



## Seasonal variations, metal distribution and water quality in the Todos os Santos River, Southeastern Brazil: a multivariate analysis

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### ABSTRACT

In aquatic habitats, metal contamination from natural and anthropogenic sources continues to pose a concern for human and environmental health. Thus, it is important to complete monitoring studies to assess patterns and the extent of metal contamination in these ecosystems. The purpose of this work was to determine the concentrations of 31 chemical elements and water quality parameters of the Todos os Santos River located in the Mucuri Valley, Minas Gerais, Brazil. A multivariate statistical analysis was used to determine any seasonal and spatial patterns from the data. Results demonstrated that metals including Al, Fe, and Ni exceeded Brazilian and international guidelines nutrients as P also exceed water quality standards. Principal components analysis indicated distinct geographical and seasonal patterns for multiple elements with hierarchical cluster analysis confirming the observed spatial patterns of contamination in the Todos os Santos River.

**Key words:** toxic pollutants, metals, water quality, environment.

### INTRODUCTION

Anthropogenic activities carried out in urban and rural areas generate pollutants that are usually discharged into rivers without prior treatment. These activities include industrial activities, use of pesticides, fertilizers, and manures. Rivers, lakes, and seas have received large amounts of wastewater from domestic and industrial sources,

thus endangering the living beings that use these water resources on a daily basis (Ohe et al. 2004, Jordão et al. 2007). Therefore, water bodies may be contaminated with complex, ill-defined mixtures of chemicals and most freshwater organisms will be exposed, to varying degrees, to this contamination (Scalon et al. 2013). The toxic elements produced are relocated by the action of rain, contaminating soils and waterways that surround these areas (Ren et al. 2004, Rezende et al. 2011).

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Among the contaminants present in waters, metals stand out. In aquatic environments, metals may come from various natural and anthropogenic sources, such as atmospheric deposition, geological weathering, agricultural activities and residential and industrial products (Weber et al. 2013). High concentrations of these pollutants have been demonstrated to cause adverse effects in the human body, such as heart and neurological problems and skin cancer, affecting many ecosystems (Chiba et al. 2011, Chang and Ling 2014). The Todos os Santos River (TSR) is located in Teófilo Otoni (Mucuri Valley, Minas Gerais State, Brazil). This water system receives a waste discharge of various origins, especially in parts of the river that run through urban areas. However, there are few studies on the environmental conditions of this river and the possible types of contamination that could lead to health risks for the local populations. Recently, a study conducted by Blanc et al. 2014 at the Todos os Santos River pointed out concentrations of aluminum, phosphorus, and iron above the maximum levels permitted by Brazilian law (CONAMA 2005) and the World Health Organization (WHO 2004).

The objective of the present study was to determine the metal concentrations, physical and chemical parameters in TSR water samples during periods of rain and drought, to assess spatial and temporal patterns in water quality using multivariate statistical analyses.

#### MATERIALS AND METHODS

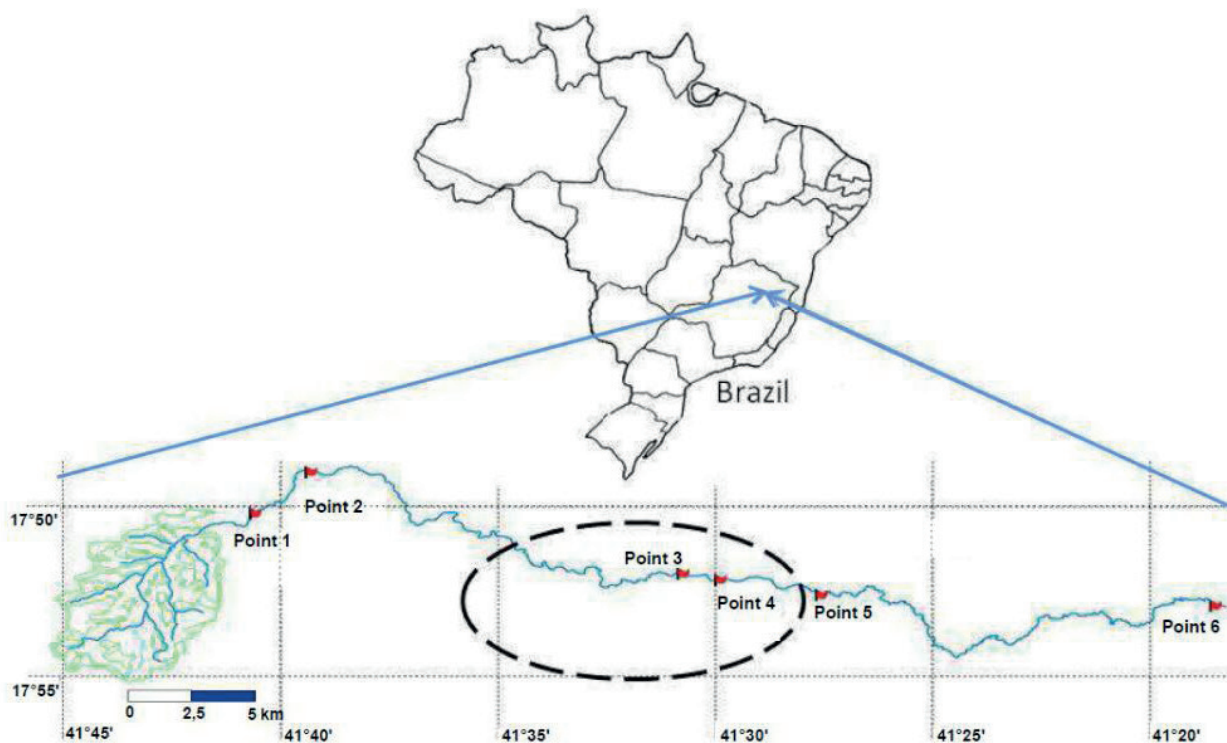
Samples were taken over a period of eight months in 2012, comprising periods of drought, which include the months from May to September, and the rainy season, which lasts from October to December. Two points are located upstream the selected urban area and near the source of the river (points 1 and 2); two other points are located downstream the urban area (points 5 and 6), and two are located within

the urban area, which is in a region with severe contamination (points 3 and 4). At each sample site, about 1 L of water was collected according to the CETESB standards (CETESB 2012), using metal-free polypropylene bottles. The samples were stored at 4°C until analysis, and a total sample volume of 100 mL was collected for the physical and chemical analyses.

The geographic coordinates of each point were determined using a Garmin 60CSx GPS receiver. The geographical location and altitude of the sampling sites are 17°50'S 41°40'W and 598.4 m (P-1), 17°48'S 41°39'W and 550.8 m (P-2); 17°51'S 41°30'W and 328.5 m (P-3), 17°52'S 41°29'W 319 m (P-4), 17°52'S 41°27'W and 310 m (P-5); 17°52'S 41°18'W and 272.5 m (P-6). The water collection points (n=6) were defined based on several parameters, such as the proximity to urban centers and water use within a radius of 74 km (Fig. 1).

The physical and chemical parameters measured were pH, dissolved oxygen, turbidity, conductivity, and temperature, using a pH-meter (power meter model mPA-210), an oximeter (model DO5519), a turbidimeter (Poly Control, model AP-2000), and a conductivity meter (model mCA – 150p) for conductivity and temperature, respectively. The measurements were made following the instruction manuals of each equipment. The dissolved oxygen, conductivity and temperature were determined *in situ*, and pH and turbidity were analyzed in the laboratory. High purity deionized water (resistivity 18.2 M Ω cm) obtained by the Milli-Q system (Millipore®) was used throughout the study and for preparing the calibration standards.

The determination of metals was performed by an inductively coupled plasma mass spectrometer (ICP-MS, ELAN DRC II, PerkinElmer), according to the method of Lawrence et al. 2006 with modifications. The equipment was installed in a clean room class 1000 in the laboratory of



**Figure 1** - Points of water samples collected from Todos os Santos River. Point 1 and Point 2 are located upstream the urban area of Teófilo Otoni city and near the source of the river; points 3 and 4 are located within the urban area, and points 5 and 6 are located downstream the urban area.

toxicology and properties of metals, Universidade de São Paulo (USP-Brazil). The determination of iron (Fe) levels in the collected samples was carried out with a spectrophotometer (Siqueira et al. 2009). For this, we used a spectrophotometer SP-220-Brazil.

The following metals were tested in surface water samples  $^{107}\text{Ag}$ ,  $^{27}\text{Al}$ ,  $^{75}\text{As}$ ,  $^{138}\text{Ba}$ ,  $^9\text{Be}$ ,  $^{209}\text{Bi}$ ,  $^{44}\text{Ca}$ ,  $^{111}\text{Cd}$ ,  $^{59}\text{Co}$ ,  $^{133}\text{Cs}$ ,  $^{63}\text{Cu}$ ,  $^{69}\text{Ga}$ ,  $^{202}\text{Hg}$ ,  $^{115}\text{In}$ ,  $^{39}\text{K}$ ,  $^7\text{Li}$ ,  $^{55}\text{Mn}$ ,  $^{23}\text{Na}$ ,  $^{60}\text{Ni}$ ,  $^{31}\text{P}$ ,  $^{208}\text{Pb}$ ,  $^{32}\text{S}$ ,  $^{82}\text{Se}$ ,  $^{28}\text{Si}$ ,  $^{88}\text{Sr}$ ,  $^{205}\text{Tl}$ ,  $^{238}\text{U}$ ,  $^{51}\text{V}$ ,  $^{184}\text{W}$  and  $^{66}\text{Zn}$ . The limits of detection (LOD) method for these elements were 0.002; 0.005; 0.0002; 0.003; 0.001; 0.01; 0.0001; 0.001; 0.001; 0.0006; 0.01; 0.0005; 0.009; 0.0007; 0.05; 0.002; 0.0001; 0.005; 0.0009; 0.4; 0.0001; 8.0; 0.001; 0.09; 0.0002; 0.06; 0.0001; 0.001; 0.005 and 0.0008  $\mu\text{g L}^{-1}$ , respectively. For this, were used calibration standard solutions from PerkinElmer (USA).

All reagents used were of analytical quality except high purity  $\text{HNO}_3$ , which was submitted

to distillation at a temperature below its boiling point using a Quartz distiller (Kürner). High purity deionized water (resistivity 18.2  $\text{M } \Omega \cdot \text{cm}$ ) obtained by the Milli-Q system (Millipore®) was used throughout the study. Quality control for the determination of metals in the water samples was carried out via analysis of water standard reference materials (Aluminum, Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Potassium, Selenium, Silver, Silicon, Sodium, Strontium, Thallium, Uranium, Vanadium, Zinc) from the National Institute of Standards and Technology (NIST 1640, Trace Elements in Natural Water). The reference samples were analyzed before and after ten runs of ordinary water samples. There were no statistical differences between the concentration values obtained for the reference materials and the “target-values” for 95% confidence intervals using the T-test. In the

multivariate analysis, the data were arranged in a matrix consisting of variables (columns), such as the concentration of each identified constituent; the objects (rows) were the sampled populations. The matrix was self-scaled before PCA and HCA were performed, the latter using the algorithm of means (Laurence et al. 2006). Data were analyzed using chemometrics software in MATLAB version 5.3 and the package PLS\_Toolbox (Version 2.0).

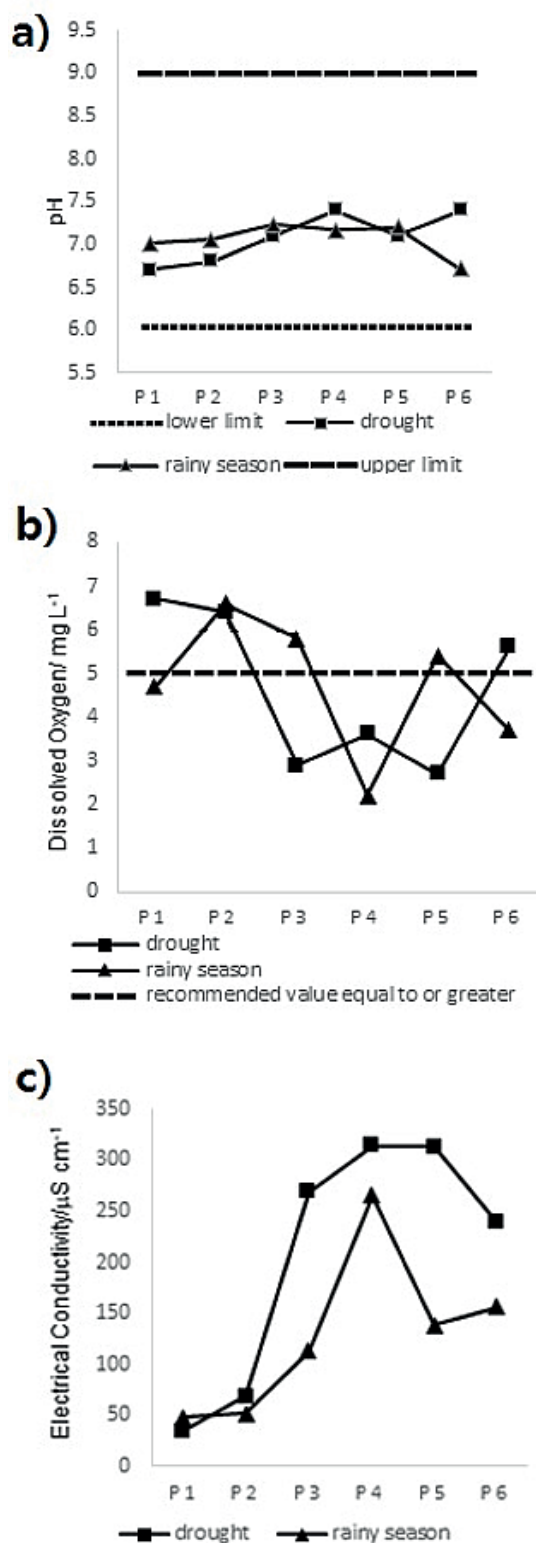
## RESULTS AND DISCUSSION

The average results of physical and chemical analyses in periods of drought and rain are shown in Fig. 2. During the dry period, the pH ranged from 6.7 to 7.4, and the turbidity varied between 4.4 and 58 NTU. These values of pH and turbidity are in agreement with the recommendations by the Resolution 357 of CONAMA/2005 (pH from 6.0 to 9.0 and turbidity until 100 NTU). The levels of dissolved oxygen (DO) were in disagreement with the resolution at points P-3, P-4 and P-5, ranging from 2.7 to 6.7 mg L<sup>-1</sup>.

During the rainy period, the pH and turbidity ranged from 6.7 to 7.2 and 4.8 to 89 NTU, respectively. The DO values in the rainy period ranged from 2.2 to 6.6 mg L<sup>-1</sup>; locations P-1, P-4, and P-6 were below the established minimum value (5 mg L<sup>-1</sup> DO) by the Resolution 357 of CONAMA/2005.

Dissolved oxygen is essential to aquatic life (Jordão et al. 2007), and low values are associated to the presence of oxidable substances, such as biodegradable organic matter and ions of lower oxidation state as Fe (II) and Mn (II) (Von Sperling 1996). This situation can lead to problems for the organisms living in the river because reduced oxygen in the water is not conducive to the survival of aerobic organisms and it is essential for the maintenance of the natural processes (CETESB 2001).

In both seasons, the electrical conductivity of TSR exhibited high values when passing through



**Figure 2** - Physical and chemical parameters: a) pH, b) dissolved oxygen, c) electrical conductivity for the water samples from the Todos os Santos River.



the urban perimeter of Teófilo Otoni city (P-3 and P-4). In the dry season, the values at points P-3, P-4, P-5 and P-6 ranged from 239 to 314  $\mu\text{S cm}^{-1}$ . During the rainy season, these same points ranged from 113 to 265  $\mu\text{S cm}^{-1}$ . Therefore, 66.7% of the assessed points (P3 to P6) suggested anthropogenic changes in this parameter during the two seasons.

Regarding the physical and chemical parameters, the samples collected in both periods (i.e., drought and rainy) presented similar results for electrical conductivity and turbidity. For dissolved oxygen, similar results were found for locations 3, 4 and 5 during the drought season.

The mean values of trace elements analyzed during the dry and rainy seasons are showed in Tables I and II. It can be seen that the elements aluminum, iron, and phosphorus were above those permitted by local regulations during both periods.

During the dry season, changes in the Al and Fe levels may be due to the inappropriate disposal of solid wastes, which can be observed along the route of the river; alternatively, these elements may be characteristic of the soil in this region. Lixiviation may also be considered given the high concentrations of aluminum. Elevated levels of P are related to domestic waste dumps in the riverbed (Christophoridis et al. 2009) as well as fertilizer used near the river (Rothwell et al. 2011).

In the rainy season, excessive levels of Ni were found. This may have been caused by industrial activities in the region (ATSDR 2005) and even the use of agricultural fertilizers contaminated by this metal (Campos et al. 2005), causing significant amounts of these contaminants to be eliminated in the river.

Matlab software was used to discover principal components (PCs) on water metal concentration series. Table III presented all the PCA eigenvalues for these water metals, and Table IV showed the corresponding principal component loadings. According to Table III, two PCs were selected and the first principal component (PC1) was a measure

of all elements less than Cr, Ni, Se, Ag and Hg which are indicative of primary contaminants; the second principal component (PC2) was primarily attributed to all elements less than Cd, Na, Be, Hg, Ag, Ta, Ga, Bi, In, Fe, P and S which is indicative of a second contaminant. In this way, the dataset resulted in two PCs, explaining 47.05% of the variance. These two independent principal components seemed to dominate the contamination data.

We performed an exploratory analysis using principal components analysis (PCA) and hierarchical cluster analysis (HCA), as shown in Fig. 3, in which the letters identify the collection month (i.e., A, May; B, June; C, July; D, September; and E, December). Fourteen principal components explained 96.2% of the variance. The PC1 and PC2 components accumulated the higher variances and were used for the differentiation of samples from the collection sites. The other components of accumulated minor variances were not enough to differentiate samples from collection sites. Thus, the sample in the PCA was grouped into six groups (G1 to G6). In this way, we can identify whether the samples collected in the month of December exhibited any similarities, as indicated by their position at the top (i.e., positive) part of PC2, which explained 12.5% of the total variance, and the left (i.e., negative) part of PC1, which explained 34.6%.

However, the samples lying at the bottom (i.e., negative) part of PC2 and the negative part of PC1 exhibit similarities across several months of collection, such as the samples from location 1 in the months of May, June, July, and September. Samples from area 2 came in this quadrant in the months of May, June, and September. From location 3, only the sample collected in July was in this quadrant; from location 4, the samples from June and September were similar to the points above and from area 6, only the sample collected in September was in that quadrant. Considering the arrangement of the samples with positive scores for both PC1 and PC2, the samples that most closely resemble each other are the ones from location

**TABLE I**  
**Mean values of trace element concentrations in water samples during the dry season (sample concentration  $\pm$  standard deviation in  $\mu\text{g L}^{-1}$ ). RMV in  $\mu\text{g L}^{-1}$  (Recommended Maximum values according to CONAMA 2005).**

Elements	Collecting Points						RMV
	P-1	P-2	P-3	P-4	P-5	P-6	
Ag	1.640 $\pm$ 0.178	0.973 $\pm$ 0.167	0.431 $\pm$ 0.062	0.379 $\pm$ 0.038	0.104 $\pm$ 0.014	0.128 $\pm$ 0.051	10.000
Al	27.870 $\pm$ 4.160	*455.280 $\pm$ 24.050	*447.080 $\pm$ 78.960	*233.950 $\pm$ 19.690	*721.530 $\pm$ 182.150	689.970 $\pm$ 73.900	100.000
As	0.156 $\pm$ 0.038	0.173 $\pm$ 0.051	0.289 $\pm$ 0.088	0.342 $\pm$ 0.082	0.516 $\pm$ 0.121	0.334 $\pm$ 0.066	10.000
Ba	20.540 $\pm$ 0.253	33.540 $\pm$ 0.375	36.510 $\pm$ 2.362	63.430 $\pm$ 9.676	56.060 $\pm$ 4.595	40.220 $\pm$ 0.407	700.000
Be	0.001 $\pm$ 0.000	0.064 $\pm$ 0.068	0.078 $\pm$ 0.048	0.032 $\pm$ 0.120	0.411 $\pm$ 0.203	0.642 $\pm$ 0.140	40.000
Bi	0.011 $\pm$ 0.004	0.016 $\pm$ 0.006	0.020 $\pm$ 0.007	0.013 $\pm$ 0.006	0.020 $\pm$ 0.005	0.023 $\pm$ 0.004	
Ca	897.000 $\pm$ 86.000	2762.000 $\pm$ 239.000	11045.000 $\pm$ 654.000	12655.000 $\pm$ 766.000	13158.000 $\pm$ 171.000	8629.000 $\pm$ 347.000	
Cd	0.001 $\pm$ 0.003	0.005 $\pm$ 0.011	0.014 $\pm$ 0.005	0.017 $\pm$ 0.007	0.024 $\pm$ 0.013	0.016 $\pm$ 0.062	1.000
Co	0.018 $\pm$ 0.007	0.061 $\pm$ 0.010	0.432 $\pm$ 0.043	0.353 $\pm$ 0.031	0.329 $\pm$ 0.046	0.231 $\pm$ 0.012	50.000
Cs	0.258 $\pm$ 0.006	0.302 $\pm$ 0.010	0.239 $\pm$ 0.023	0.270 $\pm$ 0.012	0.290 $\pm$ 0.034	0.218 $\pm$ 0.016	
Cu	0.139 $\pm$ 0.028	0.162 $\pm$ 0.045	1.600 $\pm$ 0.060	0.656 $\pm$ 0.050	1.190 $\pm$ 0.247	7.357 $\pm$ 0.043	9.000
Fe	*881.200 $\pm$ 1.200	*1281.700 $\pm$ 2.100	*2484.300 $\pm$ 2.200	*3425.900 $\pm$ 1.700	*5945.600 $\pm$ 1.600	*3239.300 $\pm$ 1.700	300.000
Ga	0.528 $\pm$ 0.029	1.013 $\pm$ 0.048	1.079 $\pm$ 0.087	1.632 $\pm$ 0.054	1.900 $\pm$ 0.211	1.376 $\pm$ 0.068	
Hg	0.027 $\pm$ 0.008	0.019 $\pm$ 0.003	0.003 $\pm$ 0.011	0.031 $\pm$ 0.005	0.012 $\pm$ 0.004	0.017 $\pm$ 0.002	0.200
In	0.006 $\pm$ 0.003	0.005 $\pm$ 0.001	0.006 $\pm$ 0.002	0.006 $\pm$ 0.001	0.005 $\pm$ 0.001	0.006 $\pm$ 0.003	
K	357.000 $\pm$ 8.000	1106.000 $\pm$ 64.000	4565.000 $\pm$ 506.000	5360.000 $\pm$ 157.000	6759.000 $\pm$ 849.000	5834.000 $\pm$ 193.000	
Li	0.309 $\pm$ 0.144	0.475 $\pm$ 0.181	1.008 $\pm$ 0.280	345.974 $\pm$ 0.948	2.568 $\pm$ 0.211	2.478 $\pm$ 0.093	2500.000
Mn	15.720 $\pm$ 0.210	28.880 $\pm$ 1.360	66.040 $\pm$ 2.490	134.000 $\pm$ 4.110	181.670 $\pm$ 15.800	70.220 $\pm$ 1.940	100.000
Na	2033.000 $\pm$ 70.000	3345.000 $\pm$ 182.000	12525.000 $\pm$ 1690.000	15892.000 $\pm$ 808.000	17228.000 $\pm$ 2684.000	23958.000 $\pm$ 587.000	
Ni	0.280 $\pm$ 0.410	0.910 $\pm$ 0.058	1.780 $\pm$ 0.132	1.810 $\pm$ 0.154	1.140 $\pm$ 0.140	1.510 $\pm$ 0.099	25.000
P	*25.800 $\pm$ 10.810	*103.600 $\pm$ 11.100	*841.900 $\pm$ 24.800	*612.730 $\pm$ 14.178	*1167.590 $\pm$ 24.600	*269.030 $\pm$ 15.110	20.000
Pb	0.018 $\pm$ 0.013	0.098 $\pm$ 0.015	2.175 $\pm$ 0.176	3.670 $\pm$ 0.090	2.014 $\pm$ 0.270	0.875 $\pm$ 0.250	10.000
S	281.800 $\pm$ 141.200	281.400 $\pm$ 68.400	417.500 $\pm$ 57.580	412.200 $\pm$ 80.300	366.945 $\pm$ 70.600	294.200 $\pm$ 92.130	
Se	1.145 $\pm$ 1.481	0.962 $\pm$ 1.546	0.564 $\pm$ 0.161	2.146 $\pm$ 1.411	1.592 $\pm$ 1.157	0.543 $\pm$ 1.452	10.000
Si	3585.000 $\pm$ 128.000	4873.000 $\pm$ 120.000	8499.000 $\pm$ 155.000	10299.000 $\pm$ 211.000	9502.000 $\pm$ 223.000	10699.000 $\pm$ 287.000	
Sr	14.970 $\pm$ 0.152	28.994 $\pm$ 0.397	62.250 $\pm$ 2.020	82.570 $\pm$ 1.600	73.370 $\pm$ 4.500	43.050 $\pm$ 0.817	
Tl	0.015 $\pm$ 0.004	0.044 $\pm$ 0.008	0.017 $\pm$ 0.002	0.027 $\pm$ 0.006	0.015 $\pm$ 0.004	0.015 $\pm$ 0.005	
U	0.004 $\pm$ 0.005	0.116 $\pm$ 0.020	0.096 $\pm$ 0.016	0.191 $\pm$ 0.015	0.163 $\pm$ 0.040	0.192 $\pm$ 0.023	20.000
V	0.031 $\pm$ 0.002	0.883 $\pm$ 0.026	0.748 $\pm$ 0.088	1.679 $\pm$ 0.079	2.059 $\pm$ 0.343	1.598 $\pm$ 0.295	100.000
W	0.025 $\pm$ 0.005	0.012 $\pm$ 0.003	0.057 $\pm$ 0.003	0.018 $\pm$ 0.008	0.035 $\pm$ 0.014	0.020 $\pm$ 0.008	
Zn	3.460 $\pm$ 0.233	9.086 $\pm$ 0.174	26.180 $\pm$ 1.760	19.825 $\pm$ 0.508	14.558 $\pm$ 1.22	8.107 $\pm$ 0.285	180.000

\*Above the maximum value permitted by Resolution 357 of CONAMA/2005.

**TABLE II**  
**Mean values of trace elements in water samples during the rainy season (sample concentration  $\pm$  standard deviation in  $\mu\text{g L}^{-1}$ ). RMV in  $\mu\text{g L}^{-1}$  (Recommended Maximum Values according to CONAMA 2005).**

Elements	Collecting Points						RMV
	P-1	P-2	P-3	P-4	P-5	P-6	
Ag	0.039 $\pm$ 0.073	0.043 $\pm$ 0.068	ND	ND	ND	ND	10.000
Al	*109.080 $\pm$ 0.857	*244.890 $\pm$ 9.253	*272.520 $\pm$ 20.550	*768.890 $\pm$ 49.930	*600.700 $\pm$ 33.280	*2831.800 $\pm$ 141.900	100.000
As	0.025 $\pm$ 0.191	ND	ND	0.275 $\pm$ 0.169	0.315 $\pm$ 0.173	0.715 $\pm$ 0.193	10.000
Ba	27.451 $\pm$ 0.099	28.705 $\pm$ 0.266	29.408 $\pm$ 0.681	83.411 $\pm$ 1.338	43.042 $\pm$ 0.583	73.350 $\pm$ 1.111	700.000
Be	0.001 $\pm$ 0.000	0.009 $\pm$ 0.004	0.078 $\pm$ 0.032	0.022 $\pm$ 0.060	0.632 $\pm$ 0.109	0.511 $\pm$ 0.073	40.000
Bi	ND	ND	ND	ND	ND	ND	
Ca	1569.000 $\pm$ 98.000	1642.000 $\pm$ 79.000	3714.000 $\pm$ 126.000	8913.000 $\pm$ 74.000	5004.000 $\pm$ 55.000	4440.830 $\pm$ 121.870	
Cd	ND	ND	ND	ND	ND	ND	1.000
Co	0.027 $\pm$ 0.036	ND	ND	0.173 $\pm$ 0.070	0.001 $\pm$ 0.039	0.317 $\pm$ 0.039	50.000
Cs	0.370 $\pm$ 0.021	0.328 $\pm$ 0.064	0.120 $\pm$ 0.011	0.217 $\pm$ 0.044	0.096 $\pm$ 0.035	0.435 $\pm$ 0.102	
Cu	3.767 $\pm$ 0.261	0.657 $\pm$ 0.155	7.672 $\pm$ 0.195	1.758 $\pm$ 0.025	7.368 $\pm$ 1.262	5.775 $\pm$ 0.313	9.000
Fe	*1217.390 $\pm$ 0.010	*570.050 $\pm$ 0.020	193.240 $\pm$ 0.100	231.880 $\pm$ 0.300	188.410 $\pm$ 1.100	*1043.480 $\pm$ 3.200	300.000
Ga	0.032 $\pm$ 0.016	0.856 $\pm$ 0.041	0.996 $\pm$ 0.054	1.456 $\pm$ 0.048	1.698 $\pm$ 0.113	1.859 $\pm$ 0.055	
Hg	0.001 $\pm$ 0.000	0.011 $\pm$ 0.001	0.001 $\pm$ 0.000	0.057 $\pm$ 0.004	0.007 $\pm$ 0.001	0.013 $\pm$ 0.001	0.200
In	0.003 $\pm$ 0.000	0.002 $\pm$ 0.000	0.002 $\pm$ 0.000	0.003 $\pm$ 0.000	0.001 $\pm$ 0.000	0.005 $\pm$ 0.000	
K	1753.000 $\pm$ 11.000	2217.000 $\pm$ 9.000	2022.000 $\pm$ 18.000	3714.000 $\pm$ 101.000	2520.000 $\pm$ 67.000	3259.000 $\pm$ 20.000	
Li	7.420 $\pm$ 0.241	0.000 $\pm$ 0.000	0.340 $\pm$ 0.244	0.577 $\pm$ 0.372	0.605 $\pm$ 0.456	2.023 $\pm$ 0.085	2500.000
Mn	25.785 $\pm$ 0.452	6.281 $\pm$ 0.151	5.209 $\pm$ 0.119	78.914 $\pm$ 2.314	13.912 $\pm$ 0.236	52.151 $\pm$ 1.353	100.000
Na	426.000 $\pm$ 10.000	480.000 $\pm$ 4.000	1084.000 $\pm$ 28.000	2433.000 $\pm$ 16.000	1143.000 $\pm$ 15.000	1397.000 $\pm$ 8.000	
Ni	*90.701 $\pm$ 1.637	11.172 $\pm$ 0.303	9.853 $\pm$ 0.243	10.413 $\pm$ 0.207	23.843 $\pm$ 0.526	*31.316 $\pm$ 0.330	25.000
P	*61.750 $\pm$ 8.940	*31.960 $\pm$ 7.680	*183.250 $\pm$ 12.770	*461.590 $\pm$ 17.470	*164.420 $\pm$ 14.400	*192.310 $\pm$ 14.160	20.000
Pb	ND	ND	ND	2.547 $\pm$ 0.217	0.186 $\pm$ 0.064	ND	10.000
S	217.400 $\pm$ 100.400	211.100 $\pm$ 45.800	395.300 $\pm$ 36.440	441.260 $\pm$ 90.670	321.820 $\pm$ 62.080	276.320 $\pm$ 73.130	
Se	0.494 $\pm$ 2.381	1.591 $\pm$ 0.934	1.644 $\pm$ 1.545	2.507 $\pm$ 2.603	0.987 $\pm$ 2.023	1.811 $\pm$ 0.412	10.000
Si	4087 $\pm$ 31	4358 $\pm$ 24	5209 $\pm$ 893	6673 $\pm$ 91	6854 $\pm$ 944	9984 $\pm$ 188	
Sr	21.520 $\pm$ 0.044	23.431 $\pm$ 0.033	44.827 $\pm$ 0.665	94.550 $\pm$ 2.127	66.943 $\pm$ 1.090	68.690 $\pm$ 0.278	
Tl	ND	0.002 $\pm$ 0.000	0.001 $\pm$ 0.000	0.0000 $\pm$ 0.00	ND	ND	
U	ND	ND	ND	0.227 $\pm$ 0.005	0.031 $\pm$ 0.041	0.448 $\pm$ 0.144	20.000
V	ND	ND	ND	1.756 $\pm$ 0.135	1.084 $\pm$ 0.111	5.388 $\pm$ 0.240	100.000
W	0.021 $\pm$ 0.002	0.009 $\pm$ 0.007	0.042 $\pm$ 0.005	0.023 $\pm$ 0.012	0.012 $\pm$ 0.014	0.006 $\pm$ 0.001	
Zn	23.820 $\pm$ 1.149	8.862 $\pm$ 0.464	29.740 $\pm$ 0.838	40.170 $\pm$ 0.655	29.650 $\pm$ 0.840	17.320 $\pm$ 0.375	180.000

\*Above the maximum value permitted by Resolution 357 of CONAMA 2005. ND = Not detected (Below LOD).

**TABLE III**  
Eigenvalues of PCA for water metal analysis datasets.

Component	Eigenvalue	Variance	Cumulative variance %
1	10.375	34.585	34.585
2	3.739	12.463	47.048
3	3.216	10.719	57.767
4	2.565	8.549	66.316
5	1.859	6.196	72.512
6	1.601	5.335	77.848
7	1.293	4.311	82.159
8	1.154	3.846	86.004
9	0.850	2.835	88.839
10	0.575	1.918	90.757
11	0.479	1.595	92.353
12	0.460	1.534	93.887
13	0.395	1.318	95.205
14	0.297	0.990	96.195

3 collected in May, area 5 in June, location 6 in July and location 4 in May. Regarding the samples with negative values of PC1 and positive values of PC2, this group of samples comprises those from point 2 collected in July, location 3 in June and September, area 4 in July, location 5 in May, July, and September and point 6 in July.

This distribution of water samples collected at different locations and in different months is explained by influences on the elemental content, as represented in the graph of weights (Fig. 4). In the positive region of PC2 and negative region of PC1, the elements that have the strongest influence are Ni, Cr, and Se. The influence of Ag, Hg, and In is strong in the region in which both PC1 and PC2 are negative. When PC1 and PC2 are both positive, the elements Cu, Li, Ce, Zn, Al, Sr, Ba, Ur, Va, As, Pb, K, Co, Ca and Mn stand out. For the region in which PC2 is negative and PC1 is positive, clustering is due to the levels of Be, Na, Cd, P, Fe, Ta, Bi, Ga and S.

### CONCLUSIONS

The levels of dissolved oxygen during the dry and rainy period were in disagreement with the

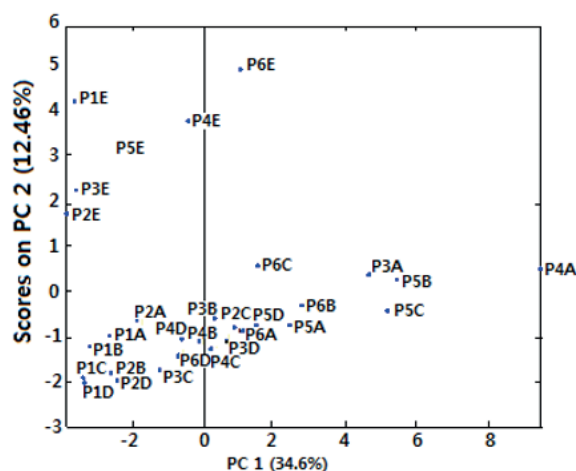
local regulations for points 3, 4, 5. The electrical conductivity of TSR exhibited high values in both seasons for points 3 and 4.

During the dry season the metals aluminum (points 2, 3, 4, 5) and iron (points 1-6) are outside the range permitted. For rainy season, aluminum (points 1-6), iron (points 1, 2, 6) and nickel (points 1, 6) exhibited high levels. The nonmetal phosphorus was found in disagreement with the legislation in the 6 points analysed for both seasons.

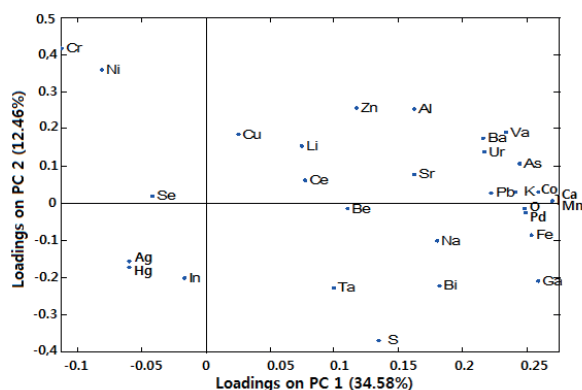
**TABLE IV**  
Data for principal components 1 and 2 of the water analysis datasets.

Components	PC1	PC2
Cr	-0.113	0.4183
Mn	0.270	0.0062
Co	0.260	0.0301
Cu	0.025	0.1855
Pb	0.223	0.0269
Cd	0.248	-0.0140
Li	0.075	0.1542
Al	0.162	0.2544
Na	0.180	-0.1006
Ba	0.216	0.1750
K	0.241	0.0298
As	0.245	0.1077
Be	0.110	-0.0155
Hg	-0.060	-0.1735
Ni	-0.081	0.3595
Ag	-0.060	-0.1574
Se	-0.042	0.0191
Ta	0.100	-0.2274
Ur	0.217	0.1388
Zn	0.117	0.2575
Va	0.234	0.1902
Ga	0.259	-0.2083
Sr	0.162	0.0764
Bi	0.182	-0.2222
Ca	0.276	0.0223
Ce	0.077	0.0616
In	-0.017	-0.2016
Fe	0.254	-0.0866
P	0.249	-0.0244
S	0.134	-0.3704





**Figure 3** - Scores of water samples collected in different months based on the metal content of the Todos os Santos River.



**Figure 4** - Loadings representing the influence of different elements on spectroscopic readings of water samples collected at various locations along the Todos os Santos River.

Exploratory analysis using PCA and HCA demonstrated that there are similarities among samples collected in different months at various locations, and together with the other dates, it can be suggested that TSR is facing a contamination problem that can influence the living beings that depend of this water source to survive.

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