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SOIL AND RIVER SEDIMENTS RADIONUCLIDES MONITORING AT CENTRO EXPERIMENTAL ARAMAR: AN HISTORICAL OVERVIEW

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ABSTRACT

In order to evaluate possible effects to the environment resulting from the implementation of the Centro Tecnológico da Marinha – Centro Experimental Aramar (CTMSP-CEA) at Iperó in São Paulo state, Brazil, which came into operation in 1989, an Environmental Monitoring Program (PMA) was established in October, 1987. One of the aims of this program is to monitor the soil and river sediments radionuclides levels at CEA and beyond its boundary. The utilization of statistical tools to evaluate the results of radiometric environmental monitoring is a procedure required by National Nuclear Energy Commission (CNEN). The box plot is a simple statistical tool for displaying data. The central tendency and dispersion of the results as well as the observation of unusual results (outliers) in the dataset are easily visualized. Control chart is a graph that maps data and provides a picture of how a process is performing over time. A control chart always has a central line for the mean, an upper line for the upper control limit and a lower line for the lower control limit. Box plots and control charts were used to visualize the annual amount of natural uranium, lead-214, actinium-228 and lead-212 in soil and river sediment detected between 1987 and 2011, considering the measurements of all monitored places each year. This historical observation shows that, in average, the results obtained are below than the 1987-1988 levels (CEA's pre-operational) or below than the backgrounds radionuclides values.

1. INTRODUCTION

Brazilian Navy develops a nuclear program research which consists of build up nuclear-propelled submarines. The Centro Tecnológico da Marinha – Centro Experimental Aramar (CTMSP-CEA), located at Iperó in São Paulo state, Brazil, is the research center responsible for developing the equipments and technology required for nuclear fuel cycle obtaining [1,2].

In order to evaluate possible effects to the environment resulting from the implementation of the center, which came into operation in 1989, an Environmental Monitoring Program (PMA) was established in October, 1987. The Laboratório Radioecológico (LARE/CTMSP-CEA, Brazil) is responsible for the PMA carrying out [1-3]. One of the aims of this program is to monitor the soil and river sediments radionuclides levels at CEA and beyond its boundary [3].

The historical overview is important to show a general panorama of the influence of CEA's operation on the environment along the years. The data amount associated with measurements dispersion, since every process has deviation, reinforces the utilization of statistical tools to evaluate the results as well. Also, National Nuclear Energy Commission

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(CNEN) is the Brazilian agency responsible for controlling Brazil's nuclear activities and the utilization of statistical tools to evaluate the results of radiometric environmental monitoring is a procedure required by this agency through the Brazilian Standards CNEN-NN-3.01 and PR-3.01-008 [4, 5].

The aim of this work is to show an historical overview of the amount of the radionuclides natural uranium, lead-214, actinium-228 and lead-212 detected in soil and river sediment at CEA and its surrounds using the box plot and control charts statistical tool.

2. METHODS

2.1. Sample Collecting and Preparation

Soil and river sediments samples were collected every six months along different places covering the Center area and about 10 km radius from CEA's meteorological tower. Soil samples were collected from 12 different places. River sediments were collected from Ipanema river, Sorocaba river and Ferro's Stream. Until 2007, river sediments were collected from 14 different places. After that, 8 different places were used for samples collecting.

The samples were completely dried in an oven at 125 °C. Dried samples were then sieved and the fraction < 120 mesh granulometry was separated and used for all analysis.

2.2. Radionuclides Determination by Gamma Spectrometry

Soil and sediment samples (an amount of 100 g each, placed in polyethylene flasks) were analyzed by gamma spectrometry by using a 65 cm^3 Ge intrinsic detector with a relative efficiency of 40% and a resolution of 1.9 keV (FWHM) for the 1332 keV peak of ^{60}Co. Until 2002, the detector was coupled to a 4096 multichannel analyzer which was connected to a microcomputer and the spectra were analyzed using the software Maestro-EGG Ortec. Since 2003, the detector was coupled to a 8192 multichannel analyzer which was connected to a microcomputer and the spectra were analyzed using the software Genie2000 (Canberra). The energy efficiency curve was obtained using a set of gamma ray reference source. The' ^{238}U natural series' activity was estimated from the 351.9 keV gamma line of ^{214}Pb. The' ^{232}Th natural series' activity was estimated from the ^{228}Ac emission at 911.1 keV and ^{212}Pb at 238.6 keV. The samples were sealed and the measurements were made one month later to ensure equilibrium between the isotopes and its daughters [6]. The counting time used was 180 min. The gamma spectrometry system calibration has been periodically checked by participating in the Brazilian National Intercomparison Program (PNI) conducted by Instituto de Radioproteção e Dosimetria (IRD/CNEN – Brazil) [7].

2.3. Uranium Determination by Fluorometry

River sediment uranium extraction: 1.000 g of the sample was transferred to a 300 mL high form beaker. 100 mL of distilled water, 1.0 mL of concentrated HNO_3 and 10.0 mL of concentrated HCl were then added to the beaker. The mixture was heated at 95 °C to reduce the volume to approximately 10 mL. After that, the mixture was cooled and filtered to a 100

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mL volumetric flask which volume was completed with distilled water. A 25 mL aliquot was transferred to a 50 mL Nessler tube and extracted with 5 mL of trioctylphosphine oxide/hexane 0.48% (w/v).

Soil uranium extraction: 1.000 g of the sample was transferred to a 300 mL high form beaker. 25 mL of distilled water, 25 mL of concentrated HNO_3, 2.0 mL of H_2O_2 30% and 5.0 mL of concentrated H_2SO_4 were then added to the beaker. The mixture, covered with a watch glass, was boiled for 40 min. After that, the mixture was cooled and filtered to a 100 mL volumetric flask which volume was completed with distilled water. A 25 mL aliquot was transferred to a 50 mL Nessler tube and extracted with 5 mL of trioctylphosphine oxide/hexane 0.48% (w/v).

The fluorometry analysis was carried out by placing 100 μL of the extracted uranium in a platinum crucible which solvent was evaporated under an infrared light and then calcined at 710 °C for 15 min in a furnace. After that, 400 mg of flux (a mix of 45.5 parts of Na_2CO_3, 45.5 parts of K_2CO_3 and 9 parts of NaF) was added to the crucible and then the mixture was fused together at 710 °C for 5 min. The fused disk was cooled in a dessicator and exposed to an ultraviolet radiation source by using a Galvanek - Morrison type digital fluorometer CNEN-IEN, model 5015 [8]. The intensity of the fluorescence is measured and its comparison with the fluorescence of a uranium standard disc allows the calculation of the sample uranium concentration.

2.4. Statistical Analysis

2.4.1. Box plots

A box plot is a graphical depiction of both central tendency and dispersion of the results and is helpful for interpreting the distribution of data, since it can easily show whether the data is skewed and if there are unusual observations (outliers) in the dataset. Box plot are also very useful when large numbers of observations are involved and when two or more datasets are being compared. Fig. 1 shows an example of a box plot [9-12].

The box itself contains the middle 50% of the data. The horizontal line in the box indicates the median value of the data and the small circle indicates the mean. The upper edge (hinge) of the box is defined as the 75^{th} percentile of the data set, and the lower hinge the 25^{th} percentile. The vertical lines are called “whiskers” and its ends indicate the minimum and maximum data values, unless outliers are present [10, 11]. The length of the vertical lines indicates visually how far from the middle of the distribution the extreme values are. Data points that lie outside the ends of the whiskers are suspected to be outliers. The outliers can be determined as follow:

Upper inner value = 75^{th} percentile value + (1.5 x interquartile range), where the interquartile range = 75^{th} percentile value - 25^{th} percentile value. Lower inner value = 25^{th} percentile value - (1.5 x interquartile range). Data points that lie outside of the fence values are considered to be outliers [10, 11].

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Box plots were used in this work to visualize the annual amount of radionuclides detected in soil between 1987 and 2011, considering all sampling locations measurements obtained during each year.

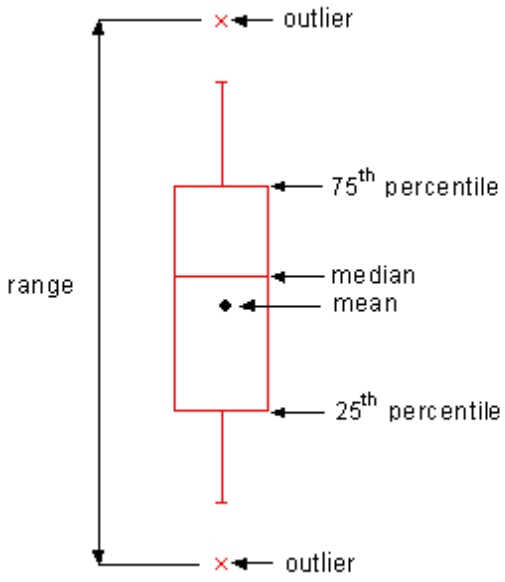

Figure 1: Box plot representation.

2.4.2. Control charts

A control chart is a graphic display used to verify process stability over time, i.e., a process that has displayed a certain degree of consistency in the past and is expected to continue to do so in the future. This consistency is characterized by a stream of data falling within control limits based on ±3 standard deviations of the mean (99.73% probability of data being within these limits). A control chart always has a central line for the mean, an upper line for the upper control limit (+3sigma) and a lower line for the lower control limit (-3sigma). These control limits are chosen so that if the process is in control, nearly all of the samples points will fall between them. These lines are determined from historical data and the goal of using a control chart is to achieve and maintain process stability. As long as the points plot within the control limits, the process is assumed to be in control, and no action is necessary [12,13]. Fig. 2 shows an example of a control chart.

Every process has variation. Some variation may be the result of causes which are not normally present in the process. This could be special cause variation. Some variation is simply the result of numerous, ever-present differences in the process. By comparing current data to these lines, it is possible to draw conclusions about whether the process variation is in control or out of control, affected by special causes of variation.

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In this work, control charts were used to visualize the annual average amount of radionuclides detected in river sediment between 1987 and 2011, considering all sampling locations measurements obtained during each year.

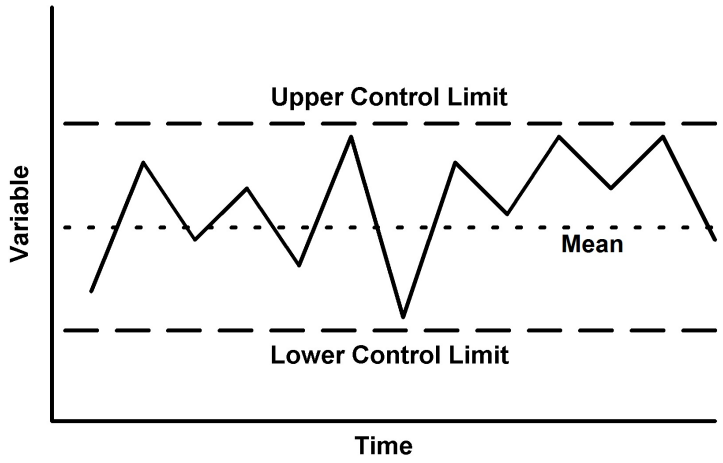

Figure 2: Control chart representation.

3. RESULTS AND DISCUSSION

CEA´s pre-operational, performed during 1987 and 1988, was conducted by Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN - Brazil). The pre-operational results presented in this work as well as the methods used to obtain these results are described at IPEN 233 Publication [14]. Table 1 shows the values of LLD along the years for all radionuclides measured in soil and river sediments in this work.

Fig. 3 and 4 shows, respectively, box plots for annual amount of natural uranium and ^{214}Pb in soil monitored from 1987 to 2011. Each box contains all data collected during the year at all collecting points. In this case, no distinction involving a particular sampling location is established.

Fig. 3 shows that the amount of natural uranium detected in soil along the years are, in average, bellow the 1987-1988 levels (CEA's pre-operational), except for 1989 and 1990. Also, the presence of outliers is observed along the years. Outliers can occur by chance in any distribution, but they are often indicative either of measurement error or a valid situation which require attention but must be treated as an isolated situation.

Even considering the higher values, compared to the pre-operational values, and the outliers, the higher amount of natural uranium detected from 1987 to 2011 is within the typical concentration range for natural uranium in soil (0.3-11.7 mg/kg) [15], since 120 Bq/kg is equivalent to 4.7 mg/kg of natural uranium, considering the natural uranium specific activity as 25,300 Bq/g [15].

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Table 1: Low Level Detection limits (LLD) along the years for radionuclides in soil and river sediment by using gamma spectrometry (^{214}Pb, ^{228}Ac and ^{212}Pb) and fluorometry (natural uranium).

	Radionuclide	1989 - 1998	1999 - 2003	2004 - 2012
	natural uranium	25	1	1
Soil	^{214}Pb	10	10	50
(Bq/kg)	^{228}Ac	10	10	10
	^{212}Pb	10	10	10
	natural uranium	25	1	1
River Sediment	^{214}Pb	10	10	50
(Bq/kg)	^{228}Ac	10	10	10
	^{212}Pb	10	10	10

Fig. 4 shows that, in general, the amount of ^{214}Pb along the years is consistent. After 2003, the amount of ^{214}Pb present in the samples was below the detection limit..

Figs. 5 and 6 shows, respectively, box plots for annual amount of ^{228}Ac and ^{212}Pb in soil monitored from 1987 to 2011. Also here, each box contains all data collected during the year at all collecting points. The results show that the amount of ^{228}Ac and ^{212}Pb detected in soil along the years are, in average, bellow the 1987-1988 levels (CEA's pre-operational). Also, a correlation is observed for both graphs indicating equilibrium between the two radionuclides. The amount of ^{228}Ac detected in the years of 2006 and 2008 was below the detection limit. The amount of ^{212}Pb detected during 2004 -2008 was also below the detection limit.

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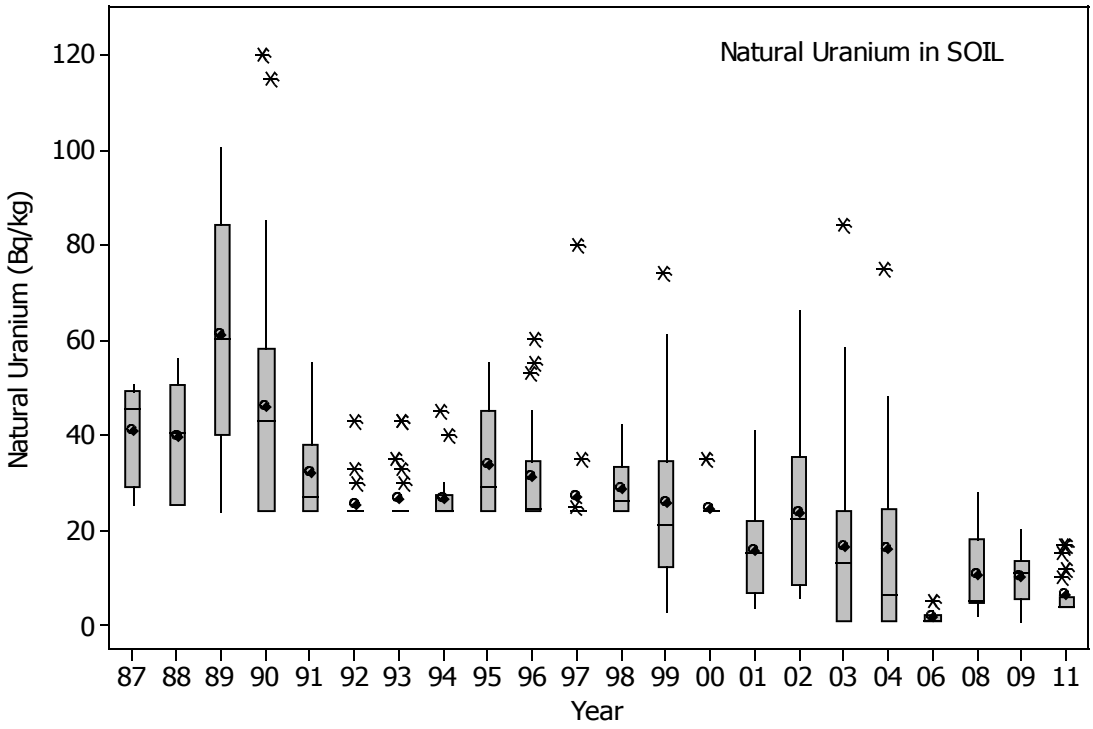

Figure 3: Box plots for annual amount of natural uranium detected in soil from 1987 to 2011, considering all sampling locations.

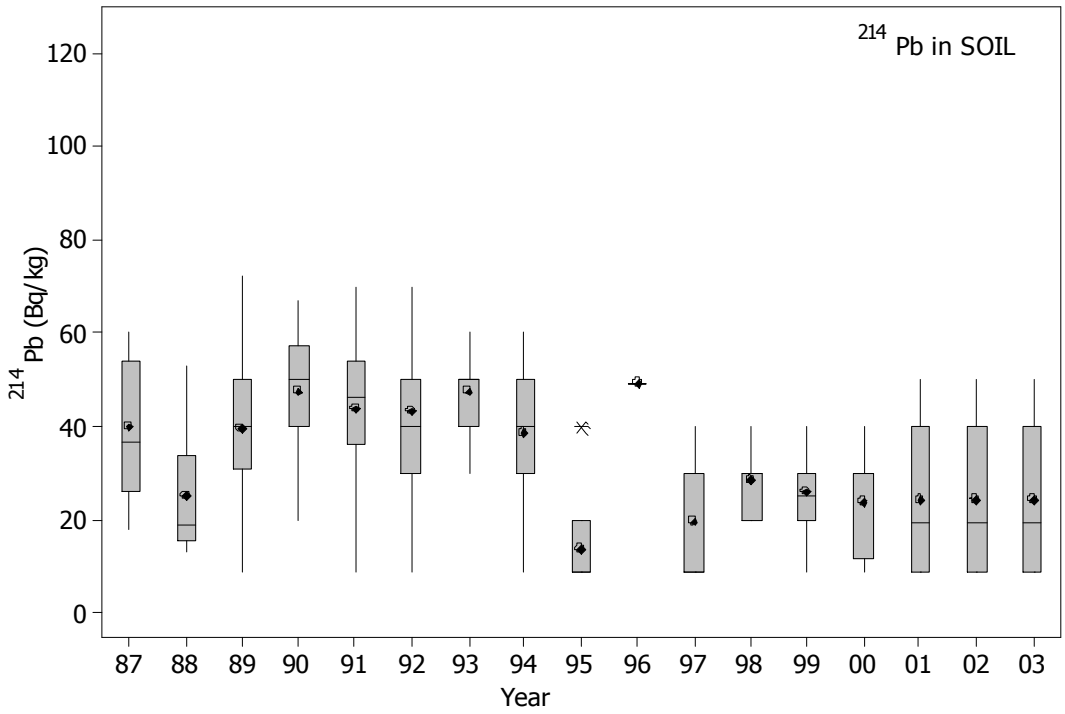

Figure 4: Box plots for annual amount of ^{214}Pb detected in soil from 1987 to 2003, considering all sampling locations.

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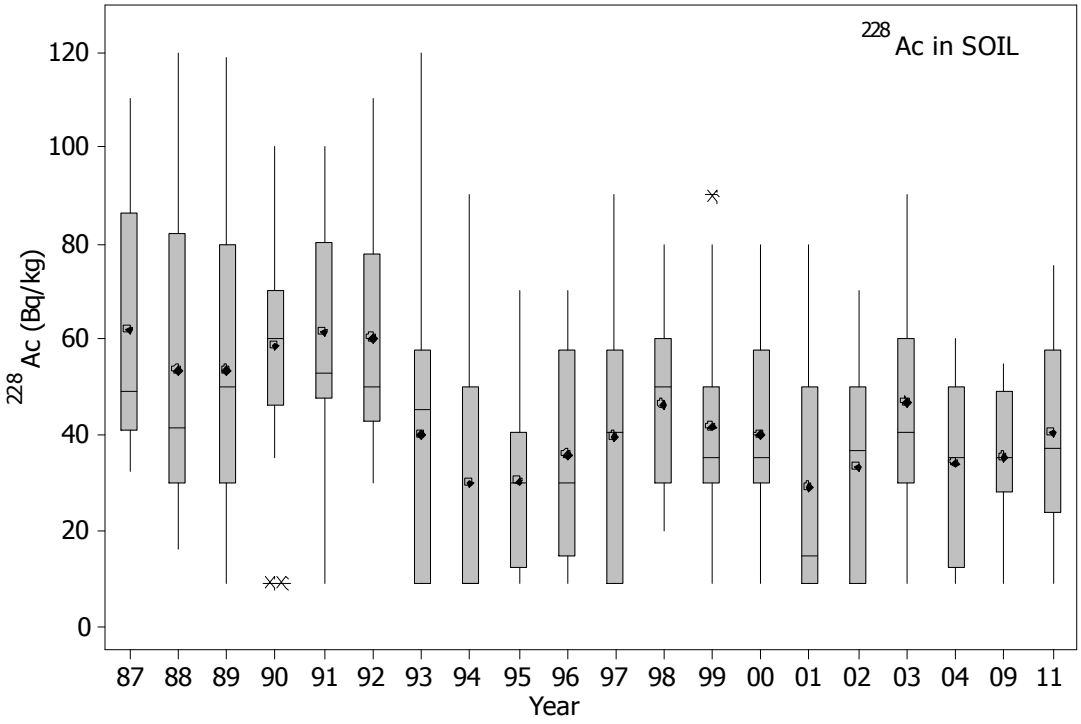

Figure 5: Box plots for annual amount of ^{228}Ac detected in soil from 1987 to 2011, considering all sampling locations.

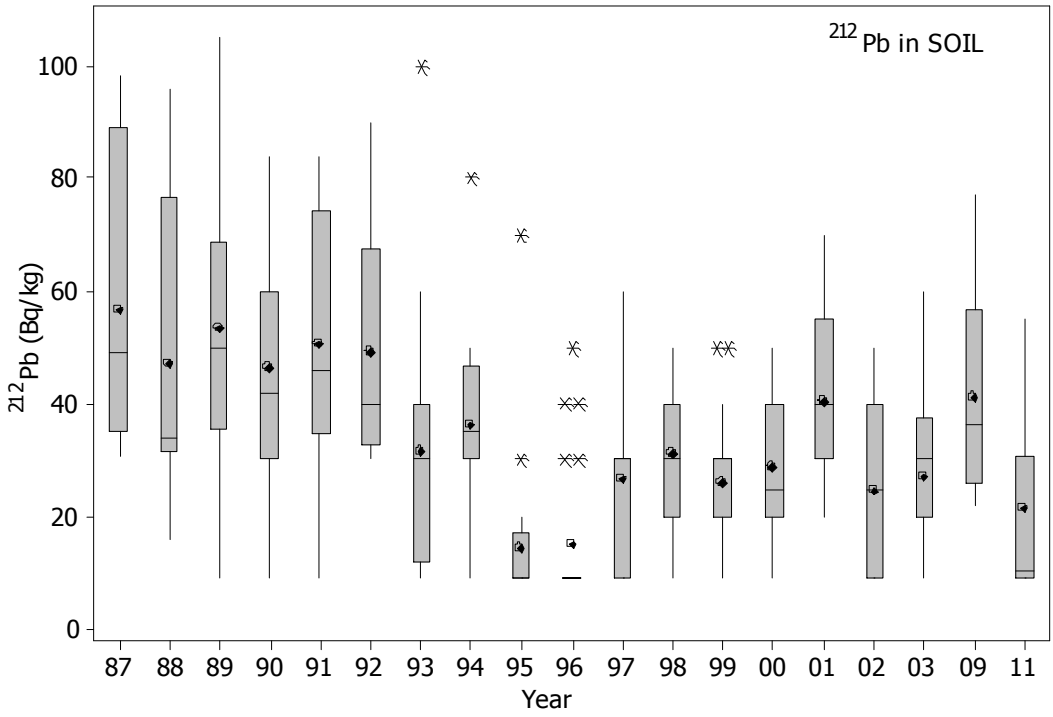

Figure 6: Box plots for annual amount of ^{212}Pb detected in soil from 1987 to 2011, considering all sampling locations.

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In order to use control charts for individual measurements it is necessary a normal distribution for the population. On the other hand, according to the central theorem of limit, the distribution of the measurements average can be approximately considered as normal [16]. For this reason, the annual average amounts of the radionuclides were used to build the control charts. Figs. 7 to 10 show control charts for annual average amount of natural uranium, ^{214}Pb, ^{228}Ac and ^{212}Pb, respectively, detected in river sediment from 1987 to 2011, considering all sampling locations.

Fig. 7 shows that the average amount of natural uranium was kept along the years between the control limits, meaning that the process is assumed to be in control. Even though the average amount of natural uranium are between the control limits, some years monitoring show, in average, results above CEA's pre-operational values. However, the maximum average value found was around 63 Bq/kg (2.5 mg/kg), which is consistent with the average amount of natural uranium already found in river sediment in other places [17,18]. It can be observed that in the last ten years the annual average values found have remained below the mean.

Also, some fluctuation in the average amount of uranium detected in river sediment along the years can be attributed to seasonal variation in response to changes in the hydrological regime. Periods with low-flow conditions leads to transport of finer-grained particulates, longer contact times between sediment and water and generally higher organic contents all of which favor the sorption of uranium by the sediment [19].

Fig. 8 shows that the amount of ^{214}Pb detected along the years remained below the CEA's pre-operational values. After 2003, the amount of ^{214}Pb present in the samples was below the detection limit.

Figs. 9 and 10 show that even though isolated annual average values failed out the upper control limits, all the annual average values for ^{228}Ac and ^{212}Pb remained below the CEA's pre-operational values. It can also be observed that since 1995 the annual average values found for both radionuclides have remained below the mean. Also, a correlation is observed for both graphs indicating equilibrium between the two radionuclides.

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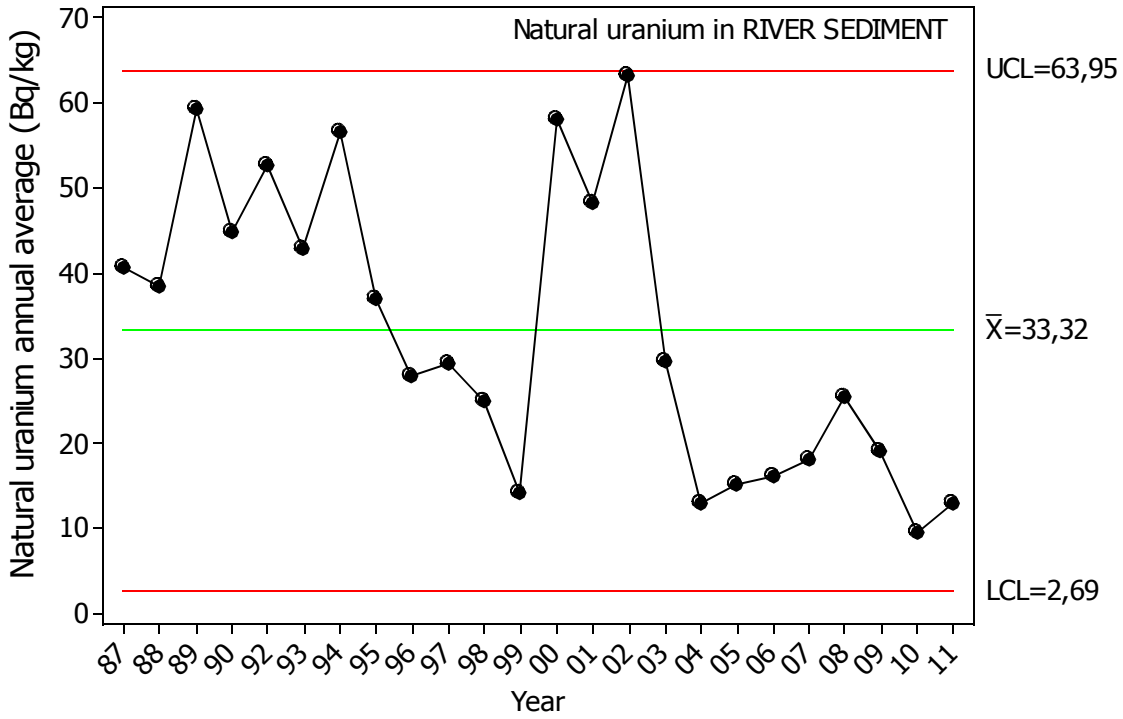

Figure 7: Control charts for annual average amount of natural uranium detected in river sediment from 1987 to 2011, considering all sampling locations. UCL = Upper Control Limit, LCL = Lower Control Limit, $\bar{X}$ = mean.

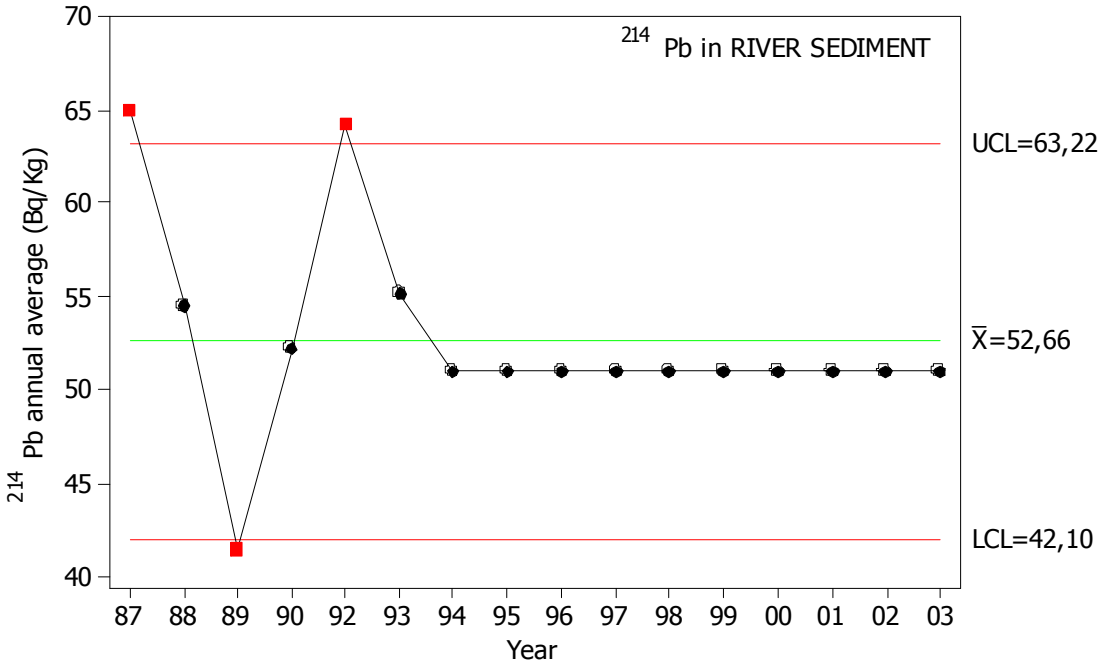

Figure 8: Control charts for annual average amount of ^{214}Pb detected in river sediment from 1987 to 2003, considering all sampling locations. UCL = Upper Control Limit, LCL = Lower Control Limit, $\bar{X}$ = mean.

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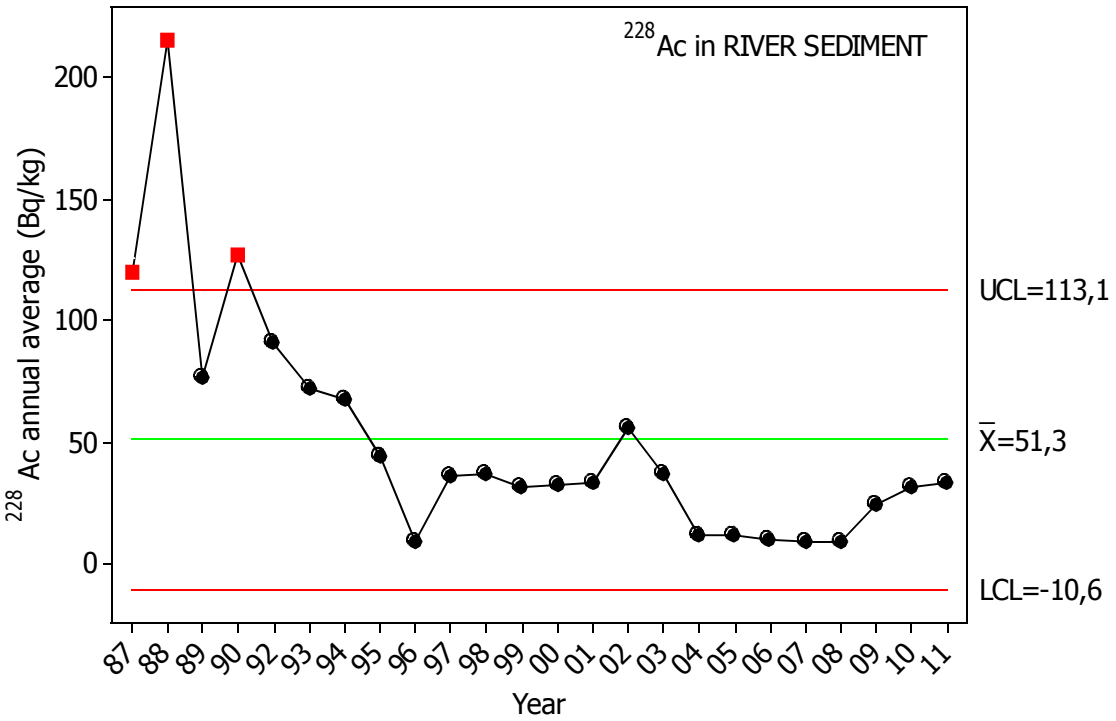

Figure 9: Control charts for annual average amount of ^{228}Ac detected in river sediment from 1987 to 2011, considering all sampling locations. UCL = Upper Control Limit, LCL = Lower Control Limit, $\overline{X}$ = mean.

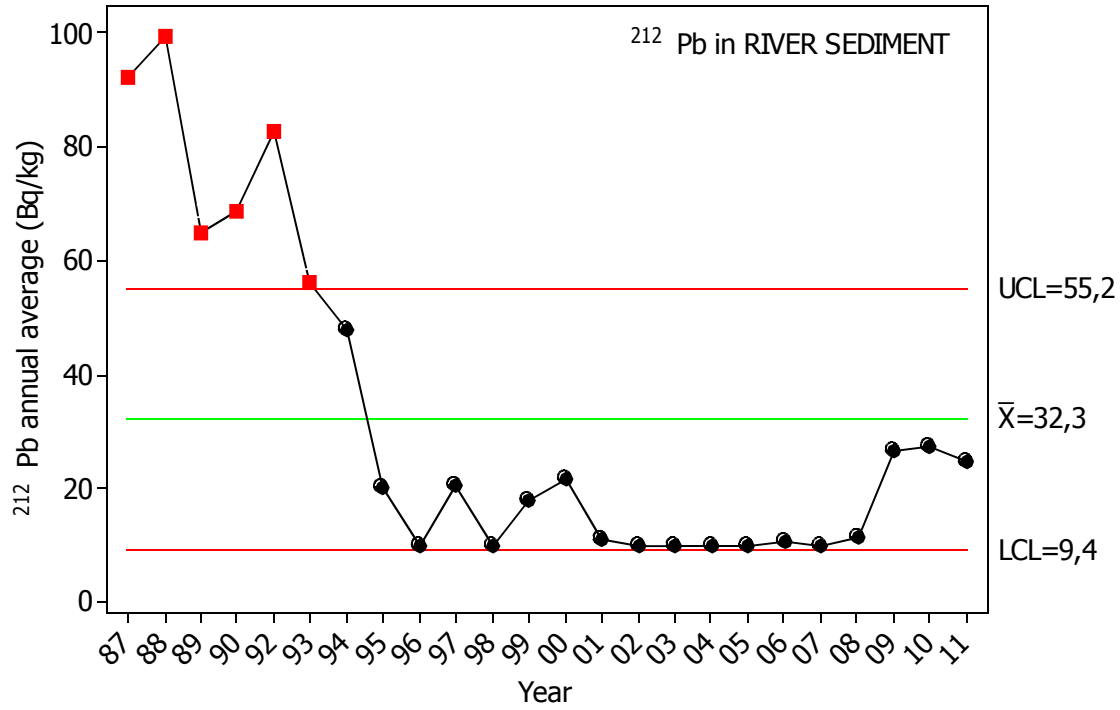

Figure 10: Control charts for annual average amount of ^{212}Pb detected in river sediment from 1987 to 2011, considering all sampling locations. UCL = Upper Control Limit, LCL = Lower Control Limit, $\overline{X}$ = mean.

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4. CONCLUSIONS

The historical observation of radionuclides monitoring in soil and river sediment shows that, in average, the results obtained are below than the 1987-1988 levels (CEA's pre-operational) or below than backgrounds radionuclides values. All statistical methods presented in this work proved to be useful to visualize and evaluate high number analysis results datasets.

REFERENCES

1. "Conheça o programa nuclear da Marinha", www.mar.mil.br/pnm/pnm.htm (2013).
2. "Centro Tecnológico da Marinha em São Paulo", www.mar.mil.br/ctmsp/conheca_centro (2013).
3. Centro Tecnológico da Marinha em São Paulo, Programa de Monitoração Ambiental do CEA (PMA). Documento nº A18.02-0200 – PG - 0003 – 2007.
4. Comissão Nacional de Energia Nuclear (CNEN) - **CNEN-NN-3.01, "**Diretrizes básicas de proteção radiológica", Rio de Janeiro, Brazil (2005).
5. Comissão Nacional de Energia Nuclear (CNEN) - **Posição Regulatória 3.01/008,** "Programa de monitoração radiológica ambiental", Rio de Janeiro, Brazil (2005).
6. M.A.P.V. Moraes, T.F.L. Daltro, "Environmental gamma radiation and natural radioactivity in soils in Centro Experimental Aramar (CTMSP-Brazil) and region", *Radiation Protection Dosimetry*, **87**, pp. 207-211 (2000).
7. L. Tauhata, M. E. C. M. Vianna, A. E. Oliveira, A. C. Ferreira, M. J. C. Bragança, A. F. Clain, R. Q. Faria, "The Brazilian National Intercomparison Program (PNI/IRD/CNEN): evaluation of 15 years of data", *Journal of Environmental Radioactivity*, **86**, pp. 384-390 (2006).
8. American Society for Testing and Materials – ASTM. Annual Book of ASTM Standards - Water and Environmental Technology, Section 11.02, pp. 516 – 522 (1986).
9. R. McGill, J.W. Tukey, W.A. Larsen, "Variations of box plots", *The American Statistician*, **32**, pp. 12-16 (1978).
10. M. Frigge, D.C. Hoaglin, B. Iglewicz, "Some implementations of the boxplot", *The American Statistician*, **43**, pp. 50–54 (1989).
11. D.C. Montgomery, *Design and Analysis of Experiments*, 6th ed., John Wiley & Sons, New York, pp. 25 (2005).
12. D.C. Montgomery, *Introduction to Statistical Quality Control*, 5th ed., John Wiley & Sons, New York, pp. 50; pp. 150 (2005).
13. Associação Brasileira de Normas Técnicas (ABNT) - **NB-1326,** "Controle estatístico para prevenção e detecção de desvios da qualidade, durante processos de fabricação, por meio de gráficos", Rio de Janeiro, Brazil, 1990.
14. G. Hiromoto, V.M.F. Jacomino, L. Venturini, S.R. D. Moreira, A.M.P.L. Gordon, C.L. Duarte, B.R.S. Pecequilo, B.P. Mazzilli, "Programa de monitoração ambiental da usina de enriquecimento de urânio almirante Álvaro Alberto", Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN) – Publicação 233, novembro de 1988. São Paulo, 75p.
15. A. Bleise, P.R. Danesi, W. Burkart, "Properties, use and health effects of depleted uranium (DU): a general overview", *Journal of Environmental Radioactivity*, **64**, pp. 93-112 (2003).

ISBN: **978-85-99141-05-2**

16. Estatística aplicada ao sistema de medição. Porto Alegre: Siqueira Campos Associados, julho - 2012. 231 p. Apostila do curso. pp. 109.
17. M.R. Scott, "Thorium and uranium concentrations and isotope ratios in river sediments", *Earth and Planetary Science Letters*, **4**, pp. 245-252 (1968).
18. M.E. Ketterer, W.C. Wetzel, R. R. Layman, G. Matisoff, E.C. Bonniwell, "Isotopic studies of sources of uranium in sediments of the Ashtabula river, Ohio, USA", *Environmental Science & Technology*, **34**, pp. 966-972 (2000).
19. A.J. Plater, M. Ivanovich, R.E. Dugdale, "Uranium series disequilibrium in river sediments and waters: the significance of anomalous activity ratios", *Applied Geochemistry*, **7**, pp. 101-110 (1992).

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