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APPLYING MULTI-INCREMENTAL SAMPLING METHODOLOGY TO SOILS FOR RADIOLOGICAL AND ENVIRONMENTAL RISKS EVALUATION

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ABSTRACT

Multi-increment soil sampling is a methodology that allows evaluating environmental liability inside decision unit, providing a representative aliquot for laboratory analysis with associated uncertainties lower than conventional sampling. The literature has reported much works about environmental liabilities evaluation in soil using multi-increment sampling however, for nuclear facilities soils are practically nonexistent. Therefore, aim of this study was to determinate radionuclides concentration (by Gamma spectroscopy), major and minor constituents (by X-ray fluorescence spectrometry) and metals (by Inductively Coupled Plasma-Atomic Emission Spectrometry) in soils of nuclear material storage facilities in Nuclear and Energy Research Institute (IPEN/CNEN-SP) using multi-increment sampling. The natural radionuclides (^{210}Pb, ^{226}Ra, ^{228}Ra, ^{238}U), major and minor constituents (MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, and others) and metals (Cr, Fe, Co, Ni, Zn, As, Pb, and other) were determined in 120 soil samples, in-depth between 0 and 150 mm at 30 quadrants. The results showed specific activity of 57 ± 16 Bq kg-1 (210Pb), 51 ± 22 Bq kg-1 (226Ra), 81 ± 12 Bq kg-1 (228Ra) and 48 ± 14 Bq kg-1 (238U), corresponding uncontaminated soil, according reference values. With regarding metals concentration, results also were lower than values reference. The statistical tests showed that methodology is efficient for environmental impact studies and monitoring programs and adequate to attend established conditions in IPEN-CNEN / SP environmental licensing.

1. INTRODUCTION

The environmental liability evaluation soil depends on several factors including planning and sampling strategies. If these parameters making well establish we can have a representative and economically feasible sample. The literature has reported that discrete sampling strategy, also called individual sampling, allows a good evaluation of environmental liabilities. However, it is very expensive since the cost is towering because a significant number of samples should be analyzed. Thus, an alternative to minimize costs in chemical analyzes is multi-increment sampling [1].

Multi-increment sampling is a methodology that provides one representative and a reproducible sample of elements and compounds average concentration at a given decision unit [2]. The number of soil increments to be collected in each decision unit should be least 30, with mass between five to fifty grams [3]. Each sample should be dried, desegregated and sieved [4].

The multi-increment sampling protocol described in document Incremental Sampling Methodology and has been used for environmental evaluation of soil in several cases. However, for liabilities of nuclear material are practically nonexistent [5].

In this context, aim this study was to compare discrete sampling with multi increment for evaluation environmental liabilities of surface soil in sites that keep nuclear materials under safeguard.

Thus, in soil samples collected at the adjacent area to nuclear materials deposit, under the safeguard of the Nuclear and Energy Research Institute (IPEN/CNEN-SP) were determinate. The major and minor constituents (Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, Fe_2O_3 and others) by Wavelength Dispersion X-ray Fluorescence spectrometer's (WDXRF), trace elements (Cr, Ni, As, Pb and others) by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-OES) and radionuclides (^{210}Pb, ^{226}Ra, ^{228}Ra and ^{238}U) by gamma spectroscopy.

2. MATERIALS AND METHODS

2.1. Sampling

The sampling of soil was taking according to Manual de Gerenciamento de Áreas Contaminadas [4] and Protocolo de Orientação Técnica [5]. An area of 480 m^2, adjacent to nuclear material deposit, under safeguard protection of the Nuclear and Energy Research Institute (IPEN/CNEN-SP), was divided into 30 equal parts, with 16 m^2 each. Using a stainless steel manual sampler with 2.5 cm diameter and 10 cm depth, in each part four single samples were collected named, I, IA, IB and IC, add up to 120 samples. The "I" samples was numbered from 1 to 30 formed the individual set. The “IA” samples of each part were aggregated producing a composed sample of 30 increments, named “MIA”. Likewise for “IB” and “IC” producing “MIB” and “MIC” samples. All samples were identified and stored in zip lock bags.

In the laboratory, each sample was weighed and placed in an oven at 50 ° C for 48 h, then ground in an agate mortar and sieved to use fraction <2 mm. After the procedure, the composite samples (MIA, MIB and MIC) was spread on a stainless steel tray and divided into 30 equal parts. From each part, about 5 g of the sample was removed, which were also aggregated, forming a new composite sample.

2.2. X-ray fluorescence analysis

The major and minor constituents analyzes (Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, Fe_2O_3) were carried out using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF) procedure according to by Scapin et al. 2015 [6].

2.3. ICP-OES analysis

The trace elements analysis (Li, Be, B, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Sr, Mo, Ag, Cd, In, Sn, Sb, Te, Ba, Ta, Hg, Pb Bi and U) were carried out using inductively coupled plasma source atomic emission spectrometry (ICP-OES) procedure according SMWW 3120 b method (2012).

2.4. Radionuclides analysis

Using following methodologies by gamma spectroscopy the radionuclides were determined. The direct calculation at peak of 186.2 keV considering the contribution of ^{235}U at same peak (185.7 keV) for ^{226}Ra isotope; Secular equilibrium with ^{228}Ac in HpGe coaxial detector for ^{228}Ra isotope; Secular equilibrium with ^{234}Th in low energy detector HpGe for isotope ^{238}U; Direct determination at peak of 46.5 keV for the ^{210}Pb isotope.

2.5. Statistical tools

The analytical results and comparison between individual sampling with multi-increment sampling was evaluated through following statistical tests

a) Principal component analysis (PCA) - PCA was used to evaluate the variance between individual samples with multi-increment. A matrix was constructed considering individual samples (I-1 to I-30) and multi-increment (MIA, MIB and MIC) as variables and respective analytical results obtained by WDXRF, ICP-OES and gamma spectroscopy as cases, using Statistic 7.0 software. The variable values in reason of having different units were standardized using "Standardizing Data" function, Eq.1.

$$\text{Std. Score} = (\text{raw score - mean})/\text{Std. deviation} \tag{1}$$

Subsequently, using "Main components & Classification analysis" and "Correlation" functions, scores and cosine squares factor were calculated based on correlation for each variable. For visualization of the variance was plotted the graph in 2D using larger weight factors.

b) The Chauvenet test was applied for the detection of the outliers, Eq. 2 [7].

$$|X_i - \bar{X}| > Kn * s \tag{2}$$

Where X_i is a measured value, X is the average value, $Kn$is the Chauvenet's coefficient and s is the standard deviation.

c) After the exclusion of outliers, mean ($\bar{X}$), standard deviation (σ) and relative standard deviation (RSD%) for compounds determined by WDXRF, ICP-OES and radionuclides were calculated.

d) The comparison the individual samples mean with multi-increment was evaluated through the Student's t-test and Pearson's correlation. The criterion of acceptability for the null hypothesis was if $t_{\text{experimental}} < t_{\text{theoretical}}$ the means are statistically equal.

3. RESULTS AND DISCUSSION

3.1. PCA Analysis

The PCA analysis showed that two factors describe the correlation between individual samples with multi-increment in terms of variance; Factor 1 (32%) and Factor 2 (26%). In Fig. 1 it can be observed four distinct sets, "A" set with multi-increment samples (MIA, MIB and MIC) and three ‘B”, “C”, and “D”, with individual samples. The “B” set showed major number samples and intersected with “A” set, demonstrating homogeneity between the sets mentioned. In addition, four samples excluded from the sets (I-29, I-16, I-4 and I-24) it can be observed, demonstrating probable outliers.

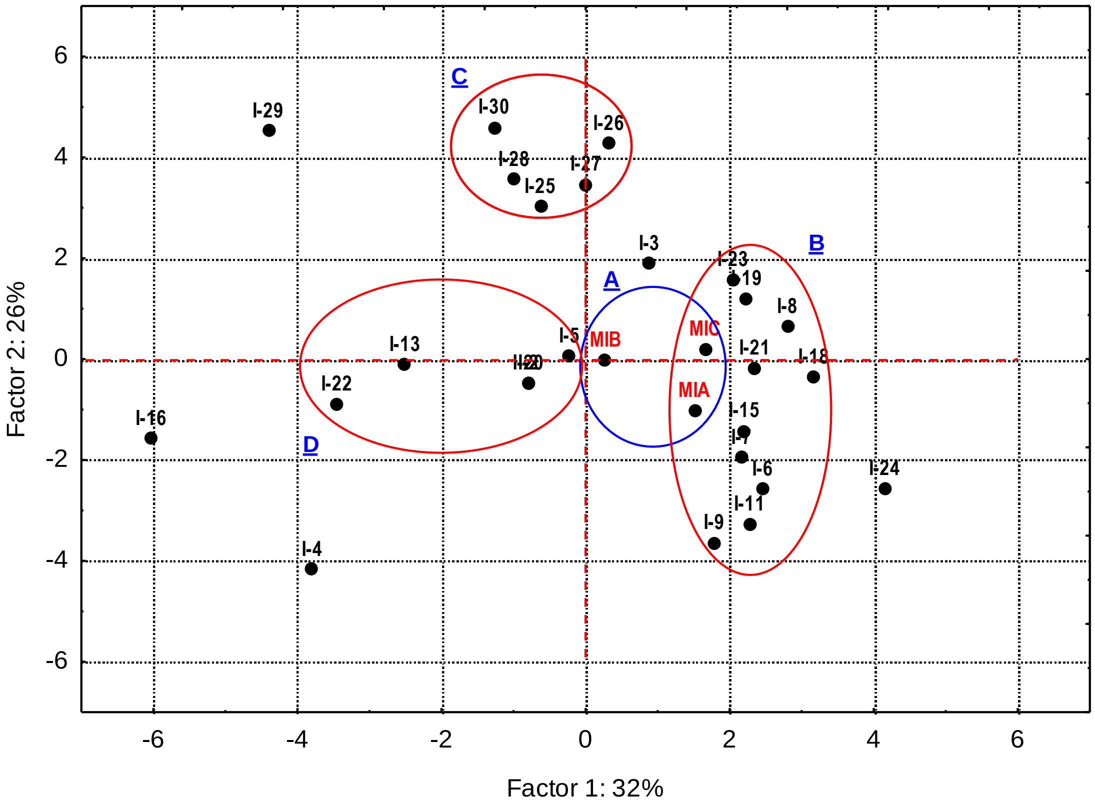

Figure 1: Projection of all samples factor-plane (1x2)

The Chauvenet test applied for the detection of the outliers provided a new set with 15 samples. The PCA applied on new set showed that two factors also describe the variance between samples, Factor 1 (26%) and Factor 2 (21%). In Fig. 2, two sets of samples it can observe; "A" set with 10 individual samples including the multi-increments (MIA, MIB, and MIC) and "B" set made by only three samples. Two samples outside the sets (I-10 and I-11) it can also observe. The comparison Fig. 1 and Fig. 2 show that the exclusion of outliers allowed reducing sets number and have individual samples more representative. In addition, the multi-increment samples (MIA, MIB, and MIC) present the same variance in both figures, demonstrating that multi-increment sampling is representative for the evaluation of nuclear liabilities of the area proposed in this study.

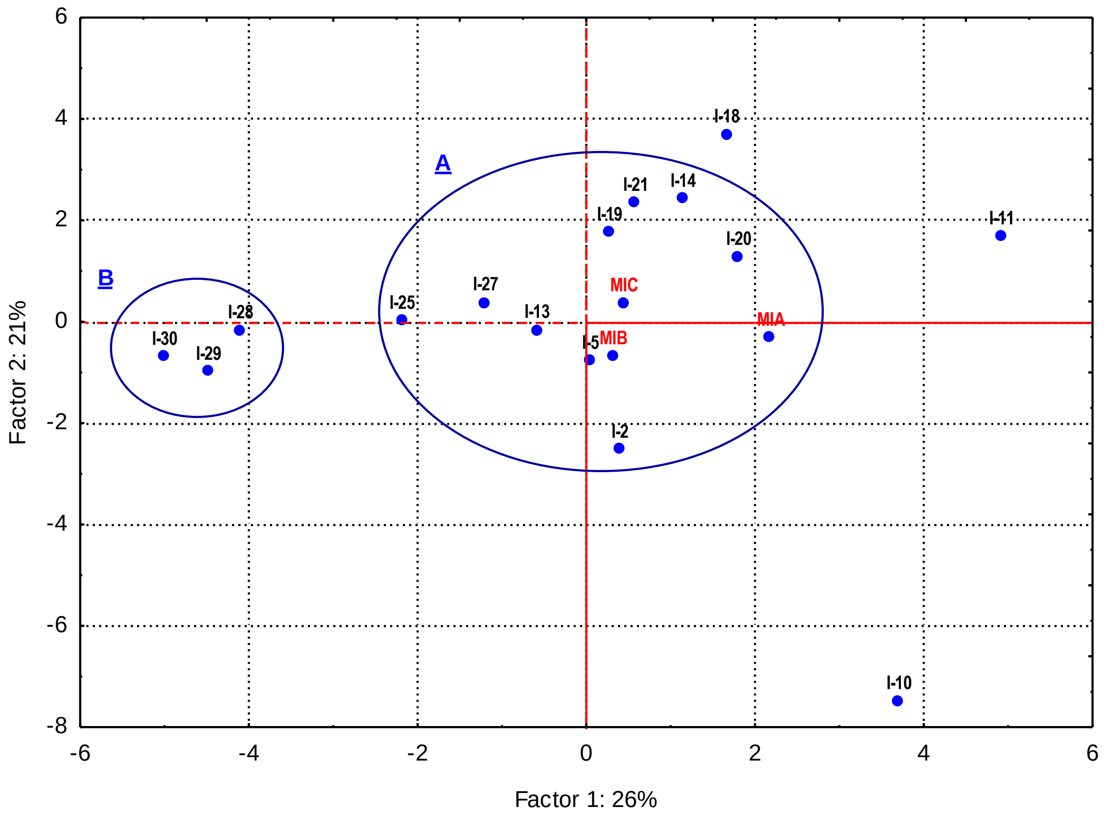

Figure 2 - Projection of the factor plan after excluding outlier samples (1x2)

3.2. Analysis results by WDXRF

In Table 1, average contents ($\bar{X} \pm \sigma$) and relative standard deviation (RSD %) after exclusion of the outliers for individual sample (I) and multi-increment (MI) sample, are presented for Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2 and Fe_2O_3. In addition, an average of compounds for individual sample (I) and multi-increment (MI) sample, loss on ignition (LOI), Pearson's correlation (ρ) and $t_{\text{experimental}}$ and $t_{\text{theoretical}}$ calculated by Student's t-test for comparison of an average between an individual with multi-increment samples.

The Pearson correlation value showed a perfect positive correlation (1.00), showing that in terms of the major and minor constituents, the individual samples are statistically equal to the multi-increment sample. The $t_{\text{experimental}}$ value (0.03) was lower than $t_{\text{theoretical}}$ (2.31), corroborated the Pearson correlation test that is, confirming the equality between the samples.

Table 1 – Results for an individual (I) and multi-increment (MI) samples by WDXRF

Compound	$\bar{X} \pm \sigma$ (I) (%)	RSD%	$\bar{X} \pm \sigma$ (MI) (%)	RSD%
Al_2O_3	32,6±0,7	2,1	32,5±0,5	1,4
SiO_2	43±2	5,3	44,2±0,3	0,7
P_2O_5	0,11±0,02	20	0,11±0,01	10
K_2O	1,8±0,2	14	1,81±0,06	3
CaO	0,4±0,2	39	0,6±0,2	30

TiO_2	1,5±0,1	3	1,48±0,03	2
Fe_2O_3	7,2±0,3	4	7,0±0,3	5
LOI	13±2	14	11,7±0,6	5
average	11±16	144	11±16	147
ρ			1,00	
$t_{\text{experimental}}$			0,03	
$t_{\text{theoretical}}$			2,31	

3.3. Analysis results by ICP-OES

The results obtained by inductively coupled plasma source atomic emission spectrometry (ICP-OES) showed: Co <0.2 mg kg $^{-1}$, Li, Be, As, Se, Mo, Ag, Cd, In, Sn, Sb, Te, Ta, Hg Bi and U < 5mg kg^{-1} for all individual (I) and multi-increment (MI) samples, lower than the detection limit of the method (LQ).

In Table 2, average contents ($\bar{X} \pm \sigma$) and relative standard deviation (RSD %) after exclusion of the outliers for individual sample (I) and multi-increment (MI) sample, are presented for B, Na, Mg, V, Cr, Mn, Ni, Cu, Zn, Ga, Sr, Ba and Pb. In addition, an average of elements for individual sample (I) and multi-increment (MI) sample, loss on ignition (LOI), Pearson's correlation (ρ) and $t_{\text{experimental}}$ and $t_{\text{theoretical}}$ calculated by Student's t-test for comparison of an average between an individual with multi-increment samples.

The Pearson correlation value showed a positive correlation (0.98), showing that in terms of the trace elements, the individual samples also are statistically equal to the multi-increment sample. The $t_{\text{experimental}}$ value (0.62) was also lower than $t_{\text{theoretical}}$ (2.18) corroborated the Pearson correlation test that is, confirming the equality between the samples.

Table 2 – Results for an individual (I) and multi-increment (MI) samples by ICP-OES

Elements	$\bar{X}\pm\sigma$ (I) (mg kg^{-1})	RSD%	$\bar{X}\pm\sigma$ (MI) (mg kg^{-1})	RSD%
B	23±11	48	27±3	11
Na	118±20	17	98±16	16
Mg	113±46	41	127±18	14
V	34±11	34	30±2	8
Cr	16±6	35	13±2	13
Mn	30±19	62	33±6	17
Ni	4±3	83	4±1	36
Cu	14±7	48	13±1	9
Zn	25±9	36	21±4	19
Ga	10±3	29	9±1	11
Sr	5±2	34	4±1	18
Ba	15±6	37	16±3	17
Pb	15±7	45	10±2	19
average	32±38	119	31±38	119
ρ			0,98	
$t_{\text{experimental}}$			0,62	
$t_{\text{theoretical}}$			2,18	

3.3. Analysis results by Gamma spectroscopic

In Table 3, average contents ($\bar{X}$ ± σ) and relative standard deviation (RSD %) for individual sample (I) and multi-increment (MI) sample, are presented for ^{210}Pb, ^{226}Ra, ^{228}Ra and ^{238}U. In addition, an average of elements for individual sample (I) and multi-increment (MI) sample, loss on ignition (LOI), Pearson's correlation (ρ) and $t_{\text{experimental}}$ and $t_{\text{theoretical}}$ calculated by Student's t-test for comparison of an average between an individual with multi-increment samples.

The Pearson correlation value showed a positive correlation (0.97), showing that in terms of the radionuclides, the individual samples also are statistically equal to the multi-increment sample. The $t_{\text{experimental}}$ value (1.46) was also lower than $t_{\text{theoretical}}$ (3.18) corroborated the Pearson correlation test that is, confirming the equality between the samples.

Table 3 – Results for an individual (I) and multi-increment (MI) samples by gamma spectroscopy

Radionuclides	$\bar{X}$±σ (I) (Bq kg^{-1})	RSD%	$\bar{X}$±σ (MI) (Bq kg^{-1})	RDS%
^{210}Pb	62±13	21	58±6	10
^{226}Ra	50±7	14	52±7	13
^{228}Ra	83±7	8	81±1	11
^{238}U	56±10	19	49±4	8
average	63±14	22	60±15	25
ρ			0,97	
$t_{\text{experimental}}$			1,46	
$t_{\text{theoretical}}$			3,18	

4. CONCLUSIONS

The results showed that multi-increment sampling methodology provides a representative and economically viable sample for the evaluation of nuclear soil liabilities. , since the levels of the largest and smallest constituents, trace elements and natural radionuclides determined in the individual samples are statistically the same determined in the multi-increment sample. The contents of major and minor constituents, trace elements and natural radionuclides determined at the individual samples are statistically equals as those determined in the multi-increment sample. In addition, adjacent area to the nuclear material deposit, under the safeguard of Nuclear and Energy Research Institute (IPEN-CNEN / SP), isn't impacted by radionuclides as well as toxic metals since the determined contents are fewer guidelines established by legislation [8, 9]. The multi-increment sampling methodology it can use to licensing of polluting activities. Depending on the complexity of the impact caused it can use as a starting point for more complex evaluations.

REFERENCES

1. C. Jorge, “Estratégias de amostragem discreta versus incremental,” Laboratório nacional de engenharia civil, http://repositorio.lnec.pt:8080/jspui/handle/123456789/1001181, (2010).

2. “ALS Enviromental”, http://www.caslab.com/Search/?cx=007942417317104073234%3Abl98jywii1m&cof=FORID%3A11&ie=UTF-8&q=multiincrement&sa=Search, (2019).

3. STATE OF HAWAII DEPARTMENT OF HEALTH, Office of Hazard Evaluation and Emergency Response. Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan, Section 4: Soil Sample Collection Approaches. Hawai – EUA. 2008.

4. Companhia de Tecnologia de Saneamento Ambiental. Caderno da Gestão de Conhecimento – Técnicas de Investigação de Áreas Contaminadas (Parte 1). São Paulo, SP: CETESB, 2012.

5. ITRC - Interstate Technology & Regulatory Council. Incremental Sampling Methodology. ISM-1. Washington, D.C.: Interstate Technology & Regulatory Council. 2012.

6. S. N. Guilhen, F. M. Oliveira, W. S. Filho, M. E.B. Cotrim, S. K. sakaTa, M. A. Scapin, “Assessment of major and trace elements in soil and sediments from Osamu Utsumi Uranium Mine by WDXRF ", *International Nuclear Atlantic Conference - INAC 2015*, São Paulo, October 4-9, http://repositorio.ipen.br/handle/123456789/23935 (2015).

7. “Aplicação da difração e fluorescência de raios X (WDXRF): ensaios em argilominerais”, http://www.teses.usp.br/teses/disponiveis/85/85134/tde-07052007-161852/pt-br.php (2003).

8. COMPANHIA AMBIENTAL DO ESTADO DE SÃO PAULO. “Decisão de Diretoria Nº 256/2016/E, de 22 de novembro de 2016” https://www.cetesb.sp.gov.br/wp-content/uploads/2014/12/DD-256-2016-E-Valores-Orientadores-Dioxinas-e-Furanos-2016-Intranet.pdf (2016).

9. CONAMA – CONSELHO NACIONAL DO MEIO AMBIENTE. “Altera a Resolução CONAMA n. 420, de 28 de dezembro de 2009, que dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e dá outras providências." http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=702