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Contiguous urban rivers should not be necessarily submitted to the same management plan: the case of Tietê and Pinheiros Rivers (São Paulo-Brazil)

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ABSTRACT

The management of urban water resources plays an important role for developing countries. The Tietê and Pinheiros Rivers (São Paulo, Brazil) are affected by domestic and industrial effluents and by the diffuse pollution. This research aimed to quantify 134 variables in the water of Tietê and Pinheiros Rivers (approximately 7,200 and 6,600 analyses, respectively) from August 2007 to December 2008. The idea was to verify if the fact that both rivers are located in the same basin is enough to consider the application of a single management plan for both. Data showed that the rivers presented significant anthropogenic interference. The results suggested that such rivers must be subjected to individual management plans since there were exclusive occurrences (variables that were only detected in one of the rivers). Moreover, there was a statistically significant difference between rainy and dry periods for eleven variables ($p^* < 0.05$, ANOVA), reinforcing the special importance of the temporal component within the monitoring program. It is expected that this study subsidize environmental recovery programs in the Tietê River, to which is recommendable to focus on prosecution of illegal wastewater releases, and in the Pinheiros River, to which special attention is suggested to the pollution derived from the pesticides load to the water body.

Key words: environmental monitoring, metropolitan region of São Paulo (MRSP), urban rivers, water pollution, water quality, watershed management.

INTRODUCTION

Urban rivers are usually submitted to various anthropogenic impacts not only on their quantitative aspects, but also on their qualitative characteristics. These effects include decreasing of the water quality, threatening of the aquatic biota, changing of the pristine conditions of flow and of other hydraulic conditions. Many recent researches have been linking land-use and vegetation presence or absence with the nutrient levels in the water bodies. Industrial, domestic effluents and runoff might contribute to the increase of heavy metals concentrations in the water, as well as organic and inorganic compounds. Besides, factors like geomorphology and climate also play an important role on the water quality (Turner and Rabalais 2003, Blanchoud et al. 2007, Galbraith and Burns 2007, Bedore et al. 2008, Göbel et al. 2007, Miserendino et al. 2008).

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Compared to non-urban aquatic systems, urban rivers tend to be more influenced by runoff from stormflows events through diffuse pollution. These stormflows are frequently able to increase total suspended solids, cadmium, copper, lead and zinc concentrations, as well as sodium and sulfate (from road deicers), and to decrease dissolved oxygen. Moreover, macroinvertebrate communities in urban rivers have few sensitive species and are dominated by tolerant species (Fuchs et al. 1997, Tong and Chen 2002, Gray 2004). One of the greatest environmental problems in developing countries is to control the diffuse pollution originated from urban and rural runoff (Tucci 2004). However, in these countries, the relative importance of diffuse pollution is smaller than the importance of pollution from point sources. Therefore, Brazilian urban rivers are subordinated not only to runoff from stormflows, but also, and mainly, to domestic and industrial discharges, which contribute to the water quality decrease. Summarily, wastewater and stormwater management is progressively becoming a complex task for the megacities around the world (Varis et al. 2006).

The Tietê and Pinheiros Rivers are two aquatic systems located in São Paulo State (Southeast Brazil). According to Abraham et al. (2007), it is assumed that untreated domestic wastewater from 10 million inhabitants is daily discharged into the Tietê River. These authors observed high concentrations of pathogenic microorganisms (*E. coli*, *Shiguella flexneri* and *S. boydii*) in the Tietê River (in the city of São Paulo), which could show that the poor water quality of this aquatic system might even cause negative effects on public health. Therefore, an accented pollution process has been occurring in the Tietê River since 1950 as a consequence of domestic and industrial effluents release. The Tietê River flows through São Paulo State and receives the water of the Pinheiros River in São Paulo City. The Pinheiros River's flow direction had been reversed into Billings Reservoir until 1992, in order to increase the electricity generation. After 1992, however, with the increase of the pollution process, this procedure was prohibited, except in cases of flood control in São Paulo (Braga 2000, Silva et al. 2002). In this last case, Pedreira Dam and Pumping Station convey the water from the Pinheiros River to the reservoir in order to prevent flooding in the urban area.

The main motivation for this research was to find out if two contiguous urban rivers tend to be similar or different when it comes to water quality. Thus, a consequence of this study was the analysis of the relative importance of the spatial scale (in terms of basin or sub-basin) in the handling of water resources. The Tietê and Pinheiros Rivers may be included in the same basin or, contrarily, in different sub-basins, depending on the spatial scale. The present study was performed to answer the following question: *Is it possible to delineate the same water quality management plan for both rivers or is it imperative to establish different plans for each aquatic system, disregarding their spatial proximity and taking into account their peculiarities and exclusive occurrences of some water variables?*

To reach an accurate answer, this study aimed to determine the specific characteristics of the water quality of these two urban rivers in São Paulo State (Brazil) through an intense monitoring program that was conducted for about seventeen months. As a specific objective, this research aimed to compare the results of the Tietê and Pinheiros Rivers, considering the contributions of the drainage sub-basins for each aquatic system. The idea was to investigate the influence and the relative importance of the land use patterns of each urban sub-basin in the presence (and, consequently, in the concentrations) or in the absence of some water quality variables in samples of each river.

MATERIALS AND METHODS

Two sampling stations were considered (Fig. 1), one of them in the Tietê River (TIE), immediately upstream to its confluence with the Pinheiros River, and other in the Pinheiros River (PIN), about 15 km upstream of its mouth.

Sampling campaigns were performed from August 2007 to December 2008, through the quantification of 134 biological, chemical and physical variables in the water, following APHA (2005) methods. The laboratories in charge of all the analyses were *Laboratório Ambiental* and *Ecolabor* (both certified by ABNT – the Brazilian Authority on Technical Norms). The frequency of analysis varied from substance to substance (e.g. weekly, biweekly, monthly, bimonthly), but the total number of data was about 7,200 for the Tietê

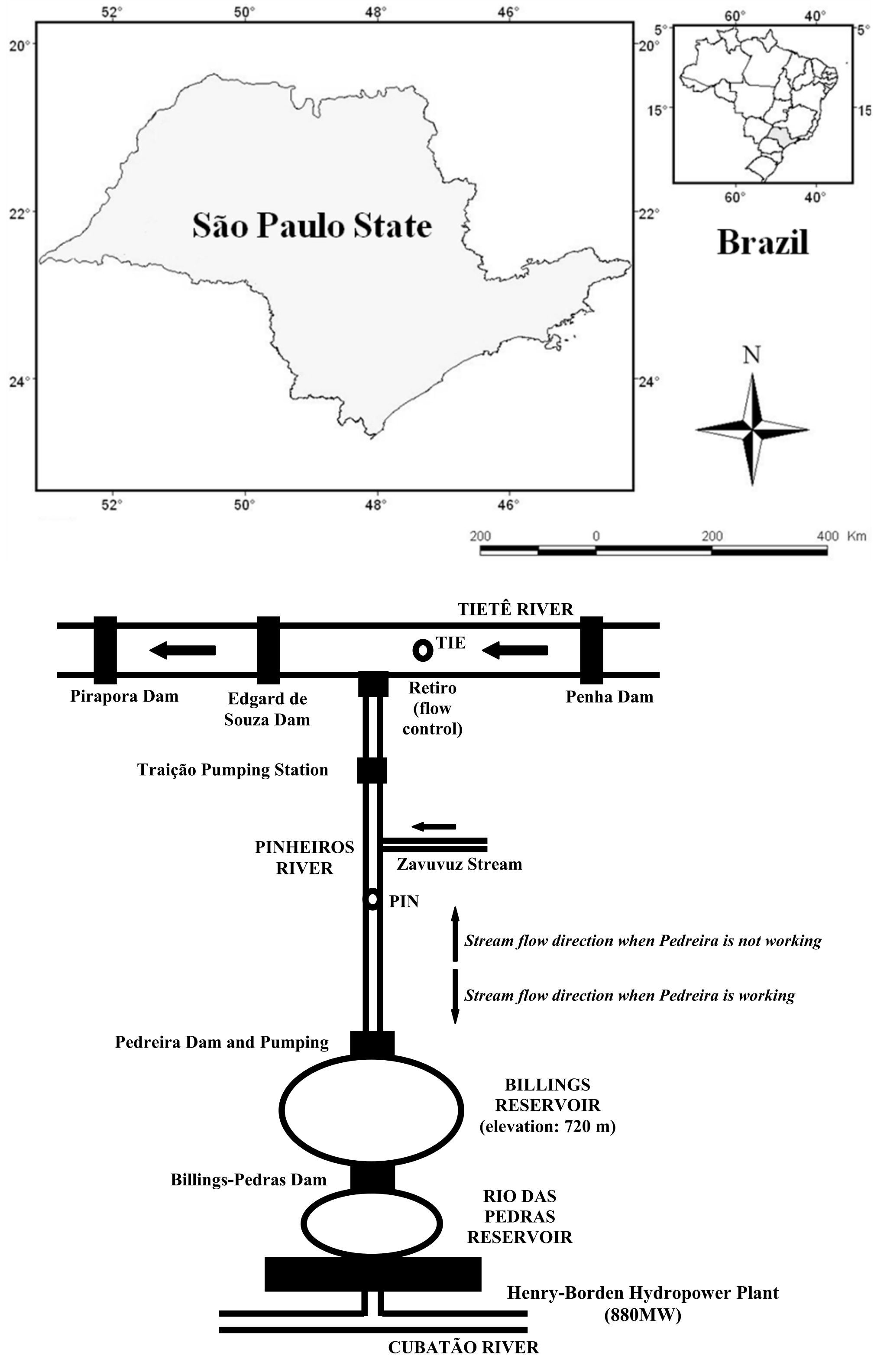

Fig. 1 – Scheme of sampling stations in the Tietê (TIE) and Pinheiros (PIN) Rivers, which are located in São Paulo State (Brazil).

River and 6,600 for the Pinheiros River. For this reason, we present not only the mean, minimum and maximum values or concentrations of each variable, but also the coefficient of variation (C.V.) for each case in order to highlight the temporal component of the monitoring program. The C.V. was calculated by dividing the standard deviation by the mean of a given variable and multiplying the result by 100%.

For practical purposes, all the variables were allocated in three possible cases according to their respective concentrations and values:

i) *Case A ("exclusivity")* – the variable was detected either in the Tietê River or in the Pinheiros River;

ii) *Case B ("presence")* – the variable was detected in both rivers:

- Case B-TIE – the maximum value was higher in the Tietê River;
- Case B-PIN – the maximum value was higher in the Pinheiros River;

iii) *Case C ("absence")* – the variable was detected in none of the rivers for all samples, considering the detection limit for each variable.

This division significantly helped the identification of the exclusive occurrences in each river (Case A) and the river whose sample presented the most critical value when the variable was detected in both (Case B). Also, it was useful to segregate those variables that were not observed in the aquatic systems for any sample (Case C). Variables from Cases A and B were submitted to statistical analyses in order to verify the significance of their temporal variation. Therefore, the hydrologic year 2007-2008 was divided into wet period (from October 2007 to March 2008) and dry period (from April to September 2008). The statistical procedures were conducted through the Analysis of Variance (ANOVA) for all detected water variables to assess the differences between the rainy and dry seasons, under the probability of 95% ($p^* < 0.05$). The software Systat 10® was used for this purpose.

RESULTS AND DISCUSSION

The monitoring program results (Table I) are shown for those variables that presented concentrations or values higher than the respective detection limit. All this data are available in the website of the Brazilian State Attorney (http://www.mp.sp.gov.br). The substances are presented in alphabetical order, with their mean, minimum, maximum concentrations and, additionally, the coefficient of variation and the total number of samples for each case. When it comes to the organic compounds, it is important to observe the high concentrations of 1.1-Dichloroethene (maximum of 13.0 $\mu g.L^{-1}$ in the Tietê River and 17.0 $\mu g.L^{-1}$ in the Pinheiros River), Chloroform (maximum of 13.0 $\mu g.L^{-1}$ in the Tietê River and 43.0 $\mu g.L^{-1}$ in the Pinheiros River), Methylene Chloride (maximum of 75.0 $\mu g.L^{-1}$ in the Tietê River and 15.0 $\mu g.L^{-1}$ in the Pinheiros River) and Toluene (reaching 106.0 $\mu g.L^{-1}$ in the Tietê River and 215.0 $\mu g.L^{-1}$ in the Pinheiros River).

Among the metals in the water samples, Lead concentrations were high, particularly in the Tietê River (maximum of 0.15 $\mu g.L^{-1}$), as Chromium concentrations in the Pinheiros River (maximum of 0.31 $mg.L^{-1}$ for both total and trivalent Chromium). Soluble Iron concentrations were higher in the Pinheiros River in comparison to the Tietê River (maximum of 14.3 $mg.L^{-1}$ *versus* 3.8 $mg.L^{-1}$).

Thermotolerant Coliforms concentrations were similar in both rivers, since the highest values were about 10^7 $MPN.L^{-1}$. Enterovirus was detected in both rivers, but *Cryptosporidium* sp. and *Giardia* sp. were absent for all samples. Biochemical Oxygen Demand and Chemical Oxygen Demand were greater in the Tietê River (434 $mg.L^{-1}$ and 860 $mg.L^{-1}$ as maximum values, respectively). The highest concentrations of Total Phosphorus and Ammonia-Nitrogen, which are nutrients straightly related to the eutrophication, were 14.0 $mg.L^{-1}$ (mean: 0.76 $mg.L^{-1}$) and 99.0 $mg.L^{-1}$ (mean: 23.3 $mg.L^{-1}$) for the Tietê River, respectively, and 5.4 $mg.L^{-1}$ (mean: 0.54 $mg.L^{-1}$) and 117 $mg.L^{-1}$ (mean: 25.5 $mg.L^{-1}$) for the Pinheiros River. Dissolved Oxygen concentrations and Turbidity values varied from 0.3 $mg.L^{-1}$ to 7.3 $mg.L^{-1}$ and 2 NTU to 107 NTU (Tietê River) and from < 0.1 $mg.L^{-1}$ to 5.3 $mg.L^{-1}$ and 5 NTU to 217 NTU (Pinheiros River).

Concerning Case A ("exclusivity") variables, 11 variables were only detected in the Tietê River, including 9 organic compounds, 1 metal and 1 metalloid. On

TABLE I

Results of the quantification of biological, chemical and physical variables that were detected in the Tietê and/or in Pinheiros Rivers (São Paulo State, Brazil) with their mean (Mean), minimum (Min) and maximum (Max) values, besides the coefficient of variation (C.V.) and the respective number of samples (N) for each case.

Variable	Tietê River				
	N	Mean	Min	Max	C.V. (%)
1.1-Dichloroethene	15	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	13.0 μg.L^{-1}	172.1
1.2-Diphenylhydrazine	11	0.05 μg.L^{-1}	< 0.05 μg.L^{-1}	0.29 μg.L^{-1}	162.8
2,4-D	16	0.066 μg.L^{-1}	< 0.0024 μg.L^{-1}	0.874 μg.L^{-1}	330.1
2.4-Dichlorophenol	17	0.7 μg.L^{-1}	< 0.003 μg.L^{-1}	8.2 μg.L^{-1}	287.3
2.4-Dinitrotoluene	2	0.1 μg.L^{-1}	< 0.1 μg.L^{-1}	0.1 μg.L^{-1}	33.2
2.4.5-T	17	0.2 μg.L^{-1}	< 0.0042 μg.L^{-1}	3.0 μg.L^{-1}	348.5
2.4.6-Trichlorophenol	17	0.009 μg.L^{-1}	< 0.005 μg.L^{-1}	0.11 μg.L^{-1}	293.9
2-Chlorophenol	2	0.1 μg.L^{-1}	0.1 μg.L^{-1}	0.1 μg.L^{-1}	—
4.4-DDD	12	< 0.0005 μg.L^{-1}	< 0.0005 μg.L^{-1}	< 0.0005 μg.L^{-1}	—
4.4-DDE	12	0.001 μg.L^{-1}	< 0.0005 μg.L^{-1}	0.005 μg.L^{-1}	177.5
Acroleine	10	1.6 μg.L^{-1}	< 0.5 μg.L^{-1}	13 μg.L^{-1}	252.5
Alachlor	14	< 0.0008 μg.L^{-1}	< 0.0008 μg.L^{-1}	< 0.0008 μg.L^{-1}	—
Aldrin+Dieldrin	16	< 0.0007 μg.L^{-1}	< 0.0007 μg.L^{-1}	< 0.0007 μg.L^{-1}	—
Alfa-BHC	13	0.005 μg.L^{-1}	< 0.0008 μg.L^{-1}	0.062 μg.L^{-1}	332.5
Aluminum (soluble)	18	0.42 mg.L^{-1}	< 0.1 mg.L^{-1}	2.3 mg.L^{-1}	120.0
Ammonia-nitrogen	331	23.3 mg.L^{-1}	0.2 mg.L^{-1}	99.0 mg.L^{-1}	61.2
Anthracene	13	0.043 μg.L^{-1}	< 0.012 μg.L^{-1}	0.486 μg.L^{-1}	310.2
Antimonium	18	0.0046 μg.L^{-1}	< 0.0019 μg.L^{-1}	15.0 μg.L^{-1}	157.5
Apparent color	457	304 C.U.	3 C.U.	956 C.U.	61.6
Asbestos*	13	4.4 Mf.L^{-1}	< 1.0 Mf.L^{-1}	7.4 Mf.L^{-1}	51.0
Barium	18	0.045 mg.L^{-1}	< 0.01 mg.L^{-1}	0.078 mg.L^{-1}	47.9
Bentazon	17	0.2 μg.L^{-1}	< 0.0042 μg.L^{-1}	1.4 μg.L^{-1}	206.2
Benz(a)Anthracene	17	0.017 μg.L^{-1}	< 0.031 μg.L^{-1}	0.04 μg.L^{-1}	35.1
Biochemical Oxygen Demand	455	121 mg.L^{-1}	< 2 mg.L^{-1}	434 mg.L^{-1}	55.4
Bis (2-ethylhexyl)adipate	10	0.5 μg.L^{-1}	< 0.1 μg.L^{-1}	1.0 μg.L^{-1}	31.3
Bis (2-ethylhexyl)ftalate	13	1.0 μg.L^{-1}	< 1.0 μg.L^{-1}	7.2 μg.L^{-1}	182.6
Boron	17	0.069	0.036 mg.L^{-1}	0.200 mg.L^{-1}	53.7
Bromates	7	0.01 μg.L^{-1}	< 0.01 μg.L^{-1}	0.04 μg.L^{-1}	111.1
Cadmium	17	< 0.001 mg.L^{-1}	< 0.001 mg.L^{-1}	0.001 mg.L^{-1}	—
Carbofuran	13	0.04 μg.L^{-1}	< 0.05 μg.L^{-1}	0.31 μg.L^{-1}	187.2
Chemical Oxygen Demand	458	118 mg.L^{-1}	12 mg.L^{-1}	860 mg.L^{-1}	60.3
Chlorides	18	78 mg.L^{-1}	40 mg.L^{-1}	132 mg.L 1	37.5
Chloroform	18	< 5.0 μg.L^{-1}	< 5.0 μg.L^{-1}	13.0 μg.L^{-1}	—
Chromium (total)	18	0.02 mg.L^{-1}	< 0.005 mg.L^{-1}	0.06 mg.L^{-1}	95.9
Chromium (trivalent)	18	0.016 mg.L^{-1}	< 0.005 mg.L^{-1}	0.055 mg.L^{-1}	104.0
Cis-1.2-Dichloroethene	18	3.2 μg.L^{-1}	< 2.0 μg.L^{-1}	3.4 μg.L^{-1}	11.2
Cobalt	18	0.005 mg.L^{-1}	< 0.005 mg.L^{-1}	0.004 mg.L^{-1}	107.8

TABLE I (continuation)

Variable	Tietê River				
	N	Mean	Min	Max	C.V. (%)
Condutivity	353	544 μS.cm^{-1}	7 μS.cm^{-1}	1,510 μS.cm^{-1}	27.1
Copper (total)	17	0.030 mg.L^{-1}	< 0.005 mg.L^{-1}	0.08 mg.L^{-1}	85.1
Cyanide	17	0.02 mg.L^{-1}	< 0.005 mg.L^{-1}	0.06 mg.L^{-1}	133.0
Detergents	455	2.0 mg.L^{-1}	< 0.05 mg.L^{-1}	36.0 mg.L^{-1}	1,477
Dissolved oxygen	213	1.9 mg.L^{-1}	0.3 mg.L^{-1}	7.3 mg.L^{-1}	55.6
Endosulfan	16	0.012 μg.L^{-1}	< 0.001 μg.L^{-1}	0.162 μg.L^{-1}	348.6
Endrin	16	0.009 μg.L^{-1}	< 0.0005 μg.L^{-1}	0.067 μg.L^{-1}	226.5
Enterovirus	64	—	Absent	Present	—
Ethylbenzene	14	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	3.0 μg.L^{-1}	—
Fluoranthene	7	< 0.03 μg.L^{-1}	< 0.03 μg.L^{-1}	< 0.03 μg.L^{-1}	—
Hexachlorobutadiene	14	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	—
Iron (soluble)	303	0.3 mg.L^{-1}	< 0.05 mg.L^{-1}	3.8 mg.L^{-1}	136.5
Lead	17	0.02 μg.L^{-1}	< 0.01 μg.L^{-1}	0.15 μg.L^{-1}	227.2
Manganese (soluble)	302	0.1 mg.L^{-1}	< 0.05 mg.L^{-1}	1.9 mg.L^{-1}	81.1
Manganese (total)	13	0.20 mg.L^{-1}	0.08 mg.L^{-1}	0.27 mg.L^{-1}	36.4
Methylene Chloride	18	9.2 μg.L^{-1}	< 2.0 μg.L^{-1}	75.0 μg.L^{-1}	201.4
Nickel	11	< 0.05 μg.L^{-1}	< 0.05 μg.L^{-1}	0.09 μg.L^{-1}	—
Nitrate	16	1.0 mg.L^{-1}	< 0.1 mg.L^{-1}	13.0 mg.L^{-1}	303.0
Oxamyl	9	< 0.05 μg.L^{-}	< 0.05 μg.L^{-1}	< 0.05 μg.L^{-1}	—
pH	225	7.18	5.09	11.20	7.8
Phenols	20	0.08 μg.L^{-1}	< 0.01 μg.L^{-1}	0.53 μg.L^{-1}	141.6
Phosphorus	309	0.76 mg.L^{-1}	< 0.2 mg.L^{-1}	14.0 mg.L^{-1}	161.9
Sedimentable solids	329	0.65 mL.L^{-1}	< 0.1 mL.L^{-1}	15.0 mL.L^{-1}	176.5
Silver	13	0.002 mg.L^{-1}	< 0.002 mg.L^{-1}	0.007 mg.L^{-1}	107.3
Temperature	216	23°C (73.4°F)	12°C (53.6°F)	28°C (82.4°F)	13.0
Tetrachloroethylene	14	2.4 μg.L^{-1}	< 2.0 μg.L^{-1}	14.0 μg.L^{-1}	134.0
Thermotolerant coliforms	347	1×10^6 MPN.L^{-1}	Absent	13×10^6 MPN.L^{-1}	189.6
Tin (total)	17	0.10 mg.L^{-1}	< 0.02 mg.L^{-1}	0.31 mg.L^{-1}	87.2
Toluene	14	46.6 μg.L^{-1}	< 4.0 μg.L^{-1}	106.0 μg.L^{-1}	93.8
Total dissolved solids	136	283 mg.L^{-1}	< 10 mg.L^{-1}	592 mg.L^{-1}	33.8
Total suspended solids	300	46 mg.L^{-1}	< 10 mg.L^{-1}	990 mg.L^{-1}	183.0
Trichloroethylene	14	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	3.0 μg.L^{-1}	—
Turbidity	236	35 NTU	2 NTU	107 NTU	64.3
Vanadium	13	< 0.01 mg.L^{-}	< 0.01 mg.L^{-1}	0.01 mg.L^{-1}	—
Vinyl Chloride	17	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	12.0 μg.L^{-1}	—
Zinc	13	0.15 mg.L^{-1}	0.02 mg.L^{-1}	0.34 mg.L^{-1}	78.7

TABLE I (continuation)

Variable	Pinheiros River				
	N	Mean	Min	Max	C.V. (%)
1.1-Dichloroethene	14	2.1 μg.L^{-1}	< 2.0 μg.L^{-1}	17.0 μg.L^{-1}	199.6
1.2-Diphenylhydrazine	8	< 0.05 μg.L^{-1}	< 0.05 μg.L^{-1}	< 0.05 μg.L^{-1}	—
2,4-D	7	< 0.0024 μg.L^{-1}	< 0.0024 μg.L^{-1}	< 0.0024 μg.L^{-1}	—
2.4-Dichlorophenol	7	1.5 μg.L^{-1}	< 0.003 μg.L^{-1}	10.8 μg.L^{-1}	264.3
2.4-Dinitrotoluene	2	0.1 μg.L^{-1}	< 0.1 μg.L^{-1}	0.1 μg.L^{-1}	51.1
2.4.5-T	7	< 0.0042 μg.L^{-1}	< 0.0042 μg.L^{-1}	< 0.0042 μg.L^{-1}	—
2.4.6-Trichlorophenol	7	< 0.005 μg.L^{-1}	< 0.005 μg.L^{-1}	< 0.005 μg.L^{-1}	—
2-Chlorophenol	2	0.1 μg.L^{-1}	0.1 μg.L^{-1}	0.1μg.L^{-1}	—
4.4-DDD	14	0.004 μg.L^{-1}	< 0.0005 μg.L^{-1}	0.053 μg.L^{-1}	350.9
4.4-DDE	14	0.185 μg.L^{-1}	< 0.0005 μg.L^{-1}	2.6 μg.L^{-1}	373.7
Acroleine	12	1.6 μg.L^{-1}	< 0.5 μg.L^{-1}	13 μg.L^{-1}	231.9
Alachlor	14	0.0199 μg.L^{-1}	< 0.0008 μg.L^{-1}	0.075 μg.L^{-1}	348.0
Aldrin+Dieldrin	17	0.0018 μg.L^{-1}	< 0.0007 μg.L^{-1}	0.02 μg.L^{-1}	271.4
Alfa-BHC	14	0.003 μg.L^{-1}	< 0.0008 μg.L^{-1}	0.031 μg.L^{-1}	308.2
Aluminum (soluble)	17	0.24 mg.L^{-1}	< 0.1 mg.L^{-1}	0.5 mg.L^{-1}	51.5
Ammonia-nitrogen	326	25.5 mg.L^{-1}	0.5 mg.L^{-1}	117.0 mg.L^{-1}	56.2
Anthracene	14	0.047 μg.L^{-1}	< 0.012 μg.L^{-1}	0.583 μg.L^{-1}	326.6
Antimonium	17	< 0.0019 μg.L^{-1}	< 0.0019 μg.L^{-1}	< 0.0019 μg.L^{-1}	—
Apparent color	456	425 C.U.	20 C.U.	2,580 C.U.	68.8
Asbestos*	13	8.4 Mf.L^{-1}	< 1.0 Mf.L^{-1}	50.9 Mf.L^{-1}	156.4
Barium	17	0.059 mg.L^{-1}	< 0.01 mg.L^{-1}	0.14 mg.L^{-1}	55.7
Bentazon	8	0.6 μg.L^{-1}	< 0.0042 μg.L^{-1}	4.9 μg.L^{-1}	281.9
Benz(a)Anthracene	8	0.019	< 0.031 μg.L^{-1}	0.04 μg.L^{-1}	46.7
Biochemical Oxygen Demand	454	117 mg.L^{-1}	< 2 mg.L^{-1}	271 mg.L^{-1}	47.6
Bis (2-ethylhexyl)adipate	12	0.5 μg.L^{-1}	< 0.1 μg.L^{-1}	1.0 μg.L^{-1}	5.5
Bis (2-ethylhexyl)ftalate	14	2.2 μg.L^{-1}	< 1.0 μg.L^{-1}	12.0 μg.L^{-1}	175.2
Boron	17	0.042	< 0.027 mg.L^{-1}	0.094 mg.L 1	43.8
Bromates	8	0.01 μg.L^{-1}	< 0.01 μg.L^{-1}	0.04 μg.L^{-1}	113.1
Cadmium	16	< 0.001 mg.L^{-1}	< 0.001 mg.L^{-1}	< 0.001 mg.L^{-1}	—
Carbofuran	13	0.12 μg.L^{-1}	< 0.05 μg.L^{-1}	0.76 μg.L^{-1}	187.6
Chemical Oxygen Demand	457	120 mg.L^{-1}	20 mg.L^{-1}	614 mg.L^{-1}	49.1
Chlorides	17	58 mg.L^{-1}	30 mg.L^{-1}	116 mg.L^{-1}	46.7
Chloroform	17	6.6 μg.L^{-1}	< 5.0 μg.L^{-1}	43.0 μg.L^{-1}	150.1
Chromium (total)	17	0.02 mg.L^{-1}	< 0.005 mg.L^{-1}	0.31 mg.L^{-1}	316.6
Chromium (trivalent)	17	0.023 mg.L^{-1}	< 0.005 mg.L^{-1}	0.31 mg.L^{-1}	329.2
Cis-1.2-Dichloroethene	17	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	—
Cobalt	16	0.005 mg.L^{-1}	< 0.005 mg.L^{-1}	0.006 mg.L^{-1}	104.2

TABLE I (continuation)

Variable	Pinheiros River				
	N	Mean	Min	Max	C.V. (%)
Condutivity	454	500 μS.cm^{-1}	4 μS.cm^{-1}	1,440 μS.cm^{-1}	33.1
Copper (total)	16	0.016 mg.L^{-1}	< 0.005 mg.L^{-1}	0.05 mg.L^{-1}	85.8
Cyanide	17	0.01 mg.L^{-1}	< 0.005 mg.L^{-1}	0.035 mg.L^{-1}	116.8
Detergents	258	1.9 mg.L^{-1}	< 0.05 mg.L^{-1}	11 mg.L^{-1}	94.1
Dissolved oxygen	303	1.6 mg.L^{-1}	< 0.1 mg.L^{-1}	5.3 mg.L^{-1}	63.8
Endosulfan	8	< 0.001 μg.L^{-1}	< 0.001 μg.L^{-1}	< 0.001 μg.L^{-1}	—
Endrin	8	< 0.0005 μg.L^{-1}	< 0.0005 μg.L^{-1}	< 0.0005 μg.L^{-1}	—
Enterovirus	56	—	Absent	Present	—
Ethylbenzene	13	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	2.5 μg.L^{-1}	—
Fluoranthene	6	0.03 μg.L^{-1}	< 0.03 μg.L^{-1}	0.08 μg.L^{-1}	103.0
Hexachlorobutadiene	13	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	6.0 μg.L^{-1}	—
Iron (soluble)	103	2.1 mg.L^{-1}	< 0.05 mg.L^{-1}	14.3 mg.L^{-1}	160.0
Lead	16	< 0.01 μg.L^{-1}	< 0.01 μg.L^{-1}	0.032 μg.L^{-1}	—
Manganese (soluble)	102	0.2 mg.L^{-1}	< 0.05 mg.L^{-1}	2.2 mg.L^{-1}	82.4
Manganese (total)	12	0.23 mg.L^{-1}	0.1 mg.L^{-1}	0.63 mg.L^{-1}	65.9
Methylene Chloride	17	2.9 μg.L^{-1}	< 2.0 μg.L^{-1}	15.0 μg.L^{-1}	141.8
Nickel	12	< 0.05 μg.L^{-1}	< 0.05 μg.L^{-1}	0.03 μg.L^{-1}	—
Nitrate	15	0.1 mg.L^{-1}	< 0.1 mg.L^{-1}	0.5 mg.L^{-1}	110.9
Oxamyl	9	0.1 μg.L^{-1}	< 0.05 μg.L^{-1}	0.9 μg.L^{-1}	263.7
pH	316	7.10	3.00	10.70	7.4
Phenols	9	0.04 μg.L^{-1}	< 0.01 μg.L^{-1}	0.16 μg.L^{-1}	150.5
Phosphorus	299	0.59 mg.L^{-1}	< 0.2 mg.L^{-1}	5.4 mg.L^{-1}	128.6
Sedimentable solids	325	1.1 mL.L^{-1}	< 0.1 mL.L^{-1}	10.1 mL.L^{-1}	787.2
Silver	12	0.002 mg.L^{-1}	< 0.002 mg.L^{-1}	0.003 mg.L^{-1}	111.5
Temperature	307	23°C (73.4°F)	16°C (60.8°F)	33°C (91.4°F)	12.4
Tetrachloroethylene	13	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	—
Thermotolerant coliforms	258	3 × 10^5 MPN.L^{-1}	Absent	12 × 10^6 MPN.L^{-1}	296.3
Tin (total)	17	0.10 mg.L^{-1}	< 0.02 mg.L^{-1}	0.51 mg.L^{-1}	119.0
Toluene	13	85.4 μg.L^{-1}	< 4.0 μg.L^{-1}	215.0 μg.L^{-1}	77.0
Total dissolved solids	99	245 mg.L^{-1}	86 mg.L^{-1}	455 mg.L^{-1}	36.7
Total suspended solids	297	37 mg.L^{-1}	< 10 mg.L^{-1}	340 mg.L^{-1}	123.3
Trichloroethylene	13	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	3.0 μg.L^{-1}	—
Turbidity	326	56 NTU	5 NTU	217 NTU	70.1
Vanadium	12	< 0.01 mg.L^{-}	< 0.01 mg.L^{-1}	0.03 mg.L^{-1}	—
Vinyl Chloride	15	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	< 2.0 μg.L^{-1}	—
Zinc	11	0.07 mg.L^{-1}	0.04 mg.L^{-1}	0.16 mg.L^{-1}	64.3

* Mf.L^{-1}: Millions of fibers per Liter.

the other hand, 6 substances were exclusively detected in the Pinheiros River, being all of them organic compounds (Table II).

Five variables exclusively detected in the Tietê River (2.4-D, 2.4.5-T, 2.4.6-Trichlorophenol, Endosulfan and Endrin) are organic compounds normally used in agriculture to control plagues, like weeds, insects and fungus, although agricultural activities are not preponderant in the Tietê sub-basin (there are only some vegetable belts in the upper part of the basin). All these pesticides present chlorine in their molecular structure. Four other organic substances, which were also only observed in the Tietê River, may be related with industrial activities that take place in the respective sub-basin: 1.2-Diphenylhydrazine, Cis-1.2-Dichloroethene, Vinyl Chloride and Tetrachloroethylene. The degradation of 1.2-Diphenylhydrazine promotes the formation of several other products that may be associated with the slow disappearance of its overall toxicity (Muneer et al. 2002). This cited study ratified that this substance presents a high level of toxicity, even through its degradation products.

Cis-1.2-Dichloroethene and Vinyl Chloride in turn are recognized as biodegradation products of Trichloroethylene and Tetrachloroetylene (Bradley et al. 1998). Tetrachloroetylene sources to the Tietê River may include dry cleaning establishments and metal degreasing activities. The anoxic conditions found in the Tietê River (the mean and minimum concentrations of dissolved oxygen were 1.9 mg.L^{-1} and 0.3 mg.L^{-1}, respectively) were probably able to stimulate the degradation of Tetrachloroetylene to Dichloroethene and Vinyl Chloride through anaerobic reductive dechlorination, as verified by other researchers in lab-scale experiments (Bradley et al. 2008, Duhamel et al. 2002). Cadmium and Antimonium concentrations in the Tietê River may be associated with the clandestine discharges of metallurgical units, which are common in the surrounding area, and with the effluents of oil-handling industry.

When it comes to the substances exclusively detected in the Pinheiros River, all of them are organic compounds, four of which are used to decrease plagues infestation (three are chlorinated). Agricultural activities in the Pinheiros River sub-basin are almost inexistent. Therefore, it is assumed that a possible source of these compounds may be the application of insecticides in the river margins to eliminate mosquitoes and other vectors, mainly organophosphate compounds like Themephos and Cipermetrine (aleatory application) and Betacyfluthrin (daily application), according to Morais et al. (2007). Some authors consider the Pinheiros River as a large urban breeding of the mosquito *Culex quinquefasciatus* and state that this situation was aggravated since the pumping of its water to Billings Reservoir was interrupted (Bracco et al. 1997, Morais et al. 2006, Andrade et al. 2007, Silva-Filha et al. 2008).

In the case of Alachlor, this herbicide has relatively rapid transformation rates and, consequently, its overall occurrence and concentration may be underestimated without data on the degradation products, as verified by Kolpin et al. (1998) for North-American groundwater. Fluoranthene occurrence may be related with effluents of coal combustion, vehicular exhaust, tire degradation and lubricating oils industry (Manoli et al. 2000), which are widespread in the Pinheiros River sub-basin. Sealed areas, such as streets and other urban sites, are successively re-enriched by PAHs (Polycyclic Aromatic Hydrocarbons) like Fluoranthene, for instance. The input of this substance into the aquatic systems is controlled by the location and activation of particle sources and, consequently, urban runoff plays an important role over these processes (Krein and Schorer 2000, Hwang and Foster 2006). Hexachlorobutadiene in turn is also related with industrial activities. This aliphatic compound is extremely volatile and some recent researches have been linking hexachlorobutadiene exposure with possible carcinogenic effects to human (Tchounwou et al. 1998, Green et al. 2003, Staples et al. 2003, Juang et al. 2009).

Table III presents the variables that were placed in Case B ("presence") category, with "TIE" meaning that the highest value was found in the Tietê River and "PIN" denoting the same for the Pinheiros River.

In synthesis, 56 variables were detected in both rivers, but the highest values or concentrations of 26 were found in the Tietê River and 22 in the Pinheiros River. Case B-TIE variables included diverse groups: 5 organic compounds, 2 nutrients, 6 physical variables, 7 metals, 1 non-metallic substance, 2 ions and 1 biological variable, besides BOD and COD, which are indic-

TABLE II
Case A ("exclusivity") variables, which were exclusively detected either in the Tietê or in Pinheiros River, including some information about each one.

Variable	Information
Tietê River	
1.2-Diphenylhydrazine	Organic compound used to produce some dyes and to make certain medicines
2.4-D	Organic compound used as herbicide
2.4.5-T	Organic compound used as herbicide
2.4.6-Trichlorophenol	Organic compound used as fungicide
Antimonium	Metalloid used for metal blending and as a component for storage batteries
Cadmium	Metal used for batteries manufacture
Cis-1.2-Dichloroethene	Organic compound used in the manufacture of solvents
Endosulfan	Organic compound used as insecticide and fungicide
Endrin	Organic compound used as insecticide
Tetrachloroethylene	Organic compound used for dry cleaning and metal degreasing
Vinyl Chloride	Organic compound whose polymerization produces PVC, a thermoplastic resin that is largely used worldwide
Pinheiros River	
4.4-DDD	Organic compound used as insecticide
Alachlor	Organic compound used as herbicide
Aldrin+Dieldrin	Organic compound used as insecticide
Fluoranthene	Organic compound, usually a byproduct of combustion process
Hexachloro-butadiene	Organic compound, usually a byproduct of industrial plants that deal with hydrochloric acid
Oxamyl	Organic compound used as nematocide

References: ATSDR (1999), PANNA (2009), TOXMAP (2009).

ators of degradable organic matter by biochemical or chemical processes, respectively. When it comes to Case B-PIN variables, the distribution was: 9 organic compounds, 1 nutrient, 3 physical variables and 8 metals, besides Asbestos. The Tietê River water presented the highest values of BOD (Biochemical Oxygen Demand), Conductivity, Detergents, Phosphorus, Solids (Sedimentable, Dissolved and Suspended) and Thermotolerant Coliforms, which are straightly related to organic matter pollution derived from domestic wastewater. Chloroform concentrations were high (reaching 43.0 $\mu g.L^{-1}$ in the Pinheiros River and 13.0 $\mu g.L^{-1}$ in the Tietê River), when compared to the mean concentration for European rivers, for instance, which is about 0.5 $\mu g.L^{-1}$ (McCulloch 2003). The same happens for Aluminum (maximum of 2.3 $mg.L^{-1}$ in the Tietê River), Chromium (maximum of 0.31 $mg.L^{-1}$ in the Pinheiros River) and Iron (maximum of 14.3 $mg.L^{-1}$ in the Pinheiros River).

When we assessed the temporal component of the monitoring program, the Analysis of Variance (ANOVA) with variables from Case A and B (altogether 73 variables) suggested that only 11 variables were considered statistically different comparing the rainy and dry periods (Table IV). These variables were directly influenced by the rainfall in the urban area, e.g. Total suspended solids, which were higher in the rainy months. On the other hand, Apparent color, Chemical Oxygen Demand and Conductivity, which are variables that may be related with industrial effluents, presented

TABLE III
Case B ("presence") variables, which were detected both in the Tietê and Pinheiros Rivers.

Variable	Highest concentration/value	Variable	Highest concentration/value
1.1-Dichloroethene	PIN	Cyanide	TIE
2.4-Dichlorophenol	PIN	Detergents	TIE
2.4-Dinitrotoluene	TIE = PIN	Dissolved Oxygen	TIE
2-Chlorophenol	TIE = PIN	Enterovirus	TIE = PIN
4.4-DDE	PIN	Ethylbenzene	TIE
Acroleine	TIE = PIN	Iron (soluble)	PIN
Alfa-BHC	TIE	Lead	TIE
Aluminum (soluble)	TIE	pH	TIE
Ammonia-nitrogen	PIN	Phenols	TIE
Anthracene	PIN	Phosphorus	TIE
Apparent color	PIN	Manganese (soluble)	PIN
Asbestos	PIN	Manganese (total)	TIE
Barium	PIN	Methylene Chloride	TIE
Bentazon	PIN	Nickel	TIE
Benz(a)Anthracene	TIE = PIN	Nitrate	TIE
Biochemical Oxygen Demand	TIE	Sedimentable solids	TIE
Bis (2-ethylhexyl)adipate	TIE = PIN	Silver	TIE
Bis (2-ethylhexyl)ftalate	PIN	Temperature	PIN
Boron	TIE	Thermotolerant Coliforms	TIE
Bromates	TIE = PIN	Tin (total)	PIN
Carbofuran	PIN	Toluene	PIN
Chemical Oxygen Demand	TIE	Total dissolved solids	TIE
Chlorides	TIE	Total suspended solids	TIE
Chloroform	PIN	Trichloroethylene	TIE = PIN
Chromium (total)	PIN	Turbidity	PIN
Chromium (trivalent)	PIN	Vanadium	PIN
Cobalt	PIN	Zinc	TIE
Copper (total)	TIE	TOTAL: TIE (26 variables), PIN (22 variables), TIE = PIN (8 variables)	
Condutivity	TIE		

their highest values in the dry season, possibly as a consequence of lower river flows and smaller capacity of dilution.

The remaining 61 variables that were not aforementioned (51 organic compounds, 8 metals and 2 biological variables) were placed in Case C ("total absence") since they were not detected in any sample, considering the detection limit: 1.1.1-Trichloroethane, 1.1.2.2-Tetrachloroethane, 1.2.4-Trichlorobenzene, 1.2-Dichlorobenzene, 1.2-Dichloroethane, 1.2-Dichloropropane, 1.2-trans-Dichloroethene, 1.3-Dichlorobenzene, 1.3-Dichloropropene, 1.4-Dichlorobenzene, 2.4-Dinitrophenol, 2.4.5-TP, 2.4-Dimetylphenol, 2-Methyl-4.6-Dinitrophenol, 3.3-Dichlorobenzidine, 4.4-DDT, Acenaphtene, Acrylamide, Aldicarb, Arsene, Atrazine, Benz(a)-Pyrene, Benzene, Benzo(b)Fluoranthene, Benzo(k)Fluoranthene, Beryllium, Beta-BHC, Bis (2-Chloroethyl-ether), Bis (2-Chloroisopropyl-ether), Chlordane, Chlorobenzene, Chromium (hexavalent), Chrysene, Copper (soluble), *Cryptosporidium* sp., Dalapon, Demeton, Dibenz(a,h)anthracene, Dieldrin, Dinoseb, Endosulfan sulfate, Fluorene, *Giardia* sp., Guthion, Heptachloro,

TABLE IV
List of variables that presented statistically significant differences during the dry and rainy periods in the Tietê and/or Pinheiros Rivers. Observation: p* indicates statistical significance.

Variable	Tietê River	Pinheiros River	Observation
Apparent color	$p^* < 0.05$	$p^* < 0.05$	Higher in the dry period
Chemical Oxygen Demand	$p^* < 0.05$	$p^* < 0.05$	Higher in the dry period
Conductivity	$p^* < 0.05$	$p^* < 0.05$	Higher in the dry period
Dissolved oxygen	$p^* < 0.05$	$p > 0.05$ (NSS)	Higher in the dry period
pH	$p^* < 0.05$	$p^* < 0.05$	Higher in the rainy period
Phosphorus	$p^* < 0.05$	$p^* < 0.05$	Higher in the rainy period
Sedimentable solids	$p^* < 0.05$	$p > 0.05$ (NSS)	Higher in the rainy period
Temperature	$p^* < 0.05$	$p^* < 0.05$	Higher in the rainy period
Total dissolved solids	$p^* < 0.05$	$p > 0.05$ (NSS)	Higher in the dry period
Total suspended solids	$p^* < 0.05$	$p^* < 0.05$	Higher in the rainy period
Turbidity	$p^* < 0.05$	$p^* < 0.05$	Higher in the dry period

NSS: the difference was not statistically significant.

Hexachlorobenzene, Hexachloroethane, Indeno (1.2.3-cd) pyrene, Lindane, Lithium, Malathion, Mercury, Methyl-bromide, Molinate, Pentachlorophenol, Polychlorinated biphenyls, Selenium, Styrene, Toxaphene, Uranium and Xylene.

Among the metals allocated in Case C, we highlight Chromium (hexavalent), Lithium, Mercury and Uranium, which were absent. They are toxic heavy metals that may exert detrimental effects not only on human health but also on the whole environment (Davydova 2005). *Cryptosporidium* sp. and *Giardia* sp. were also absent for all samples of the Tietê and Pinheiros Rivers. *Giardia* sp. causes an intestinal illness called giardiasis or "beaver fever" and *Cryptosporidium* sp. is responsible for a similar illness called cryptosporidiosis, which is characterized by gastroenteritis (Franco et al. 2001, Hachich 2002, Heller et al. 2004).

A considerable level of differences was found for the studied urban rivers, not only between the aquatic systems themselves, but also considering the same river in distinct periods of the hydrologic cycle (i.e. dry and wet seasons). Case A variables particularly represent a key information, since the Tietê River and the Pinheiros River presented some exclusive occurrences. Therefore, the imperative is to analyze each river separately and to establish individualized recovery plans for each one, taking into account, besides the seasonal fluctuation, the fact that all exclusive variables of the Pinheiros River are organic compounds and, on the other hand, the exclusive water variables in the Tietê River included, besides some organic substances, a metal and a metalloid.

CONCLUSIONS

The water quality monitoring of the Tietê and Pinheiros Rivers (Metropolitan Region of São Paulo), through an intense program that performed the quantification of biological, chemical and physical variables for about seventeen months (August, 2007 to December, 2008) enabled the authors to conclude that:

i. It is not advisable to adopt the same management program of water resources or control procedures for the sub-basins of both rivers. The results showed that, despite the fact that they are located in the same basin, the contribution of the drainage sub-basin area was relevant and determined some exclusive water variables occurrences for these urban aquatic systems;

ii. The temporal variation of the results presented a significant importance for only eleven variables, among the seventy three that were assessed. These variables were influenced by rainfall events and different seasonal precipitation patterns. Some of these variables were statistically different within the dry and rainy months only for the Tietê River (e.g. Dissolved Oxygen, Sedimentable solids and

Total dissolved solids), which suggested that the temporal component is even more important for the former aquatic system and that this river is possibly more susceptible to the urban runoff;

iii. In general, the Tietê River seemed to be more affected by domestic wastewater in comparison to the Pinheiros River, since high concentrations of Phosphorus, Ammonia-Nitrogen, BOD and detergents were observed in the former river. Nevertheless, by analyzing the variables of exclusive occurrence, it was possible to find out that the Tietê River is also submitted to impacts from industry, from the inappropriate disposal of batteries and solvents and from dry cleaning and metal degreasing activities;

iv. The Pinheiros River in turn also presented some exclusive occurrences, mainly organochlorinated compounds, although the Pinheiros sub-basin has almost none agricultural activities. Therefore, these occurrences were associated with the application of insecticides on the river margins to reduce mosquitoes infestation, which is a current practice in the area. Besides, the carcinogenic substance was exclusively detected in the water of this river, characterizing a public health concern;

v. The rivers are severely polluted by a great number of substances, with diverse origins from the respective sub-basin. Particularly, the concentrations of Aluminum, Ammonia-Nitrogen, Chloroform, Cyanide, Detergents, Phosphorus and Solids were high in both rivers, which may provide significant risks to the water quality, to the aquatic systems balance and to the public health as well.

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RESUMO

O gerenciamento dos recursos hídricos urbanos desempenha um papel importante para os países em desenvolvimento. Os rios Tietê e Pinheiros (São Paulo, Brasil) são afetados por efluentes domésticos e industriais e pela poluição difusa. Esta pesquisa teve como objetivo quantificar 134 variáveis da água dos rios Tietê e Pinheiros (aproximadamente 7.200 e 6.600 análises, respectivamente) de Agosto de 2007 a Dezembro de 2008. A ideia foi verificar se o fato de os dois rios se localizarem na mesma bacia hidrográfica é suficiente para que se considere a aplicação de um único plano de manejo para ambos. Os dados mostraram que os rios apresentam significativa interferência antrópica. Os resultados sugeriram que tais rios devem ser submetidos a planos individuais de gerenciamento, uma vez que houve ocorrências exclusivas (variáveis que foram detectadas em apenas um dos rios). Além disso, houve diferença estatisticamente significativa entre os períodos seco e chuvoso para onze variáveis ($p^* < 0{,}05$, ANOVA), o que reforça a especial importância da componente temporal do programa de monitoramento. Espera-se que esse estudo ofereça subsídios para programas de recuperação ambiental do rio Tietê, para o qual é recomendado foco na repressão de lançamentos clandestinos de águas residuárias, e do rio Pinheiros, para o qual se sugere especial atenção à poluição derivada do aporte de pesticidas ao corpo de água.

Palavras-chave: monitoramento ambiental, região metropolitana de São Paulo (RMSP), rios urbanos, poluição da água, qualidade da água, gestão de bacias hidrográficas.

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