

ENVIRONMENTAL MONITORING PROGRAMME OF CENTRO EXPERIMENTAL ARAMAR: RADIOMETRIC AND CHEMICAL PARAMETERS IN FRESHWATER SAMPLES

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ABSTRACT

Experimental results are described obtained with gamma spectrometry , alpha and beta gross counts, liquid scintillation and fluorometry techniques for the measurement of background radiation and several other techniques for chemical parameters analysis in surface water samples collected in Centro Experimental Aramar and surroundings, from 1988 to 2011. The estimated average background radiation concentrations in water samples in this region is low, related to the Low Level Detection limits of the techniques, and the chemical parameters values are compared with the limits established by CONAMA (Comissão Nacional do Meio Ambiente /Brasil - a governmental Brazilian institution for environmental protection). There are good water quality parameters, and low interference in the environment in Centro Experimental Aramar and region .

Keywords: Water samples; Water quality parameters; Gamma spectrometry; Environmental protection

1. INTRODUCTION

The Centro Tecnológico da Marinha (CTMSP) is a military research organization, located in S.Paulo city (Brazil), whose objectives are to set up nuclear and energy systems for Brazilian Naval Ship propulsion. These projects are being developed in Centro Experimental Aramar, located at Ipero city (100 km from S.Paulo).The investigation of background radiation concentrations and chemical parameters in water samples of the Centro Experimental Aramar and region are of great significance because the CTMSP industrial nuclear research programme is being assembled in this centre [1]. Therefore, surface water samples from environmental stations have been collected and analysed systematically, since 1988 (2nd

semester), by using the gamma spectrometry, alpha and beta gross counts, liquid scintillation and fluorometry techniques [2,3] and several other techniques for water chemical parameter analysis [4]. The main objective is to estimate the quality water parameters and verify the possible interference in the environment. The measurements were performed in addition to the Environmental Monitoring Programme, carried out by the Radioecological laboratory in this region [5]. This study provides a reference level for the purposes of water quality parameters analysis and comparative monitoring, specifically, knowledge of radioactive concentrations and water chemical parameters is a basic task in determining the quality parameters, background levels, transfer, dosimetry and environmental conditions implications.

2. MATERIALS AND METHODS

The Environmental Monitoring Programme has been conducted by the Radiation Protection and Environmental Control Department (CTMSP) and is being systematically carried out in this centre and region (this region corresponds to an area defined by a 10 km radius circle), by collecting and analysing soils, fish, grass, water, milk, harvest and air samples in 124 environmental stations, since 1988 [2,3,5]. Surface water samples are collected in 11 environmental stations, distributed on Ipanema river (five sample points: 1,2,3,4,8), Sorocaba river (four sample points: 5,6,7,9) and in Ferro's stream (two sample points: 13,15), located in the vicinity of this nuclear research centre, as can be seen in figure 1.

The sample preparation methodologies are described in references [5,6]. The frequency of the collected and analysed samples has been different along the years, caused by technical conditions, but in general it was monthly [5].

The gamma spectrometry, alpha and beta gross counts, liquid scintillation and fluorometry measurements are well known techniques employed in several kinds of analysis [4,5]. Gamma spectrometry was performed by using two 65 cm³ Ge intrinsic detector with a relative efficiency of 40% and a resolution of 1.9 keV (FWHM) for the 1332 keV peak of ⁶⁰Co. This detector was coupled to a 8192 multichannel which was connected to a microcomputer. Spectra was analysed using the software GENIE2000(CANBERRA). The energy efficiency curve was obtained by a set of gamma ray reference sources. The ²³⁸U natural series's activity was estimated from de 351.9 keV and 609.3 keV gamma lines of ²¹⁴Pb and ²¹⁴Bi, respectively. The ²³²Th natural series's activity was estimated from the ²²⁸Ac emission at 911.1 keV. The samples were sealed and the measurements were made one month later to ensure equilibrium between the isotopes and its daughters [7]. The gamma spectrometry system calibration has been periodically checked by participating in a National Inter comparison Programme (P.N.I.) for water sample analysis, conducted by Secondary Standard Dosimetry Laboratory (IRD/CNEN/BRAZIL) [8].

Fluorometry measurements were made by using a digital fluorometry detector model 5015 and the methodology of analysis is described in reference [4]. Tritium counting was performed with a Beckmann (model LS-5801) liquid scintillation spectrometer, utilizing polyethylene vials containing 10 mL of Ultima Gold XR (scintillation) and 1 mL of the distillate sample. The samples were counted during 100 minutes. The counting regions were selected by taking into account the quench level of the samples. Previously, the tritium spectrum was calibrated using Beckman/Spectrum Analysis software calibration, by

measuring a set of ^3H standards ($(761 \pm 5\%)$ dps : activity in 01/02/1991) with different levels of quenching (called #H number). The reproducibility counting efficiency is 1% [9].

Alpha and Beta gross counts were performed in a Berthold LB-770-2 low level counter, containing ten proportional gas detectors. The efficiencies previously determined were 13% for alpha counting, by using a calibrated ^{230}Th alpha source, and 34% for beta counting, by using a calibrated ^{90}Sr beta source.

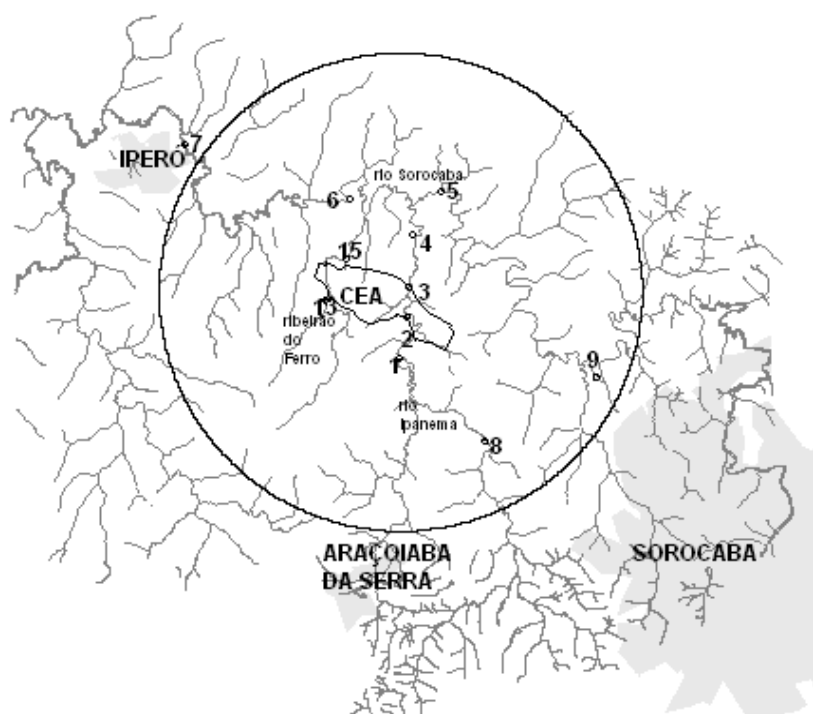


Figure 1. Location of Centro Experimental Aramar (CEA) and the region defined by the 10 km circle radius, the eleven water sampling points: 1,2,3,4,5,6,7,8,9,13 and 15, the main cities around: Sorocaba, Iperó and Araçoiaba da Serra, and the Sorocaba river (Rio Sorocaba), Ipanema river (Rio Ipanema), Ferro stream (Ribeirão do Ferro)

The specific techniques used in preparation and analysis of the environmental samples were taken of the standards methods, described in details in reference [4]. The no-radioactive parameters analysed, the employed methodology and equipment are cited following :

- a) Flame Atomic Absorption Spectrometric method [4][section 3111]: aluminium, soluble iron, total iron, manganese, zinc / (Atomic Absorption Spectrophotometer – Hitachi-model Z-8100 polarized Zeeman) ;

- b) Electrothermal Atomic Absorption Spectrometric method [4][section 3113] : lead ,copper, nickel, chromium / (Atomic Absorption Spectrophotometer–Hitachi-model Z-8100 polarized Zeeman with graphite furnace) ;
- c) Flame Emission Photometric method [4][section 3500]: potassium, sodium / (Micronal–model B262) ;
- d) Electrometric method [4][section 4500]: pH / (Analion–model IA601)
- e) Turbidity method [4][section 2130]: turbidity
- f) Visual Comparison method [4][section 2120] : Colour
- g) Titrimetric method [4][section 4500]: N-ammoniacal, chloride, Biochemical Oxygen Demand(BOD), Dissolved oxygen(DO), orthophosphate, total phosphate, Chemical Oxygen Demand(COD) [section 5220] / (Procyon-model Sa720)
- h) Colorimetric method (Spectrophotometer) [4][section4500]:N-nitrate, N-nitrite / (Micronal-model B382)
- i) Ion Selective Electrode method [4][section 4500]: fluoride / (Procyon-model Sa720)
- j) Electrical Conductivity method [4][section 2520]: electrical conductivity/(Micronal-model B331)

3. RESULTS AND DISCUSSION

The low level detection limits (LLD) [22], related to the ^{214}Pb (^{238}U -series) and ^{228}Ac (^{232}Th -series) radionuclides, measured by the gamma spectrometry technique, are shown in table1. These values are variables, because the software and the preparing methodology changed along the years [5]. Nowadays, the ^{214}Pb LLD value is lower than 0.20 Bq/L and the ^{228}Ac LLD value is lower than 0.30 Bq/L in the water samples.

Table 1. Low Level Detection limits (LLD) determined in surface water analysis in all environmental samples, by using gamma spectrometry technique (^{214}Pb and ^{228}Ac concentrations in Bq/L), fluorometry technique (U concentrations in Bq/L units) and alpha and beta gross counts technique (alpha and beta concentrations in Bq/L).

(* values were obtained in the pre-operational conditions [3]).

Year	^{214}Pb	^{228}Ac	U natural	Alpha counts	Beta counts
1988 *	0.27	0.48	0.025	0.13	0.10
1991	0.37	0.48	0.13	0.13	0.10
1992 to 1995	0.40	0.50	0.13	0.13	0.10
1996 to 1999	0.20	0.30	0.13	0.13	0.10
2000 to 2004	0.20	0.30	0.005	0.13	0.10
2005-2011	0.20	0.30	0.0025	0.13	0.10

The ^{214}Pb and ^{228}Ac concentrations obtained in all samples were LLD values. Those values are in good accordance with the data obtained in the pre-operational conditions [3], denoting a low natural radioactivity in Centro Experimental Aramar and region [9]. The paper published in reference [10] state a contrasting situation: the values of ^{238}U and ^{232}Th concentrations obtained in water rivers nearby uranium mines were enhanced in comparison with concentrations measured in other rivers, indicating an increase of natural radioactivity.

The LLD value for tritium measurement, by using the liquid scintillation technique, is 14.8 Bq/L [9]. Tritium activities (Bq/L) were measured in fourteen surface water samples, from 1990 to 1999 and the results obtained provided an estimate average of (25.9 ± 2.1) Bq/L. The results published in reference [11] indicate tritium activity levels between 0.6 Bq/L (LLD value) and 3.6 Bq/L, in rivers of different origin. In spite of this, both values are compatible with the tritium limit concentration in drinking water of 740 Bq/L, recommended by EPA(U.S.A.) [12] and 100 Bq/L for waters intended for human consumption [11], thus confirming a low natural tritium radioactivity in Centro Experimental Aramar and region [9].

Uranium concentration results obtained by fluorometry analysis in all samples were LLD values, in agreement with the data obtained in the pre-operational conditions [3], and the data presented in a similar environmental monitoring programme [13]. These LLD values are also shown in table1 and are distinct, because the software and the preparing methodology changed along the years [5].

The LLD values for alpha and beta total counts monitored in these samples are also presented in table1. Alpha and beta results obtained in the majority of the samples analysed were LLD values (more than 95%). By analysing the complementary results (5%), the maximum and average values obtained were, respectively: 0.30 Bq/L and 0.20 Bq/L for alpha counts and 0.80 Bq/L and 0.40 Bq/L for beta counts. The results published in reference [14] divulge alpha activity between 0.06 Bq/L and 0.13 Bq/L and beta activity between 0.14 Bq/L and 0.36 Bq/L in surface water around a proposed uranium mining site, and the results of alpha activity in water published in reference [15], indicate a value of 0.05 Bq/L. Also, the limits proposed by EPA(U.S.A.) [4] establish that if the average annual concentrations are less than 0.56 Bq/L (15 pCi/L) for alpha gross counts and less than 1.85 Bq/L (50 pCi/L) for beta gross counts, no further analysis is required. By taking into account these limits, it is not necessary to identify the alpha and beta specific radioactive contaminants in the water samples of the Aramar Environmental Monitoring Programme .

The evaluated water quality chemical parameters, related to the sampling points, river location(those rivers are classified as “class 2”), average, maximum and minimum values and tolerable limit values defined by CONAMA [16], are shown in tables 2, 3 and 4.

Most of the water quality chemical parameters of the Ipanema river and Ferro stream are lower than the established limits suggested by CONAMA. The parameters pH, color and turbidity are also in agreement with the CONAMA limits in all sample points. Metal concentration like copper, nickel and lead are very low. Aluminium concentrations were about 10% higher than CONAMA limits in some months, in all sampling points. N-Ammoniacal, N-nitrate, sodium and BOD are in low concentrations and DO is in high concentrations in the Ipanema river and Ferro stream. The main human activities developed in this region are agricultural. Therefore, the water quality parameters of this river and stream can be considered good.

The turbidity, copper, nickel and lead parameters evaluated in the Sorocaba river are comparable with the CONAMA limits, iron and aluminium concentrations are a little higher

Table 2. Calculated water quality parameters of Ipanema river (maximum, minimum and average (avr) values). The CONAMA limits are also presented. (* There are no established limits).

Parameters and units	SAMPLE 8			SAMPLE 1			SAMPLE 2			SAMPLE 3			SAMPLE 4			CONAMA LIMITS
	Avr	Max	Min	Avr	Max	Min	Avr	Max	Min	Avr	Max	Min	Avr	Max	Min	
pH	7.0	8.0	6.3	6.7	7.07	6.34	7.1	8.1	6.1	6.88	7.21	6.64	7.1	7.9	5.8	6.0 to 9.0
Turbidity (FTU)	28	200	5.9	25.43	51.88	12.6	22.5	144	3.2	26.96	43.7	11.5	24.5	141	3.1	100
Colour (colour unit)	19	78	5	19.8	84.29	8.64	19.4	99.3	5	22.9	106.43	9	23	192.14	5	75
El.conductivity (µS/cm)	101	162.2	53.1	86.79	119	64.55	90	151.3	49.5	87.49	132.2	66.88	93.5	139.8	50.9	*
Copper (µg/L)	3.87	12.3	<0.03	4.2	16	<0.01	4.21	8.4	<0.02	3.65	10.9	<0.03	3.85	10	<0.01	20
Nickel (µg/L)	15.62	90	<1	15.55	90	<1	14.98	90	<1	15.57	90	<1	15.15	90	<1	25
Lead (µg/L)	2.84	8.1	<0.15	2.99	8	<0.15	3.2	8.08	<0.15	3.45	7.92	<0.15	3.18	8.55	<0.15	30
Zinc (µg/L)	18.19	29.09	<0.03	19.12	31	<0.05	18.68	30.27	<0.04	19.08	30.64	<0.03	17.88	27.27	<0.03	180
Chromium (µg/L)	8.62	30	<1	8.62	30	<1	9.44	30	<1	8.64	30	<1	8.64	30	<1.09	*
Aluminium (mg/L)	0.83	1.96	<0.2	0.66	1.2	<0.2	0.74	1.59	<0.21	0.73	1.36	<0.18	0.88	2.32	<0.26	0.1
Manganese (mg/L)	0.14	0.18	<0.1	0.13	0.28	<0.1	0.11	0.14	<0.09	0.12	0.16	<0.1	0.12	0.2	<0.1	0.1
Soluble Iron (mg/L)	0.27	0.35	<0.2	0.33	0.49	<0.18	0.36	0.52	<0.25	0.33	0.44	0.22	0.43	1.46	0.22	0.3
Total Iron (mg/L)	2.13	4.65	0.23	1.48	2.67	0.23	1.64	3.06	0.24	1.75	3.24	0.31	1.8	3.59	0.23	*
N-Nitrate (mg/L)	0.88	2.48	<0.27	0.37	0.6	0.16	0.6	2.08	0.2	0.36	0.6	<0.19	0.69	1.83	<0.23	10
N-Nitrite (mg/L)	0.466	2.48	<0.01	0.01	0.04	0.01	0.366	2.08	<0.01	0.01	0.03	<0.01	0.338	1.83	<0.01	1
N-Ammoniacal (mg/L)	0.294	2.17	<0.02	0.07	0.13	<0.03	0.065	0.3	<0.02	0.07	0.13	<0.02	0.08	0.51	<0.02	0.02
Fluoride (mg/L)	0.19	0.20	<0.12	0.14	0.18	<0.12	0.14	0.21	<0.12	0.13	0.21	<0.12	0.19	0.19	<0.12	1.4
Sodium (mg/L)	5.1	10.4	2.83	4.01	5.33	2.87	4.75	8.4	2.5	3.99	5.11	2.89	4.8	8.3	2.4	*
Potassium (mg/L)	3.41	8.2	1.8	3.36	5.18	2.07	3.33	6.6	2.04	3.44	5.28	2.06	3.33	6.8	2.02	*
Chloride (mg/L)	4.77	10	<1.7	2.15	3.64	<1.46	4.48	7.4	<1.3	2.21	3.7	<1.48	4.41	7.4	<1.55	250
Total solids (mg/L)	96.38	230	<3.97	95.37	146	<3.64	90.54	116	<3.71	94.97	116	<3.71	95.20	175	51	500
COD (mg/L)	20.33	32	<9.46	15.55	21.75	<9.33	21.63	29	<1	16.03	24.8	<8.99	18.5	29	<1	*
BOD (mg/L)	2.23	4.8	<1	1.59	4.5	<1.05	1.53	2.5	<1	1.65	7.14	<0.72	1.62	2.9	<1	5
DO (mg/L)	6.4	8.7	5.07	5.92	6.59	4.85	7.1	9.2	5.6	6.87	8.04	6.2	7.08	9.2	5.5	5
Orthophosphate (mg/L)	0.043	0.16	<0.005	0.03	0.05	<0.01	0.020	0.053	<0.005	0.03	0.05	<0.01	0.022	0.058	<0.005	*
Total Phosphate (mg/L)	0.068	0.25	0.009	0.03	0.07	<0.01	0.037	0.22	0.008	0.04	0.14	<0.02	0.050	0.25	0.001	0.025

**Table 3. Calculated water quality parameters of Sorocaba river (maximum, minimum and average (avr) values).
The CONAMA limits are also presented.
(* There is no established limits).**

Parameters and Units	SAMPLE 9			SAMPLE 5			SAMPLE 6			SAMPLE 7			CONAMA LIMITS
	Avr	Max	Min	Avr	Max	Min	Avr	Max	Min	Avr	Max	Min	
pH	6.8	7.5	5.6	6.6	6.81	6.4	6.85	7.8	5.9	6.71	6.97	6.55	6.0 to 9.0
Turbidity (FTU)	22.5	70	3.5	30.2	82.5	13.54	21.5	81.67	3.3	30.02	89.11	10.4	100
Colour (colour units)	17	50	10	19.44	72.86	10.42	16.5	66	5	22.74	116.67	10.8	75
El. Conductivity (µS/cm)	166	271	18.8	171.02	245.83	136.4	166	271	84	166.85	234.5	137.6	‡
Copper (µg/L)	4.47	9.18	<0.01	5.25	13.4	<0.03	3.92	9.1	<0.01	4.06	9.3	<0.01	20
Nickel (µg/L)	16.35	30	<1.33	16	90	<0.14	17.14	90	<1.6	18.35	90	<1.91	25
S Lead (µg/L)	4.36	13.2	<0.1	3.93	10.94	<0.1	3.94	11.33	<0.1	3.65	10.5	<0.1	30
O Zinc (µg/L)	18.76	27.1	<0.02	18.34	27.45	<0.02	18.2	28.64	<0.02	19.54	33	<0.02	180
R Chromium (µg/L)	9.17	10	<1.17	8.24	20	<1.33	8.07	20	<1.33	9.17	30	<1.2	‡
O Aluminium (mg/L)	1.28	2.43	0.25	1.8	4.48	<0.46	1.47	2.61	0.45	1.64	4.64	<0.44	0.1
C Manganese (mg/L)	0.18	0.2	<0.13	0.19	0.25	<0.14	0.18	0.22	0.13	0.17	0.23	<0.1	0.1
A Soluble iron (mg/L)	0.27	0.4	0.14	0.26	0.43	<0.17	0.27	0.4	<0.19	0.3	0.5	0.2	0.3
B Total iron (mg/L)	2.04	2.46	0.16	2.48	4.54	0.12	2.35	5.57	0.16	2.12	3.53	0.18	‡
A N-Nitrate (mg/L)	0.65	5.67	<0.14	0.48	2.74	<0.21	0.61	1.21	<0.14	0.39	0.61	<0.2	10
N-Nitrite (mg/L)	0.287	2.5	<0.01	0.24	2.59	0.01	0.183	1.08	<0.01	0.16	1.52	<0.01	1
R N-Ammoniacal (mg/L)	2.15	4.55	0.21	2	2.97	0.94	1.94	4.79	0.04	1.84	3.01	0.87	0.02
I Fluoride (mg/L)	1.6	1.81	<0.12	0.79	1.31	0.29	0.6	1.29	<0.12	0.86	1.36	0.35	1.4
V Sodium (mg/L)	13.7	23.3	4.2	13.52	23.45	4.93	13.4	22.2	4.4	13.92	23.69	9.62	‡
E Potassium (mg/L)	4.6	8.64	2.2	4.96	7.79	2.9	4.6	7.4	2.7	4.83	7.54	2.94	‡
R Chloride (mg/L)	12	22	6.1	10.05	13.4	7.19	12	22	6.1	9.51	13.5	7.24	250
Total solids (mg/L)	158.5	240	<28.5	162.06	235.5	<24.64	136.9	248	<25.2	149.87	226.83	<23.42	500
COD (mg/L)	31.5	66	<1	26.59	40	9.15	27	69	<14	23.84	33.6	7.79	‡
BOD (mg/L)	4.3	11.1	1.2	6.38	23	3.23	3.6	4.6	1	5	11	3.44	5
DO (mg/L)	2.5	7.5	0.39	1.74	3.29	0.81	2.75	7.9	1.24	2.62	4.06	1.5	5
Orthophosphate (mg/L)	0.08	0.25	<0.02	0.06	0.14	<0.02	0.073	0.21	0.012	0.07	0.18	<0.02	‡
Total Phosphate (mg/L)	0.100	0.35	0.021	0.08	0.17	<0.02	0.100	0.38	0.025	0.19	1.62	<0.02	0.025

Table 4. Calculated water quality parameters of Ferro stream (maximum, minimum and average (avr) values).

The CONAMA limits are also presented.

(* There is no established limit).

Parameters and units		SAMPLE 13			SAMPLE 15			CONAMA LIMITS
		Avr	Max	Min	Avr	Max	Min	
F E R R O S T R E A M	pH	7.32	8.0	6.1	7.26	8.1	3.9	6.0 to 9.0
	Turbidity (FTU)	9.87	44	2.9	11.33	43	2.8	100
	Colour (colour units)	14.72	40	5	14.31	60	5	75
	El. Conductivity (µS/cm)	136.7	217.4	64.8	142.5	263.2	83.2	*
	Copper (µg/L)	3.49	8.3	<0.04	2.3	3.6	<1.5	20
	Nickel (µg/L)	16.13	90	<1	2.17	4.2	.11	25
	Lead (µg/L)	2.05	3.42	<1	3.82	5.93	<1.7	30
	Zinc (µg/L)	17.43	24.55	<0.02	20	20	<20	180
	Chromium (µg/L)	8.46	30	<1	1	<1	<1	*
	Aluminium (mg/L)	0.33	0.88	<0.14	0.22	0.3	<0.2	0.1
	Manganese (mg/L)	0.11	0.15	<0.09	0.17	0.2	<0.1	0.1
	Soluble iron (mg/L)	0.27	0.51	0.13	0.36	0.46	<0.3	0.3
	Total iron (mg/L)	0.84	1.4	0.6	0.82	0.9	0.8	*
	N-Nitrate (mg/L)	0.35	0.92	0.023	0.375	1.02	<0.14	10
	N-Nitrite (mg/L)	0.36	0.92	<0.01	0.32	0.54	<0.01	1
	N-Ammoniacal (mg/L)	0.111	0.7	<0.02	0.059	0.15	0.01	0.02
	Fluoride (mg/L)	0.395	0.61	<0.12	0.17	0.17	<0.12	1.4
	Sodium (mg/L)	5.6	14.5	3.5	5.9	16.6	3.1	*
	Potassium (mg/L)	3.6	7.6	1.9	4.1	13.3	1.8	*
	Chloride (mg/L)	1.64	2.5	<1.3	2.6	5.75	<1.3	250
Total solids (mg/L)	132.2	259	<6.3	138.4	269	87	500	
COD (mg/L)	15.4	59	<6.9	15.6	34	<14	*	
BOD (mg/L)	1.5	2.9	0.92	1.85	3.0	<1	5	
DO (mg/L)	7.4	8.8	5.2	7.27	8.8	5.4	5	
Orthophosphate (mg/L)	0.04	0.08	<0.01	0.033	0.09	0.013	*	
Total Phosphate (mg/L)	0.05	0.3	<0.03	0.052	0.22	<0.005	0.025	

than the limits; BOD, sodium and N-ammoniacal parameters are found in higher concentrations and DO in lower concentrations, in accordance with data obtained in reference [17]. This is due probably because the higher volume of sewages added to the river every day. The COD concentration is approximately 5 times higher than the BOD concentration. It suggests that non-biodegradable materials, like soaps are added to the river too. Phosphate and N-ammoniacal concentrations were found to be higher than the CONAMA limits.

The variable aluminium levels found in the rivers and stream is explained by the fact that the studied area is a transition region between Seasonal Semi deciduous Forest and Savannah Forest (Cerrado), where is usual to find high concentrations of aluminium and iron [18,19]. An old iron mine already worked in the local [17]. Another noteworthy finding is that fluoride concentrations were low in the two rivers and stream.

Those cited rivers and stream characteristics may be found in most rivers that pass nearby the urban centres in a tropical area, and are influenced by the land use region [18,20,21].

4. CONCLUSIONS

The assessment realized in eleven environmental sample points located at Centro Experimental Aramar and region, by taking into account the radioactive level and the water quality chemical parameters, collected and measured in the period from 1988 to 2011, indicates accordance, mainly with pre-operational values and governmental limits, and we conclude that practically there are no changes in the water quality parameters in that sampling points analysed.

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