed in groups [2]. The elements Na and K (%) (alkali metals) presented mean values lower than the reference values. In the case of the alkaline earth metal Ba, its concentrations in all samples were higher than the UCC values. Among the transition metals, only in samples NASO6 and NASO7 were the concentrations of Cr and Zn lower than UCC values. Meanwhile, the mean concentrations of Co and Fe were lower than the results provided by Rollinson, et al [2].

Table II: Mean, minimum and maximum concentrations, mg kg^{-1}, of the inorganic chemical elements and reference values from UCC.

Element	Mean	Min	Max	UCC	Element	Mean	Min	Max	UCC
	mg kg^{-1}					mg kg^{-1}			
As	1.82	0.92	4.58	1.5	**Rb**	100	75	126	110
Ba	779	592	891	668	**Sb**	0.2	0.2	0.3	0.2
Br	14.1	8.7	20.4	1.6	**Sc**	8	5	11	11
Co	9	3	13	10	**Se**	2.713	1.93	3.403	0.083
Cr	40	21	61	35	**Ta**	1.6	0.9	2.2	2.2
Cs	1.9	1.3	2.4	3.7	**Tb**	0.9	0.4	1.4	0.7
Fe (%)	3.2	2.2	4.1	3.5	**Th**	13	10	15	10
Hf	8.9	6.3	11.8	5.8	**U**	1.3	0.9	2.4	2.5
K (%)	2.26	1.81	2.67	2.87	**Zn**	87	48	111	71
Na	1976	1154	3565	2560					

Among the volatile and semi-metals elements, the elements As and Sb were not detected in all spring soil samples. The elements Cs and Rb were detected in all samples and presented lower averages than the UCC.

In all samples, the U element presented values lower than the reference values. In the case of Th, all values were higher than those provided in UCC 2].

In Table III, the concentration values of the REE normalized by Post-Archean Australian Shale (PAAS) [2;10] are presented. The purpose of using normalized values is to avoid the Oddo-Harkins rule, which describes an irregular pattern observed in the distribution of atomic or molar masses of elements, particularly in the REE group [2]. Among the Light REE (LREE) (La, Ce, and Nd), Nd was the only one not detected in all samples, only in NASO2, NASO3, NASO5 and NASO6. For the Middle REE (MREE) (Sm, Eu, Tb), Tb was not detected only in NASO6. In the case of Heavy REE (HREE) (Yb and Lu), all samples showed concentrations for these elements. Comparing the results obtained among the LREE, La was found to have higher values in NASO4 and NASO7, Ce exhibited higher concentrations in NASO1, NASO2, NASO4 and NASO5, and Nd showed elevated levels in NASO2 compared to reference values.

Regarding the MREE, Sm concentrations were notably higher in NASO1, NASO2, NASO4, and NASO7. Eu showed elevated levels in NASO1, NASO4, and NASO5, and Tb exhibited increased concentrations in NASO1, NASO2, NASO4, and NASO5. As for the HREE, Yb concentrations surpassed the PAAS values in NASO1, NASO2, NASO4, and NASO7, while Lu exhibited elevated levels in NASO1, NASO2, NASO3, and NASO4.

Organic matter and clay have a strong affinity for REE. Sample NASO2 presented the highest percentage of organic matter, and consequently, all REE, except for La and Tb, in this sample, have concentrations above the PAAS reference values. It is precisely in this spring that the highest percentage of clay is also present.

Table III: Concentration values, mg kg^{-1}, of REE normalized with PASS and their minimum and maximum values.

	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
NASO1	34,0	81,9	-	5,85	1,13	0,92	3,04	0,52
NASO2	36,2	83,7	68,7	5,92	0,94	0,75	3,13	0,44
NASO3	31,8	68,6	26,3	5,08	0,93	0,53	2,76	0,44
NASO4	50,5	94,2	-	8,20	1,51	0,91	3,54	0,59
NASO5	34,9	114,1	20,4	3,36	1,51	1,16	1,96	0,35
NASO6	34,6	62,6	20,2	3,33	0,58	-	1,94	0,35
NASO7	45,3	52,2	-	7,12	0,96	0,38	3,38	0,35
Min	31,8	52,2	20,2	3,33	0,58	0,38	1,94	0,35
Max	50,5	114,1	68,7	8,20	1,51	1,16	3,54	0,59
PAAS	38,2	79,6	33,9	5,55	1,08	0,77	2,82	0,43

- not determined

4. Conclusions

The present work undertook the inorganic chemical characterization of the soil from seven water springs located in the RPPN Fazenda Renópolis, using Instrumental Neutron Activation Analysis that proved effective in determining trace elements. The elements As, Ba, Cr, Hf, Se, Tb, Th and Zn showed concentrations higher than the UCC reference values. The inorganic chemical characterization has revealed important information about the composition and characteristics of the soils at each location. The variation in particle size distribution, as well as the other analysed physicochemical parameters, contributes to a better understanding of the factors influencing the formation and composition of soils in these springs.

For future research, these concentrations values of elements determined by INAA (specifically REEs) and physicochemical parameters will be employed to understand the geological formations to which the springs are subjected.

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