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PRELIMINARY CHEMICAL QUALITY EVALUATION OF IPEN´S GROUNDWATERS FOR STABLE ELEMENTS

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ABSTRACT

IPEN has implemented an Environmental Monitoring Program, which has as main objective the life and property safety in its plant of 478,000 m^2. As a research and production facility, many chemical, biological and radioactive products are manipulated in its laboratories. To assure that its activities do not lead to groundwater resources contamination, the environmental program includes chemical quality evaluation of six wells installed in different areas of the institute. Throughout 2009, four sampling campaigns were performed according to international references. The samples collected were analyzed at the Chemistry and Environmental Diagnosis Center - CQMA applying techniques such as ICP-OES, CV-AAS, GFAA and ion chromatography, in order to quantify metals, semimetals and anions. The results were compared to intervention values defined by current Brazilian environmental laws. Elements commonly present in groundwater such as hardness due to calcium and magnesium, sodium, chloride and sulfate were detected in $mg.L^{-1}$ levels, but in concentrations much lower than national drinking water standards. Among the six hundred and forty-five analyses carried out, it was observed that only 1.2% of the results were not in compliance with the regulatory values. Those non-compliant values are presented and discussed in this work. It was observed that there is no evidence of contamination by the evaluated compounds in IPEN´s groundwater.

1. INTRODUTION

The Environmental Monitoring Program from Nuclear and Energy Research Institute - Ipen also covers groundwater resources. Ipen is located on Upper Tiete Basin that is the most populated hydrological unity in Brazil. Accordingly to Hirata, et al. [1] there is no information about the total number of operational wells or the total exploited volume. On Hirata's initial estimation the Upper Tiete Basin has 9 thousand operational wells and 315million cubic meters exploited every year, mostly in Sao Paulo City.

Considering that Upper Tiete Basin has no governmental groundwater management program, many other human activities could cause degradation of groundwater quality and production. Considering this scenario, Ipen's monitoring program intends to evaluate the present situation and the impact of its activities on groundwater quality. This work will describe and discuss the results obtained during 2009 on four sample collection campaigns, performed on March, July, September, and November, from six monitoring wells located inside Ipen's facility.

The obtained results were compared with regulatory values, established by Sao Paulo environmental agency, CETESB [2] and with Brazil National Council for the Environment- CONAMA Resolution 420 [3]. The legal standards established by Regulation 518 [4] from Brazilian Ministry of Health for potable water quality were also used to compare with the obtained results for the studied wells.

2. LOCALIZATION

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.

The six 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 1.

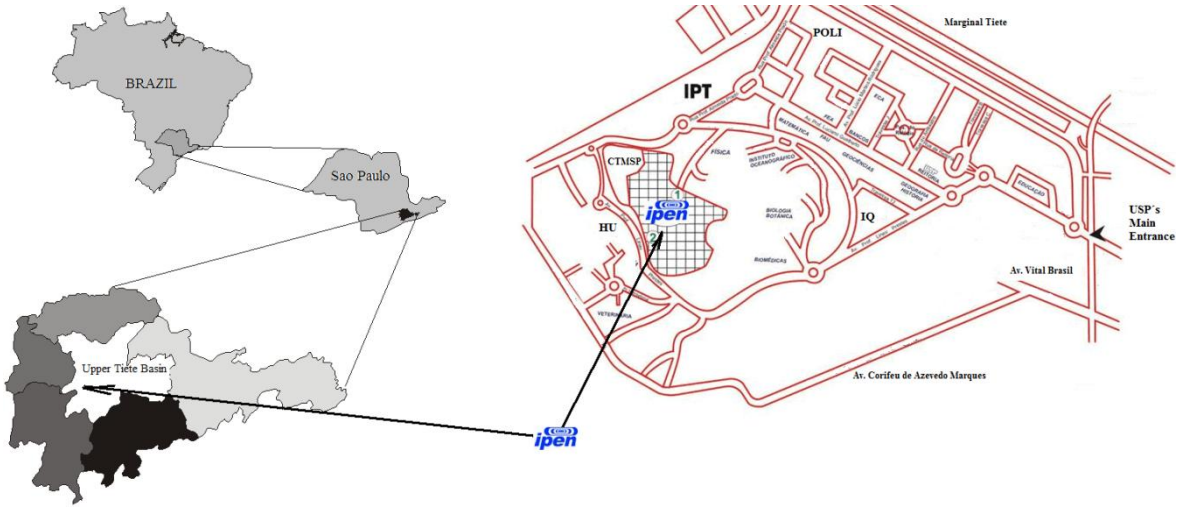

Figure 1: Ipen's location on Upper Tiete Basin.

Table 1 : Wells location inside Ipen's facility.

Wells identification	Location
AP-01	North entrance
AP-02	UITAR - LRR
AP-03	CQMA
AP-04	Safeguard Warehouse
AP-05	Perimetral Route
AP-06	Behind UITAR - LRR

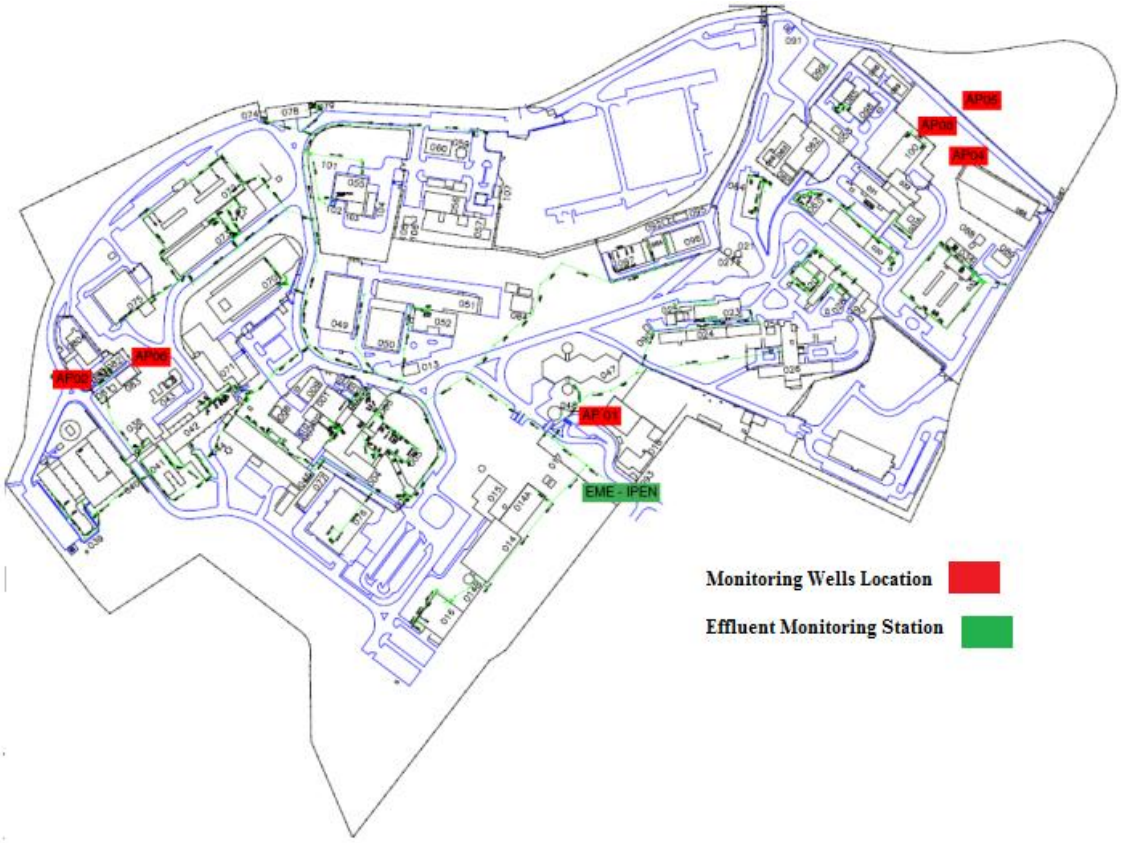

Figure 2: Monitoring well´s location inside Ipen´s facility.

3. METHODS:

3.1. Analytical procedure:

Based on each element required sensibility, the metal and semimetal concentration were measured by inductively coupled optical emission spectrometry – ICP-OES, Cold Vapor Atomic Absorption Spectrometry CV-AAS or Graphite Furnace atomic Absorption Spectrometry GF-AAS.

The following instruments were used:

- ICP-OES, Espectro Flame M 120, from Spectro Analytical Instruments; with axial torch, with Meinhard nebulizer and Scott Chamber.
- GF-AAS AAnalyst 800, from Perkin Elmer with flow injection system FIAS – 400.
- Ion chromatograph system, model DX-120, from DIONEX Corporation, with a conductivity detector with auto regenerated suppressor was used accordingly to LEMES [5] and Standard Method 4110B [6].

All samples were previously filtered on 0.45µm membrane (Millex- from Millipore), as required for anion measurements. Each element corresponding analytical curve was prepared using multi elementary standard solutions as previously described by COTRIM [7] DANTAS et. al. [8] and FURUSAWA [9].

3.2. Sampling:

All sample collection and preservation was according to São Paulo State Environment Agency- CETESB´s Collection Guide [10] and APHA [6]. Those references specify from the flask type, sample volume, preservation procedures and reactive, to sample expiration date for each parameter.

4. RESULTS:

Throughout 2009, four campaigns were executed evenly distributed in the months of March, July, September and November. No sample was collected in AP-01 (well located near North Main Entrance), due the low water level.

Average ground water monitoring results (n=3) obtained from tubular wells, and standard deviation are presented on Table 2. Those results were compared with intervention/regulatory values for groundwater samples established by CETESB [10]. Elements, such as calcium, magnesium, potassium and anions such as chloride and sulfate were the main compounds found in Ipen's groundwater.

Manganese and Aluminum were found above CETESB´s intervention value [10], in the following periods and locations:

- Aluminum in AP-03 during March campaign.
- Manganese in AP-05 in every collection period.

It is noticed that iron, aluminum and manganese are abundantly found on tropical soils, as stated by CETESB [11] on a report issued on 2001. That causes some questions about the integrity of the retention filters inside the monitoring wells.

In AP-03 in November and in AP-04 in September, the nitrate values were above CETESB´s intervention value. Those values are linked to a sewer leakage that occurred close to the groundwater collection site. A proper maintenance was performed to avoid future non-compliant values. Concerning AP-04, it was observed a single occurrence, so there is no need to future mitigatory actions.

Cobalt was above CETESB´s intervention value for the following samples:

- AP-02: September;
- AP-03: July, September and November;
- AP-04: September and November;
- AP-05: July, September and November;
- AP-06: July, September and November.

Considering that in Brazil, the majority of cobalt values on ground water samples were above cobalt intervention value of $5\mu g.L^{-1}$, it was proposed by CETESB a regulatory value revision to $70\ \mu g.L^{-1}$. That revision was stated by CETESB in a directory meeting and properly documented [10]. Later the revised value adopted by NATIONAL COUNCIL FOR THE ENVIRONMENT –CONAMA, on its resolution #420/2009 [4] for Contaminated Areas management guidance.

Table 2: Ground water chemical analysis results obtained on 2009.

Parameter	AP-2				AP-03				AP-04				AP-05				AP-06			
	March	July	July	September	March	July	September	November	March	July	September	November	March	July	September	November	March	July	September	November
In situ																				
pH	4.63	5.32	5.65	5.78	5.51	6.24	5.62	6.22	6.06	5.49	4.99	5.68	5.46	6.05	6.82	6.32	5.79	5.30	6.47	6.32
Conductivity. µS/cm	290.00	34.00	51.00	53.00	117.00	113.00	165.00	166.00	55.00	77.00	78.00	79.00	80.00	143.00	133.00	142.00	39.00	36.00	47.00	39.00
Turbidity. NTU	6.00	10.00	999.00	6.32	4.00	10.00	4.00	10.00	22.00	1.00	3.00	10.00	24.00	10.00	485.00	110.00	2.00	10.00	8.00	10.00
Temperature. °C	23.00	21.50	22.00	19.70	23.10	19.70	19.60	24.10	23.00	21.60	19.70	24.10	22.90	19.70	20.40	23.90	22.90	21.30	19.70	24.10
Dissolved oxigen. mgO$_2$/L	6.49	8.00	7.55	6.48	6.65	8.46	5.81	4.52	6.73	8.18	5.83	4.70	6.32	8.46	4.35	4.67	6.92	7.91	5.95	4.97
Inorganic																				
Al (µg/L)	36 ± 1	72 ± 1	4.3 ± 0.01	183 ± 1	537 ± 1	< 1	< 1	< 1	< 1	19 ± 1	< 1	< 1	< 1	64 ± 0.5	< 1	< 1	< 1	4.8 ± 0.1	< 1	< 1
Sb (µg/L)	<1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	< 1	< 1
As(µg/L)	NA	< 1	< 1	<1	NA	< 1	<1	<1	NA	< 1	<1	<1	NA	< 1	<1	<1	NA	<1	<1	<1
Ba (µg/L)	56 ± 1	34 ± 1	< 10	26 ± 1	177 ± 1	190 ± 1	377 ± 1	371 ± 1	<10	13 ± 1	19 ± 1	22 ± 2	95 ± 1	68 ± 1	65 ± 5	65 ± 1	79 ± 1	52 ± 1	50 ± 1	60 ± 1
B (µg/L)	30 ± 1	< 20	< 20	< 20	40 ± 1	< 20	< 20	< 20	31 ± 1	< 20	< 20	< 20	28 ± 1	< 20	< 20	< 20	30 ± 1	< 20	< 20	< 20
Cd (µg/L)	< 0.1	0.2 ± 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb (µg/L)	1 ± 1	1 ± 1	< 1	<1	< 1	< 1	< 1	< 1	< 1	1 ± 1	< 1	< 1	< 1	1 ± 1	< 1	< 1	< 1	< 1	< 1	< 1
Cl- (mg/L)	6.12	6.33	NA	4.72	4.43	4.53	7.01	12.20	5.08	7.40	12.80	7.82	8.03	10.70	6.07	6.74	4.45	4.16	3.84	4.50
Co (µg/L)	< 10	< 10	< 10	28 ± 1	< 10	13 ± 3	31 ± 11	30 ± 1	< 10	< 10	28 ± 3	22 ± 3	< 10	18 ± 1	33 ± 2	39 ± 1	< 10	12 ± 2	29 ± 1	18 ± 1
Cu (µg/L)	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Cr (µg/L)	< 10	< 10	< 10	< 10	< 10	< 10	< 10	13 ± 1	< 10	< 10	< 10	12 ± 2	< 10	< 10	< 10	11 ± 1	< 10	< 10	< 10	11 ± 1
Fe (µg/L)	< 20	< 20	< 20	137 ± 8	221 ± 1	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	74 ± 3	< 20	91 ± 1	< 20	< 20	< 20	< 20
F- (mg/L)	0.03	0.09	NA	<0.05	0.05	1.59	<0.05	0.06	<0.025	0.04	0.06	<0.05	0.02	0.07	<0.05	<0.05	0.03	0.04	<0.05	<0.05
Mn (µg/L)	9 ± 1	< 2	< 2	< 2	2 ± 1	13 ± 1	14 ± 1	16 ± 1	< 2	24 ± 1	32 ± 1	44 ± 1	1970 ± 10	1090 ± 10	1210 ± 20	1610 ± 13	2 ± 1	6.5 ± 0.1	35 ± 1	41 ± 3
Hg (µg/L)	NA	< 0.8	< 0.8	< 0.8	NA	< 0.8	< 0.8	< 0.8	NA	< 0.8	< 0.8	< 0.8	NA	< 0.8	< 0.8	< 0.8	NA	< 0.8	< 0.8	< 0.8
Mo (µg/L)	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 20	< 10	< 10	< 10	< 20	< 10	< 10	< 10	< 20	< 10	< 10	< 10	< 20
NO3- (mg/L)	6.60	5.85	NA	9.92	6.50	<0.05	2.09	31.50	3.60	4.86	41.80	2.20	4.61	0.21	0.41	1.22	7.36	7.64	9.27	9.53
NO3-N (µg/L)	2138.40	1895.40	NA	3214.08	2106.00	<16	677.16	10206.00	1166.40	1574.64	13543.20	712.80	1493.64	68.04	132.84	395.28	2384.64	2475.36	3003.48	3087.72
NO2 (mg/L)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NO2-N (mg/L)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ni (µg/L)	< 10	< 10	< 10	< 10	< 10	< 10	< 10	17 ± 1	< 10	< 10	< 10	13 ± 1	< 10	< 10	< 10	15 ± 1	< 10	< 10	< 10	16 ± 1
Ag (µg/L)	< 2	< 2	< 2	13 ± 1	< 2	< 2	14 ± 2	15 ± 2	< 2	< 2	16 ± 2	12 ± 2	< 2	< 2	15 ± 1	14 ± 2	< 2	< 2	14 ± 1	14 ± 5
Se (µg/L)	1 ± 1	< 1	< 1	< 1	< 1	< 1	< 0.1	< 1	< 1	< 1	< 0.1	< 1	< 1	< 1	< 0.1	< 1	< 1	< 1	< 0.1	< 1
Na (mg/L)	2.67 ± 0.003	3.05 ± 0.01	7.27 ± 0.01	6.42 ± 0.01	2.19 ± 0.01	2.49 ± 0.01	10.0 ± 0.01	9.51 ± 0.04	4.37 ± 0.01	6.27 ± 0.02	5.25 ± 0.01	5.44 ± 0.01	5.65 ± 0.02	3.83 ± 0.01	3.69 ± 0.01	4.38 ± 0.01	2.31 ± 0.01	2.08 ± 0.01	1.62 ± 0.01	1.88 ± 0.01
SO4-2 (mg/L)	<0.2	1.14	NA	2.90	18.80	5.25	19.40	0.99	11.20	17.30	0.42	19.10	9.42	21.20	12.20	9.77	1.13	1.17	1.43	0.77
Zn (µg/L)	22 ± 1	18 ± 1	< 1	4 ± 1	11 ± 1	< 1	12 ± 1	5 ± 1	8 ± 1	11 ± 01	12 ± 1	14 ± 1	5 ± 1	6.8 ± 0.1	4 ± 1	5 ± 1	66 ± 1	171 ± 1	109 ± 1	100 ± 20
Ca(mg/L)	0.467 ± 0.005	0.283 ± 0.002	0.187 ± 0.001	1.45 ± 0.02	18.2 ± 0.1	16.8 ± 0.1	17.6 ± 0.3	18.4 ± 0.1	3.72 ± 0.02	4.42 ± 0.02	4.85 0.06	4.91 ± 0.03	4.38 ± 0.03	10.6 ± 0.05	7.03 ± 0.07	3.68 ± 0.03	3.15 ± 0.02	3.28 ± 0.01	4.29 ± 0.08	2.75 ± 0.04
Mg (mg/L)	0.377 ± 0.007	0.326 ± 0.008	0.051 ± 0.007	0.401 ± 0.011	2.38 ± 0.01	2.66 ± 0.01	2.40 ± 0.03	2.58 ± 0.01	0.444 ± 0.006	0.517 ± 0.001	0.503 ± 0.010	0.537 ± 0.01	1.47 ± 0.01	3.50 ± 0.01	1.87 ± 0.01	1.19 ± 0.02	0.499 ± 0.001	0.522 ± 0.008	0.483 ± 0.010	0.489 ± 0.004
Hardness (mgCaCO$_3$/L)	2.72	2.05	0.68	5.27	55.25	52.90	53.83	56.57	11.12	13.17	14.18	14.47	16.99	40.88	25.25	14.09	9.92	10.34	12.70	9.43
Be (µg/L)	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Br- (mg/L)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sn (mg/L)	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060	< 0.060
P (mg/L)	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	0.089 ± 0.003	0.055 ± 0.001	0.029 ± 0.005	< 0.020	< 0.020	< 0.020	0.118 ± 0.003	0.075 ± 0.001	< 0.020	0.197 ± 0.003	< 0.020	< 0.020	0.247 ± 0.003	< 0.020
PO4-3(mg/L)	<0.05	<0.05	NA	<0.05	<0.05	<0.05	<0.05	0.93	<0.05	<0.05	0.27	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	1.53	<0.05
PO4-3 -P(mg/L)	<0.016	<0.016	NA	<0.016	<0.016	<0.016	<0.016	0.30	<0.016	<0.016	0.09	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	0.50	<0.016
Li (mg/L)	0.014 ± 0.001	< 0.010	< 0.010	< 0.010	0.016 ± 0.001	0.012 ± 0.001	0.017 ± 0.001	0.017 ± 0.001	0.013 ± 0.001	< 0.010	< 0.010	< 0.010	0.013 ± 0.001	< 0.010	< 0.010	< 0.010	0.014 ± 0.001	< 0.010	< 0.010	< 0.010
K (mg/L)	1.24 ± 0.01	0.978 ± 0.001	0.925 ± 0.001	1.40 ± 0.01	4.81 ± 0.01	4.07 ± 0.01	3.47 ± 0.01	3.38 ± 0.01	2.48 ± 0.01	3.70 ± 0.01	3.62 ± 0.002	3.43 ± 0.01	2.08± 0.01	15.0 ± 0.01	5.18 ± 0.03	2.58 ± 0.01	1.81 ± 0.01	1.58 ± 0.01	2.12 ± 0.01	1.93 ± 0.01
Si (mg/L)	2.50 ± 0.01	2.39 ± 0.01	6.91 ± 0.02	5.62 ± 0.03	5.85 ± 0.05	4.69 ± 0.01	15.5 ± 0.7	15.6 ± 0.2	2.26 ± 0.001	1.21 ± 0.01	1.28 ± 0.01	1.22 ± 0.02	1.41 ± 0.01	2.86 ± 0.01	1.89 ± 0.01	1.44 ± 0.03	1.79 ± 0.001	1.54 ± 0.01	1.46 ± 0.04	1.58 ± 0.05
Sr (mg/L)	< 0.010	< 0.010	< 0.010	< 0.010	0.199 ± 0.003	0.267 ± 0.002	0.546 ± 0.006	0.567 ± 0.001	0.023 ± 0.001	0.023 ± 0.001	0.023 ± 0.001	0.030 ± 0.003	0.025 ± 0.001	0.074 ± 0.001	0.048 ± 0.002	0.033 ± 0.002	0.176 ± 0.01	0.223 ± 0.002	0.250 ± 0.003	0.173 ± 0.001
Ti (mg/L)	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040	< 0.040
V (mg/L)	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030

After those considerations, and also adopting the new revised cobalt intervention value, it was observed that the maximum value found for Cobalt was 39 $\mu g.L^{-1}$, in AP-05, in November. So it is possible to state that cobalt levels on Ipen´s ground water present no risk to human health.

In six hundred and forty five analysis performed on Ipen´s ground water samples, throughout 2009, with the stable compounds chemical evaluation purpose, it was observed values above CETESB´s intervention values for only 1.2% of results.

The main stable chemical compounds that presented values above CETESB´s intervention values were Manganese and Nitrate. The manganese presence above the regulatory limits is caused by soil contamination, probably due to non-retained material on the well filter. The nitrate presence in AP-03 was originated in a sewer leakage, later repaired. The non-compliant value presented in AP-04 did not repeat, in the following campaigns and remain fourteen times lower than CETESB´s intervention value.

5. CONCLUSION

Concerning the evaluation performed during the year of 2009, that monitored stable compounds, on six groundwater monitoring wells, inside Ipen´s facility, it was possible to observe the following: Manganese was found above the regulatory value in AP-05, this is an element with a natural high concentration occurrence on tropical soils. It was noticed that the intervention value was established based on physical and sensorial evaluation of water for human consumption and not based on any safety limits. When Cobalt concentrations were evaluated on groundwater samples, the intervention value stated by CETESB [11] is 5 $\mu g.L^{-1}$. However, CETESB later identified this value needed a revision for 70 $\mu g.L^{-1}$, as it is stated on NATIONAL COUNCIL FOR THE ENVIRONMENT - CONAMA´s Resolution for contaminated areas (available on CONAMA´s Website). Considering the revised value for cobalt, 100% of values found on collected samples are below intervention value. It was found for AP-03 and AP-04, nitrate concentrations higher than the CETESB´s intervention value. Concerning AP-04, that was an isolated result and no other event occurred in any of the following collection campaigns. Concerning AP-03, new sample collections will be performed to identify the source of nitrate, to solve this sanitary non conformity. Only macro elements (Ca, Mg, K) and anions (Chloride and sulfate), usually found in water, were measured in groundwater samples. The other elements concentration was below quantification limits and consequently way below regulatory values. Accordingly to the groundwater evaluation results obtained in this work samples, there is no heavy metal contamination evidence on Ipen´s ground water.

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