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ESTIMATED POLLUTANT LOAD FROM NUCLEAR AND ENERGY RESEARCH INSTITUTE (IPEN/CNEN-SP, BRAZIL)

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ABSTRACT

Quantifying the pollutant load in a receiving water body is one of the needed steps to keep its original standards, irrespective of its releases source. Monitoring, and thus, controlling the amount of pollutants to be destined to the water body means ensuring water quality, keeping it free of excessive pollution and harm to human health and the environment. Hence, this paper aims to estimate the pollutant load of sanitary wastewater released by the Nuclear and Energy Research Institute (IPEN / CNEN-SP) during 2015 and 2016. The assay of Cd, Pb, Cu, Cr, Zn, Ba, Ni, Mn, Fe, B and Sn were performed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and As, Hg and Se by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). The metals and total fixed solids pollutant load estimative carried out, employed wastewater flow measurement, using bromide (Br-) as tracer and the annual water consumption at IPEN. This evaluation is performed annually by IPEN since 2006 as part of the Environmental Monitoring Program (PMA-Q), in order to comply with the current environmental legislation and the Term of Adjustment of Conduct requirements, agreed with the Brazilian Institute of Environment and Renewable Natural Resources (IBAMA).

1. INTRODUCTION

The National Council of Environment (CONAMA) published on May 13th, 2011, the Resolution# 430, that provides guidelines and standards regarding the release of wastewater in water bodies. This resolution states that only previously treated wastewater can be released in water bodies. Also minimum requirements and conditions to wastewater releases are established in this Resolution and others in force, as well. Thus, to all potentially affecting substances, maximum allowed values were established for the operation of a receiving water body [1].

The 28th paragraph of the Resolution# 430/11, requires that a “Polluting Load Declaration” must to be presented every year up to March 31st, by the operational responsible of the potential polluting source, referring to the previous year. The environmental organ has to establish the maximum polluting load of the substance release likely to be present or being formed in its productive process [1].

The CONAMA Resolution# 357/05 defines polluting load as the quantity of a specific polluting released in the receiving water body [2]. The wastewater flow rate (quantitative variable) and the substances concentrations in this wastewater (qualitative variable) are required variables, because these are conditions changing on time. Then, the total released load is quantified. Any change in the release patterns can be identified (e.g. changes between dry and rainy periods) [3].

The estimate of the polluting load received in a given water body is the beginning of the monitoring and controlling procedures. The estimated amount of total solids and metals released at IPEN were evaluated in order to meet the environmental regulations [2,5,6], since 2013. At that time, no compromise of the water body goals were observed under Ipen monitoring program.
As a continuous and yearly process, this paperwork discusses the 2015 and 2016 estimates of metals polluting load (Ba, Sn, Cd, B, Cr, Cu, Fe, Mn, Pb, Ni e Zn) and fixed total solids released. This activity is part of the Environmental Monitoring Program for Chemical Compounds (PMA-Q). The wastewater flow rate measured by Silva, e al. [5], and the polluting load estimates from Marques et al. in 2013 and 2014 [6] are compared with the more recent values measured in the present work. The IPEN water consumption between 2012 and 2016 [7] were used to correct the estimated quantities.

2. MATERIALS AND METHODS

2.1. Sampling Wastewater

The wastewater samples were collected at the Wastewater Monitoring Station (EME), located near to the north entrance of IPEN (geographical coordinates 23°33'43.48"S 46°44'11.71"W).

Collection was performed by the means of a peristaltic pump, with 1 L.min-1 flow rate, working 8 hours a day, 5 times a week. The collection process meets ANA-CETESB guide to the collection and preservation of environmental samples [8] and the Standard Methods for the Examination of Water and Wastewater [9]. Samples were prepared and essayed at Environment and Chemistry Center (CQMA) at IPEN.

In 2015, collection was regularly carried out in march, April and May, and in 2016 in June, July, September and November. Collections were not carried out every month due to problems with the collection system.

2.2. Metals and Semimetals Determination

To measure the metals and semimetals (Cd, Pb, Cu, Cr, Zn, Ba, Ni, Mn, Fe, B e Sn), the Inductively coupled Plasma Optical Emission Spectrometry (ICP-OES) was used. Graphite Furnace Atomic Absorption Spectrometry was used on As, Hg and Se determinations.

An aliquot of 50 mL of each daily sample was used to compound a weekly sample, acidified with nitric acid to analytes solubility preservation. These weekly samples were prepared by microwave assisted acid digestion, according to EPA 3015 [10].

2.3. Solids Determination

According to the report published by São Paulo`s Environmental Company (CETESB) in 2009, solids are all the physical material that remains as residue, even after evaporation, drying or calcination of samples [13]. The estimation of fixed total solids (FTS) allow to compare the results with the metals polluting load, since the FTS, in general, are composed of metals oxides, among other residues. So, the sum of the oxides cannot be higher than the FTS polluting loads, being used as an index of evaluation of metals polluting load.

Gravimetric method (ABNT NBR 10664/1989 - Waters – Determination of Residues (Solids) – Gravimetric Method–Method of Test) was used to solid series determination [11]. The determination of Fixe Total Solids (FTS) and Volatile Total Solids (VTS) was used to calculate Total Solids (TS), according to Equation 1.

$$TS = FTS + VTS \tag{1}$$

The FTS are the stable inorganic salts and the VTS instable inorganic salts, as ammonium salts, magnesium carbonate plus organic matter [12].

2.4. Polluting Load

To the metals and TS polluting load estimation was used the wastewater flow rate determined by Silva et al. [5], that used bromide as tracer, and IPEN annual water consumption [7]. The result obtained was 10,5 ± 3,1 $m^3.h^{-1}$. The polluting load was estimated using the Equation 2 [6].

$$m\ (x) = C\ (x).Q_{wastewater} \tag{2}$$

$m\ (x)$ = Pollutant Load of a Specific Element;
$C\ (x)$ = Amount of the element;
$Q_{wastewater}$ = Wastewater Flow Rate.

3. RESULTS & DISCUSSION

3.1. Flow Rate and Water Consumption

In 2013 and 2014, the polluting load released by IPEN was estimated by Marques et al. [6]. This estimate considers the flow rate measured by Silva et al. in an operating regime of 24 h a day, 7 days a week. In these conditions, the estimated weekly flow rate is about 1,764 $m^3.week^{-1}$. However, the IPEN`s water consumption in 2013 and 2014 was 285 e 294 $m^3.week^{-1}$, respectively [7]. These figures are incompatible with the calculated data. Suggesting the polluting load was probably super estimated. However, the water consumption data were disclosed only in 2015.

In this paperwork, the wastewater weekly flow rate was considered as changing according to the institute operating regime. The operation regime was considered to be 8 h.day-1, 5 days a week, as presented in Table 1. Therefore, a weekly flow rate has more accurate values.

Table 1: IPEN`s water consumption and flow rate estimations, considering different operating regime

Water Consumption [7]					Flow Rate Estimation [5]		Unity
2012	2013	2014	2015	2016	Operating regime 24h/7dias [4]	Operating regime 8h/5dias	
15.56	13.70	14.10	10.96	7.62	84.672	20.160	Yearly $m^3.year^{-1}$
1.30	1.14	1.18	914	635	7.056	1.680	Monthly $m^3.month^{-1}$
324	285	294	228	159	1764	420	weekly $m^3.week^{-1}$

Even considering an operating regime of 8h per day, 5 days a week, the estimated flow rate presents results above the institute water consumption, but more near of them. So this operating regime was considered more adequate to the estimations to be carried out. When compared to the estimated flow rate declared by Marques et al., a significant change is observed in the polluting load results [6].

3.2. Metals and Semimetals Polluting Load

In 2015 and 2016, the IPEN`s estimated polluting load considered changes in the flow rate, according to operating regime. The 2013 and 2014 values are compared considering the same operating regime (8h a day e 5 days a week). Some similarities are observed between 2013 and 2014 values that were kept in 2015 and 2016.

In 2015 and 2016, Ni was presented the lower polluting load released. In opposite, Fe was the metal with the highest polluting load (Fig. 2). The monthly polluting load of Cd, Pb, Cu, Cr, Zn, Sn, Ni, Ba, Mn and B (Fig. 2), in its majority, was inferior to 1,0 $kg.month^{-1}$. The single exception was observed in July 2016, when Sn and Ba exceeded 1,0 $kg.month^{-1}$.

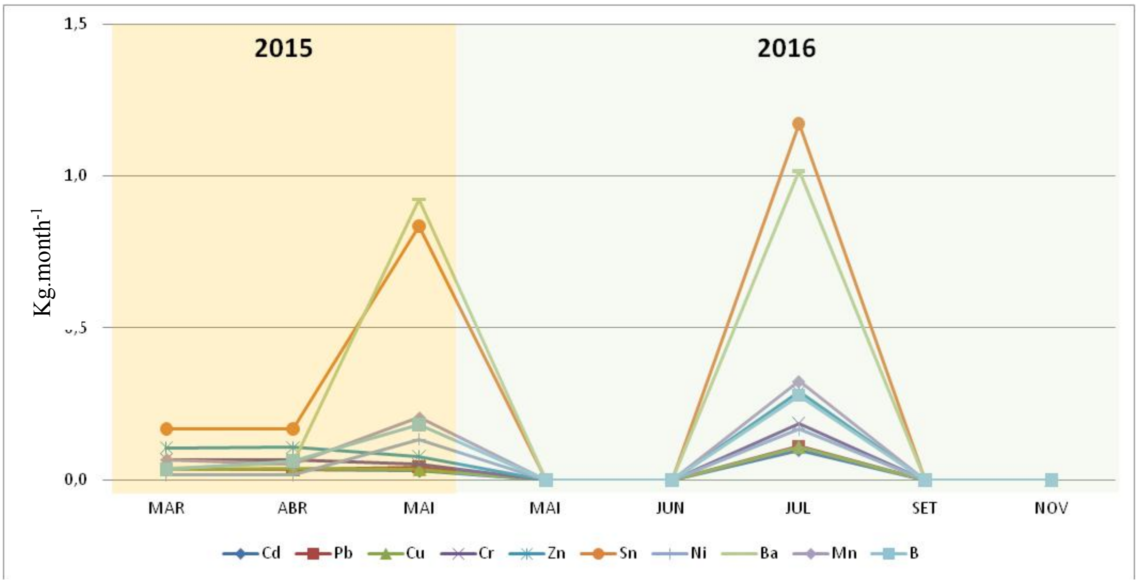

Figure 1: Metals and Semimetals Polluting Load (considering 8h a day/5 days a week as operating regime)

Between 2015 and 2016, Fe presented results between 2,0 and 8,0 kg.month^{-1} (Fig. 3). As Marques et al. [6] pointed out, the Fe monthly polluting load varied between 6,0 and 16,0 kg.month^{-1} in 2014 and 4,0 e 9,0 kg.month^{-1} in 2013, considering a superior operating regime (24h a day, 7 days a week). This variation cannot be totally explained by the difference in flow rate estimation. Considering the proper correction to the operating regime, these values would correspond to 1,4 and 3,8 kg.month^{-1} in 2013 and 2014. So, in 2015 and 2016, an increase in Fe polluting load was observed.

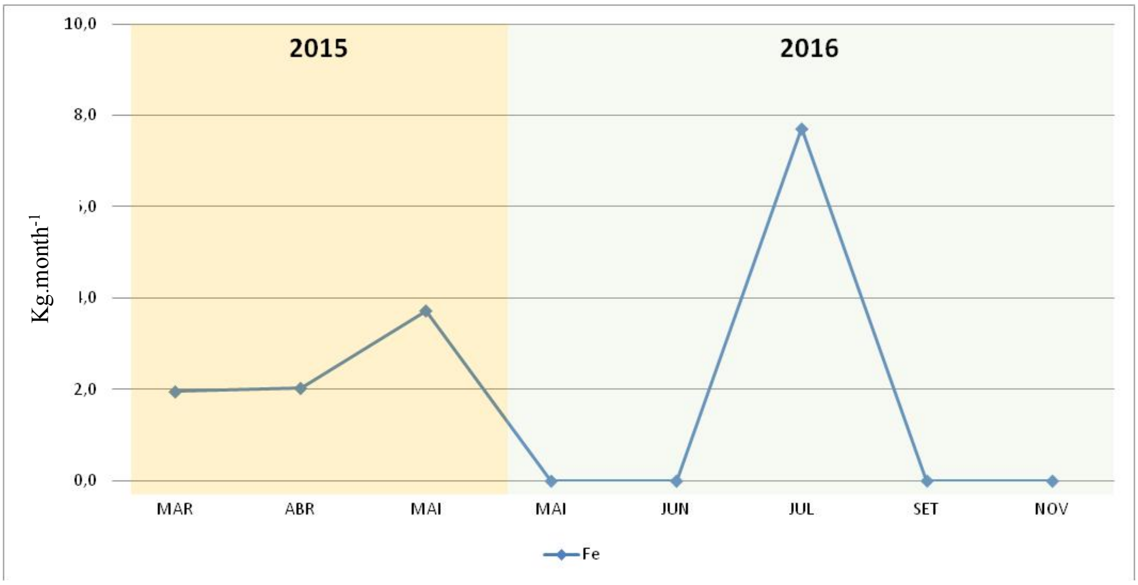

Figure 2: Iron Polluting Load considering operating regime 8h a day, 5 days a week

Fig. 4 presents the monthly average of Fe polluting load, that corresponds to 2,6 kg.month^{-1} and the 4,5 kg.month^{-1} in 2015 and 2016, respectively. While in 2013 and 2014 the monthly average was 2,6 kg.month^{-1} and 2,3 kg.month^{-1}, respectively.

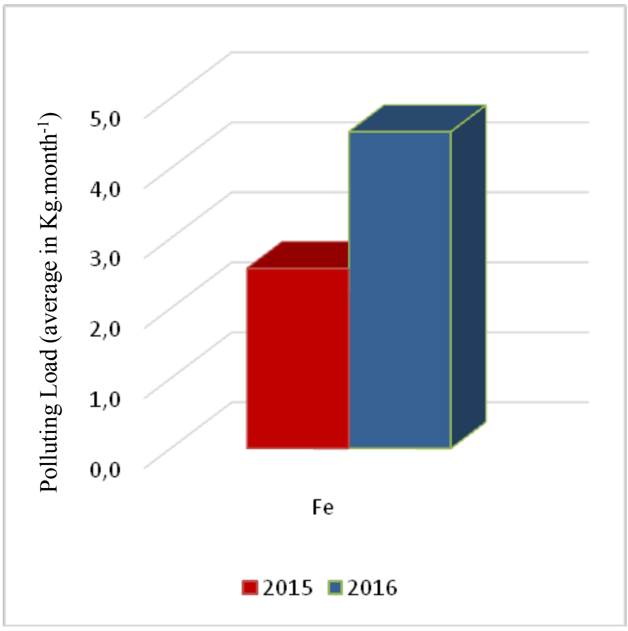

Figure 3: Monthly average of Iron polluting load in 2015 and 2016

In 2015, to other metals evaluated, the average monthly polluting load, showed in Fig. 5, decrease in the order Sn, Ba, Mn, Zn, B and Ni followed by Cd, Pb and Cu. In 2016, after Fe, the element that presented the higher polluting load was Zn, followed by Sn, Mn, Cu, Ba, Cr, Cd, Pb and B. During all the period assessed, this elements polluting load was inferior to 0,4 kg.month^{-1}. While in 2013 and 2014results were inferior to 0,7 kg.month^{-1}.

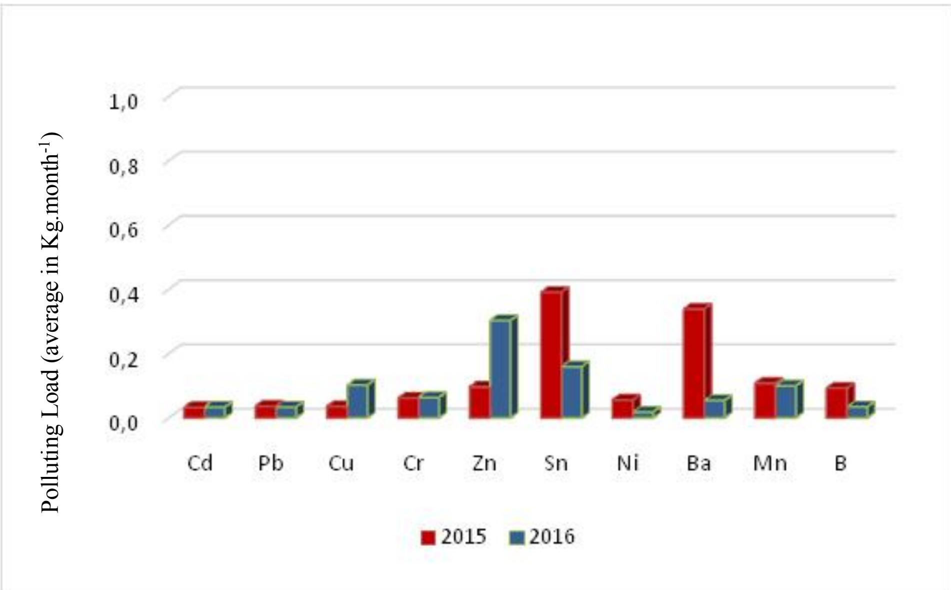

Figure 4: Average monthly polluting load for metals in 2015 and 2016

3.3. Totals Solids and its Fractions

Evaluating the Solids Series, was possible to observe that in 2015 and 2016, IPEN`s wastewater was composed in its majority by VTS, featured by organic matter, then FTS (inorganic salts, as sulfated and chlorides). The VTS correspond to 54 % and 51 % of the Total Solids, in 2015 and 2016, respectively (Fig. 6)

Considering that the FTS corresponds to metals oxides, as non-volatile substances, these were approximately 1,4 % to 4,4 % of FTS in 2015 and approximately 1,7 to 3,1 % of FTS in 2016. Therefore, the FTS polluting loads was expressively higher than the metals oxides polluting loads assessed. Probably, this low percentage of metals oxides in the FTS was obtained due to the presence of other oxides of metals not monitored in this work, like Na, K, Ca, Mg, Al, etc.

The IPEN`s water consumption has been reduced around 30 % between 2015 and 2016, the total solids polluting load was 60 % higher in the same period.

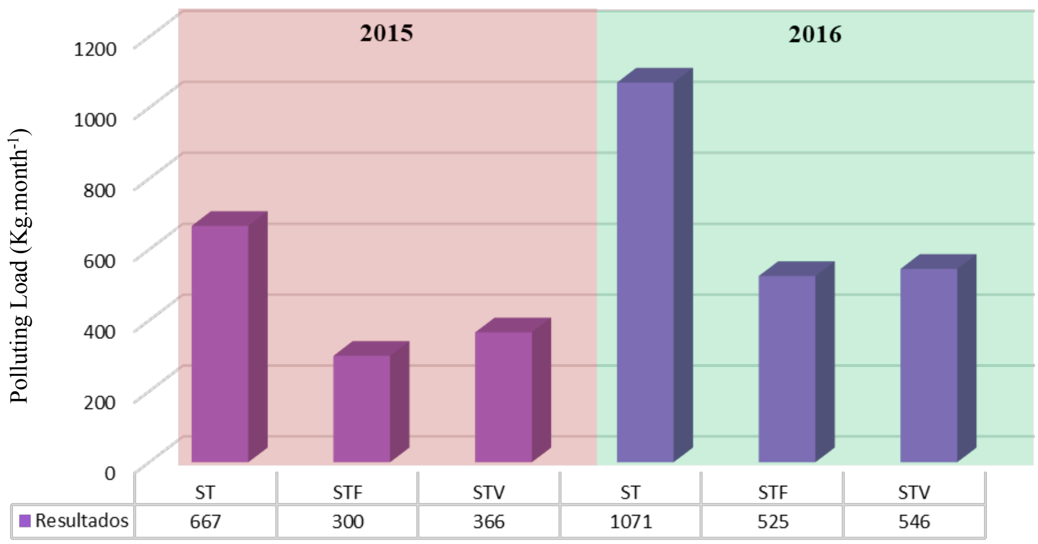

Figure 5: Monthly TS, FTS and VTS polluting loads in 2015 and 2016

3. CONCLUSIONS

Using the information published by Silva et al. [5] and Marques et al. [6], the metal and solid polluting load released by IPEN in 2015 and 2016 were estimated. These results were compared with the polluting load released in 2013 and 2014. Using the IPEN`s water consumption, the overestimation of the wastewater flow rate was identified, based on the operating regime of the institute.

IPEN`s water consumption decreased 50 % from 2012 to 2016. However, an increase in the average of metal and total solid polluting load released by the institute was observed when compared with 2013 and 2014. The appropriated operating regime were considered. The increase of Fe and STF polluting load, observed in 2015 and 2016, was not linked to any specific activity at IPEN. Moreover, the release pattern of the institute was considered to present punctual features. As concentrate in a specific period, possibly affecting the average monthly of Total Solids and Metals polluting load. The continuous reduction in the collection frequency observed, from the early monitoring years up to 2016, can increase largely the measurement uncertainty. The lack of information during these months can be considered as a non-compliance to Brazilian regulations.

More than to keep the assessment of the polluting load released, this paper contribute to improvement the estimation method. Uncertainties and sources can be identified and mitigated. Then, a metals polluting load reduction goal can be proposed, as required by the agreement firmed between IPEN and IBAMA, to meet the environmental legislations.

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