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TEMPORAL COMPORTMENT ASSESSMENT OF METALS IN GROUNDWATER ON THE CAMPUS AT IPEN/CNEN-SP

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ABSTRACT

Since 2006, Nuclear and Energy Research Institute (IPEN) performs yearly the Environmental Monitoring Program of Stable Chemical Compounds (PMA-Q).Among other parameters, metals and semi metals in groundwater, collected at Ipen's facility, are evaluated. The monitoring is conducted in nine wells, in attendance to the current Brazilian environmental legislation, which requires the monitoring of metals and semi metals in groundwater, in accordance with CETESB and CONAMA's resolutions. CETESB is the Sao Paulo State environmental regulatory agency and CONAMA is the Environmental National Council, both agencies that regulate environmental standards in Brazil and regulate Ipen's environmental activities. Besides these two environmental regulators, Ipen have to follow the request of the Term for the Adjustment of Conduct (TAC) from (IBAMA), in order to support programs to prevent and control pollution resulting from activities of Ipen's facilities. In the current PMA-Q, aluminum (Al) antimony (Sb), silver (Ag), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), zinc (Zn), boron (B), barium (Ba), calcium (Ca), iron (Fe), manganese (Mn), mercury (Hg) and nickel (Ni) are analyzed by using sensitive analytical techniques as inductively coupled plasma optical emission spectrometry (ICP-OES) and graphite furnace atomic absorption spectrometry (GF-AAS). These elements results are in this paper evaluated. Both internal and external quality controls that uses data from interlaboratory programs are discussed here. It was possible to conclude that IPEN's groundwater attends national standards and Ipen's monitoring system operates under controlled quality conditions.

Keywords: Groundwater, Metals, Monitoring; IPEN/CNEN-SP, Quality Control

1. INTRODUCTION

The groundwater is rainwater that falls and infiltrate the ground, in pores between sand, clay and rocky formation called aquifer (1); and performance a fundamental role in the maintenance in the soil humidity, river and lake flow (2)

The Environmental Monitoring Program of Stable Chemical Compounds (PMA-Q) define basics conditions to life protection and propriety at IPEN, where are handled all kind of products, being radioactive, biological and chemical. In addition to monitoring that takes place in the nine groundwater wells that are in IPEN 's facilities, there are also monitoring in the wastewater of the institution (3).

The program started in 2006 with the groundwater monitoring. The analyses results has being compare to the actual legislation, such as the Society of Environmental Sanitation Technology of State of São Paulo (CETESB), with the board directory #195-2005-E, of November 23, 2005, that set about the approval of the Guiding Values for Soil and São Paulo State Water.

And the Resolution #420, of December 28, 2009, of the National Environment Council (CONAMA), which establishes the criteria and guiding values of soil quality for the presence of chemicals and establish guidelines for the environmental management of contaminated areas by these substances as a result of anthropogenic activity (4), (5), (3).

In addition, to comply with the environmental laws, IPEN needs to be with the requirements of Adjustment and Conduct Term (TAC), the Brazilian Institute of Environmental and Renewable Natural Resources (IBAMA). IBAMA that are authorized to give the environmental licensing of activities and projects for the research, production, storage and disposal of radioactive materials, than the IPEN needs to be with the environmental regulations to operate. Among other parameters, this term requires the groundwater monitoring to investigate possible indications contaminants, such as the presence of metal and semi metal.

The contamination by metals and semi metals in aquatic environments is of concern due to their toxicity and abundance in the environment, in which there is accumulation of metals in flora and fauna, consequently enters the food chain and can cause harmful effects to various organism. The trace metals are the main causes of these harmful effects and can come from domestic and industrial wastewater within the water body (5) (6) (7).

The objective of this paper work is to evaluate the metals and semi metals, such as aluminum (Al) silver (Ag), lead (Pb), chromium (Cr), cobalt (Co), zinc (Zn), boron (B), barium (Ba), iron (Fe), manganese (Mn), mercury (Hg), calcium (Ca), nickel (Ni), antimony (Sb) and arsenic (As). Which the guiding values are, regulate by CETESB in groundwater and can be present in the eight environmental monitoring wells installed at IPEN. The study period correspond an interval between 2011 and 2014 and the results have been compared to the valid legislation. In addition, demonstrate the mode of operation of the internal and external quality control system at the Laboratory of Chemical Analysis and Environmental (LAQA) conducting the tests involved in this study.

2. MATERIALS AND METHODS

The groundwater samples collected at IPEN were held in nine monitoring wells, distributed within the institute (see Figure 1). The well, named, PM-08 started the collection in March 2012. In March 2013 the AP-05N and AP-06N- wells were opened. From March 2014 the abbreviation used to identify the wells, *AP*, have been changed to PM (Monitoring Well). The collection points and its locations are present in Table 1. The Construction characteristics of the monitoring wells installed are present in the Table 2.

Table 1 - Identification of collection wells groundwater Campus of IPEN/CNEN-SP

Wells Identification	Localization	GPS Localization*
PM-01	General Ordinance (Spots sector)	23°33'43.51"S - 46°44'13.87"W
PM-02	UITAR - LRR	23°33'59.66"S - 46°44'4.58"W
PM-03	CQMA (Industrial Complex)	23°33'40.76"S - 46°44'27.90"W
PM-04	Shed Safeguards	23°33'40.00"S - 46°44'26.58"W
PM-05	Via perimetral	23°33'36.67"S - 46°44'33.07"W
PM-06	Behind the UITAR – LRR	23°33'58.39"S - 46°44'7.43"W
PM-08	GREIC	23°33'36.51"S - 46°44'32.98"W
PM-09(AP-05N)	Via perimetral	23º33'37,3''S - 46º44'33,1''W
PM-10(AP-06N)	Behind the UITAR – LRR	23º33'38,4''S - 46º44'08,1''W

*GPS – Global Positioning System - (S – South latitude – W – West Longitude)

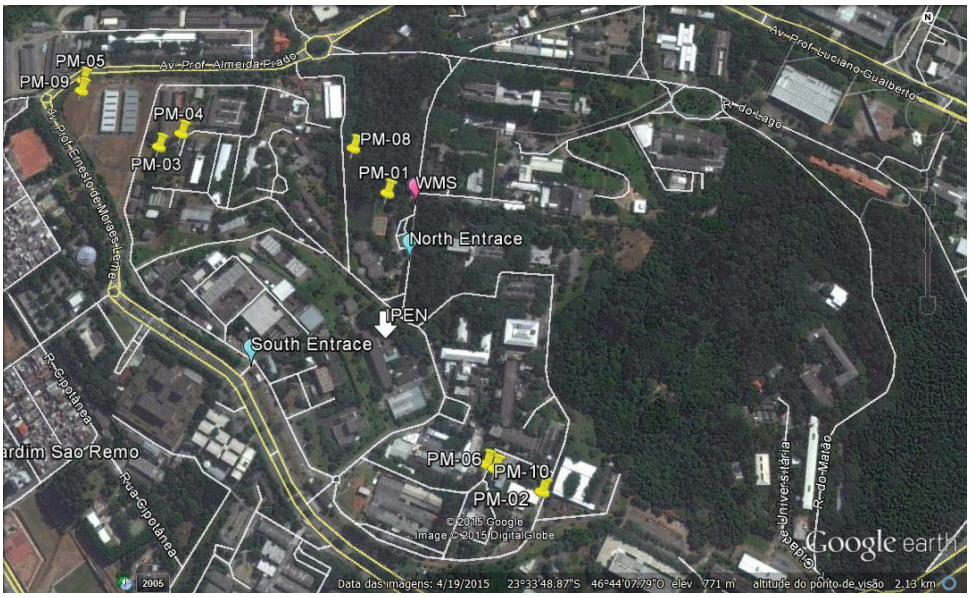

Figure 1 - IPEN's monitoring wells location.

The water samples collection followed the *National Guide Collection and Sample Preservation*, of the National Water Agency (ANA)/CETESB (8) and the *Standard Methods for the Examination of Water and Wastewater* (9). For the collection in the wells were used a depletion device (without purge), *bailer*.

Table 2 - Construction characteristics of the monitoring wells installed

Wells Identification	Depth (m)	Static level (m)	Water column (m)
PM-01	22,9	12,4	10,4
PM-02	15,9	8,6	7,4
PM-03	23,7	3,5	20,0
PM-04	19,8	4,6	14,4
PM-05	15,5	0,8	15,0
PM-06	15,7	8,0	7,2
PM-08	16,0	6,8	9,0
PM-09(AP-05N)	14,9	3,9	11,0
PM-10(AP-06N)	15,0	7,7	7,3

2.1. Metal Analysis

All analyzes were performed by IPEN's Chemical and Environmental Analysis Laboratory (LAQA). The following techniques to quantifying elementals at trace levels were employed:

- Atomic Absorption Spectrometry with Cold Vapor Generator (CVAAS):
  - Mercury;
- Atomic Absorption Spectrometry with graphite furnace (GF-AAS):
  - Arsenic, antimony;
- Optical Emission Spectrometry with Inductively Coupled Plasma Source (ICP-OES):
  - Aluminum, barium, boron, cobalt, lead, chromium, iron, manganese, nickel, silver, calcium and zinc

2.2. Internal and External Quality Control

Internal Quality Control (IQC) consists in a series of actions that allow the control chart construction with elemental results of SRM 1643e reference material, manufactured by NIST (National Institute of Standards and Technology) and traceable to SI in the GF-AAS analysis.

To ICP-OES analysis, Background Equivalent Concentration (BEC) was performed, that test consists of phosphorus (P) and manganese (Mn) measurements at Background level, to demonstrate the technique adequate sensitivity and detection limit.

External Quality Control (EQC) was performed by several proficiency tests provided mostly by *Rede Metrologica do Rio Grande do Sul*, from 2010 until 2014. EQC data corresponds to LAQA performance as per Z-score criteria. Z-score was calculated by interlaboratory program providers as stated in ISO / DIS 13528:2005 - *Statistical methods for use in proficiency testing by interlaboratory comparisons* (6). Z-score of each laboratory average (n = 3) was obtained by the equation 1:

$$Z = \frac{(x_i - x^{**})}{s^{**}} \qquad (1)$$

Where: x_i = the arithmetic average of the results obtained by the participant;

x^{**} = the value average of the robust set of data;

s^{**} = the robust diversion.

Laboratories performances were classified as SATISFACTORY, QUESTIONABLE or UNSATISFACTORY, to each of the measure, considering the following criteria:

If: $|Z| \leq 2$ Satisfactory results

$2 < |Z| < 3$ Questionable results

$|Z| \geq 3$ Unsatisfactory results

2.3. Brazilian Environmental Regulation

Brazilian Environmental regulation used in this work are the CETESB recommended values for Groundwater and CONAMA Resolution #420. Standards of inorganic substances stated in Brazilian regulations to groundwater, are present in Table 3.

The CETESB reviewed the recommended values in 2014, in these news values the iron, aluminum and manganese elements is no longer in the legislation, once that these elements when appears with high concentration, they are related in the wells construction, and not in eventual contamination in the study area. Besides, these elements give taste and color for the water.

To demonstrate the temporal comportment of these elements in study, between 2011 and 2014, will be used the CETESB old and the new legislation.

Table 3 - Environmental standards of inorganic chemicals in groundwater (4) (5) (10)

	CETESB - Decision of Board #195-2005-E	**CONAMA Resolution # 420/2009**	**CETESB -Decision of Board #045/2014/E/C/I**
Elements	**Concentration ($\mu g.L^{-1}$)**	**Concentration ($\mu g.L^{-1}$)**	**Concentration ($\mu g.L^{-1}$)**
Arsenic (As)	10	10	10
Aluminum (Al)	200	3500	-
Antimony (Sb)	5	5	5
Boron (B)	500	500	2400
Lead (Pb)	10	10	10
Cobalt (Co)	5	70	70
Chromium (Cr)	50	50	50
Barium (Ba)	700	700	700
Iron (Fe)	300	2450	-
Manganese (Mn)	400	400	-
Mercury (Hg)	1	1	1
Nickel(Ni)	20	20	70
Zinc (Zn)	5000	1050	1800
Silver (Ag)	50	50	50

3. RESULTS AND DISCUSSION

3.1. Ipen's Groundwater status

The elements, arsenic, antimony, boron, lead, cobalt, chromium, barium, mercury, zinc and silver were below the recommended values. Iron, manganese and aluminum had values above the recommend values. The iron ad values above the recommended in four wells, as PM-01 (AP-01), PM-05, PM-06 and PM-09 (AP-05N), manganese in three wells, as PM-01 (AP-01), PM-05 and PM-09 (AP-05N) and aluminum had in two wells, as PM-02 and PM-03.

Iron in PM-01 (AP-01) wells, from 2011 to 2014, had the recommended values above the former CETESB legislation, also in the PM-05 in the years 2011 and 2012, in the PM-06, in only in one collection, in May 2012 and the PM-09 (AP-05N), in the years 2013 and 2014. However, in 2014, as mentioned in the item 2.3 iron is no longer in the new review of the legislation, so all the data from iron concentration is satisfactory after 2014. Iron used to be regulated because gives to water of color and taste. Higher results from iron came from the soil and tells more about well filter status than about water itself.

The same was observed with manganese, in 2011 and 2012 in the well PM-01. From 2011 to 2013, in the wells PM-05 and PM-09 (AP-05N), and in 2014 only in the well PM-05, but equal as iron, manganese is no longer in the new review of the legislation and these higher values came from the soil.

Aluminum in the year 2011 the only well that presented recommend values above the legislation was PM-02. In 2013, in the well PM-03, only one collection, in March, presented values above. Equal iron and manganese, this element is no longer in the legislation and the values for these three elements after 2014 is satisfactory.

In 2014, arsenic and lead exceeding values were reported. Lead in PM-01 and arsenic in PM-09 (AP-05N).

3.2. Quality control data:

The individual laboratory Proficiency performance obtained from 2010 and 2014, for arsenic, iron, calcium, mercury and nickel are presented in Figure 2.

Calcium was the element with 100% of the results satisfactory. The elements arsenic had one result questionable, iron had one unsatisfactory result and nickel had two unsatisfactory results. The mercury element had four unsatisfactory result, from twelve test.

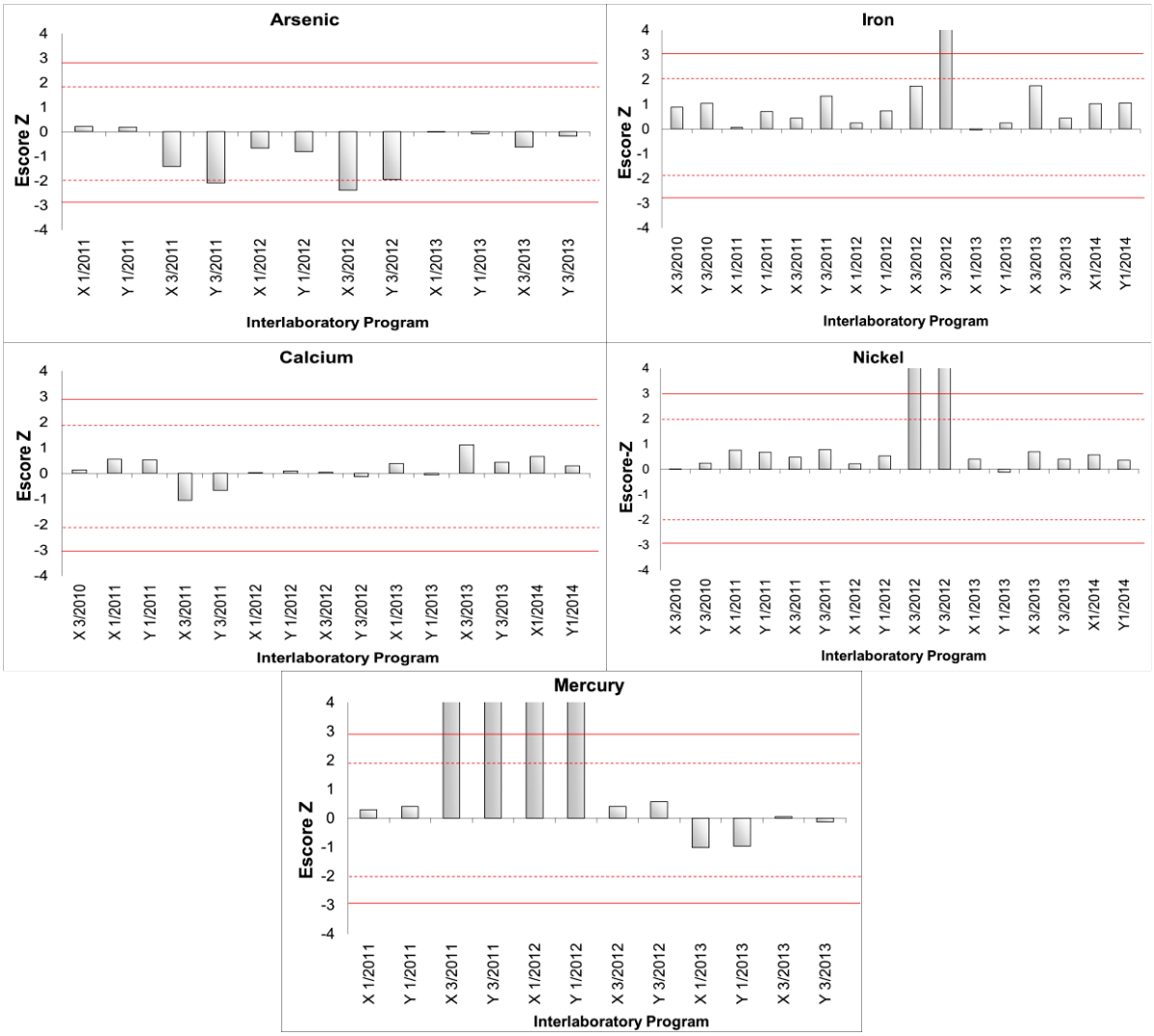

Figure 2 - Data from arsenic, iron, nickel, calcium and mercury in water's interlaboratory program, from 2010 to 2014

The unsatisfactory or questionable results main causes were as following:

- Reagent Contamination;
- Incorrect results expression, such as incorrect chemical form or incorrect measurements unity;
- Test condition, instrumental degradation, such as standards and analytical curve.

These problems were identified also in the internal quality control so corrective measures were taken to ensured satisfactory values in the following interlaboratory programs rounds.

3.3. Internal Quality Control

Every sample batch had as internal quality control blank, standard addition, reference material and replicate samples for every metal. As reference material for recovery evaluation, in the GF-AAS, it was used the NIST – SRM 1643e. This reference material was used to evaluate the reproducibility and the element recovery by comparison with its certificated and reference values.

From ICP-OES, besides the blank and the standard addition, the BEC solution was past for verification. One example from the results are present in Table 4. To be considered satisfactory the Mn need to be with 0,01 $mg.L^{-1}$ and P need to be with 0,3 $mg.L^{-1}$. All the results from BEC was satisfactory.

Table 4 - Example from BEC analysis from water analysis, from 2014

BEC's elements	Concentration, $mg.L^{-1}$
BEC Mn	0,009
BEC P	0,346

4. CONCLUSIONS

Elemental analysis studied in this paperwork at Ipen's groundwater had satisfactory results in most of interlaboratory programs. All questionable or unsatisfactory results were investigated and the main cause was identified, discussed and solved. Training actions among all personal in charge of sample collection, analysis and result expression were frequently performed. Non-compliant iron results between 2011 to 2013, were related to geologic characteristic of the soil where wells were located. Internal and external quality control helped to keep analytical analyses under specified conditions concerning precision, recovery and traceability. With these Quality control tools, it was possible to identify all analytical errors and solve then. These actions gave a higher confidence to Metal analysis at Ipen's groundwater.

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