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STUDY OF GROUNDWATER COLLECTION PROTOCOLS ON THE IPEN /CNEN-SP CAMPUS

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ABSTRACT

As per Brazilian Health Ministry´s evaluation, industry is the second activity that most contaminates the soil in Sao Paulo Metropolitan region. In order to assess this scenario and keep a continuous logging of IPEN´s installations effect over chemical compounds levels, and to improve the installation radioactive logging, in the region under its campus influence, since 2006, IPEN performs the groundwater monitoring, in the region where it is located. Collections are performed bimonthly in seven monitoring wells, evaluating 17 parameters. These values are compared to the ones established by CONAMA 396/08 Resolution, which provides the groundwater classification and environmental guidelines to chemically stable compounds. So far IPEN keeps the wells in good conditions and performs sampling methods studies to adequate it to current legal standards. The groundwater collection method and the wells characterization, concerning the anionic species content (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{-3} e SO_4^{-2}), are evaluated in the present study. The purge procedure requirement was also evaluated. The well purging is the procedure for withdrawing water from inside the well, so the collection is performed only after the water level restoration, thereby ensuring that the water collected represents the aquifer. The use of "bailer", which requires purging, and a called “low flow pump”, which requires no purging for sample collection, was also evaluated. These methods were selected in this study because they are recommended by CETESB 6410/88, the local standard to groundwater sample collection. Thus some anions concentrations in groundwater sampled with different purging procedures and collection were compared. The concentration change in each well performed with the same collection procedure was compared with the other collection methods variation in order to evaluate if these are equivalents. From the results obtained in this comparative study was possible to optimize the collect methods, shaping changes in sampling protocol, with neither invalidate nor lose the historic program data.

1. INTRODUCTION

According to National Environment Council (CONAMA) Resolution´s 396/08, groundwater is the water that occurs naturally or artificially in the underground (1). This water source commonly occurs in pores or empty parts of rocks. Feitosa, et al (2008) (2) states the groundwater source is the biggest global reservoir of fresh water as a liquid, that constitutes about 10.3 million km^3.

Groundwater is very important to keep the soil humidity, rivers flow, lakes and wetlands, rivers ever greening during the drought period. Its importance must be considered in the hydrological cycle as a solution to the problem of hydric resources access in some regions, and also contributes to the pollution control. (World Resources Institute apud in Rebouças, 1999) (3)

Groundwater have different features, because absorbs some rock species or species from the reservoir region, and generally it is subjected to several modifications. Groundwater could become cleaner, or depending on the way which travels, could become contaminated. These water resources do not have defined physical limits, hence its contamination can affect other regions, other underground sources or even surface water. At last groundwater could become a river fount or at least feeding it. Due to the likely contact between water of a region, groundwater assessment must be evaluated, mainly in regions of wide vulnerability. The water characterization to define quality parameters and the reservoir class (aquifer) must be framed. Even more, under industrial, agricultural, or urban activities, it is important to establish actions in order to keep the original groundwater quality standards, mainly because its decontamination process can be extremely slow and expensive.

In this work, the groundwater anions characterization (F^-, Cl^-, Br^- NO_2^-, NO_3^-, $PO4^{-3}$ e $SO4^{-2}$) was performed at IPEN/CNEN-SP *campus*, through the ion chromatography technique (4). The goal was to reach the water chemical classification of seven monitoring wells (AP-01, AP-02, AP-03, AP-04, AP-05, AP-06 e AP-08). Samples need to be adequately collected and conserved to the hydro chemical studies are performed with affectivity, because the water collected should represents the real conditions of the aquifer. Also the collected samples could not derive of the stagnant water within the well. Thus the collection methods, for instance, bailer system and electric pump, that require the well purge, and the low-flow system, that do not requires purge (recommended method by CETESB 6410/88 Standard) (5), were evaluated. Through Hydrographs was evaluated the anion concentration and it was analyzed collection methods influence over anions results. This study allowed improving the groundwater collection methods, and ensuring the validity and representativeness of the essays performed in the IPEN/CNEN-SP Program of Groundwater Assessment (PMA-Q).

2. OBJECTIVE

This work intends to evaluate different groundwater collection procedures and to characterize groundwater of seven monitoring wells installed at IPEN/CNEN-SP. Furthermore it was proposed the water chemical classification to each well.

3. MATERIAL & METHOD

3.1. Collection Samples Procedure

The sampling was performed between January/2012 and November/2012. As an exhausting device was used the bailer and an electric drive pump (model: GRUNDFOS CS18 of ½ HP and 10L/min of output). The collections were performed with bailers, high flow pump and a low-flow pump (Sauber System Ambiental), that does not require the well purge. The procedure applied to each collect is showed in the Table 1.

Ipen facility is located inside São Paulo University Campus in West side of São Paulo City in a total area of 478,000 m^2, in coordinates UTM 7.392 km and 7.395 km North and 322 km and 326 km East, that is represented in Figure 1. The Upper Tiete Basin Committee is divided on five sub-committees: Tiete-Cabeceiras, Billings-Tamanduatei, Juqueri-Cantareira, Cotia-Guarapiranga e Pinheiros-Pirapora. Ipen is locates on Sub-Committee Penha-Pinheiros, between Jaguare, Pirajussara and Pinheiros Rivers. (6)

Table 1: Collection procedures

	Jan/2012	Mar/2012	Mai/2012	Jul/2012	Set/2012	Nov/2012
Purge	Yes	Yes	Yes	No	No	No
Collection method	High-flow pump	High-flow pump	High-flow pump	*Bailer*	Low-flow pump	*Bailer*

The seven monitoring wells (see Figure 2) were positioned close to buildings associated with significant radioactivity or chemical manipulation, such as the Nuclear reactor, Solid Residual Storage facility and Uranium reprocessing unity. Those wells position was chosen, together with many other safety devices, intent to identify an early contamination generated by operational buildings, as identified on Table 2.

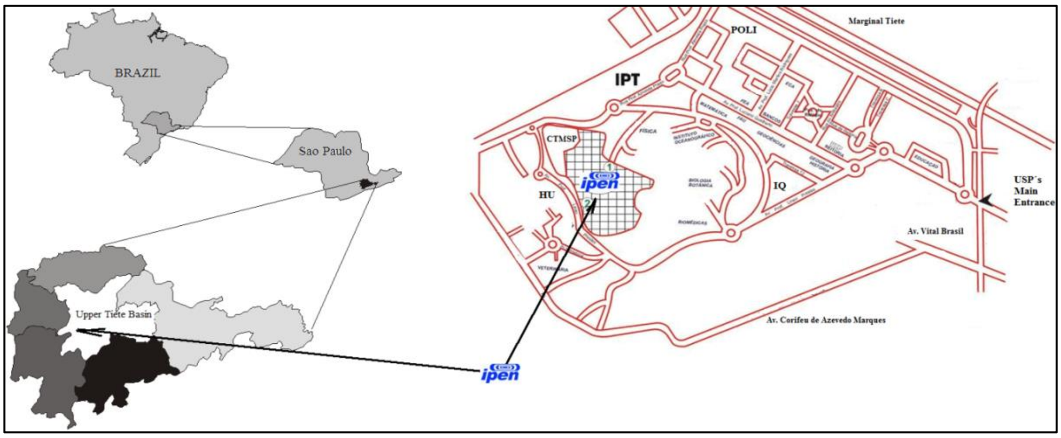


Figure 1: Ipen's location on Upper Tiete Basin

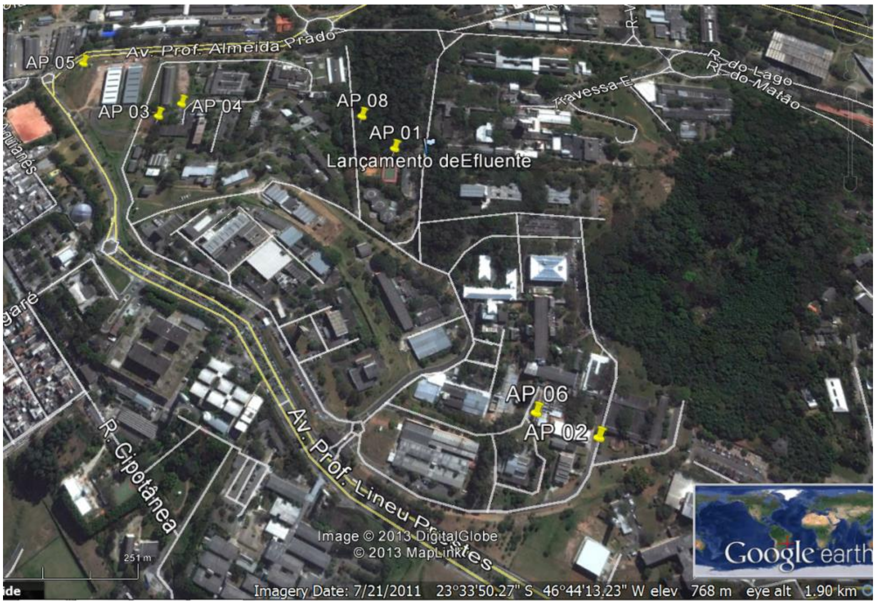


Figure 2: Monitoring well´s location inside Ipen´s facility

Table 2: Wells location inside Ipen's facility

Wells identification	Location	Location (GPS)
AP-01	North entrance	23°33'43.51"S 46°44'13.87"W
AP-02	UITAR - LRR	23°33'59.66"S 46°44'4.58"W
AP-03	CQMA	23°33'40.76"S 46°44'27.90"W
AP-04	Safeguard Warehouse	23°33'40.00"S 46°44'26.58"W
AP-05	Perimetral Route	23°33'36.67"S 46°44'33.07"W
AP-06	Behind UITAR - LRR	23°33'58.39"S 46°44'7.43"W
AP-08	Greic	23°33'36.51"S 46°44'32.98"W

3.2. Sample Preparation

The samples were filtered with membrane of 0.45µm pore (Millipore) using vacuum and 0.45um filtration cartridges (Millex, Millipore). All samples were analyzed upon 48hs from the collection time.

3.3. Essay Method

The anions essay was performed in an ion chromatograph system, model DX-120, from DIONEX Corporation, with a conductivity detector with auto regenerated suppressor was used accordingly to LEMES and Standard Method 4110B.

3.3. Statistical Data Treatment

The Analysis of Variance (ANOVA) was used in the sampling method comparison. The variances of the anions analysis were calculated to the collection procedures described below:

- Applying purge and high flow pump;
- Without purge and using "*bailer*" (twice); and
- Without purge and using low flow pump (once)

The ANOVA is a parametric test that compares the mean and the dispersion between data groups with the data dispersion observed within the groups. (7)
To the comparison between F_{cal} and the F_{critic}, obtained from the F distribution, the ANOVA adopts the criteria below:

- If $F_{cal} < F_{critic}$, then the means are not expressively different (H0 Null Hypothesis)
- If $F_{cal} > F_{critic}$, then at least one of the means is expressively different (H1).

The samples were analyzed and evaluated according to the wells conditions, and the data were statistically treated through the data analysis tool called ANOVA, to evaluate the sampling protocol equivalence. In this study the null hypothesis was that all sample collection procedures were statistically comparable or equivalent.

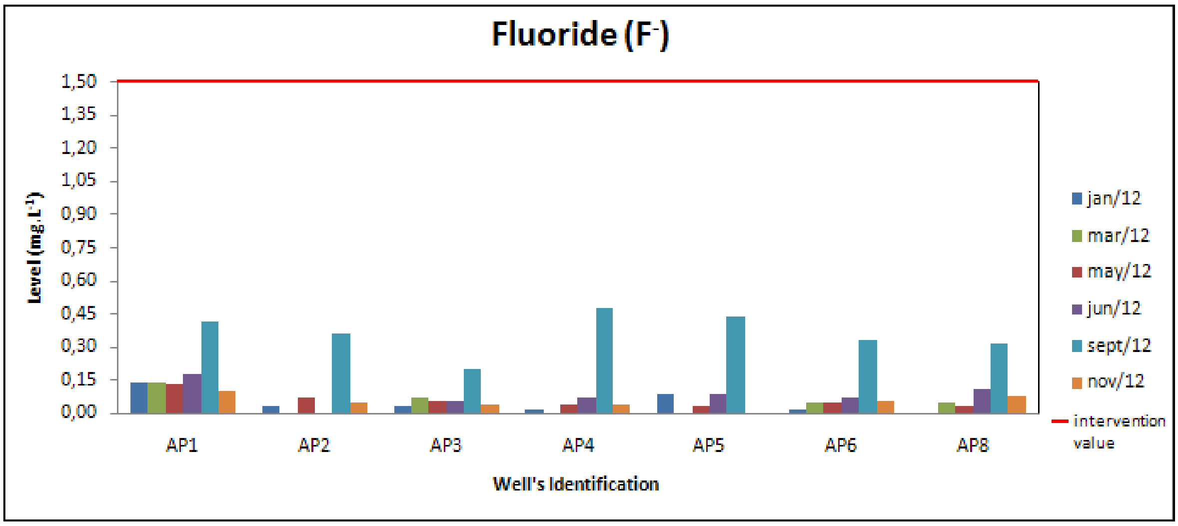
4. RESULTS & DISCUSSION

4.1. Results of Ion Chromatography Analysis

Anion concentration results, monitored in 2012, were compared with the Brazilian legal requirements (1), to assess IPEN´s influence over the region's groundwater.

4.1.1. Fluoride (F^-)

In groundwater, the Brazilian intervention value for fluoride is 1.5 $mg.L^{-1}$, according to CONAMA (1).



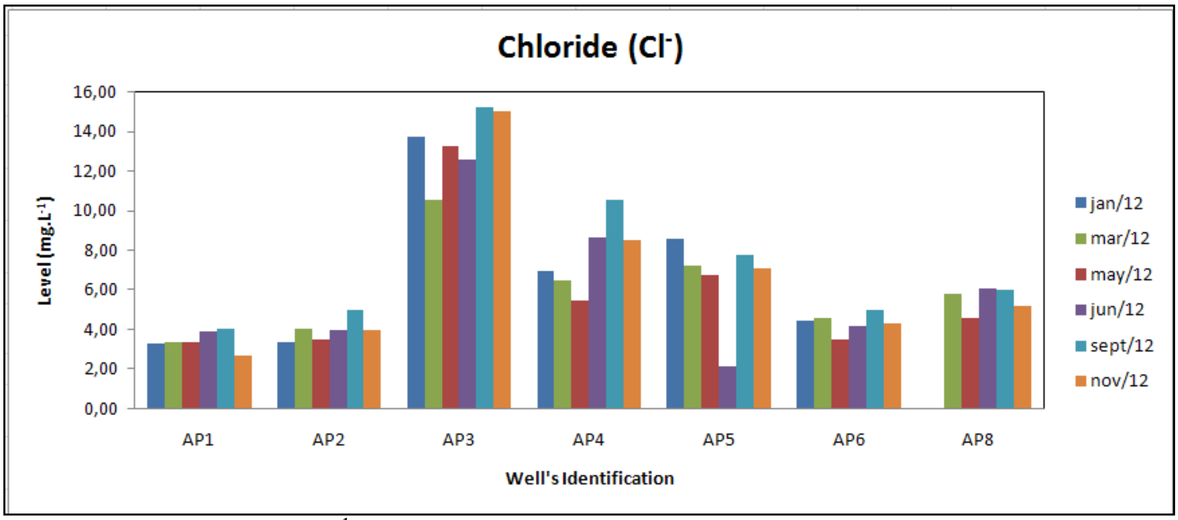
Detection Limit <0.02 $mg.L^{-1}$.

Figure 3: Fluoride concentration per well and per collection in 2012.

Figure 3 presents the fluoride concentration measured in each well in six collections in 2012. These values were bellowing the intervention value (1) in all monitored wells, and all collection campaigns under all the sample collection methods, independently of the variations.

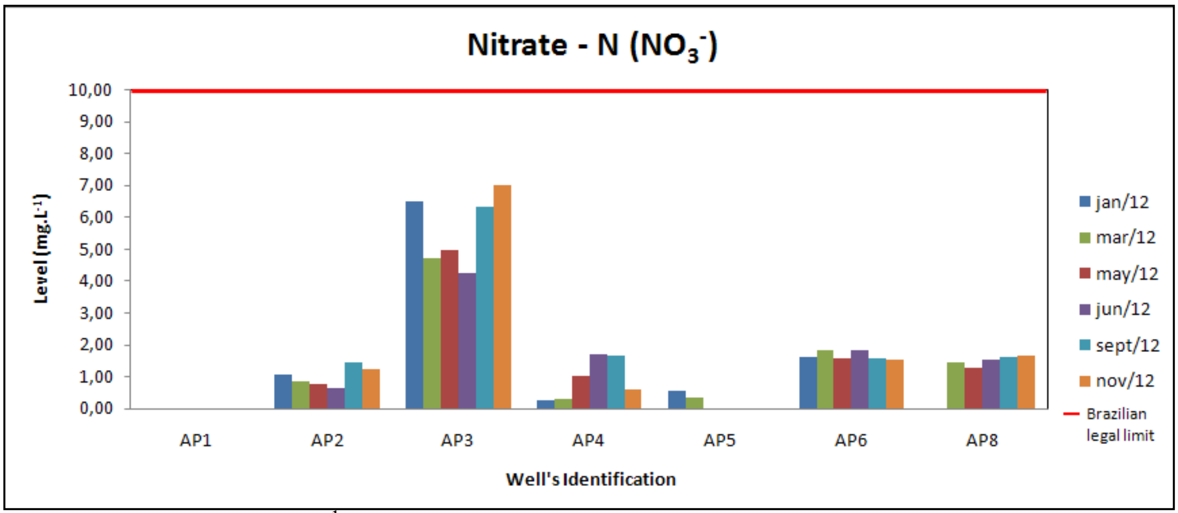
4.1.2. Chloride (Cl^-)

Chloride is considered one of the main ions in groundwater, in other words, chloride is commonly found in large levels, when compared to others. It is highly solvable and deliquescent (tend to absorbing water and become liquid) and it is extremely stable in solutions. Groundwater normally presents levels lower than 100 mg/L but when chloride is found in levels too higher than this it can indicates pollution by dump or landfill (2). Chloride´s maximum consumption concentration limit is 250 mg L^{-1}, according to CONAMA 396 Resolution (1). Figure 4 presents chloride concentration obtained in 2012. Independently of the variations presented, by wells, sample collection method and collection time, the chloride levels are lower than the maximum limit specified to consumption, at Ipen facility.



Detection Limit <0.1 mg.L^{-1}.

Figure 4: Chloride concentration (mg.L^{-1}) results per well and per collection, in 2012.



Detection limit <0.1 mg L^{-1}.

Figure 5: Nitrate-N concentration (mg.L^{-1}) results per well and per collection, in 2012.

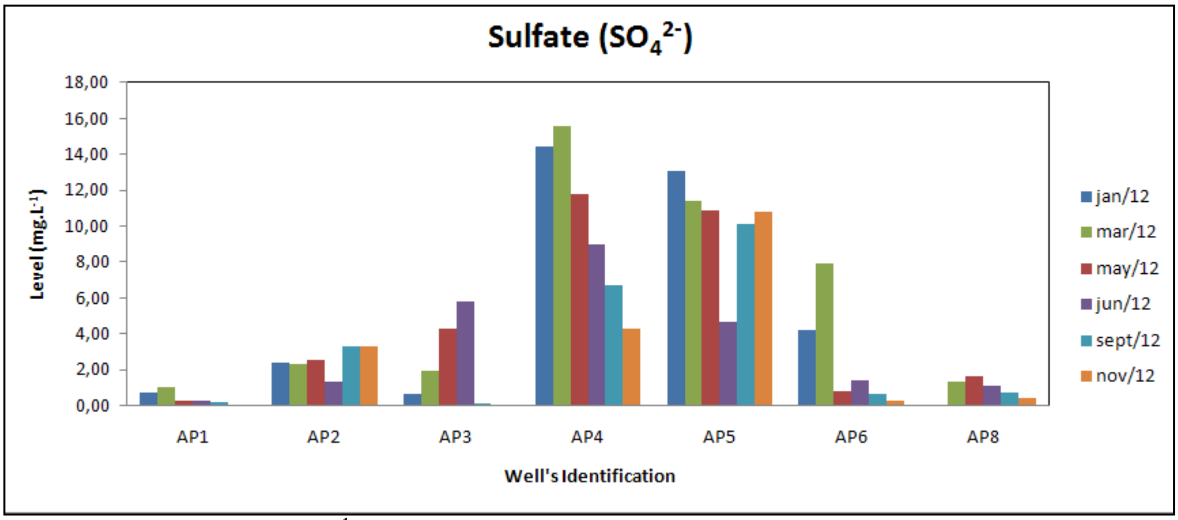
4.1.3. Nitrate-N and Nitrite-N (NO_3^--N & NO_2^--N)

All of the Nitrates are solvable and stable in aqueous solutions. High levels (upper than 5 mg/L), in groundwater, indicates contamination by anthropogenic activities, as well as sewage discharge, septic tanks, landfills, cemeteries, nitrogen fertilizers, animal waste, etc.

Related to the nitrogen cycle, in presence of a particular bacteria the ammonia (NH_3) oxidizes to nitrite (NO_2^-) the nitrite oxidizes to nitrate (NO_3^-), showing that the presence of nitrite indicates recent pollution (8). Nitrate´s Brazilian legal limit in groundwater is up to 10 mg L^{-1} (1). The results obtained in the analysis around 2012 are presented in the Figure 5. Considering nitrate-N results in all Ipen´s monitoring wells are according Brazilian legislation. In all monitoring wells, during 2012 campaign, there were no nitrite values above the quantification limit (0.10 mg.L^{-1}).

4.1.4. Sulfate (SO_4^{2-})

As well as chloride, sulfate is considered a main ion in nature waters, highly deliquescent; some of this species are very solvable and in general are stable. Commonly presents levels lower than 100 mg L^{-1}, in groundwater (2). The Brazilian Law established the limit of 250 mg/L (1). The results obtained in the analysis around 2012 are presented in the Figure 6. Considering sulfate the values measured in all monitoring wells were also under the Brazilian legal limit. (1).



Detection Limit <0.1 mg.L^{-1}.

Figure 6: Sulfate concentration (mg.L^{-1}) results per well and per collection, in 2012.

4.2. Collection Protocol Assessment

By the anion measured concentration, in addition to the data treatment through the statistical ANOVA test, it was possible to verify the collection protocol equivalence depends on the anion that is assessed. To fluoride, F_{cal} was higher than F_{critic}, hence the collection protocols using "bailer" and high flow pump are expressively different of low flow pump collection method. Due to the water well agitation, during the sampling process using either *"bailer"* or high flow pump, the calcium, iron and barium levels increase, bearing on straight in the fluorides solubility.

In case of Chloride there was no have expressive differences between all of the collection protocols studied ($F_{cal} < F_{critic}$), although the AP-04 well presented expressive differences between the collection methods.

Concerning nitrate-N and sulfate (Figures 5 and 6), it was possible to evaluate the collection protocols do not present expressive differences (n= 6 and α = 0,05), to Ipen´s monitoring wells.

4.3. Chemical Groundwater Classification

The Piper Diagram is presented in the Figure 7 to perform the chemical groundwater classification. The assessments were based on the results from January, March and September of 2012, which were the analysis we had results of sulfate, chloride and bicarbonate to all of the wells.

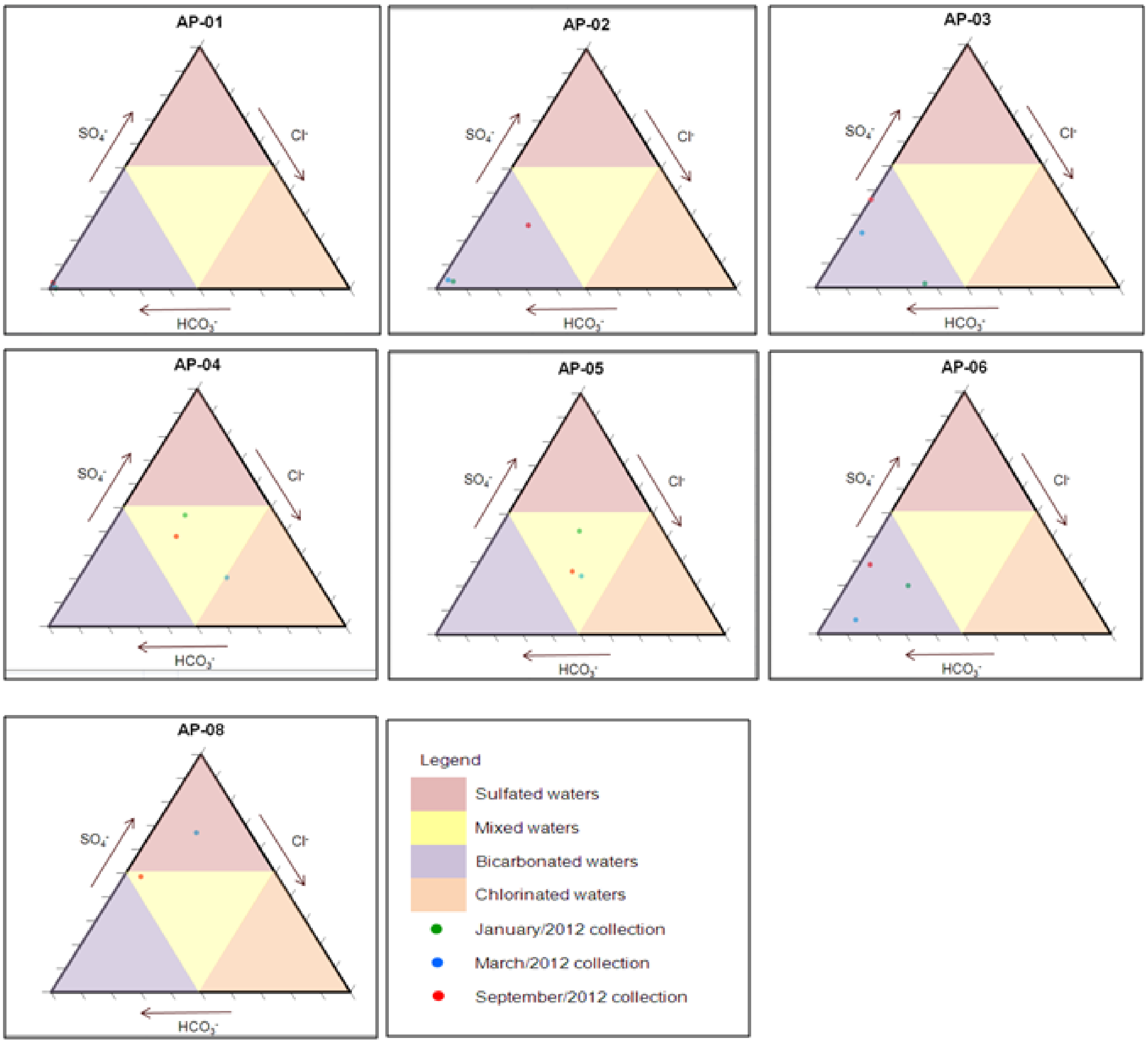


Figure 7: Piper diagram to Ipen´s chemical groundwater classification.

5. CONCLUSION

Although the collection protocol is not expressively influenced in the chloride, nitrate-N and sulfate results in groundwater samples collected at IPEN/CNEN, expressive differences were found to fluoride results. However apart from observed variations, all anion monitored in Ipen´s groundwaters are in accordance with Brazilian legislation.

There were no nitrite-N and phosphate-P results above the quantification limit.

According to the Piper Diagram, the wells are chemically classified as:

- **Bicarbonated Waters**: AP-01, AP-02, AP-03 e AP-06;
- **Mixed Waters**: AP-04 e AP-05.

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