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USE OF MEAN REGULATORY QUOTIENTS IN WASTEWATERS FROM IPEN-CNEN/SP, BRAZIL

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ABSTRACT

IPEN has been carrying out an Environmental Monitoring Program since 2007, which includes analyses of stable chemical compounds in the wastewater generated by the institute. Throughout 2009 seven hundred and eighty metals, semimetals and anions analyses were performed. Aiming a global evaluation of the results, it was applied a guideline-compliant quotient, as defined by Long et al. [1]. That quotient was calculated as an average of the division result of the individual substance concentration in the effluent by its respective guideline values. The resulting index provides a method of accounting for both the presence and the concentrations of multiple chemicals in wastewaters, relative to its legal compliance. It was considered in this work as guidelines the legal values established by São Paulo 8468 state law (article 19-A) [2]. For barium, boron and manganese, legal standards defined by CONAMA 357/05[3] article 34 were assumed as guidelines. This quotient main advantage is to allow a simultaneous comparison of several substances, with different effects and concentration levels. Additionally they are easy to be understood because only one index per sample is obtained. Indexes around 1 indicate the analyzed substances are present in the wastewater in concentration close to the legal guidelines. The use of the average regulatory quotients in wastewaters from Ipen showed that the analyzed substances are present in levels between 0.69 and 4.28% of the legal value for effluents releasing in public sewer system. The quotients indicated that Ipen wastewater was in accordance with current State environmental regulation.

1. INTRODUCTION

In many environmental studies, it is adopted a quality quotient concept: for water quality indexes[4,5] for sediment quality guidelines [1] and for risk assessment evaluations indexes[6]. As long as the matrix, the calculation model and the interpretation concepts were carefully selected, those indexes demonstrated to be useful tools. Each index presents a variety of approaches to make easier the environmental diagnosis.

Is this river contaminated? Can I drink this water? Is the effluent compliant with legal standards? Sometimes a yes or no question is not so simple to answer. Especially when several parameters must be monitored with different concentration levels, associated risks and biological effects. In this work, the quotient concept was adopted considering wastewater legal requirements that must be fulfilled in order to release an effluent in to public sewer system. The stable compounds concentration found on Ipen´s effluent was compared with State and National legal values. It was also discussed the quotient validity to perform both legal and environmental diagnosis, its advantages, assumptions and limitations.

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2. METHODS

2.1. Wastewater collection and analysis:

Sampling and analysis are presented elsewhere [7]. According to Sao Paulo´s State law decree 8468/76 [2], in order to release a wastewater on public sewer system there are 24 physical and chemical criteria that must be fulfilled, which are presented on Table 1.

Physical and chemical characterizations are supposed to be performed previously to every wastewater release. This requirement is imposed to Ipen; therefore, sample collection is performed on a daily basis. During the year of 2009, 107 samples were collected and analyzed, obtained 708 results. Thirty-seven parameters were monitored along 36 weeks of 2009.

Table 1: Effluent Legal values to be released into public sewer system[2].

Parameter	São Paulo State Decree 8468/76 art. 19-A
Settable material(1)	≤ 20 mL/L
pH(2)	≥6 e ≤10
Temperature(2)	<40°C
N-Hexane Extractable Material(1)	≤ 150 mg/L
Light organic solvents(1)	Absent
Total Arsenic *	≤ 1.5 mg/L
Total Cadmium *	≤ 1.5 mg/L
Total Lead*	≤ 1.5 mg/L
Total Copper *	≤ 1.5 mg/L
Hexavalent Chromium(1)	≤ 1.5 mg/L
Total Mercury *	≤ 1.5 mg/L
Total Silver *	≤ 1.5 mg/L
Total Selenium *	≤1.5 mg/L
Total Chromium *	≤ 5.0 mg/L
Total Zinc *	≤ 5.0 mg/L
Total Tin *	≤ 4.0 mg/L
Total Nickel *	≤ 2.0 mg/L
Total Elemental Content (Sum of all assign elements*)	≤ 5.0 mg/L
Total Cyanide (1)	≤ 0.2 mg/L
Total Phenols(1)	≤ 5.0 mg/L
Soluble Iron	≤ 15 mg/L
Fluoride(2)	≤ 10.0 mg/L
Sulfide (1)	≤ 1.0 mg/L
Sulfate(2)	≤ 1000 mg/L

(1) Not monitored in 2009.
(2) Monitored but not used in to the Quotient calculation.

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2.2. Quotient calculation:

In this study, it was used the same quotient calculation $\bar{Q}$ as defined by Long et al. [1]. The calculation of $\bar{Q}$ is a three-step process. First, each chemical concentration in the sample is divided by legal values, resulting in an individual concentration ratio Q, presented in equation 1. Then, all Q values are summed for each compound, every monitoring week and finally divided by the total number of measured compounds, as presented in equation 2. The result is a single unitless index of relative degree of compliance with current regulation, presented on percentage format, for a particular monitoring week.

The legal criterion, in this study was defined by Sao Paulo State Decree 8468, article 19A, listed in Table 1 [2] The CONAMA resolution 357/05 [3] and 397/08 [8], article 34 were used as legal standard to barium, boron, manganese. The Q value, showed in Equation 1, should imply in an estimated value how close the sample is from legal requirements for an individual parameter.

$$\boldsymbol{Q} = \frac{\boldsymbol{SubstanceConcentration}}{\boldsymbol{Legal\,Standard}} \qquad (1)$$

To evaluate and to compare samples collected on different weeks, it was used a total average quotient $\bar{Q}$, calculate as per equation 2.

$$\bar{\boldsymbol{Q}} = \frac{\sum_{i=1}^{i=n} \boldsymbol{Q}}{\boldsymbol{n}} \qquad (2)$$

Q = is the individual Q defined in equation 1
n = is the total number of analyzed substances for each sample, per week.

In this work, it was considered the use of 9 metals (Ag, Ba, Cd, Fe, Mn, Ni, Pb, Sn and Zn), 2 semi-metals (B and As) and 1 non-metal (Se) to perform the quotient calculation. By legal requirement, those elements must be summed, as an individual criteria (See Table 1). pH, temperature, fluoride and sulfate were monitored, but not used in $\bar{Q}$ calculation. Those parameters were excluded because by definition $\bar{Q}$ values must be applied to a similar group of substances or elements. The similarity criteria could be associated to chemical behavior, chemical hazard or risk, or to biological effects. So in this evaluation it was selected to work with trace elements that already were grouped by legal definition.

When chemical concentration was lower than the method quantitation limit, that chemical was not included in the calculation and the denominator was adjusted accordingly. By Long´s definition [1], this only can be performed when the legal criteria is much higher than method quantification limit, like it happens in this study.

Quotients values close to the 100% indicate that effluent average concentration is close to the legal value [2, 3, 8]. Quotients higher than 100% are regulatory non-compliant. Any value under 100% meets legal environmental requirements.

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3. RESULTS

The results of individual elements (n=13) quotient Q and total average quotient $\overline{Q}$ by monitoring week (n=36) are presented in Table 2. Only substances with concentration higher than the analytical method quantitation limit were considered to Q calculation.

Ipen´s effluent total average quotient $\overline{Q}$, on 36 monitoring weeks was between 0.69% and 4.28% of the regulatory value. With those results it is possible to state that Ipen's effluent is compliant with Sao Paulo's State regulation, considering the studied trace elements.

The objective, i.e. to use a quotient to evaluate Ipen´s effluent, was met with an easily understandable, regulatory compliant index. The model adopted allows that the number of chemical in the sample that exceeds their respective regulatory level can be summed as an indication of presence of these substances at the legal limitation level. After Table 2 evaluation, it was observed that one chemical compound lower than regulatory limit will affect the final quotient in a similar way as a non-detected substance. That means it will contribute to an average quotient lower than 100%.

However this assumption could give the false idea that two extremely different effluents concerning the chemical properties would have a similar characteristic, simply because they have similar total quotients. This can be noticed in Figure 1, where it is presented the average, maximum and minimum total quotients per week. Ipen's effluent presents an average quotient around 1.8%, and during several weeks no significant change was observed on the average quotient value. However the maximum quotient and the individual element quotient, presented in Figure 2, exhibits a significant variation in the same period of time.

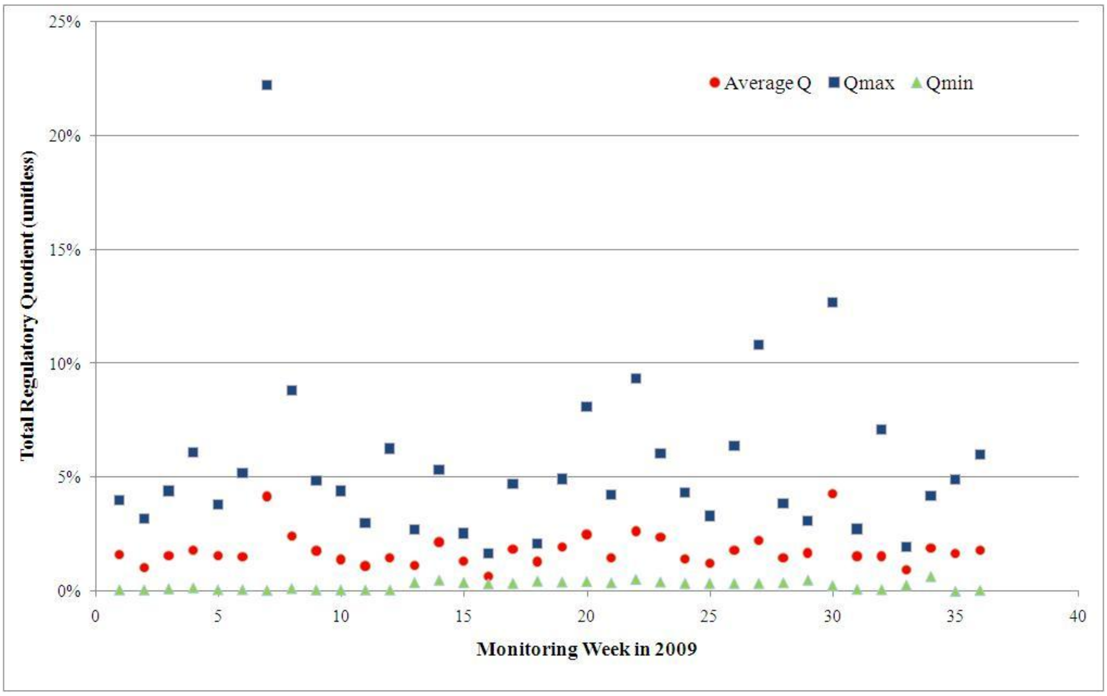

Figure 1: Average, maximum and minimum total quotient, per monitoring week.

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Individual quotients, presented in Table 3, permit the identification of critical parameters related to current regulation, or any particular element trend (see Figure 2) that could lead to a future non-compliant status. Using Ipen's effluent as an example, it is possible to notice that Boron was not present on early week's wastewater. On week 12, Boron increased up to week 30 reaching 12.68% of regulatory limit. This kind of trend identification permits to adopt reduction emission goals and corrective measures.

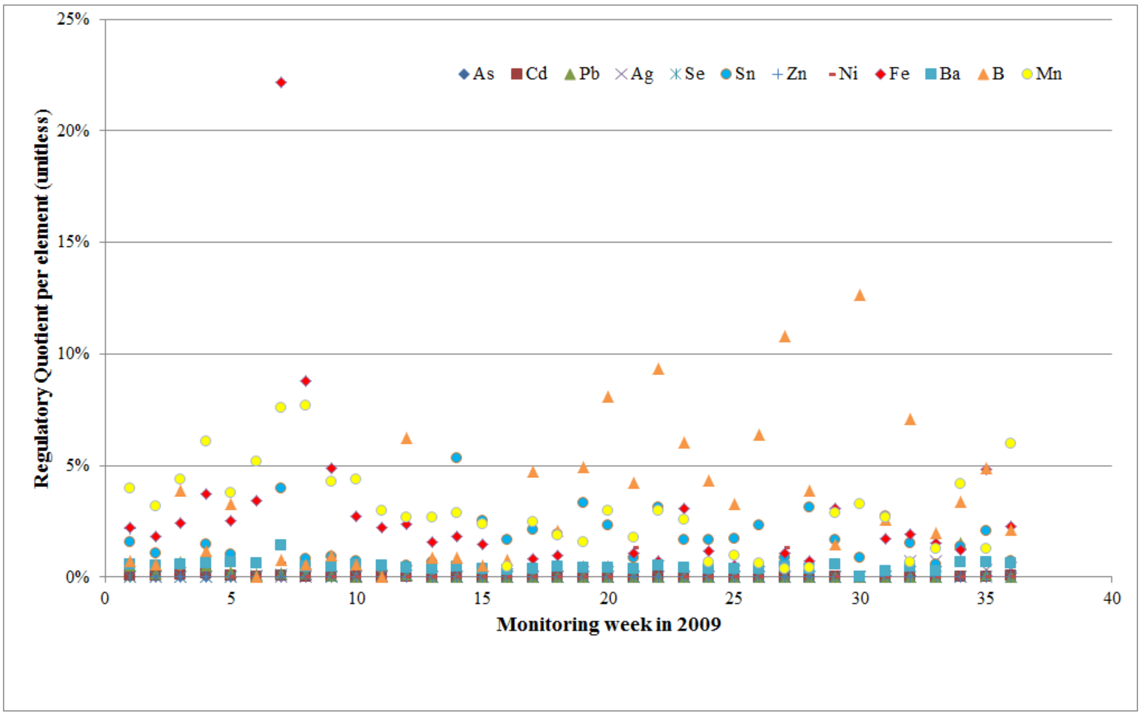

Figure 2: Individual element quotient per monitoring week.

This is the reason to recommend a multi-parametric index to the evaluation of a routinely generated wastewater that may not fit the evaluation of non-routinely operations. At Ipen's monitoring program, the use of a regulatory index should not preclude examination of the individual chemical data, but may help the general public presentation or discussion about regulatory compliance operations.

Considering there are no legal guidelines for long term wastewater evaluation or risk assessment, associated to an emission reduction, some environmental state or national organisms may oppose the use of this index. However it is recognized in current literature that such tool can be "predictive of the presence or absence" of toxic effects with a quantifiable degree of confidence. It could be an advantage to use a site related regulatory index to some particular purposes, like:

- To establish a plant environmental performance or an emission reduction goal,
- To reduce a complex data matrix into a simple quotient.
- To present to the general public, in a simply and quantitative manner, any plant regulatory compliance.

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Table 2: Average Quotient, as per Long et al [1], for Ipen´s effluent during the year 2009.

Parameter	February			March			April				
	1	2	3	4	5	6	7	8	9	10	11
Week	-	-	-	-	-	-	-	-	-	-	-
As	0.07%	0.07%	0.12%	0.17%	0.08%	-	0.05%	-	-	-	-
Cd	0.54%	0.17%	0.69%	0.54%	0.21%	0.15%	0.17%	0.17%	0.07%	-	-
Pb	-	-	-	-	-	-	-	-	-	-	-
Ag	-	-	-	-	-	0.08%	0.11%	0.13%	-	0.07%	0.07%
Se	1.56%	1.06%	0.54%	1.46%	1.02%	0.62%	4.00%	0.82%	0.92%	0.72%	0.44%
Sn	2.18%	-	-	-	-	-	-	-	-	-	-
Zn	0.65%	0.55%	0.60%	0.55%	-	-	0.65%	-	-	-	-
Ni	3.74%	1.35%	1.02%	1.89%	1.11%	0.69%	4.67%	0.91%	0.94%	0.74%	0.46%
Fe	0.60%	0.52%	0.56%	0.62%	0.66%	0.62%	1.44%	0.48%	0.50%	0.60%	0.54%
Ba	0.72%	0.60%	3.90%	1.20%	3.26%	-	0.80%	0.56%	0.98%	0.60%	-
B	4.00%	3.20%	4.40%	6.10%	3.80%	5.20%	7.60%	7.70%	4.30%	4.40%	3.00%
Mn	10	9	9	9	8	7	10	8	7	7	6
n	**1.63%**	**1.04%**	**1.58%**	**1.80%**	**1.58%**	**1.54%**	**4.17%**	**2.45%**	**1.80%**	**1.41%**	**1.13%**
Q	4.00%	3.20%	4.40%	6.10%	3.80%	5.20%	22.20%	8.80%	4.87%	4.40%	3.00%

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Table 2: Average Quotient, as per Long et al [1], for Ipen´s effluent during the year 2009.(cont.)

Parameter	May				June			July	August
	12	13	14	15	16	17	18	19	20
Week	-	-	-	-	-	-	-	-	-
As	-	-	-	-	-	-	-	-	-
Cd	0.11%	-	-	-	-	-	-	-	-
Pb	0.27%	-	-	-	-	-	-	-	-
Ag	0.07%	-	-	-	-	-	-	-	-
Se	0.52%	0.70%	5.33%	2.53%	1.67%	2.13%	1.93%	3.33%	2.33%
Sn	-	-	-	-	-	-	-	-	-
Zn	-	-	-	-	-	-	-	-	-
Ni	0.65%	0.70%	1.60%	0.76%	0.50%	0.64%	0.58%	1.00%	0.70%
Fe	0.42%	0.40%	0.50%	0.40%	0.34%	0.36%	0.46%	0.42%	0.44%
Ba	6.26%	0.86%	0.88%	0.54%	0.76%	4.72%	2.10%	4.92%	8.08%
B	2.70%	2.70%	2.90%	2.40%	0.47%	2.50%	1.90%	1.60%	3.00%
Mn	9	6	6	6	6	6	6	6	6
n	**1.49%**	**1.15%**	**2.17%**	**1.36%**	**0.69%**	**1.87%**	**1.32%**	**1.96%**	**2.50%**
Q	6.26%	2.70%	5.33%	2.53%	1.67%	4.72%	2.10%	4.92%	8.08%

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Table 2: Average Quotient, as per Long et al [1], for Ipen´s effluent during the year 2009.(cont.)

Parameter	September				October				
	21	22	23	24	25	26	27	28	29
Week	-	-	-	-	-	-	-	-	-
As	-	-	-	-	-	-	-	-	-
Cd	-	-	-	-	-	-	-	-	-
Pb	-	-	-	-	-	-	-	-	-
Ag	-	-	-	-	-	-	-	-	-
Se	0.87%	3.13%	1.67%	1.67%	1.73%	2.33%	0.87%	3.13%	1.67%
Sn	-	-	-	-	-	-	-	-	-
Zn	1.35%	0.60%	-	-	-	-	1.35%	0.60%	-
Ni	0.80%	1.18%	0.50%	0.50%	0.52%	0.70%	0.80%	1.18%	0.50%
Fe	0.38%	0.54%	0.42%	0.36%	0.36%	0.36%	0.48%	0.38%	0.56%
Ba	4.22%	9.34%	6.06%	4.32%	3.30%	6.38%	10.80%	3.86%	1.46%
B	1.80%	3.00%	2.60%	0.68%	1.00%	0.61%	0.36%	0.44%	2.90%
Mn	7	7	6	6	6	6	7	7	6
n	**1.50%**	**2.65%**	**2.39%**	**1.45%**	**1.24%**	**1.81%**	**2.25%**	**1.48%**	**1.70%**
Q	4.22%	9.34%	6.06%	4.32%	3.30%	6.38%	10.80%	3.86%	3.09%

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Table 2: Average Quotient, as per Long et al [1], for Ipen´s effluent during the year 2009.(cont.)

Parameter	November				Dezember		
	30	31	32	33	34	35	36
Week	-	0.09%	0.09%	-	-	-	-
As	-	-	-	-	-	0.01%	0.05%
Cd	-	-	-	-	1.53%	0.13%	-
Pb	-	-	0.73%	0.73%	-	0.30%	0.41%
Ag	-	-	-	-	-	-	-
Se	0.87%	2.73%	1.53%	0.56%	1.40%	2.07%	0.73%
Sn	-	-	-	-	-	-	-
Zn	-	-	0.65%	-	-	-	-
Ni	0.26%	0.82%	0.94%	0.39%	0.88%	0.75%	0.36%
Fe	-	0.26%	0.48%	0.28%	0.66%	0.68%	0.64%
Ba	12.68%	2.60%	7.10%	1.96%	3.38%	4.90%	2.12%
B	3.30%	2.70%	0.66%	1.30%	4.20%	1.30%	6.00%
Mn	4	7	9	7	7	9	7
n	**4.28%**	**1.55%**	**1.56%**	**0.96%**	**1.90%**	**1.66%**	**1.80%**
Q	12.68%	2.73%	7.10%	1.96%	4.20%	4.90%	6.00%

Table 3: Average, Maximum and Minimum quotient per element.

Parameter	Quotient		
	Average	Max	Min
As	0.09%	0.09%	NC
Cd	0.08%	0.17%	0.01%
Pb	0.37%	1.53%	0.07%
Ag	0.49%	0.73%	0.27%
Se	0.09%	0.13%	0.07%
Sn	1.68%	5.33%	0.44%
Zn	2.18%	2.18%	NC
Ni	0.76%	1.35%	0.55%
Sum of Metals	0.99%	4.67%	0.26%
Fe	2.66%	22.20%	0.37%
Ba	0.51%	1.44%	0.26%
B	3.71%	12.68%	0.54%
Mn	2.96%	7.70%	0.36%

NC: not calculated.

CONCLUSION

Considering the monitored parameters and by using the Ipen´s effluent concentration to calculate Q and $\bar{Q}$, as per Long et al. [1] definition, it was observed that effluent corresponds to 0.68 up to 4.28% of the regulatory standard to be released into public sewer system. So it is possible to state this effluent is compliant with Sao Paulo State wastewater regulation. Using this procedure, it was possible to propose a simple Regulatory Compliance Index with the current environmental legislation. This index also makes the effluent evaluation much easier by using just one simple and understandable value.

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