

Distribution of chemical parameters in the water of the Tucuruí Reservoir, Amazon Region - Brazil: influence of seasonality and depth of water column

Distribuição dos parâmetros químicos na água do reservatório de Tucuruí, Amazônia - Brasil: influência da sazonalidade e profundidade da coluna de água

Davis Castro dos Santos^{1*}; Simone de Fátima Pinheiro Pereira^{1}; Augusto Fernando Souza de Oliveira¹; Thiago de Melo e Silva¹; Cléber Silva e Silva²; Ronaldo Magno Rocha²; Kellen Heloizy Garcia Freitas²; Luciana Pinheiro Santos²**

¹Environmental and Analytical Chemistry Laboratory, Federal University of Pará, Augusto Correa Street, S/N - Guamá, 66075-900 - Belém - PA – Brazil

²Federal Institute of Education, Science and Technology of Pará, Almirante Barroso Street, 1155 - Marco, 66093-020 - Belém - PA – Brazil

* davisquimica@gmail.com

** simonefp@ufpa.br

Abstract

Assessment of seasonal changes in chemical parameters is an important aspect for evaluating temporal variations of lentic ecosystem (lakes and reservoirs) due to anthropogenic activities. In this study, six metals and four physicochemical parameters were evaluated, collected from fourteen sampling sites in two seasons and three depths in the Tucuruí reservoir (Tocantins River-PA). The heavy metals monitoring was done with the inductively coupled plasma atomic emission spectrometry (ICP-AES). Different multivariate statistical techniques were employed to evaluate the seasonal correlations of physicochemical parameters and metals. The seasonality influence for the temperature, pH, conductivity, Al, Fe and Mn was demonstrated by Single Factor ANOVA analysis. Turbidity and Ba showed no significant differences between two periods. The temperature and Fe in the rainy season were influenced by the depth of the water column that was not a determinant in the variability of most parameters.

Keywords: Tocantins river. Tucuruí dam. heavy metals. Water pollution.

Resumo

A avaliação de mudanças sazonais em parâmetros químicos é um aspecto importante para avaliar as variações temporais do ecossistema lêntico (lagos e reservatórios) devido a atividades antropogênicas. Neste estudo, seis metais e quatro parâmetros físico-químicos foram avaliados, coletados em quatorze locais amostrados em duas estações e três profundidades no reservatório de Tucuruí (Rio Tocantins-PA). O monitoramento de metais pesados foi feito através de espectrometria de emissão atômica com plasma indutivamente acoplado (ICP-AES). Diferentes técnicas estatísticas multivariadas foram empregadas para avaliar as correlações sazonais de parâmetros físico-químicos e metais. A influência da sazonalidade para a temperatura, pH, condutividade, Al, Fe e Mn foi demonstrada pela análise ANOVA Fator Único. Turbidez e Ba não apresentaram diferenças significativas entre os dois períodos. A temperatura e Fe na estação chuvosa foram influenciados pela profundidade da coluna de água que não foi determinante na variabilidade da maioria dos parâmetros.

Palavras-chave: Rio Tocantins. Represa de Tucuruí. metais pesados. poluição da água.

Introdução

Water contamination by toxic chemicals in rivers and lakes are of major environmental concern worldwide [1]. Moreover, heavy metals have a high tendency for biomagnification [2]. Particularly, the lentic ecosystems (lakes and reservoirs) are more prone to the problem of water contamination due to low capacity for self-purification and dispersion of pollutants [3]. There are several studies on limnological aspects of aquatic systems in different parts of the world [4].

Acidic mine discharges, industrial effluents and wastes released into water bodies may change their physicochemical characteristics and raise the concentration of heavy metals in the nature of the effluent discharged [5]. In order to understand the environmental chemistry of metals, it is necessary to include the physical and chemical parameters in varied conditions of natural systems [6].

The Tucuruí dam (Figure 1) is located in the southeast of Pará state, in the lower Tocantins River, 7.5 km upstream from the Tucuruí city, 300 km straight line from the Belém city (state capital). Its geographical position is defined by the coordinates 03° 45' south latitude and 49° 41' west longitude. The area is approximately 2,430 km², with a maximum width around 40 km and an average of 14.3 kilometers, extending over a stretch of about 170 km away, near the Marabá city and a perimeter of 3,700 km [7].

The lengthy course of the Tocantins River Basin contributes to a well-defined and stable climatic regime across this region. The north of the region is hot and humid with high rainfall. The temperature peaks at 38°C in August and September, whereas the coldest temperatures are recorded in June (about 22°C), the rainfall can be as high as 2,400 mm with a humidity rate of about 85%. Towards the south of this region the temperature drops as the latitude increases and the rainfall averages around 1,400 mm with a humidity rate of around 70% [8].

From the construction of Hydroelectric Tucuruí on the Tocantins River-PA, significant changes regarding their chemical environment were observed in the local ecosystems. An appreciable drop in the quality of water downstream was forecast. During low flow-rates most of the water is discharged through the tailrace and the quality was of reduced quality for human and environmental uses [9].

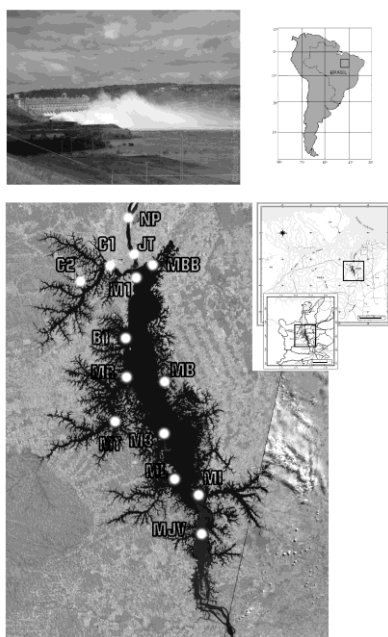


Figure 1 - Tucuruí Dam Reservoir with sampling points. Source: Adapted from Google Earth, 2018.

The regularization of the river flow prevented the seasonal flooding of the riverbanks downstream adversely affecting the natural fertilization processes. In addition, it was anticipated that

the physical barrier of the dam would trap nutrient rich organic matter disrupting the downstream food cycle. The aforementioned impact decreased the natural and agricultural productivity of the flood plain where as the dearth in organic matter had a likewise impact on the number of fish downstream [10].

The seasonal changes the balance of elements and compounds in water, resulting in significant changes of chemical, physical, biological and mineralogical properties [11]. Without forgetting that other changes are important as pH changes, changes in electrical conductivity, and ionic strength on the sorption and desorption of ions [12].

This study aimed to evaluate the influence of seasonality and depth of the water column on the distribution of physicochemical parameters (pH, turbidity, conductivity and temperature) and some metals (Al, Fe, Ba, Mn, Zn e Cd) water in the Tucuruí reservoir - Tocantins river - PA.

Material and Methods

Related to collecting and handling of water samples, followed and there are specific protocols for that described in EPA Analytical Methods (1600-series) and available for trace metals analysis.

The samples were collected at 14 sampling stations (Table 1), in two seasons in he rainy period (May) and dry period (September) and three depths (surface, middle and bottom), pH, turbidity, conductivity and temperature were evaluated according to [13]. After collecting the samples were placed in bottles properly decontaminated, kept under refrigeration at 4 ° C and preserved as recommended for [14].

Table 1. Sampling stations and geographic coordinates

Acronyms	Stations	Coordinates	
		Longitude	Latitude
C1	Caraipé 1	49°42'35.62"W	3°50'9.49"S
C2	Caraipé 2	49°48'39.98"W	3°51'48.32"S
M1	Montante 1	49°37'52.51"W	3°51'47.08"S
MBB	Montante Breu Branco	49°33'51.45"W	3°47'22.50"S
MB	Montante Belauto	49°27'52.01"W	4°14'6.74"S
MT	Montante Tucuruí	49°46'7.52"W	4°21'19.33"S
M3	Montante3	49°30'22.38"W	4°24'27.52"S
MR	Montante Repartimento	49°41'51.75"W	4°13'1.38"S
B1	Base 1	49°38'57.73"W	4° 5'26.81"S
MI	Montante Ipixuna	49°24'31.67"W	4°29'36.57"S
MJV	Montante J. Velho	49°26'31.60"W	4°33'7.07"S
ML	Montante Lontra	49°31'42.05"W	4°29'53.81"S
JT	Jusante Tucuruí	49°38'53.84"W	3°47'11.52"S
NP	Nazaré dos Patos	49°36'38.96"W	3°26'48.97"S

In laboratory mounted in the reservoir, the samples were vacuum filtered through a milipore in order to quantify only the dissolved material membrane of 0.22 µm without acid addition (soluble components) and sent for analysis of elements using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

The precision and accuracy study was performed with the analysis of standard reference material of water river (SRM 1640 NIST) where the elements are analyzed at concentrations similar to those found in the samples analyzed in this study and by analyzing multielement standard.

In relation to the river water uses by the National Environment Council (CONAMA) Resolution 357-05 (2005), the Tocantins river are considered Class II, also was used to check the maximum reference value of parameters analyzed.

Results and Discussion

Dixon test validated the results for a tabled value Q_t (0.2334) for 84 samples. The results for the physical and chemical parameters in two seasons and three water depths in the Tucuruí dam are presented in Table 2 and Table 3.

Table 2. Temperature and pH distribution of the Tucuruí dam water

Stations	Temperature (°C)						pH					
	Rainy season			Dry season			Rainy season			Dry season		
	1	2	3	1	2	3	1	2	3	1	2	3
MI	28.3	29.0	29.0	30.8	30.6	30.6	6.1	6.3	5.9	6.8	6.8	7.1
MJV	29.8	29.7	28.6	30.7	30.7	30.6	6.2	6.2	6.1	6.9	6.7	6.6
ML	30.9	29.4	28.3	32.8	31.2	30.3	6.2	4.3	5.9	6.9	6.9	6.8
M3	29.5	29.5	28.0	32.1	30.6	30.6	6.2	6.4	6.3	7.3	7.1	7.1
MB	29.0	29.0	28.5	31.0	30.5	30.5	6.1	6.4	5.9	7.2	7.1	7.0
MT	30.0	29.7	28.6	30.8	30.7	30.7	6.7	6.7	6.3	7.0	6.8	6.8
MR	29.8	29.7	28.9	30.1	30.1	30.2	6.2	6.3	6.0	7.1	6.9	6.5
B1	30.0	28.9	28.8	30.6	30.5	30.6	6.2	6.2	6.2	7.1	7.3	7.4
C1	29.8	29.6	29.1	29.2	29.1	29.0	6.2	6.3	6.2	6.8	6.9	6.8
C2	30.2	29.9	28.3	31.1	30.9	30.2	5.9	6.2	5.8	7.0	7.0	6.9
MBB	29.0	29.3	28.6	30.8	30.0	29.8	6.6	6.7	6.5	7.5	7.3	7.0
M1	29.4	29.4	28.4	30.3	29.9	29.6	7.0	7.0	6.8	7.1	7.0	6.9
NP	28.8	28.6	28.7	29.6	29.5	29.3	6.2	6.3	6.3	6.8	6.8	6.8
JT	29.0	29.0	28.8	29.6	29.5	29.4	6.1	6.5	6.6	6.6	6.6	6.5
Mean	29.5	29.3	28.6	30.6	30.2	30.1	6.2	6.2	6.2	7.0	6.9	6.9
SD	0.67	0.38	0.30	0.95	0.60	0.57	0.2	0.6	0.2	0.2	0.1	0.2
RSD (%)	2.3	1.3	1.0	3.1	2.0	1.9	4.5	9.9	4.7	3.4	2.7	3.5
Minimum	28.3	28.6	28.0	29.2	29.1	29.3	5.9	4.3	5.8	6.8	6.7	6.5
Maximum	30.9	29.9	29.1	32.8	30.9	30.7	7.0	7.0	6.8	7.5	7.3	7.4

SD - Standard Deviation; RSD - Relative Standard Deviation; 1 - Surface; 2 - Intermediate; 3 - Bottom

Table 3. Turbidity and conductivity distribution of the Tucuruí dam water

Stations	Turbidity (UNT)						Conductivity (µS/cm)					
	Rainy season			Dry season			Rainy season			Dry season		
	1	2	3	1	2	3	1	2	3	1	2	3
MI	34.0	32.6	33.1	16.2	7.1	11.3	40.0	43.0	40.0	67.0	60.0	66.0
MJV	25.1	15.9	21.3	11.5	15.3	16.9	44.0	43.0	42.0	57.0	53.0	50.0
ML	19.8	27.5	23.5	13.1	8.0	10.4	47.0	43.0	48.0	61.0	63.0	65.0
M3	12.7	10.9	8.9	25.1	20.1	20.2	47.0	46.0	45.0	68.0	67.0	66.0
MB	4.6	3.7	6.9	5.8	11.3	6.4	41.0	44.0	45.0	49.0	47.0	46.0
MT	13.9	12.5	9.8	10.3	8.3	13.1	49.0	45.0	47.0	76.0	75.0	75.0
MR	29.9	10.3	15.7	17.4	18.3	15.9	55.0	51.0	56.0	55.0	55.0	78.0
B1	7.8	8.9	11.2	16.7	10.4	6.7	47.0	45.0	44.0	56.0	55.0	55.0
C1	3.1	5.1	2.6	23.1	20.1	25.4	49.0	48.0	46.0	47.0	52.0	52.0
C2	6.9	6.6	9.9	24.5	23.9	24.4	51.0	48.0	54.0	48.0	52.0	52.0
MBB	24.7	27.8	30.1	17.7	18.5	10.0	45.0	45.0	46.0	54.0	53.0	53.0
M1	22.6	23.2	25.7	11.7	7.3	12.8	44.0	43.0	43.0	51.0	51.0	55.0
NP	36.4	35.9	19.4	24.5	25.9	23.8	45.0	45.0	44.0	56.0	51.0	51.0
JT	30.3	34.5	29.9	14.2	13.3	15.9	51.0	41.0	45.0	52.0	55.0	51.0
Mean	19.4	18.2	17.7	16.5	14.8	15.2	47.0	45.0	46.0	57.0	56.0	58.0
SD	11.2	11.5	9.7	5.9	6.3	6.3	4.0	2.6	4.3	8.4	7.4	9.9
RSD (%)	58.9	63.5	55.2	36.1	42.9	41.4	8.5	5.8	9.3	14.7	13.2	17.1
Minimum	3.1	3.7	2.6	5.8	7.1	6.4	40.0	41.0	40.0	47.0	47.0	46.0
Maximum	36.4	34.5	33.1	24.5	25.9	25.4	55.0	51.0	56.0	76.0	75.0	78.0

SD - Standard Deviation; RSD - Relative Standard Deviation; 1 - Surface; 2 - Intermediate; 3 - Bottom

For the rainy season (Figure 2), the pH of 6 points analyzed were not in accordance with resolution 357/05 of CONAMA (pH = 6-9). The pH was significantly higher in the middle tier of most

seasons (Figure 2), has the lowest values were found in the bottom layer that may be related to the photosynthetic activity of algae that pull carbon dioxide from water, reducing its acidity [15].

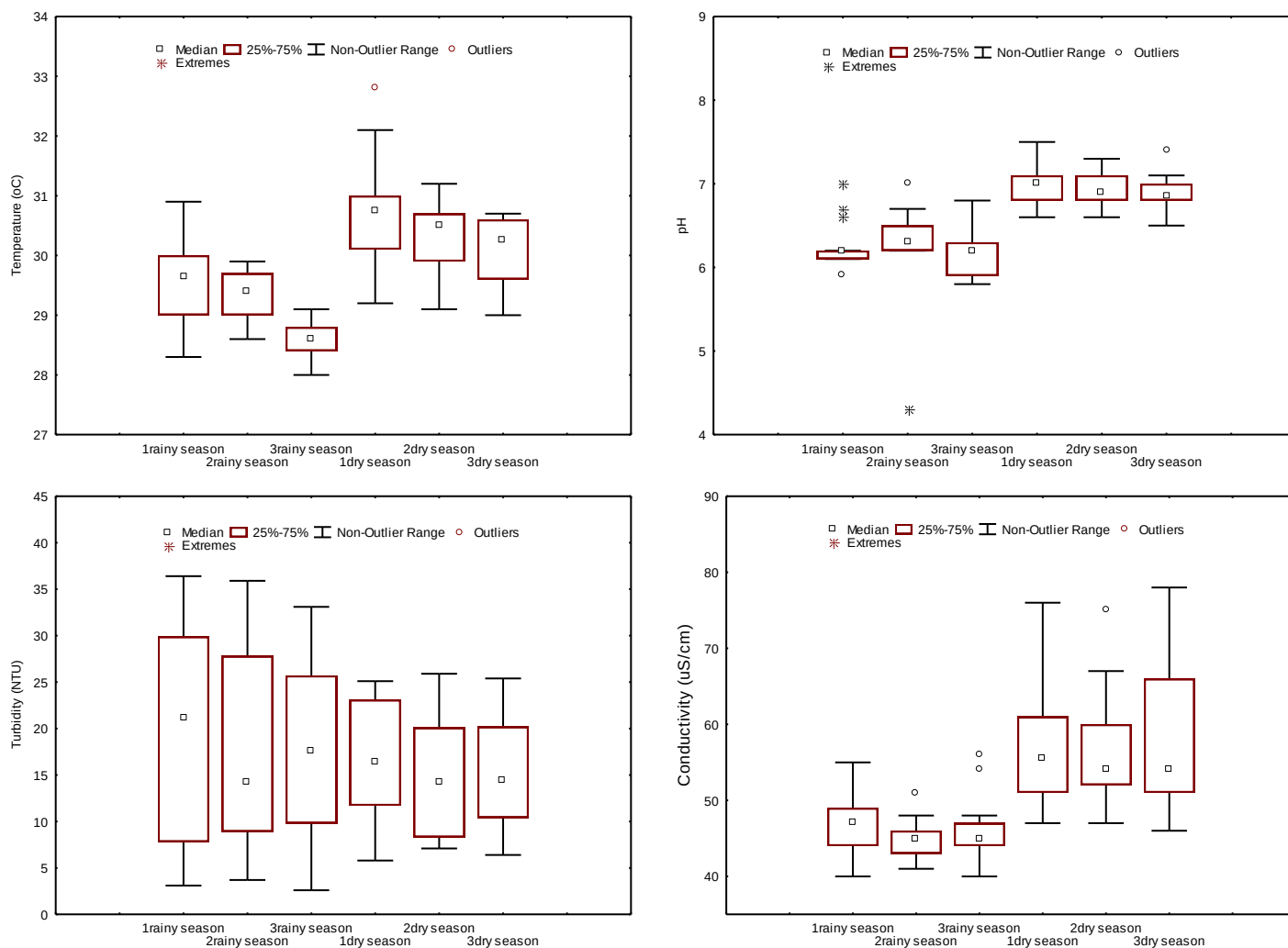


Figure 2. Physico-chemical parameters variability of water in the Tucuuruí dam

During the drought there was a decrease in pH as it increased the depth of collection. Silva et al. (2007) who studied the effect of seasonality on water quality in the sub basin of the Ponte River (Ouro Preto-MG) found pH values ranging from 5.93 to 7.71 that are consistent with the values found in this work [16].

In the Amazonian rivers, the pH of natural waters is associated with the conditions of electrolytic water. Thus, the water bodies that are near estuaries rich in electrolytes, have a pH close to neutrality (6.5 to 6.9), while the waters rich in humic and fulvic acids are normally (4.5 to 6.1) [17].

In the rainy season (Figure 2) the maximum value for turbidity (36.4 NTU), occurred in the superficial layer of the NP station, possibly caused by increased rainfall, characteristic of the collection period, acting on the material deposited in the soil (silt, sand and clay), carrying them to the water body. The values are consistent with the standards established by law.

The erosion of reservoir banks of Tucuuruí power plant is already evident and contributes to increased turbidity in the water of the study area. Pereira et al. (2007) found turbidity ranging from 17 to 34 NTU in the Murucupi river consistent with estimated values for the mean of this study during the rainy season and dry season respectively (18.46 ± 10.8 NTU) and (15.54 ± 6.2 NTU), below the levels established by CONAMA Resolution 357-05 (100 NTU) [17].

In terms of the average value of conductivity during the rainy season (Figure 2) was estimated at 46 ± 3.6 µS/cm, which is possibly related to the dissolution of carbonate rocks. The intense activity of the decomposition of submerged biomass, coupled with mineralization caused by the decrease of

oxygen in most seasons of the rainy season, can contribute to high conductivity [18]. The increase of conductivity in the dry season can be explained by the presence of strong electrolytes as ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- e SO_4^{2-} [19].

The results for the heavy metals in two seasons and three water depths in the Tucuruí dam are presented in Table 4 and Table 5. Two distinct behaviors were observed for the chemical elements: a group with high concentrations when the rainfall is relatively high (May), notably, Al and Fe and the concentration of these decreases as the rainfall is low (September) and a reverse behavior was observed for Ba, Mn, Zn and Cd, which showed an increase in levels of drought (Figure 3). The highest levels of metals in solution are observed in surface horizons, certainly due to the presence of less stable forms and the higher content of organic matter in these horizons [20].

Table 4. Al and Ba distribution of the Tucuruí dam water

Stations	Al ($\mu\text{g/L}$)						Ba ($\mu\text{g/L}$)					
	Rainy season			Dry season			Rainy season			Dry season		
	1	2	3	1	2	3	1	2	3	1	2	3
MI	560.91	584.19	504.78	44.17	40.84	51.64	21.98	22.62	22.61	23.65	24.40	23.84
MJV	210.43	208.36	370.83	39.06	17.51	17.51	34.96	34.84	25.32	52.06	52.74	60.02
ML	109.50	203.17	318.06	28.73	13.08	15.28	33.00	32.65	33.95	45.94	36.15	33.55
M3	231.91	189.88	272.76	9.18	4.74	7.83	29.06	29.07	23.08	27.63	27.10	27.01
MB	63.30	123.86	384.53	16.37	8.85	11.59	24.54	22.09	25.72	17.92	18.25	18.27
MT	27.03	17.00	212.91	23.47	21.02	19.15	40.84	40.79	51.39	64.64	62.54	67.88
MR	23.86	19.78	150.46	26.83	20.46	56.78	44.77	44.08	51.36	46.20	45.53	104.19
B1	128.11	271.83	320.73	1.64	10.71	6.83	35.08	30.33	28.81	29.15	29.06	30.15
C1	57.55	29.96	2.07	38.28	44.98	27.07	42.96	37.63	47.20	53.68	46.79	49.00
C2	19.22	16.15	283.28	44.09	23.84	31.69	49.86	45.28	51.25	78.54	60.67	62.27
MBB	322.66	360.64	370.26	33.45	16.73	10.88	25.81	24.89	26.80	38.11	29.18	29.46
M1	208.19	289.95	409.06	4.22	10.55	9.10	27.25	27.09	27.17	29.98	30.12	32.58
NP	420.84	472.23	473.10	6.46	1.50	6.67	25.40	27.92	26.58	34.15	34.57	34.39
JT	454.38	373.83	373.65	2.74	14.40	6.38	28.18	14.20	17.76	35.43	32.71	36.08
Mean	202.70	225.77	317.60	22.76	17.80	19.88	33.12	30.96	32.78	41.22	37.84	43.47
SD	176.68	178.95	130.81	15.85	12.33	16.47	8.61	8.90	12.06	16.78	13.65	23.13
RSD (%)	87.20	70.00	41.20	69.60	69.30	82.80	26.00	28.80	36.80	40.70	36.10	53.20
Minimum	19.22	17.00	2.07	1.64	1.50	6.38	21.98	14.20	17.76	17.92	18.25	18.27
Maximum	560.91	584.19	504.78	44.17	44.98	56.78	49.86	45.28	51.39	78.54	62.54	104.19

SD - Standard Deviation; RSD - Relative Standard Deviation; 1 - Surface; 2 - Intermediate; 3 - Bottom

In water, the Al is complexed and influenced by pH, temperature and the presence of ligands. The solubility is low in pH between 5.5 and 6.0. Al should have higher concentrations at depth, where the pH is lower and can occur anaerobically. If the stratification and consequent anaerobiosis is not too strong, the Al content decreases the water body as a whole, as it moves away from the rainy season.

Although the concentration of Al in natural waters is usually small, about $10^{-3} \mu\text{g/L}$ at pH = 5, in waters with low pH, the concentration of Al tends to increase, and this fact justifies the high concentrations of Al found on stations MI, ML, MB, and C2 to the bottom layers [2].

In the rainy season (Figure 3) only 10 samples were in accordance for Al, established by CONAMA 357/2005 with the maximum value of $100 \mu\text{g/L}$. Pereira et al. (2007) evaluated the Al in the industrial area. The average value found for the element was $356.0 \mu\text{g/L}$, 2.65 times above the average value of $134.42 \mu\text{g/L}$. The high Al concentrations in the rainy season almost certainly present as colloidal Al, most likely polymeric, which has low bioavailability [17].

From the boxplot for the chemical elements, it was concluded that during the period of greatest rainfall was considerable variability in the levels of Al in the superficial and intermediate layers, this did not occur in the dry season. All results for Al in the dry season are in accordance with the 357/2005.

Table 5. Fe and Mn distribution of the Tucuruí dam water

Stations	Fe (µg/L)						Mn (µg/L)					
	Rainy season			Dry season			Rainy season			Dry season		
	1	2	3	1	2	3	1	2	3	1	2	3
MI	623.88	651.63	604.82	83.35	133.30	100.06	3.36	3.40	2.97	17.04	23.99	19.42
MJV	448.11	438.58	552.95	144.64	145.11	249.49	2.53	2.98	3.41	20.54	24.13	25.43
ML	405.96	491.09	719.91	129.54	102.72	112.39	2.59	3.16	5.59	17.96	23.32	37.68
M3	490.68	444.74	485.97	60.96	56.05	66.37	3.12	2.78	2.79	18.31	19.39	20.98
MB	242.30	293.53	559.85	82.99	84.03	84.50	5.25	2.38	5.03	4.08	4.36	4.89
MT	318.09	288.57	569.50	339.16	297.93	384.10	3.00	2.24	3.74	19.41	18.80	30.84
MR	343.99	328.72	1,297	102.61	75.61	1,170	6.13	5.57	4.58	13.41	10.27	230.39
B1	343.36	504.16	558.48	22.90	32.69	25.96	2.87	3.79	3.64	6.96	7.94	7.88
C1	501.82	277.47	223.94	298.24	279.11	283.88	6.41	3.21	3.29	48.66	33.99	62.27
C2	224.05	348.92	2,186	384.03	153.62	353.60	2.85	4.31	2.24	78.08	25.71	29.46
MBB	454.43	490.50	465.34	122.11	36.81	51.17	2.99	4.12	7.21	42.32	8.55	12.22
M1	439.82	499.73	622.13	51.59	51.48	86.65	2.89	3.21	5.74	21.17	19.59	46.44
NP	615.02	688.40	667.63	297.40	290.86	323.75	5.82	6.55	5.97	47.97	48.92	55.40
JT	676.15	624.99	612.05	357.97	115.09	420.07	8.36	4.40	4.02	72.07	30.57	72.08
Mean	437.66	455.07	723.26	176.97	132.45	265.17	4.15	3.72	4.30	30.57	21.39	46.81
SD	137.86	136.4	479.42	128.15	93.16	294.44	1.86	1.20	1.42	23.38	11.80	56.59
RSD (%)	31.50	30.00	66.30	72.40	70.30	111.00	44.80	32.30	33.00	76.50	55.20	120.90
Minimum	224.05	288.57	223.94	22.90	32.69	51.17	2.53	2.24	2.24	4.08	4.36	4.89
Maximum	676.15	688.40	2,186	384.16	297.93	1,170	8.36	6.55	7.21	78.09	48.92	230.39

SD - Standard Deviation; RSD - Relative Standard Deviation; 1 - Surface; 2 - Intermediate; 3 - Bottom

The Ba is an element geochemically little mobile. The average level is 595 mg/kg in igneous rocks. Low concentrations of Ba²⁺ surface waters are the result of the low solubility of Ba sulfate (barite) and the fact that this element is easily adsorbed by hydroxides and metal oxides may occur naturally in water in the form of carbonate minerals and in some sources from industrial activities and the extraction of bauxite [17].

In the rainy season (Figure 3) on the Ba showed variability relative (Figure 3) could be explained by the low solubility of barite, which is the main source of enrichment of the element to the biota, as in the dry season there was an increase in levels, this may be associated with reduction in lake volume indicating that the element is not added to the lake by solubilization of minerals from the soil which forms the dam area [21].

Fe is not the main cation in continental surface waters, but is usually studied in rivers, lakes and reservoirs because they constitute the essential trace element for living beings, but also has the biogeochemical cycle interfering with other nutrients, especially phosphorus [21].

The prevalence of each form depends on the pH, for example, with a pH above 4.8 the solubility of the ion Fe³⁺ is less than 10 µg/L. Moreover, its concentration is low (even zero) in oxygenated waters exceptionally, in the form of Fe(OH)₃ colloids is very small in oxidizing environments, but at low water (low oxygen concentrations) have Fe generally between 1,000 and 10,000 µg/L. The solubility of iron also depends on the concentrations of SO₄²⁻ and CO₂ present in the aquatic system [2].

During the rainy season (Figure 3) the highest concentrations of Fe are given in the bottom layer of the seasons, while the lowest concentrations occurred in the surface layer. These values can be justified due to the effects of seasonality on dark minerals (mafic) patients with Fe: magnetite, biotite, pyrite, pyroxene, amphibole. The highest concentration of Fe occurred in the bottom layers in most monitoring stations, not presenting itself in terms of average, according to CONAMA Resolution 357/2005 that determines the maximum value of 300 µg/L for Fe. In the dry period, a decrease of over 75 % on average in terms of Fe, this decrease may be related to decreased rainfall acting on Fe-rich minerals, showing the relationship between the mobility of this metal and seasonality.

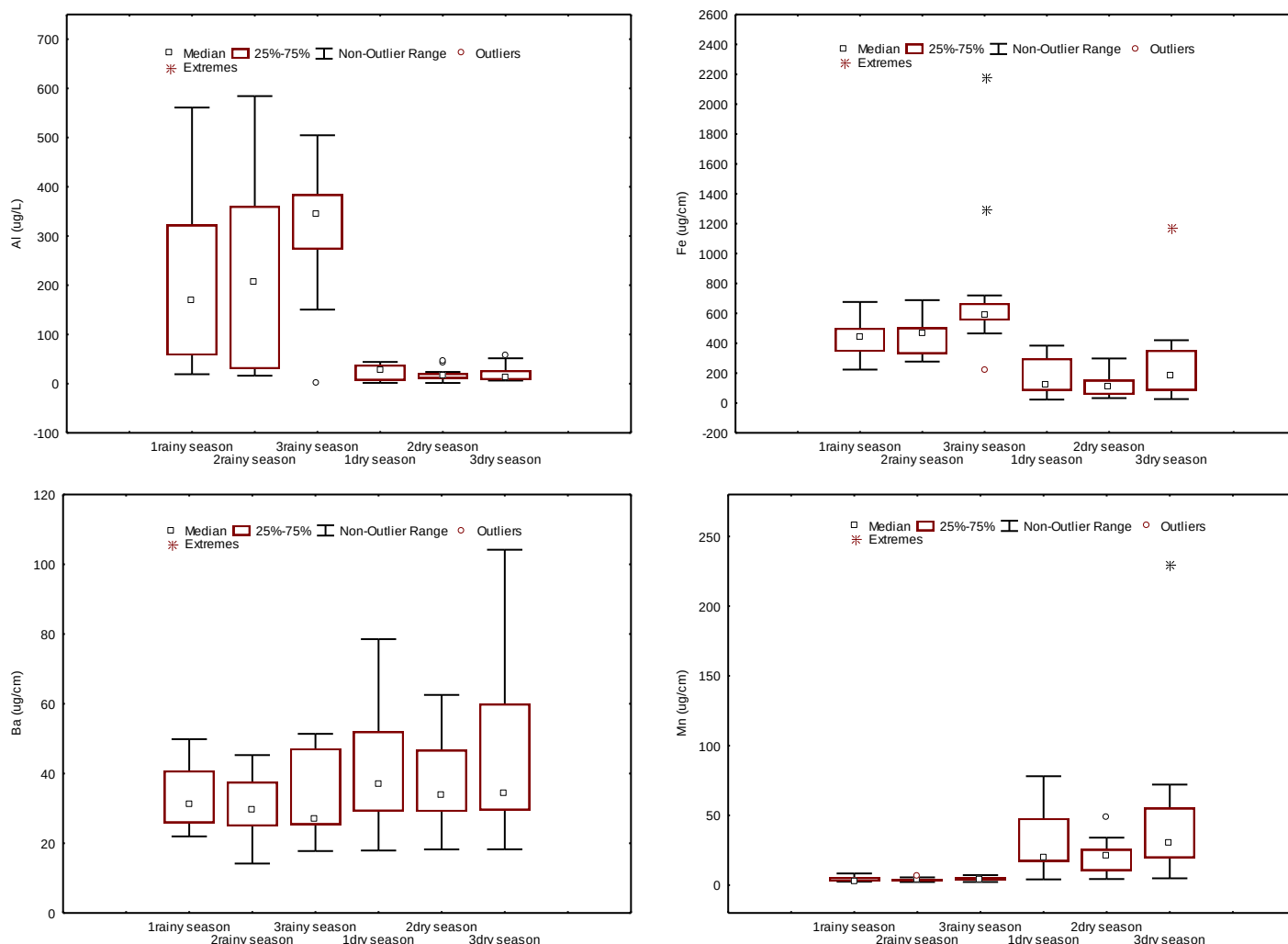


Figure 3. Metals variability in water from the Tucuruí dam

The behavior of Mn in the waters is very similar to Fe in their most diverse, at concentrations below 0.001 µg/L in natural surface water. The contribution of submerged land for the reservoir characteristics limnochemical Tucuruí can be especially important for adsorption into its components and the dissolution of Mn oxides and hydroxides in reducing environment [17]. Mn data suggest that the bottom waters in the dry season are anoxic (higher Mn^{2+}) than in the wet season when manganese is oxidised and presumably precipitated as manganese hydrous oxides.

In terms of average levels of Mn in the dry season ($32,93 \pm 30,6$ µg/L) (Figure 3) has risen by about eight times compared to the rainy season ($4,16 \pm 1,5$ µg/L) Mn concentrations are within the limits allowed by the law of which is to CONAMA 357-2005 (100 µg/L).

Zn concentration in the rainy season ranged from <0,05 µg/L a 39,48 µg/L. The highest Zn concentrations were found in the surface layer of C1 station (39,48 µg/L) and the bottom layer of the MR station (24,24 µg/L), while the lowest concentrations occurred in the surface layer and intermediate station JT, in the same period. All values for the element Zn are in accordance with the maximum allowable value (MAV) by legislation (180 µg/L) in both seasons. At some points the Zn can not be detected by the technique of ICP-AES with a detection limit of 0,05 µg/L.

The Cd was found at most stations to values below the detection limit of the analytical technique (<0,55 µg/L), Cd is usually present in natural waters at concentrations below 1 µg/L and is bioaccumulative.

The influence of seasonality was demonstrated through the analysis of single factor ANOVA for the parameters temperature, pH, conductivity, Al, Fe and Mn ($F_{calculated} > F_{critical}$), turbidity and Ba showed no significant differences between the two periods. Kamble *et al.* (2009) also showed that

significantly influences the seasonality of some physical and chemical parameters [22]. The depth of the water column influenced the temperature and Fe in the rainy season is not determinant in the variability of other parameters. From the bivariate analysis, there was an inverse correlation between Mn in the middle layer, in the dry season with the pH of the surface layer in the dry period (-0.718) showing that the decrease in pH of natural waters causes an increased concentration of metal ions dissolved in water slightly acidic.

Other important relationships occurred between the variables, especially the Pearson's correlations (Table between Al and turbid surface layer (0.727), intermediate (0.840) and bottom (0.760), and turbidity Al intermediate layer (0.835) and bottom (0.769) of the rainy season; Fe layer, the rainy season turbidity layer (0.732) rainy season, Fe layer (0.767) and intermediate (0.882), with the rainy season turbidity middle tier of the rainy season; Fe layer, the rainy season turbidity layer background rainy season (0.751) that can demonstrate that increased particulate matter carried by the rains is responsible for the increased turbidity in the rainy season is positively correlated with increasing concentration of Al and Fe in this period [23].

Opposite pattern was observed for Mn in the middle layer that correlated positively with turbidity in the bottom layer in the dry season (0.744) occurs when the reduction of particulate matter. Inverse correlations were found between Al and the surface layer temperature (-0.762), temperature and Al intermediate layer (-0.758), temperature and Fe layer, the rainy season (-0.708) Mn surface layer, the rainy season and temperature intermediate layer, drought period (-0.740), the negative correlations found between Al, Fe and Mn with temperature show that there is influence of climatic conditions on the concentration of elements present in the reservoir.

The Ba showed an opposite behavior with temperature, the correlations were found with the temperature of the Ba layer (0.705) and intermediate (0.751) rainy season; Ba with temperature layer, the rainy season (0.754), with the drought period Ba temperature intermediate layer, the rainy season (0.730). The Ba was correlated to the conductivity may indicate that the element is available in ionic form and that the rock-forming minerals in the region have soluble Ba in its constitution or may be related to contamination of anthropogenic origin related to the use of products such as fluossilicato Ba (BaSF_6), used to neutralize soil acidity.

The presence of Ba in the ionic form is evidenced by the increase of element concentration in the dry season when there are reductions in the volume of lake water. The correlations for the Ba and conductivity were superficial layer (0.763) rainy season; Ba background layer, with the drought period the surface layer conductivity rainy season (0.744); Ba layer (0.702), intermediate (0.760) and bottom (0.764) with conductivity intermediate layer of the rainy season; Ba surface layer (0.755) and bottom (.762) with the conductivity in the bottom layer of the rainy season; Ba drought period with conductivity bottom layer of the rainy season (0.726). Similar behavior was found for Fe also correlated with the surface layer conductivity, the rainy season (0.763); Fe bottom layer, with the drought period the surface layer conductivity, the rainy season (0.748) with the Fe bottom layer of conductivity rainy season (0.743); Fe drought period with conductivity bottom layer of the rainy season (0.713).

The elements Ba, Al and Fe and Ba were inversely correlated indicating different origins for the two elements. The Ba in the surface layer was correlated (-0.748), intermediate (-0.743) and bottom (-0.749) with the Al surface layer during the rainy season; Ba layer (-0.816), intermediate (-0.749) and bottom (-0.783) Al intermediate layer with the rainy season; Ba layer (-0.765) and bottom (-0.742) with Al bottom layer during the rainy season. Similar behavior was observed for Fe intermediate layer with bottom layer Ba rainy season (-0.711). Behavior with the exception of the Fe bottom layer Ba drought period (0.885) Fe bottom layer with Ba drought period (0.765) which showed a direct correlation demonstrating that the depth of the water column in some cases can change the behavior of the elements.

Fe and Al and Fe and Mn were positively correlated showing that these elements are part of the geochemistry of the region and are bound by the same source rocks forming minerals in the reservoir. Correlations were surface layer of Fe (0.865) and intermediate (0.896), the rainy season with the Al surface layer of the rainy season; Fe layer (0.745) and intermediate (0.936), with rainy season rainy Al intermediate layer; Fe intermediate layer with Al bottom layer wet season (0.758); Mn with the Fe

surface layer dry period (0.805), Mn with Fe tier drought period (0.701), Mn with Fe bottom layer drought period (0.938). The only exception was the Fe surface layer (-0.816), intermediate (-0.749) and bottom (-0.783), with rainy season rainy Al intermediate layer.

Table 6. Bivariate correlation between chemical and physico-chemical parameters in water from the Tucuruí dam

Variables	Correlation factor	Al	Ba	Fe	Mn	Temp.	pH	Conduct.	Turbidity
Al	PC	1,000							
	Sig.	-							
Ba	PC	-0,449**	1,000						
	Sig.	0,000	-						
Fe	PC	0,801**	-0,118**	1,000					
	Sig.	0,000	0,306	-					
Mn	PC	-0,435**	0,432	-0,222	1,000				
	Sig.	0,000	0,000	0,052	-				
Temp.	PC	-0,720**	0,359**	-0,726**	0,240	1,000			
	Sig.	0,000	0,001	0,000	0,036	-			
pH	PC	-0,546**	0,078	-0,716**	0,352	0,600**	1,000		
	Sig.	0,000	0,501	0,000	0,002	0,000	-		
Conduct.	PC	-0,581**	0,331**	-0,559**	0,344**	0,641**	0,508**	1,000	
	Sig.	0,000	0,003	0,000	0,002	0,000	0,000	-	
Turbidity	PC	0,576**	-0,104	0,475**	0,089	-0,344**	-0,114**	-0,252*	1,000
	Sig.	0,000	0,366	0,000	0,441	0,002	0,325	0,027	---

Conduct.: conductivity; Temp.: Temperature; (Sig) Significance; (**) Correlation with significance level of 0.01 or 99%; (*) Correlation with significance level 0.05 or 95%; (PC) Pearson Correlation.

Conclusion

From the results proposed in this study can be proven the influence of seasonality on the physical and chemical characteristics and concentration of metals in different monitoring stations resulting mainly from climatological factors, particularly rainfall depth of the water column had little influence on the parameters studied.

The highest concentrations for metals were found in the bottom layer of the monitoring stations during the month of May, the period of greatest rainfall, justified by the characteristics of the soil due to the entrainment heavy particles to the aquatic ecosystem. This impact may be related to the illegal occupation and erosion along the banks of the Tocantins River basins.

Al and Fe in the rainy season have been at odds with the standards adopted by Resolution 357-05 of the Federal CONAMA, the population that consume untreated water in the dam should be advised by the agency responsible to drink no water during this period.

Acknowledgments

Thanks to Central Laboratory (LACEN) of the ELETRONORTE (Northern Electrical Central of the Brazil), CNPq, ANEEL and Tucuruí city hall which provided logistical support for this Project.

References

- [1] A.M. Hansen; L.C. Gonzalez-Marquez. Scenarios of metal concentrations in the Arcediano Dam (State of Jalisco, Mexico). *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances & Environmental Engineering*, 45:1 (2010) 99-106.
- [2] A. Maci; M. Cara; A. Doko; J. Merkuri; M. Huta; A. Ajazi. The monitoration of water quality of Shkumbin river and its impact on the soil. *Journal of International Environmental Application & Science*, 43(2009) 285-292.
- [3] P.K. Rai. Seasonal monitoring of heavy metals and physicochemical characteristics in a lentic ecosystem of subtropical industrial region, India. *Environmental Monitoring and Assessment*, 165(2010) 407-433.
- [4] A.O. Oyewale; I. Musa. Pollution assessment of the lower basin of Lakes Kainji/Jebba, Nigeria: Heavy metal status of the waters, sediments and fishes. *Environmental Geochemistry and Health*, 28(2006) 273-281.
- [5] J.M. Nieto; A.M. Sarmiento; M. Olías; C.R. Canovas; I. Riba; J.T. Kalman; A. Delvals. Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva. Estuary. *Environment International*, 33:4(2007)_445-455.
- [6] S. Abdullah; M.A. Iqbal; M.I. Fazil. Physico chemical analysis of the freshwater at Kundalika Dam, Upli, Dist. *Global Journal of Environmental Research*, 4:1(2010) 01-05.
- [7] G.P.F. Arrifano; R.C.R. Martín-Doimeadios; M. Jiménez-Moreno; V. Ramírez-Mateos; N.F.S. Silva; J.R. Souza-Monteiro; M. Augusto-Oliveira; R.S.O. Paraense; B.M. Macchi; J.L.M. Nascimento; M. E. Crespo-Lopez. Large-scale projects in the amazon and human exposure to mercury: The case-study of the Tucuruí Dam. *Ecotoxicology and Environmental Safety*, 147(2018) 299-305.
- [8] M.P. Curtarelli; I. Ogashawara; C.A.S. Araújo; J.A. Lorenzzetti; J..A.D. Leão; E. Alcântara; J.L. Stech. Carbon dioxide emissions from Tucuruí reservoir (Amazon biome): New findings based on three-dimensional ecological model simulations. *Science of The Total Environment*, 551-552(2016) 676-694.
- [9] C.C. Arantes; DB. Fitzgerald; D.J. Hoeinghaus; K.O. Winemiller. Impacts of hydroelectric dams on fishes and fisheries in tropical rivers through the lens of functional traits. *Current Opinion in Environmental Sustainability*, 37(2019) 28-40.
- [10] J.J.L.S. Silva; M. Marques; J.M. Damásio. Impactos do desenvolvimento do potencial hidroelétrico sobre os ecossistemas aquáticos do rio Tocantins. *Ambi-Água*, 5:1 (2010) 189-203.
- [11] S.E. Shinde; T.S. Pathan; K.S. Raut; P.R. More; D.L. Sonawane. Seasonal variations in physico-chemical characteristics of Harsool - Savangi dam, district Aurangabad, India. *Ecscan*, 4:1 (2010) 37-44.
- [12] P. Zeilhofer; R.M. Moura. Hydrological changes in the northern Pantanal caused by the Manso dam: Impact analysis and suggestions for mitigation. *Ecological Engineering*, 35:1 (2009) 105-117.
- [13] American Public Health Association (APHA). Standard Methods for Examination of Water and Wastewater, American Public Health Association, 16 Th ed. Washington, 1995.

- [14] CETESB. (1998) Guia de coleta e preservação de amostras de águas, 150 p. CONAMA. (2005) Resolução do Conselho Nacional do Meio Ambiente, nº 357 de 17 de março de 2005, p. 9-24.
- [15] S. Ibechaobi; A. Gupta. Water quality in few lotic ecosystems of Manipur, India. *Pollution Research*, 252(2006) 343-346.
- [16] A.K.G. Silva; D.A. Machado; H.A.J. Nalini; J.C. Lena. A qualidade das águas na região dos garimpos de topázio imperial na sub-bacia do rio da Ponte, Ouro Preto-MG. *Revista da Escola de Minas, Ouro Preto*, 604(2007) 603-611.
- [17] S.F.P. Pereira; M.A. Lima; K.H. Freitas; C.S. Mescouto; A.F. Saraiva. Estudo químico ambiental do rio Murucupi - Barcarena, PA, Brasil, área impactada pela produção de alumínio. *Revista Ambiente & Água, Taubaté*, 23(2007) 62-82.
- [18] M.A.B. Almeida.; A. Schwarzbold. Avaliação Sazonal da Qualidade das Águas do Arroio da Cria Montenegro, RS com aplicação de um índice de qualidade de água IQA. *Revista Brasileira de Recursos Hídricos*, 81(2003) 81-97.
- [19] M. Zengin; S. Karakaplan; I. Ersoy. Determination of irrigation water quality of Lake Beysehir and other water sources used in irrigation of Cumra Plain. *Asian Journal of Chemistry*, 201(2008) 694-704.
- [20] E. Basso. Alteration of the water balance of lakes. *Lakes and Reservoirs: Research and Management*, 51(2000) 5-9.
- [21] R.G. Miranda; S.F.P. Pereira; G.R. Oliveira; D.T.V. Alves. Qualidade dos recursos hídricos da Amazônia - Rio Tapajós: avaliação de caso em relação aos elementos químicos e parâmetros físico-químicos. *Revista Ambiente & Água*, 4(2009) 75-92.
- [22] S.M. Kamble; A.H. Kamble; S.G. Narke. Study of physico-chemical parameters of Ruti dam. *Journal of Aquatic Biology*, 24:2(2009) 86-89.
- [23] S.K. Pawar; V.R. Madlapure; R.H. Tale; J.S. Pulle. Seasonal variations in water transparency, total solids, total dissolved solids, total suspended solids of Sirur dam water, Nanded, India. *Ecology, Environment and Conservation*, 121(2006) 171-173.