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# ESTIMATION OF METAL POLLUTANT LOADS FROM NUCLEAR AND ENERGY RESEARCH INSTITUTE (BRAZIL)

**Joyce R. Marques, Lucilena R. Monteiro, Sabrina M. V. Soares, Thamiris B. Stellato, Tatiane B. S. C. Silva, Douglas B. da Silva, Mainara G. Faustino, Maria A. F. Pires, Marycel E. B. Cotrim**

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
joyce.marques@usp.br

## ABSTRACT

According to National Environmental Council's (CONAMA) Resolution 357/05, pollutant load can be defined as the amount of a particular pollutant released in receiving water body; it is commonly expressed in a mass-time ratio. As specified in CONAMA's Resolution 430/11, the responsible for the pollutant source must present the Pollutant Load Declaration to environmental authorities. However, pollutant load knowledge is also important to the water quality maintenance and its environmental rating that must be kept to meet the requirements of the most restrictive use. In the control of metals releases is also important due public health matters, since they can cause harmful environmental contamination and major public health issues. Therefore this work aims to present the estimated metal pollutant load released by Nuclear and Energy Research Institute (IPEN/CNEN - Brazil), between 2013 and 2014. Results of cadmium, lead, copper, chromium, zinc, nickel, manganese, iron, barium, silver, boron and tin in composite samples (weekly) via Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and bromide (Br-) released as a tracer, to measure the wastewater flow were used to estimate Ipen's Metal Pollutant load. This study is part of the environmental assessment Program at IPEN, instituted since 2006 to the attendance of the current environmental legislation (CONAMA's Resolution 430/11, Article 19-A of State Decree 8.468/76 and State Decree 15.425/80).

## 1. INTRODUCTION

According to Brazilian Institute of Geography and Statistics (IBGE) just 55% of the Brazilian cities have sewage system, and 29% of them have sewage treatment. Analyzing deeply the IBGE data, is also possible to verify the inequality of this distribution, whereas in the south east of the country 95% of the cities have sewage system and 48% of them have sewage treatment, in the north east region of the country, just 46% of the cities have sewage system and 19% have sewage treatment [1]. Hence is extremely important the assessment of the wastewater released in the sewage system, to keep the hydric resources features providing water to the most restrict uses [2].

Besides the wastewater assessment, it is crucial the estimation of pollutant load released to know the quantity of pollutants is being released in the water body in a determined period of time. Furthermore, this quantity is limited by the current Brazilian environmental legislation, according to the water body rate [3].

As defined in CONAMA's Resolution 357/05 pollutant load is the quantity of a particular element released in a water body in a period. To perform this determination is essential to know the wastewater flow rate and the amount of the specie in the wastewater, due to the pollutant load is a mass time ratio.

The Nuclear and Energy Research Institute (IPEN/ CNEN – Brazil) is a nuclear and radioactive institution, where several activities related to the development of radiations and other technologies are carried out, generating by-products from these processes, as well as wastewater. The IPEN's wastewater is released without treatment, however to the attendance of the current Brazilian legislation, this wastewater is assessed since 2006, being part of the Environmental Monitoring Program for Chemical Compounds (PMA-Q from Portuguese), in which many parameters are evaluated. Into this program, 11 metals are assessed, since the use of metals at IPEN is frequent, evaluate these parameters is relevant to keep the environmental conditions around the institute and to do not offer any risk to the population.

Thus, the aim of this paper is to estimate the metals pollutant load, released by IPEN, in the water body during 2013 and 2014. This estimation rely on the flow rate determination and the amount of metals into IPEN's wastewater.

## 2. OBJECTIVE

Estimate the metal pollutant load (B, Sn, Cd, Ba, Cr, Cu, Fe, Mn, Pb, Ni e Zn) released by IPEN during 2013 and 2014. This estimation is based on the amount of each element, from PMA-Q, and on the estimation of the IPEN's wastewater flow rate, performed by Silva, D. B. et al. [4].

## 3. MATERIALS AND METHODS

### 3.1. Wastewater Collection

Wastewater samples monitored in PMA-Q were collected on Wastewater Assessment Station (EME), nearby the north entrance of IPEN (geographical coordinates 23°33'43.48"S and 46°44'11.71"W). EME and its location can be seen in Figure 1.


**Figure 1: EME Location at IPEN/CNEN-SP.**

Wastewater was collected as a weekly-composed sample by using a peristaltic pump with a flow rate of 1 $L.min^{-1}$ that operates 9 times per day, every hour from 8 am to 5 pm, five times per week. From each of every average 5 to 10 L daily sample. An aliquot of 50 mL was taken to compose the weekly sample, that is acidified (with nitric acid), digested using the EPA Method 3015 [5] and analyzed up to 6 months. The collection and storage process applies ANA-CETESB Guide to Collection and Preservation of Environmental Samples [6] and Standard Methods for the Examination of Water and Wastewater [7].

### 3.2. IPEN's Wastewater Flow Rate

As per Silva et al. (2013), six releases of sodium bromide were carried out from different locations inside IPEN, in order to estimate the wastewater flow. The calculation was performed according to Equation 1. As a result, the flow rate determined was 10.5 ± 3.1 $m^3.h^{-1}$ (1,680.0 ± 496 $m^3.month^{-1}$, considering 8 h per day in 20 days per month) [4]. In 2015, due the water restriction Sao Paulo city faced, IPEN water consumption was reduced to ranges between 950 to 790 $m^3.month^{-1}$.

$$Q = q.C/c \quad (1)$$

Where:

$Q$ = flow rate ($m^3.h^{-1}$);
$q$ = pump flow ($mL.min^{-1}$);
$C$ = initial tracer amount ($g.L^{-1}$);
$c$ = final amount at the collection point ($mg.L^{-1}$).

### 3.3. Amount of Metals

The amount of each metal was determined by the technique Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using a method elaborated and validated in the Chemical and Environmental Centre (CQMA) at IPEN.

All the concentrations determined as below the Limit of Quantification (LQ) were considered as equal to the LQ.

### 3.4. Determination of Residues (solids) in Wastewater

At IPEN, the determination of total residues in wastewater is carried out according to ABNT NBR 10664/1989 - Waters – Determination of Residues (Solids) - Gravimetric Method - Method of Test. Each step of the method is presented in Figure 2 [8].

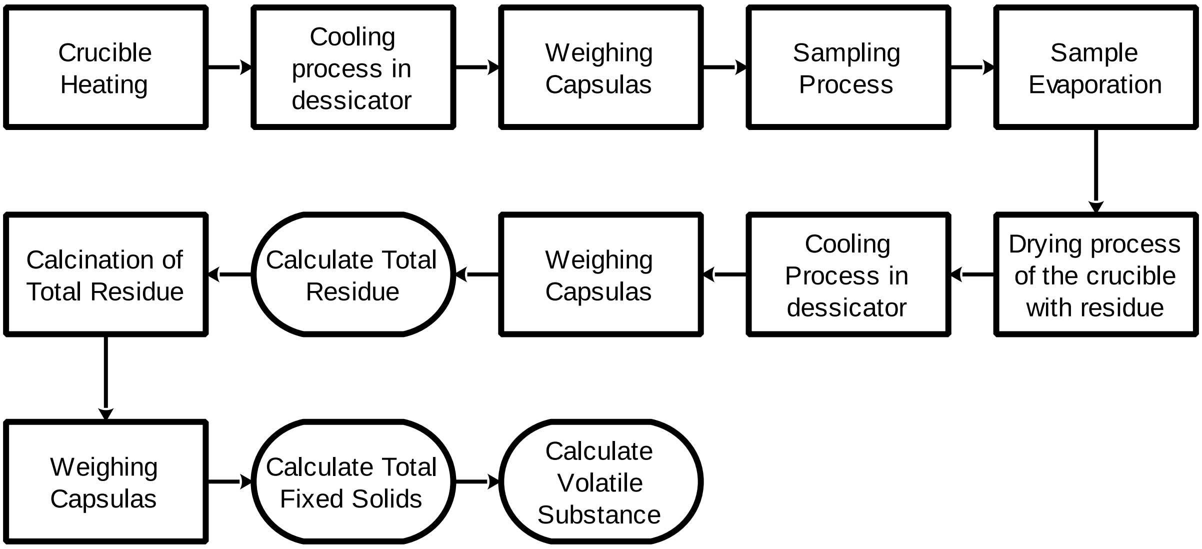



**Figure 2: Steps to the determination of residues (solids) by Gravimetric method.**

### 3.5. Pollutant Load Estimation

From the amount of each element and the wastewater flow rate, the pollutant load was estimate using the Equation 2 [9].

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

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

To consider the adequate unit of measurement the flow rate was converted to g.week$^{-1}$, according to Equation 3, because the samples analyzed were weekly composed.

$$m\ \left(\frac{g}{week}\right) = C\ \left(\frac{mg}{L}\right).\ Q_{wastewater}\left(\frac{m^3}{h}\right).\left(\frac{168\ h}{week}\right).\left(\frac{1000\ L}{m^3}\right).\left(\frac{1\ g}{1000\ mg}\right) \tag{3}$$

After that, the results correspondent to each month were added to obtain g.month$^{-1}$ results.

Additionally, pollutant load from the residue determination was calculated using same equation. Thus was possible to have the estimation of pollutant load from total residues, total fixed residues and volatile substances, hence was feasible to achieve more information and other parameters to compare and analyze the results.

## 4. RESULTS AND DISCUSSION

### 4.1. Pollutant Load released in 2013

As per Figure 3 and Figure 4, in 2013, a minority of the pollutant load was composed by nickel (aprox. 71 g.month$^{-1}$), except in April and May 2013, when the minor compound was lead (7 g.month$^{-1}$ in April and 29 g.month$^{-1}$ in May). Other metals (Cd, Pb, Cu, Cr, Zn, Sn, Ba, Mn e B) varied between 130 g.month$^{-1}$ and 700 g.month$^{-1}$, approximately.

The majority of the pollutant load during this year was composed by iron, which behavior is presented in Figure 5. Iron pollutant load remained between 4000 and 9000 $g.month^{-1}$ until June, and reached a peak in September (22000 $g.month^{-1}$) and just went out after that (until 6400 $g.month^{-1}$).

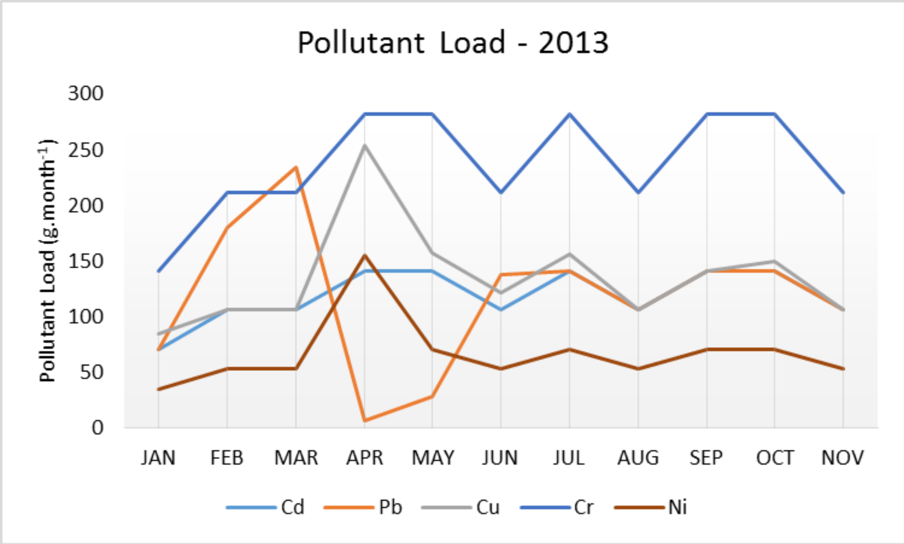



**Figure 3: Pollutant Load of Cd, Pb, Cu, Cr and Ni released by IPEN in 2013**

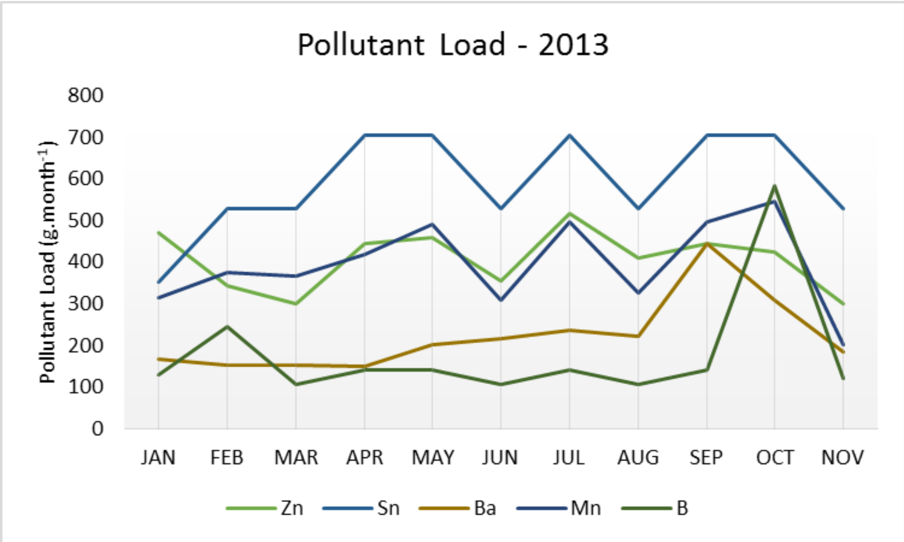



**Figure 4: Pollutant Load of Zn, Sn, Ba and Mn released by IPEN in 2013**

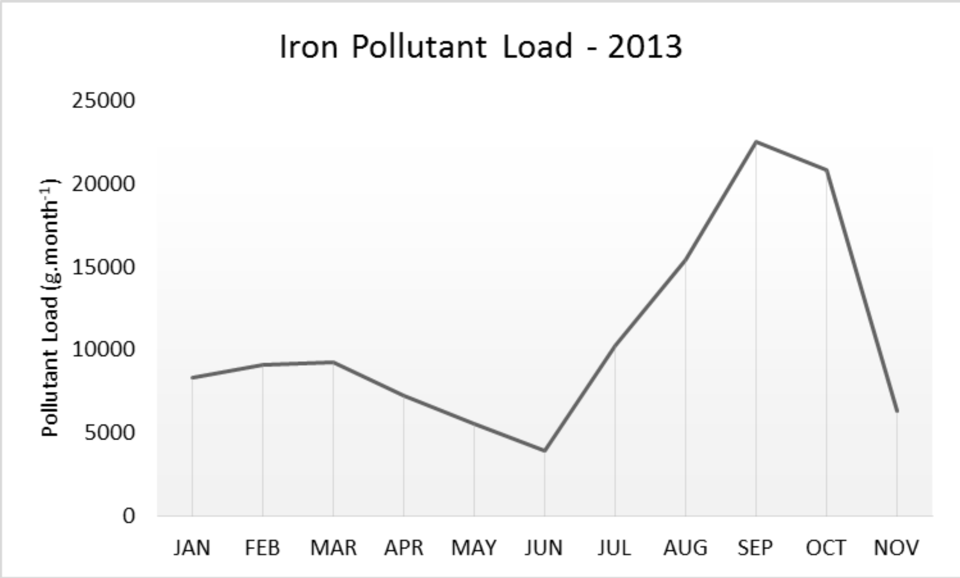



**Figure 5: Iron Pollutant Load released by IPEN in 2013**

## 4.2. Pollutant Load released in 2014

According to the Figure 6, in 2014, the minority of the pollutant load was composed by nickel as well as in 2013. The other cited metals varied between 130 $g.month^{-1}$ and 900 $g.month^{-1}$, approximately.

As presented in Figure 7, the majority of the pollutant load during 2014 was composed by iron, similarly to 2013, which pollutant load reached a peak in February (approximately 16000 $g.month^{-1}$), but after March remained stable around 8500 $g.month^{-1}$.

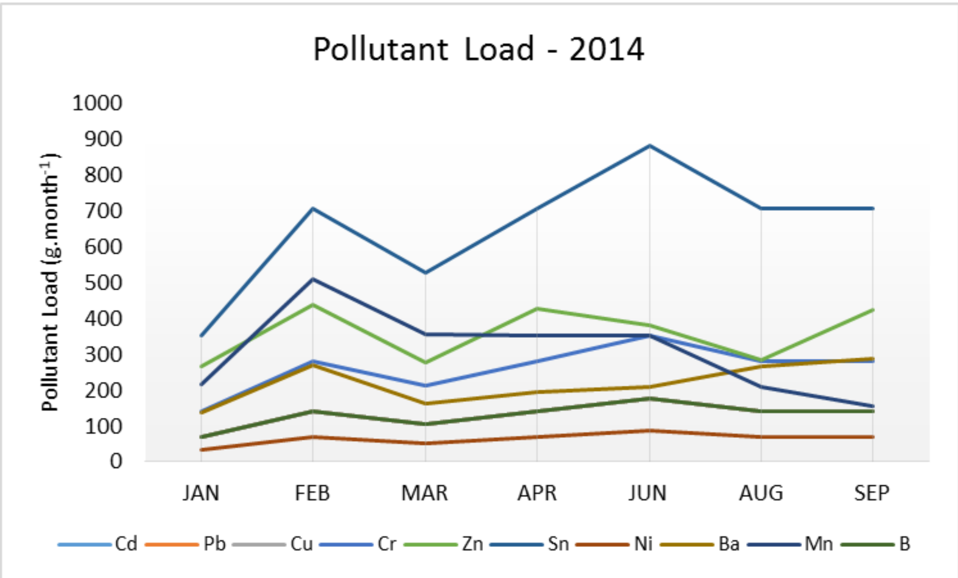



**Figure 6: Pollutant Load of Cd, Pb, Cu, Cr, Zn, Sn, Ni, Ba, Mn and B released by IPEN in 2014**

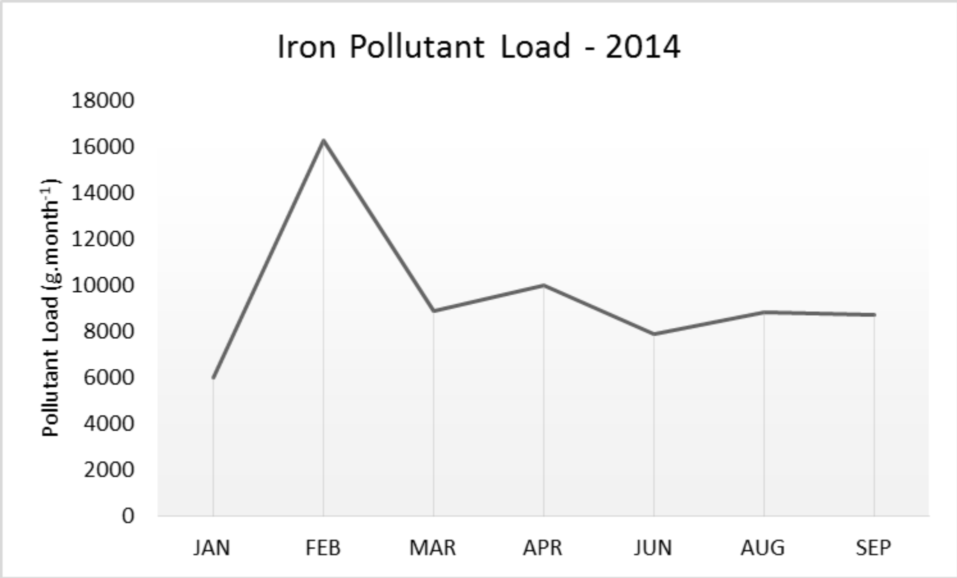



**Figure 7: Iron Pollutant Load released by IPEN in 2013**

## 4.3. Comparison of the Pollutant Load released in 2013 and 2014

As per Figure 8 and Figure 9, it is possible to state that the release pollutant load of Cd, Pb, Cr and Sn in 2013 was lower than 2014. However the release of Cu, Ni and Ba kept almost the same level, and the release of Zn, Mn, B and Fe was at least 23% less in 2014 than 2013. As a mean of metals per month, in 2014 IPEN released roughly 10% less metals than in 2013.

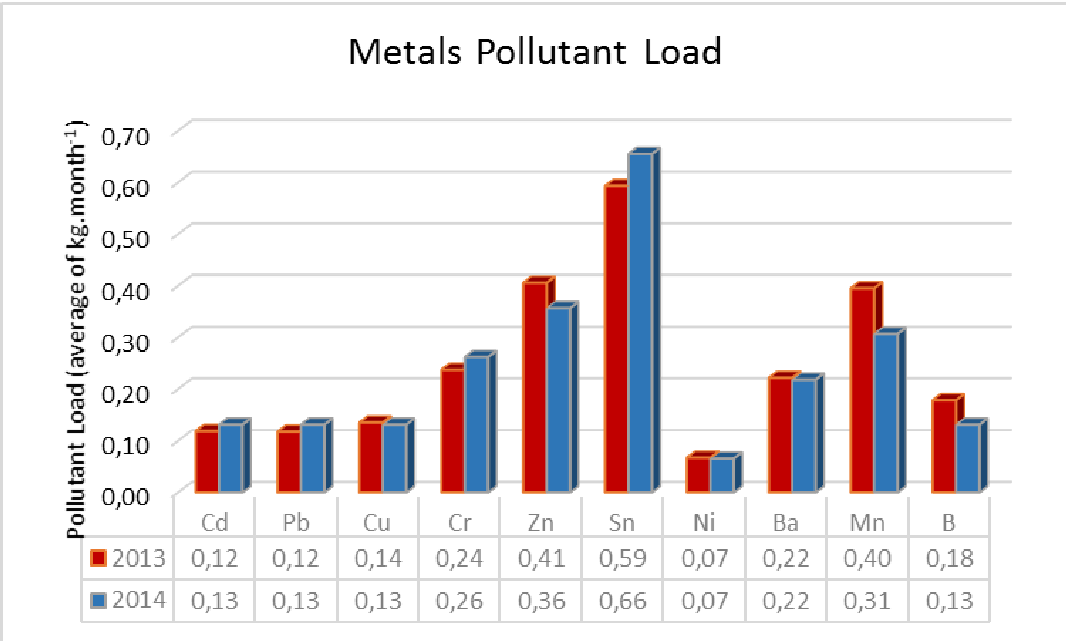



**Figure 8: Comparison of the Pollutant Load released by IPEN in 2013 and 2014**

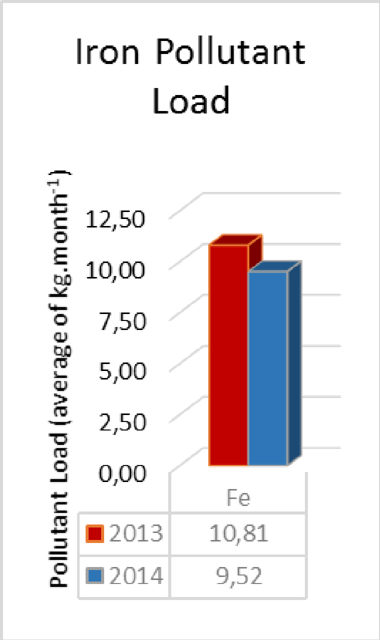
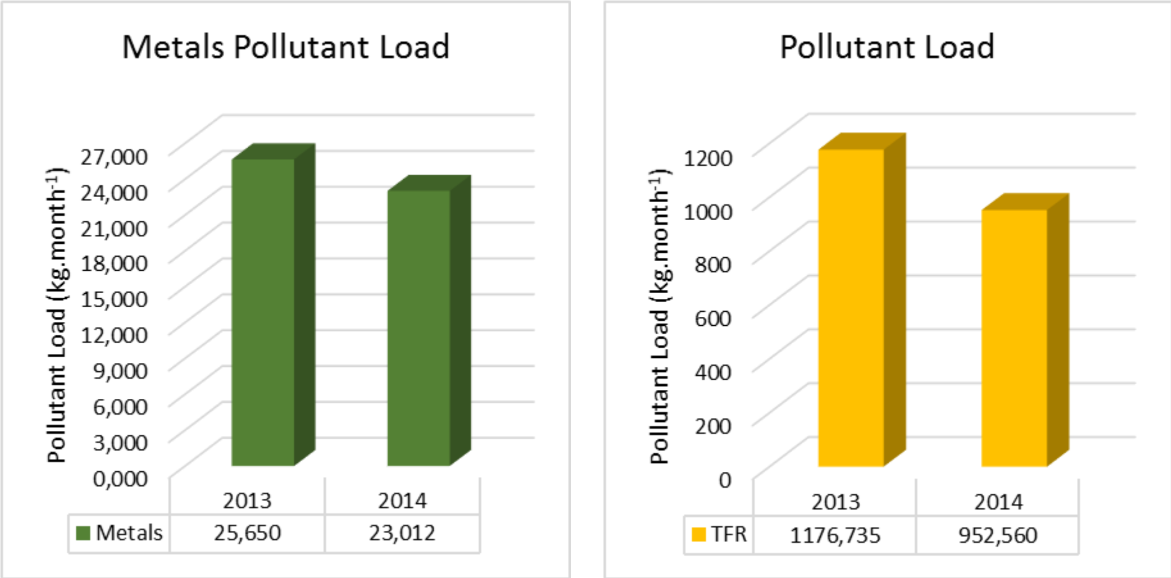



**Figure 9: Comparison of the Iron Pollutant Load released by IPEN in 2013 and 2014**

To assess whether the pollutant load results are consistent, the comparison between the pollutant load from total residues was performed. Nevertheless not just the metals amount have to be considered in this comparison, normally the metals are in the oxide form into the wastewater and the total fixed residues are composed by other metal oxides and some salts, for instance chlorides and sulfates. Hence the result was considered as coherent just if the sum of the studied metal pollutant load were lower than the pollutant load from total fixed residues.

As observed in Figure 10 was possible to verify that, even considering the most common oxides of the metals studied, the pollutant load from total fixed residues (B) was expressively bigger than the metal pollutant load (A). In 2013 metal pollutant load was 2.2% of total fixed residue in the same period. Also in 2014 the metal pollutant load corresponded to 2.4% of total fixed residue. That low contribution happens probably because other more common elements such as Na, K, Ca, Mg, Al, etc. that are not here computed and also contribute to total fixed residues.

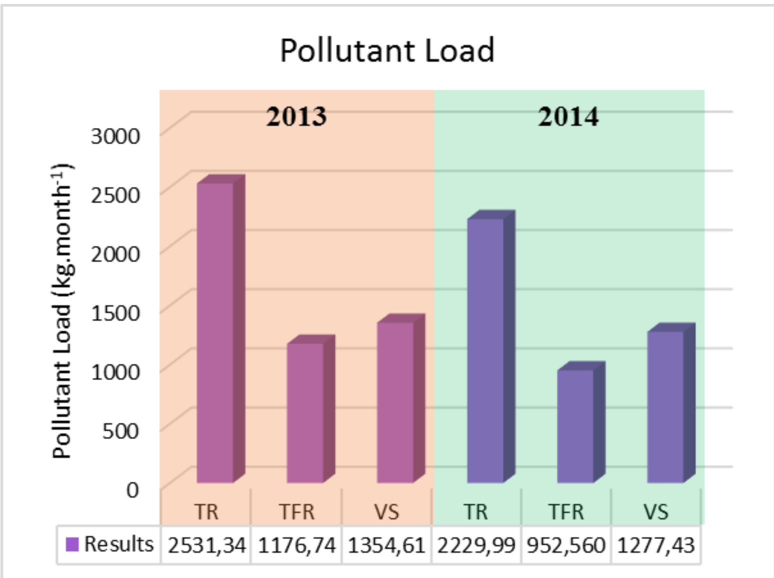
(A) (B)




Legend: TFR = Total Fixed Residues

**Figure 10: (A) Total Metal Pollutant Load released in 2013 and 2014 (considering metal oxides); (B) Pollutant Load considering the total fixed residues released in 2013 and 2014.**

In complement to the metal pollutant load the total residues pollutant load, fixed residues pollutant load and volatile substances pollutant load were estimated (see Figure 11).




Legend:
TR: Total Residues;
TFR: Total Fixed Residues;
VS: Volatile Substances;

**Figure 11: Pollutant Load From Total Residues, Total Fixed Residues and Volatile Substances released by IPEN in 2013 and 2014**

## 5. CONCLUSIONS

In this study, it was considered the average of the wastewater flow rate, so the results represents just an estimation of the metal pollutant load, some variation to more or less have to be considered as well.

IPEN's metal pollutant load and total fixed residues load in 2014 was lower than in 2013. However it was not implemented any reduction action at IPEN. This reduction was neither planned nor monitored. The water consumption estimated by the wastewater flow was around 560 to 390 L per person in 2013 and 2014. In 2015, the water consumption was estimated in 320 to 260 L per person.

Thus using the data presented in this paper will be possible to evaluate the metals released and determine a target of pollutant load for next years, and implement other actions to meet the Brazilian Environmental Legislation requirements (CONAMA's Resolution 430/11).

Finally, regarding metal concentration, IPEN meets all Brazilian Environmental Legislation Requirements (CONAMA's Resolution 430/11, Article 19-A of State Decree 8.468/76 and State Decree 15.425/80). In order to achieve better results it is mandatory to reduce wastewater flow rate by reducing water consumption.

## 6. ACKNOWLEDGMENTS

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