2024 International Nuclear Atlantic Conference – INAC 2024
Escola de Guerra Naval, Rio de Janeiro, RJ, May 6 - 10, 2024

ISBN: 978-65-594-1256-3

Pb-210 Activity Concentration Measured in Rainfall in Different Sampling Heights

J. O. Almeida Neto[1], S. R. Damatto[1],
M. F. Máduar[1], L. Leonardo[1,2] and
L. F. L. Teixeira[1]

almeida.jose@usp.br, [1] *Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes, 2242, Butantã, SP*
[2] *Centro Universitário São Camilo, Av. Nazaré, 1501, Ipiranga, SP*

1. Introduction

The nuclide ^{210}Pb, a beta emitter with a half-life of $T_{1/2} = 22.3$ years, originates from the decay sequence of ^{238}U and is present in the atmosphere as a decay product of the emanated gas ^{222}Rn ($T_{1/2} = 3.8$ days). ^{222}Rn is emitted from the Earth's surface, decaying into ^{210}Pb in the atmosphere, where it interacts with aerosol particles spanning sizes from 0.07 mm to 2 mm, resembling various atmospheric contaminants [1-2]. A minor portion of ^{210}Pb returns to Earth as dry fallout, whereas it is primarily removed from the atmosphere through rainfall washout. Its airborne concentration diminishes with increasing elevation, which is attributed to its genesis at ground level. The key mechanisms for lead removal from the atmosphere involve: i) convective updrafts; ii) large-scale rainfall precipitation; and iii) dry deposition [1].

Studies attempting to establish the activity concentration and/or deposition flux of ^{210}Pb frequently lack a thorough explanation of the sampling procedure. This article analyzes the sampling procedures in Zhang et al. (2021) [3] works using bibliometric mapping approaches to better understand the various sampler placement heights and prevalent sampling strategies. After this investigation, a case study was conducted to assess whether a variation in height above ground level, specifically 23.5 m at four distinct sampling stations, could impact the activity concentration of ^{210}Pb. It is noteworthy that the height difference in sample collection is implemented at the same site across four different elevations, situated at heights of 1.5 m, 10.3 m, 15.3 m, and 25 m.

2. Methodology

An extensive bibliometric analysis of ^{210}Pb research was conducted utilizing a comprehensive dataset sourced from Zhang et al. (2021) [3]. The dataset covered studies conducted between 1950 and 2020 across 227 diverse research sites, with access facilitated through the Elsevier and Springer platforms, encompassing literature from 170 study sites. The primary objective of this methodological approach was to thoroughly investigate sampling procedures, specifically discerning between bulk and wet deposition, and examining corresponding variations in sampling height. Notably, oceanic site observations were excluded due to their consistent height characteristics. Additionally, articles not published in English, Portuguese, or Spanish, and those inaccessible via the Elsevier and Springer platforms were excluded, ensuring a focused and linguistically accessible dataset for a comprehensive analysis.

For the experimental part of these study, four 50 cm diameter conical PVC samplers were custom-manufactured and positioned at the water tank tower (23°33'54.93"S, 46°44'5.70"W) located at the Centro de Metrologia das Radiações - Instituto de Pesquisas Energéticas e Nucleares (CMR/IPEN-CNEN/SP), São Paulo (SP), Brazil. Samplers were placed at different heights (PP1: 1.5m; PP2: 10.3m; PP3: 15.3m; PP4: 25m). To make sampling easier, each sampler was connected to 20 L size containers via hoses. Rainfall was collected from July 17, 2021 to June 9, 2022, totaling 147 samples throughout 40 field campaigns.

In the laboratory, the samples were then measured for volume, pH, and electrical conductivity (EC). Subsequently, the samples underwent filtration, acidification with HNO_3 to attain a pH of 2, and concentration to a final volume of 2 L, which was subsequently subdivided into two 1 L samples (duplicate analysis). The technique described in Moreira (1993) [4] entails precipitating materials, treating with barium and lead, changing pH, causing precipitation with sulfuric acid, and aging. The precipitate will then be transferred, washed, and solubilized. After additional treatments, lead is separated and precipitated as $PbCrO_4$. A minimum 10-day wait time is required for ^{210}Pb equilibrium with ^{210}Bi. The analysis employs a low-background gas flow proportional detector. The chemical yield is calculated gravimetrically, and the ^{210}Pb activity concentration is assessed 10 days after $PbCrO_4$ precipitation [5] enabling measurement in a low-background Berthold LB770 "10 Channel α-β Low-Level Counter" gas flow proportional detector. Samples underwent counting for 2 cycles of 200 minutes.

The software IBM SPSS® 26 Statistical Package for Social Science was used for statistical studies, which included normality tests (Shapiro-Wilk), ANOVA, and Kruskal-Wallis (KW). When the null hypothesis was rejected in ANOVA or KW tests, the 'ad-hoc' Pairwise Correlation and Bonferroni tests were used, respectively. Finally, to determine data seasonality, the Mann-Whitney U test was performed.

3. Results and Discussion

Figure IA illustrate the bibliometric mapping data, which show that 86% of the studies are conducted in the northern hemisphere. The limited research conducted in the southern hemisphere primarily focus on Oceania (16) and Antarctica (6). Due to the complexity and high cost of wet deposition samplers, 96% of the studies (Figure IB) collect samples of bulk deposition (wet + dry). In 124 studies sites, the sampler allocation height was not specified (Figure IC), with the most frequent allocation height ranging between 1 and 1.5 m.

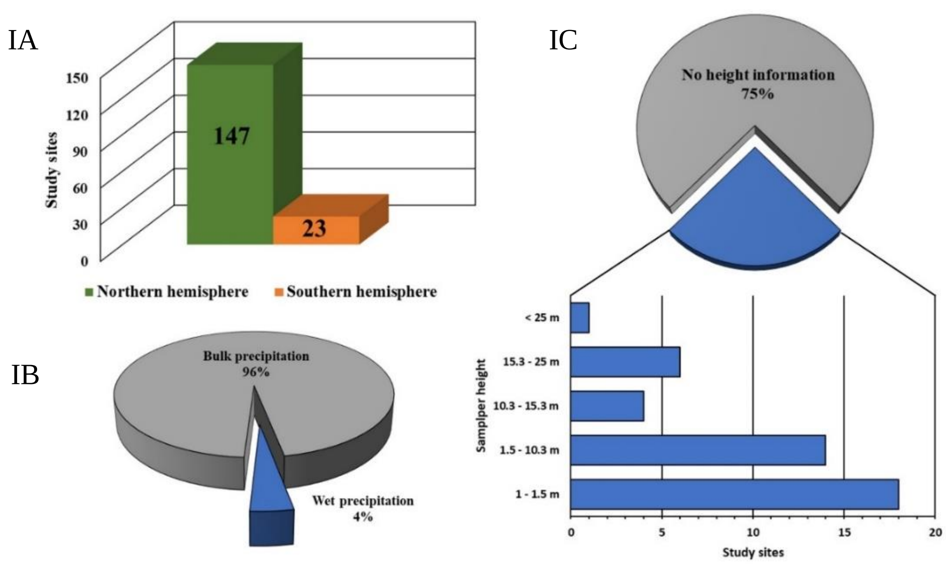

Figure IA - Hemispheric Classification of Studies; Figure IB - Types of Studied Samples; Figure IC - Analysis of Sampler Heights

Table I shows the results of monthly variation on rainfall, pH, and EC. The monthly accumulated precipitation volume varies between 3 mm (PP2 in April) and 392 mm (PP1 in January). The cumulative precipitation values (mm) for each sampler for the study period are: PP1 - 1324, PP2 - 761, PP3 - 592, and PP4 - 986. Due to the non-normal distribution of the data ($p > 0.05$), the KW test was performed, finding $H = 12.944$ and $p = 0.005$, indicating a median variation among groups. Following that, pairwise comparisons using the Point Sample Method were conducted. Pairs with significant differences ($p < 0.05$) include PP1-PP2 ($p = 0.025$) and PP1-PP3 ($p = 0.019$). The Mann-Whitney U test results show a statistically significant variation in collected volume between dry and rainy seasons ($U = 1064.5$, $p < 0.000$).

The pH values throughout the study ranged from 5.05 (PP3 in July) to 8.75 (PP1 in May), with mean values as follows: PP1 - 6.76, PP2 - 6.69, PP3 - 6.59, and PP4 - 6.18. Since the data exhibit a normal distribution, a one-way ANOVA was conducted, revealing a significant group effect on pH [$F(3,141) = 8.126$; $p < 0.05$)]. The Bonferroni post-hoc test indicated that PP4, with the most acidic samples, had a statistically different mean from the others. The Mann-Whitney U test revealed substantial seasonal variation ($U = 1015.5$, $p = 0.001$), with rainy season samples showing higher acidity.

The average electrical conductivity values (µS/cm) are as follows: PP1 - 41; PP2 - 43; PP3 - 49; PP4 - 34, varying on a daily scale from 6 µS/cm (PP4 in February) to 183 µS/cm (PP1 in August). Because the data had a non-normal distribution, the KW test was used ($H = 10.233$, $p = 0.017$), which revealed median variation between groups. The Pairwise Point Sample Comparison Test revealed a difference between PP3 and PP4 ($p = 0.015$), with sampler PP3 having the highest median rank (86) and PP4 having the lowest (56). The remaining groups did not show statistically significant differences among themselves. The reported Mann-Whitney U test revealed a statistically significant difference in EC between the dry and wet seasons ($U = 487$, $p < 0.000$), with the dry season having greater conductivities.

Table I: Monthly variation in physical-chemical analysis.

	Monthly rainfall (mm)				**Monthly pH**				**Monthly EC (µS/cm)**			
Month	**PP1**	**PP2**	**PP3**	**PP4**	**PP1**	**PP2**	**PP3**	**PP4**	**PP1**	**PP2**	**PP3**	**PP4**
Jul/21	36	14	20	31	6.50	7.13	6.20	5.42	*	*	*	*
Aug/21	32	16	19	26	6.55	6.82	6.34	6.30	183	73	35	39
Sep/21	22	13	16	19	7.06	7.37	6.98	7.33	113	123	62	82
Oct/21	159	143	83	136	6.75	6.83	6.91	6.23	44	59	65	53
Nov/21	89	67	78	92	6.71	6.81	6.47	6.30	30	24	45	25
Dec/21	225	167	186	165	6.62	6.55	6.58	6.11	38	36	41	26
Jan/22	392	193	12**	358	6.39	6.40	6.50	5.91	20	19	40	15
Feb/22	116	39	42	104	6.47	6.57	6.74	5.76	15	37	65	15
Mar/22	179	82	108	50**	6.99	6.24	6.22	5.90	20	29	33	28
Apr/22	13	3	6	5	6.51	6.69	6.85	6.67	42	47	81	50
May/22	43	20	9	*	7.81	7.22	6.71	*	32	30	44	*
Jun/22	18	6	13	*	6.81	*	6.75	*	33	*	35	*

* Not measured **Partial collection

Table II presents monthly data for volume (L) and ^{210}Pb. ^{210}Pb activity concentration ranged from 5.43 ± 0.4 mBq/L (PP1 in February) to 260 ± 26 mBq/L (PP2 in July), with monthly averages for the samplers as follows (mBq/L): PP1 – 29 ± 3; PP2 – 50 ± 4; PP3 – 35 ± 3; PP4 – 34 ± 3. Given that the study included four separate sample groups with non-normal distributions, the KW test was used, providing results $H = 4.991$ and $p = 0.172$, suggesting median similarity between groups. It is noted that the dry season has the greatest median rank (93) with fewer samples, whereas the rainy season has a lower median rank (57) with more samples. The reported Mann-Whitney U test indicates a statistically significant difference between dry and wet seasons ($U = 753$, $p < 0.000$).

Table II: Monthly rainfall and ^{210}Pb activity concentrations.

Season/Month		Monthly rainfall (L)				^{210}Pb (mBq/L) activity concentration interval - monthly mean			
Season	**Month**	**PP1**	**PP2**	**PP3**	**PP4**	**PP1**	**PP2**	**PP3**	**PP4**
Dry	Jul/21	7.1	2.7	3.9	6.1	69 ± 6	142 ± 14	57 ± 5	62 ± 2
	Aug/21	6.3	3.1	3.7	5.1	79 ± 7	35 ± 3	27 ± 2	31 ± 3
	Sep/21	4.4	2.5	3.1	3.6	64 ± 4	82 ± 4	65 ± 3	83 ± 8
Wet	Oct/21	31	28	16	27	21 ± 2	27 ± 3	34 ± 3	25 ± 3
	Nov/21	17	13	15	18	16 ± 2	71 ± 6	46 ± 2	17 ± 2
	Dec/21	44	33	36	32	39 ± 3	55 ± 5	33 ± 3	47 ± 5
	Jan/22	77	38	2.4**	70	11 ± 1	25 ± 3	81 ± 7	20 ± 3
	Feb/22	23	7.6	8.3	20	11 ± 1	43 ± 3	13 ± 1	8.8 ± 0.98
	Mar/22	35	16	21	9.9**	16 ± 1	16 ± 1	20 ± 2	17 ± 1
Dry	Apr/22	2.6	0.6	1.2	1	25 ± 1	18 ± 2	37 ± 3	55 ± 4
	May/22	8.5	3.8	1.8	*	31 ± 2	84 ± 8	32 ± 3	*
	Jun/22	3.5	1.2	2.5	*	11 ± 1	41 ± 4	8.5 ± 0.7	*

* Not measured **Partial collection

4. Conclusions

The bibliometric analysis revealed a lack of standardized sampling heights, emphasizing the case study's uniqueness. The given data and statistical parameters support the notion that a 23.5-m fluctuation cannot influence the activity concentration of ^{210}Pb. This study adds new insights into field sampling procedures, stressing the necessity of knowing how vertical orientation affects observed findings. The findings give useful recommendations for future research, laying the groundwork for better informed and effective sampling procedures in the study of ^{210}Pb activity concentration.

Acknowledgements

To CNPq (National Council for Scientific and Technological Development) for the scholarship, process n. 88887.506527/2020-00.

References

[1] M. BASKARAN. Radon: *A Tracer for Geological, Geophysical and Geochemical Studies*. Cham: Springer International Publishing (2016).

[2] K. ISAKAR; M. KIISK; E. REALO; S. SUURSOO. Lead-210 in the atmospheric air of North and South Estonia: long-term monitoring and back-trajectory calculations. *Proceedings of the Estonian Academy of Sciences*, v. 65, n. 4, pp. 442 (2016).

[3] F. ZHANG; J. WANG; M. BASKARAN; Q. ZHONG; Y. WANG; J. PAATERO; J. DU. "A global dataset of atmospheric ^{7}Be and ^{210}Pb measurements: annual air concentration and depositional flux". *Earth System Science Data*. vol. 13. pp. 2963-2994 (2021).

[4] S. R. D. MOREIRA. "*Determinação de ^{210}Pb em águas minerais da cidade de Águas da Prata.* Dissertação (Mestrado em Ciências com ênfase em Tecnologia Nuclear - Aplicações), Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP), pp. 60 (1993).

[5] D. S. M. WAKASUGI. S. R. DAMATTO. J. C. ULRICH. Natural radionuclides ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{210}Po and inorganic chemical elements determined in mineral waters from Águas de Contenda e Lambari, Brazil. *Journal of Radioanalytical and Nuclear Chemistry*, vol. 326, pp. 51-63, (2020).