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# Ecological risk assessment of a subtropical river influenced by discharges of residues from water and sewage treatment plants

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## Abstract

**Purpose** – The São Lourenço River (SLR) is used to supply potable waters for the cities of São Lourenço da Serra and Juquitiba, but receives the residues from the water treatment plants (WTPs) and sewage treatment plants (STPs), respectively. The purpose of this paper is to evaluate the impacts of the discharges of Juquitiba's WTP and STP on the quality of the SLR, by using an integrated approach based on different lines of evidence. **Design/methodology/approach** – Six sampling sites were established along the river and comprised areas situated upstream and downstream of the discharges. Five sampling surveys were performed between 2004 and 2006 for collecting water and sediment samples for ecotoxicological assays. In two of these campaigns, benthic community structure and geochemistry (metals, nutrients and sediment texture) were also assessed. **Findings** – Concentrations of P, Pe and Al in waters exceeded the national standards, but sediments were not considered to be contaminated by metals or nutrients. Water and sediments tended to exhibit marginal toxicities, excluding the sediments from JQT007 and JQT008 that were frequently toxic. Combination of geochemistry, toxicity and ecological indices indicated that some sites are not degraded, but in some stations the benthic alteration may be due to non-measured contaminants, especially in JQT007 and JQT008.

**Practical implications** – As the use of waters from SLR for public supply has increased, these results show that action should be taken in order to reverse the environmental degradation of SRL.

**Originality/value** – This research combined sediment and water quality assessments in order to provide a more suitable and reliable diagnostic of the environmental quality of the SLR.

Keywords Water, Sediment, Contamination, Environmental quality, Ecological risk assessment, Sewage Paper type Research paper

## 1. Introduction

In the recent years, the environmental monitoring programs of river basins that provide drinking waters have substantially changed worldwide. A main change in such programs involves the incorporation of sediments as an important environmental compartment that has to be evaluated together with the waters (Mozeto *et al.*, 2006), as sediments are considered a repository and a source of contaminants (Burton and Scott, 1992).

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Management of Environmental Quality: An International Journal Vol. 28 No. 2, 2017 pp. 156-174 © Emerald Publishing Limited 1477-7835 DOI 10.1108/MEQ-09-2015-0169 The purpose of assessing and monitoring the waterbodies relies in recognizing the multiple uses of water: provide the more vulnerable users with low cost services for domestic water, water for agriculture, homestead, garden, water for cattle, habitats for fish and other aquatic resources, rural enterprise water supplies, hydroelectric power, inland waterway navigation, support important cultural values and functions that are essential for local well-being and livelihoods; and might provide ecological benefits which include flood control, groundwater recharge, water harvesting, water purification, and biodiversity conservation. These uses occur at different levels (homestead, water system and catchment levels), and always as possible, the maximum possible uses should be prioritized (Food and Agriculture Organization of the United Nations, 2013).

The relationship between the possible water uses and water quality is direct. The public supply of drinking waters, for example, requires the accomplishment of some quality standards. However, some uses are conflicting and a determined waterbody can be simultaneously used for public supply and for receiving the discharges of effluents; in this case, several standards must be attended in order to allow such conflicting uses (Sperling, 1986).

The city of Juquitiba (São Paulo, Brazil) is fully inserted within the environmental protection area of the springs and is crossed by the São Lourenço River (SLR). According to the federal laws (Brasil – República Federativa, 2005), this river is classified as a Class-2 waterbody; this means that the SLR provides potable water for human consumption after conventional treatment and is also intended to the protection of aquatic life and bathing. However, the SLR receives contaminant inputs from different sources.

The public sanitation company from the State of São Paulo (SABESP) collects water from the SLR with the aim of public supply. The collected waters are treated by conventional techniques (coagulation, flocculation, decantation and filtration) before the distribution. SABESP is also responsible for collecting and treating the sewage from the cities located along the SLR basin; the treatment consists of pre-conditioning, followed by anaerobic and facultative ponds (or biological reactors) and chlorination unities, respectively. The effluents of both water treatment plant (WTP) and sewage treatment plant (STP) are discharged into the SLR. Besides, the water and sewage treatment systems require the use of chemicals (aluminum sulfate, chlorine and lime), which end discarded with the effluents.

In Brazil, the knowledge of the impacts of residues from STP and WTP is still incipient (PROSAB, 2001). Studies are required to evaluate the environmental impacts of these types of effluents; they should involve not only the chemical analyzes, but also the evaluation of the biological impacts, which are commonly measured through toxicity tests and/or community studies.

Field observations and laboratory bioassays may indicate that the presence of contaminants in sediments produces lethal or sub lethal effects on the benthic organisms, as crustaceans and insect larvae (United States Environmental Protection Agency, 2005b; Burton, 1992; CETESB, 2001). Moreover, the sediments may release the contaminants back to the water column; thus, the effects may reach not only the benthic organisms, but also the planktonic and demersal organisms. Therefore, the introduction of STP and WTP into a water body may produce environmental risks.

The ecological risk assessment (ERA) is a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (United States Environmental Protection Agency, 1992). Two major elements must be present in any ERA: characterization of effects and characterization of exposure (United States Environmental Protection Agency, 1998). These characterizations have frequently employed multiple lines of evidence (LOE) (Chapman *et al.*, 2002; Choueri *et al.*, 2010).

Geochemical methods provide information on the nature and degree of contamination, while ecotoxicological methods detect the occurrence of potential biological effects (Adams *et al.*, 1992; Petrovic and Barcelo, 2004) and provide information about both effects of and exposure to

contaminants (Castro *et al.*, 2006; Antunes *et al.*, 2008; Chapman and Anderson, 2005). The combination of toxicity tests with chemical analyses provides much more powerful information for scientific and legislative decision making.

This investigation aimed at evaluating the impacts caused by the discharges of STP and WTP into the SLR, by using different LOEs. The LOEs comprised chemical analyses and toxicity tests with water and sediments, and the analysis of the benthic community structure.

### 2. Materials and methods

#### 2.1 Study area

The SLR springs are situated in São Lourenço da Serra (SP, Brazil) in the region known as Ribeira Valley (Figure 1), on the Southwest of the metropolitan region of São Paulo (MRSP). The city of Juquitiba is situated on SW of São Lourenço da Serra (downstream SLR),



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Map of the studied are showing the sampling stations along the São Lourenço River at Juquitiba (São Paulo, Brazil) presenting 521.6 km<sup>2</sup> and 26,479 inhabitants in 2003. The region is relatively well preserved, with extensive portions of the natural Atlantic rainforest.

As previously mentioned, the SLR waters are used for public supply and for receiving residues from STP and WTP. In São Lourenço da Serra, the local WTP attends about 8,760 (62.8 percent population); it produces a load of 0.975 tons of sludge per month (16 L/s) and uses aluminum sulfate as coagulant, in the concentration of 13 mg/L (Companhia de Saneamento Básico do Estado de São Paulo, 2003). The STP attends 2,930 people (about 21 percent population). The cleaning of its filters and decanters is made every 15 days and additionally leads to the production of about 400 m<sup>3</sup> used water per month. Until December 2005, the sludge was discharged into the SLR, but currently it is introduced in the STP (Sundefeld, 2007). In Juquitiba, the WTP attends about 21,550 people (74.9 percent total population), producing monthly about 1.927 tons sludge (28 L/s) and using aluminum sulfate at 15 mg/L. Its produced sludge was discharged into the SLR until August 2006. The STP attends about 3,740 people (13 percent total population). The chemical composition of the sludge and effluents produced by these two WTPs is available in Silva (2008). Both STP effluents presented low concentrations of dissolved elements, but that from Juquitiba STP presented higher concentration of nutrients (Silva, 2008).

In addition to the STPs and WTPs, the SLR basin presents other sources of contamination, such as landfills and diffuse sources (untreated sewage, urban drainage and storm waters from urban and agricultural areas), among others.

#### 2.2 Sample collection

Water and sediment samples were collected at six sampling stations distributed along the SLR, in Juquitiba (SP, Brazil). One station was located upstream of the Juquitiba's municipal WTP or STP and two stations were positioned downstream the respective WTP and STP (Figure 1). The station JQT 002 was positioned upstream to the WTP and STP and theoretically should be the reference site (e.g. not influenced by the main contamination sources).

The water samples were collected in August 2004; March, July, October and November 2005; and March and September 2006. Surface water samples were collected using buckets, transferred to 5 L polyethylene bottles, which were previously decontaminated and then stored refrigerated at 4 °C until the use. The temperature and dissolved oxygen (DO) contents were measured in field with sensors coupled to a multi-parameter reader (YSI, model 5,100, with a membrane probe). Aliquots were separated in previously cleaned polyethylene flasks for the analyses of anions and metals (Laxen and Harrison, 1981); those for analyzing the anions were preserved refrigerated at 4 °C while those for determining the concentrations of metals were acidified with HNO<sub>3</sub> (1:1; pH < 2) and stored capped at ambient temperature.

The sediment samples were collected in March, July and November 2005, and in March and September 2006. The sediments were collected with a Petersen grab sampler ( $0.03 \text{ m}^2$ ), but in September the sample from JQT007 was not collected. Aliquots for the chemical analyses were separated and kept frozen until their use, whereas those for ecotoxicological analysis were stored refrigerated ( $\approx 4 \text{ °C}$ ) in the dark.

In March and September 2006, the macrobenthic communities were collected with the same grab sampler used in the sediments. In the field, samples were transferred to plastic flasks and fixed with tamponed formaldehyde 10 percent.

Rainfall precipitation data for each sampling period were obtained from the integrated centre of agrometeorological information (Centro integrado de informações agrometeorológicas, 2008). The total rainfall precipitation in 2006 was 1,317 mm. The drier season occurred between April and September, with mean precipitation rate of 43 mm; July was the drier month. However, during the March (summer) survey, the temperature was low, while in September the level of waters was high, because it was raining in the days before the survey.

### 2.3 Water chemistry

The concentrations of ammonia, total nitrogen (Kjeldahl) and phenols were, respectively, measured by the following methods: SMEWW 4500-NH3-D-Ammonia selective electrode method and SMEWW 4500-Norg-B-Mass–Kjeldahl Method/D-Ammonia – selective electrode method (American Public Health Association – American Water Works Association, 2012), and USEPA SW846-8270C – semi-volatile organic compounds by gas cromatography/mass spectrometry (United States Environmental Protection Agency, 1996a).

Mercury (Hg), Selenium (Se), Arsenic (As), Antimony (Sb), Lead (Pb) and Cadmium (Cd) were analyzed by atomic absorption spectrometry; Pb, Cd, Sb and Se were determined by graphite furnace, the Hg by atomization after cold vapor generation, and the As by hydrate generation (United States Environmental Protection Agency, 2005a). The resting elements (Silver – Ag; Aluminum – Al; Boron – B; Barium – Ba; Cobalt – Co; Chromium – Cr; Calcium – Ca; Copper – Cu; Iron – Fe; Potassium – K; Magnesium – Mg; Manganese – Mn; Molibdenium – Mo; Sodium – Na; Nickel – Ni; Phosphorus – P; Tin – Sn; Vanadium – V; Zinc – Zn) were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) (United States Environmental Protection Agency, 1996b).

### 2.4 Sediment properties and chemistry

The sediments were analyzed by grain size distribution, according to Mudroch and Macknight (1994). The amount of organic matter was determined by the loss by ignition and Gravimetry method (Associação Brasileira de Normas Técnicas, 1996). Concentrations of elements and oxides (SiO<sub>2</sub>, AlO<sub>3</sub>, K<sub>2</sub>O, FeO<sub>2</sub>, TiO<sub>2</sub>, MgO, CaO, P<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O, Cr, MnO, Cl, ZrO<sub>2</sub>, Ni, Zn, RbO2, SrO and SO<sub>3</sub>) were analyzed by X-ray fluorescence. To achieve that, sediments were dried and sieved through 74  $\mu$ m net, in order to separate the finer fractions. In all 20 g aliquots were disaggregated in a porcelain mortar using a pestle and deionized water; then clay and silt were separated by decantation. The clay fraction is filtered in 0.47  $\mu$ m membrane, then transferred to a glass slide to produce dry pressed tablets, that are ready for the XRF analysis. Chemical analyses of metals in sediments were made with the samples collected in September 2006, following the same protocols used for the water samples.

## 2.5 Water and sediment toxicity

The water samples were analyzed for acute toxicity through the toxicity tests with *Daphnia similis*, *D. laevis*, *Ceriodaphnia dubia or C. silvestrii* (Associação Brasileira de Normas Técnicas, 2004), according to the availability of test-organisms in the laboratorial cultures. These samples were also tested for chronic toxicity to *C. silvestrii* (Associação Brasileira de Normas Técnicas, 2005). Sediments were analyzed for acute toxicity to *Chironomus xanthus* and *Hyalella azteca* (American Society for Testing and Materials, 2000; Associação Brasileira de Normas Técnicas, 2006). Information on the quality control/quality assurance for the mentioned tests is available in Silva (2008).

#### 2.6 Benthic community

The biological samples were sorted in laboratory and then identified using identification keys for each taxonomic group (Edmonson, 1959; Righi, 1984; Pennak, 1989; Trivinho-Strixino and Strixino, 1995; Brinkhurst and Marchese, 1989; Simone, 2006). The results were compared to the classification of sediment degradation proposed by CETESB (2007) (Table I).

## 2.7 Data integration

Different approaches were used to integrate the results of sediment geochemistry, toxicity and benthic community. The first approach considered the qualitative conclusions obtained independently for chemistry, toxicity and benthos and their combination in a decision table

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(Long and Chapman, 1985). The concentrations of metals in the sediment samples were compared to the Canadian sediment quality guidelines (Canadian Council of Ministers of the Environment (CCME), 2001), considering the criteria proposed by Fairey *et al.* (2001). For the ecotoxicological data, the qualitative conclusion was obtained using the combination proposed by Abessa *et al.* (2008). For the ecological descriptors, the classification established by CETESB (2007) was adopted.

### 3. Results

#### 3.1 Water chemistry

The concentrations of ammonia, nitrogen Kjeldahl and phenols in water were below the detection limits in all samples of all sampling campaigns. The physical chemical parameters of waters are showed in Table II. Low spatial variation was observed for most the of variables, but the DO levels were slightly lower immediately after the discharges of WTP and STP. Temporal differences were observed for conductivity (higher in September 2006) and pH values, which were low in September and were below the federal standards (Brasil – República Federativa, 2005). The chemical analysis of waters from SLR showed that most of elements occur in low concentrations and present low temporal variations (Table III), excepting P, Fe and Al, which some time exceed the limits established by the federal standards (Brasil – República Federativa, 2005). As P is related to sewage or fertilizers used in agriculture, and that Al is used for disinfection of waters in WTP, these results suggest that possibly human activities may be causing this increase.

#### 3.2 Water toxicity

The majority of water samples were not toxic. However, waters from JQT003 (just after the WTP effluent), JQT006, JQT007 and JQT008 were acutely toxic to *C. silvestrii* in July/2005. Sample from JQT003 was toxic to *C. dubia* in November/2006 (Figure 2). The samples from JQT003 and JQT006 also presented chronic toxicity to *C. silvestrii* in March/2006. In September/2006, the samples from JQT002, JQT003, JQT004 and JQT008 exhibited chronic toxicity (*C. silvestrii*).

Index	Minimum	Degradation level Moderate	Strong	Table I.
Specific richness T/TD Note: T/DT, tolerant species ove Source: Adapted from CETESE	> 14 > 0.50 er total densities	6-13 0.50-0.75	< 5 > 0.75	Criterion for freshwater sediments degradation based on the benthic community

	Tempe	erature (°C)	D.O.	$(mg.L^{-1})$		pН	Conducti	vity (µS.cm <sup>-1</sup> )	
Sampling station	March	September	March	September	March	September	March	September	Table II.
JQT002	16	18	8.4	8.6	6.5	5.7	35.6	53	Values of temperature,
JQT003	16	18	8.4	7.6	6.5	5.7	36.1	52	conductivity and pH
JQT004	16	18	8.6	8.0	6.7	5.5	35.7	52	in waters from the
JQT006	15	18	8.4	8.1	6.5	5.6	36.0	51	São Lourenco River
JQT007	15	18	8.4	7.3	6.8	5.6	36.3	53	(Juquitiba, São Paulo,
JQT008	15	18	8.4	8.1	6.2	5.9	38.2	57	Brazil), in March and
CONAMA 357/05		_	> 6.0	$mg.L^{-1}O_2$	(	5.0-9.0		-	September 2006

sewage treatment plants

Water and

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28,2	Period	Station	Р	Κ	Са	Fe	Ba	Pb	B	Al	Mn	Zn	Na	Mg
	August/	JQT 002	< 0.33	0.63	2.25	0.21	0.014	< 0.001	< 0.05	0.02	0.02	0.01	2.49	0.74
	2004	JQT 003	< 0.33	0.63	2.21	0.24	0.014	< 0.001	< 0.05	0.05	0.02	0.01	2.46	0.75
		JQT 004	< 0.33	0.62	2.14	0.17	0.014	< 0.001	< 0.05	0.02	0.02	0.00	2.41	0.75
		JQT 006	< 0.33	0.65	2.29	0.14	0.015	0.002	< 0.05	0.02	0.02	0.01	2.56	0.77
162		JQT 007	< 0.33	0.67	2.27	0.16	0.015	0.002	< 0.05	0.08	0.02	0.01	2.58	0.78
102	<b>NT</b> 1/	JQT 008	< 0.33	0.76	2.20	0.19	0.015	< 0.001	< 0.05	0.02	0.00	0.01	3.25	0.80
	March/	JQT 002	0.06	0.41	2.41	0.38	0.015	< 0.001	0.00	0.06	0.01	0.01	2.50	0.85
	2005	JQ1 003	0.13	0.41	2.38	0.27	0.017	0.002	0.00	0.07	0.01	0.01	2.44	0.82
		JQ1 004	0.13	0.45	2.31	0.31	0.016	0.001	0.01	0.07	0.01	0.01	2.40	0.00
		JQ1 000	0.12	0.44	2.40	0.30	0.010	< 0.001	0.01	0.03	0.02	0.01	2.92	0.80
		JQ1 007	0.13	0.42	2.40	0.20	0.013	< 0.003	0.01	0.04	0.01	0.01	2.49	0.80
	July/2005	IOT 002	0.12	0.43	1.88	0.18	0.017	< 0.001	< 0.01	0.04	0.01	< 0.01	2.10	0.03
	July/2000	IOT 003	0.04	0.46	1.00	0.10	0.010	0.001	< 0.05	< 0.03	0.02	< 0.003	2.81	0.74
		IQT 004	0.04	0.45	1.86	017	0.018	0.001	< 0.05	< 0.03	0.02	< 0.003	2.86	0.75
		IQT 006	0.04	0.45	1.94	0.09	0.018	< 0.001	< 0.05	< 0.03	0.02	< 0.003	2.88	0.74
		<b>JQT</b> 007	0.05	0.46	2.13	0.16	0.019	< 0.001	< 0.05	< 0.03	0.02	< 0.003	2.85	0.75
		<b>JQT 008</b>	0.05	0.49	2.07	0.17	0.019	< 0.001	< 0.05	< 0.03	0.03	< 0.003	3.15	0.77
	October/	JQT 002	0.03	0.63	2.38	0.49	< 0.0001	< 0.001	< 0.05	0.28	0.01	0.00	2.50	1.00
	2005	JQT 003	0.04	0.58	2.40	0.48	< 0.0001	< 0.001	< 0.05	0.29	0.01	0.01	2.42	1.03
		JQT 004	0.03	0.57	2.34	0.46	< 0.0001	0.002	< 0.05	0.25	0.01	0.00	2.33	1.02
		JQT 006	0.03	0.64	2.44	0.45	< 0.0001	< 0.001	< 0.05	0.26	0.01	0.01	2.57	1.03
		JQT 007	0.03	0.66	2.38	0.56	< 0.0001	< 0.001	< 0.05	0.32	0.01	0.01	2.65	1.01
		JQT 008	0.05	0.69	2.52	0.51	< 0.0001	< 0.001	< 0.05	0.29	0.02	0.00	2.91	1.04
	November/	JQT 002	0.09	0.45	2.67	0.51	0.017	< 0.001	< 0.06	0.10	0.02	0.01	2.60	1.11
	2005	JQT 003	0.08	0.58	2.58	0.49	0.016	< 0.001	< 0.06	0.11	0.02	0.01	2.53	1.12
		JQT 004	0.10	0.50	2.71	0.50	0.016	0.002	< 0.06	0.13	0.03	0.10	3.10	1.17
		JQT 006	0.09	0.46	2.78	0.44	0.016	< 0.001	< 0.064	0.12	0.02	0.01	2.61	1.19
		JQ1 007	0.10	0.49	2.71	0.57	0.016	< 0.001	< 0.064	0.15	0.03	0.01	3.00	1.19
	March/	JQ1 008	0.09	0.47	2.07	0.32	0.010	< 0.001	< 0.064	0.14	0.02	0.01	2.00	1.20
	2006	JQ1 002	< 0.01	0.33	2.02	0.33	< 0.001	< 0.001	0.01	0.20	0.01	0.00	0.37	0.05
	2000	IOT 004	0.01	0.34	1.02	0.23	< 0.001	< 0.001	0.01	0.10	0.01	0.01	0.33	0.00
Table III.		IOT 006	0.02	$0.00 \\ 0.42$	2.07	0.31	< 0.001	< 0.001	0.01	0.20	0.02	0.01	0.51	0.68
Concentrations of		IOT 007	0.02	0.44	1.95	0.34	< 0.001	< 0.001	0.01	0.24	0.01	0.01	0.55	0.64
different chemical		IOT 008	0.01	0.47	2.24	0.38	< 0.001	< 0.001	0.01	0.26	0.01	0.01	0.76	0.66
elements in waters	September/	IQT 002	< 0.02	0.79	1.95	0.21	0.016	< 0.001	0.02	0.01	0.01	< 0.001	0.80	0.77
from the São	2006	JQT 003	< 0.02	0.74	1.97	0.25	0.015	< 0.001	0.02	0.01	0.01	< 0.001	0.75	0.78
Lourenço River		JQT 004	< 0.02	0.72	1.92	0.21	0.016	< 0.001	0.02	0.01	0.01	< 0.001	0.73	0.78
(Juquitiba, São Paulo,		JQT 006	< 0.02	0.73	1.97	0.26	0.014	< 0.001	< 0.064	0.02	0.01	< 0.001	0.75	0.79
Brazil). Values in bold		JQT 007	< 0.02	0.76	1.96	0.21	0.015	< 0.001	< 0.064	0.02	0.02	< 0.001	0.79	0.78
indicate levels above		JQT 008	< 0.02	0.81	2.04	0.20	0.016	< 0.001	< 0.064	0.01	0.01	< 0.001	0.85	0.80
the federal standards	CONAMA 3	357/2005	0.05	-	-	0.30	0.70	-	0.50	0.10	0.11	0.18	-	-

#### 3.3 Sediment properties and chemistry

In March 2006, all the sediment samples were considered sandy muds. In September 2006, samples from JQT002, JQT006 and JQT007 were considered sandy muds as well, those from JQT003 and JQT004 were muddy, and that from JQT008 was sandy (Table IV). However, there were evidences that sand was being exploited at JQT002 and JQT004. The quantities of OM were low in all samples, but samples under influence of the WTP (JQT004) and STP (JQT007) tended to exhibit higher levels.

The concentrations of elements and oxides obtained in the FRX are in Table V. Most of the variables did not present relevant variation in time and space, with the exception of Cr, MnO, Cl,  $ZrO_2$  and Zn, which presented certain variation among sampling stations. It was not possible to establish a clear link between the disposal of residues by WTP or STP and the concentrations of chemical substances in the SLR sediments. When the chemical





Figure 2. Acute toxicity of waters of the São Lourenço River to Ceriodaphnia dubia (Cd); Daphnia laevis (Dl); Ceriodaphnia silvestrii (Cs) and Daphnia similis (Ds) and chronic toxicity to C. silvestrii

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**Note:** Lines in the graphics show the maximum acceptable effects in the controls

analysis made with the ICP-OES is considered (Table VI), the measured concentrations are low and do not exceed the Canadian sediment quality guidelines (CCME, 2001). Moderate to high levels of aluminum were observed in sediments collected downstream in the discharge of the WTP (JQT004); aluminum sulfate is used in the water treatment. On the other hand, the concentrations were lower in the sediments collected downstream the STP.

# 3.4 Sediment toxicity

The following sediment samples from SLR presented acute toxicity: JQT008 in November 2005 (H. azteca and C. xanthus), and JQT007 in September 2006 (C. xanthus). In November 2005,

MEQ	2	31
28,2	17008 Sentember/	0 48 52 0.5
164	JC March/06	5 77 18 0.2
	T007 Sentember/06	10 77 13 1.0
	D D D D	5 70 25 1.3
	2T006 Senterr/06	9 71 20 0.2
	March/06	4 79 18 0.6
	2004 Sentember/06	95 95 1.8
	March (06	5 79 16 1.2
	2003 Sentember/06	5 85 10 0.7
		4 70 26 0.8
Table IV	1002 Sentember ()6	3 75 21 0.2
Sediment grain size distribution and Organic Matter (O.M) in samples from the	March (06	6 58 36 1.3
São Lourenço River (Juquitiba, São Paulo, Brazil)	V Arti- Ida	Clay (%) Silt (%) Sand (%) O.M. (%)

aded by USP At 12:17 28 August 2017 (PT)		
ownloa	ownloaded by USP At 12:17 28 August 2017 (PT)	

$(\mu g.g^{-1})$	March	September	March	September	March	September	March	September	March	September	March	September	March	September	March	September	March	September
	SiC	) <sub>2</sub> (%)	AIC	) <sub>3</sub> (%)	$K_{2}$	0 (%)	Fe(	) <sub>2</sub> (%)	Tić	<b>D</b> 2 (%)	Mg	0 (%)	Ca(	(%) C	$P_2C$	)2 (%)	$Na_2($	(%)
JQT002	67.4	77.4	15.8	12.8	1.8	2.7	2.7	2.0	0.56	0.47	0.41	0.40	0.17	0.26	0.31	0.23	0.14	0.15
JQT003	76.2	76.5	14.8	13.4	1.9	3.0	2.6	3.0	0.57	0.49	0.38	0.42	0.18	0.20	0.30	0.23	0.13	0.14
JQT004	78.1	62.7	13.8	20.5	1.8	2.3	2.0	3.6	0.55	0.69	0.38	0.51	0.16	0.19	0.24	0.30	0.11	0.14
JQT006	70.4	81.6	16.6	11.3	2.2	2.6	2.8	1.6	0.50	0.57	0.45	0.34	0.29	0.25	0.30	0.19	0.14	0.12
JQT007	76.1	75.2	14.8	13.9	1.8	2.2	2.5	2.2	0.53	0.56	0.42	0.40	0.22	0.18	0.27	0.19	0.11	0.14
JQT008	61.6	77.6	14.9	12.6	1.6	2.8	2.5	2.3	0.45	0.46	0.47	0.37	0.65	0.34	0.28	0.29	0.17	0.35
	Cr (r	$lg.g^{-1}$	MnO	$(\mu g.g^{-1})$	CI (F	$(g.g^{-1})$	$ZrO_2$	$(\mu g.g^{-1})$	Ni (I	$ug.g^{-1}$ )	JuZ (	$lg.g^{-1}$	$Rb_2O$	$(\mu g.g^{-1})$	SrO (	$(\mu g.g^{-1})$	SO <sub>3</sub> (F	$(g.g^{-1})$
JQT002	220	200	672	307	311	194	67	74	56	54	71	38	57	42	21	< 20	983	096
JQT003	0	182	423	528	228	0	86	35	68	64	58	0	56	57	20	22	972	1,159
JQT004	197	196	373	840	218	175	101	101	48	65	42	53	52	53	< 20	< 20	758	006
JQT006	202	235	538	284	172	0	09	72	67	70	49	0	64	40	< 20	< 20	006	757
JQT007	554	166	903	256	0	0	240	70	57	66	47	49	50	51	22	< 20	810	I
JQT008	142	194	291	355	126	0	40	56	44	99	42	36	53	68	31	42	836	919

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Table V. Concentrations of elements and oxides in sediments from the São Lourenço River (Juquitiba, São Paulo, Brazil), in March and September 2006

MEQ 28,2	Nitrite 1g.g <sup>-1</sup> )	10 10 10 20	
	Nitrate ( (ug.g <sup>-1</sup> ) (i	3.9 1.1 8.2 8.2	
166	TNK (µg.g <sup>-1</sup> )	1,952 1,687 1,787 1,262	
	Ammonia (µg.g <sup>-1</sup> )	237 250 222	
	OM (%)	3.8 3.7 4.1	
	riable Al (µg.g <sup>-1</sup> )	6,735 10,000 6,954 402	
	Aeasured vai Zn (µg.g <sup>-1</sup> )	$14 \\ 17 \\ 15 \\ 7.5$	
	$\Pr_{(\mu g. g^{-1})}$	5.4 7.3 3.7 3.7	
	Ni (µg.g <sup>-1</sup> )	5.8 5.2 0.8	
	Mg (µg.g <sup>-1</sup> )	で し し し し し し し し し し し し し	
	$C_{\rm U}$ ( $\mu g.g^{-1}$ )	4.7 7.5 1.9	
Table VI. Concentrations of	Cr (µg.g <sup>-1</sup> )	5.2 7.0 6.7 < QL en Kjeldahl	
Matter, and nitrogen compounds in sediments from the São Lourenco River	Cd (µg.g <sup>-1</sup> )	< QL < QL < QL < QL < QL , total nitrog	
(Juquitiba, São Paulo, Brazil), in September 2006	$(\mu g.g^{-1})$	JQT002 JQT004 JQT006 JQT006 JQT008 Note: TNK	

March and September 2006, the majority of samples were chronically toxic (*C. silvestrii*), including those collected upstream of the WTP and STP (Figure 3).

#### 3.5 Benthic community

The macrobenthic community of SLR in the Juquitiba region was composed by 11 taxonomic groups (to family level), as shown in Table VII. The stations located downstream





Figure 3. Acute toxicity of sediments of the São Lourenço River to Hyalela azteca (Ha) and Chironomus xanthus (Cx); and chronic toxicity to Ceriodaphnia silvestrii

Note: Lines in the graphics show the maximum acceptable effects in the controls

MEQ (JQT007 and JQT008) tended to present more species. Tubificidae was the dominant group in most of the samples, and these organisms tended to be more abundant in the stations JQT007 and JQT008. In JQT003, the abundance tended to be lower, suggesting an effect from the WTP effluent. On the other hand, abundance was greater in the stations located downstream of the STP, although the dominant species were opportunistic (as e.g. tubificids). The T/TD ratio shows this situation, since the values ranged between 0.5 and 1.0 for most of the samples, excepting JQT006 and JQT008 in September 2006.

#### 3.6 Data integration

For the integration of data, it was considered that sediments were not contaminated because no SQG exceedance was observed. Toxicity was marginal for most of sediments and only in JQT007 and JQT008 the toxicity was recurrent. For the macrobenthic community, evidences of strong alteration were observed in JQT002 (upstream to WTP and STP), JQT003, JQT004, JQT007 and JQT008. This indicates that non-measured contaminants (from unknown sources) probably are influencing the quality of SLR (Figure 4).

#### 4. Discussion

The SLR waters tended to present low concentrations of metals and other ions; however, the levels of P, Fe and Al above federal standards for freshwaters and the toxicity exhibited for some samples may indicate the influence of anthropic sources of contamination. In addition to the local sources, the SLR receives the effluents from the STP and WTP situated upstream (in the city of São Lourenço da Serra) and other unknown sources (Cutolo *et al.*, 2008). Such contamination sources could explain toxicity and high levels of P, Al and Fe, as samples from JQT002 eventually indicated toxicity and moderate to poor water quality. Effluents from WTPs and sewage are widely known by their potential to pollute the environment and cause negative effects to the biota (Jarvie *et al.*, 2006; Aerni *et al.*, 2004; Baronti *et al.*, 2000). The effluents from the WTPs and STPs of São Lourenço da Serra and Juquitiba were considered toxic to aquatic invertebrates (Silva, 2008). However, toxicities did not correlate to the levels of metals and nutrients, as observed by Rodgher *et al.* (2005) for the Tietê River. Moreover, there were not relevant alterations in the physical parameters of water along the SLR, with exception of the slight reduction in the DO levels just after the WTP and STP of Juquitiba.

Regarding the sediments, the textures showed a temporal change. Sediments from most of the stations tended to present higher percentages of sands and higher amounts of OM during the summer (excepting JQT008). The difference in textures may be explained by the turbulent river flux during the rainy season, which is capable to remobilize the fine particles and carry them downstream. Besides, the influence of sand extraction close to JQT002 and JQT004 may have an additional influence on the grain size distribution and should be considered. On the other hand, the higher OM contents in the summer are explained by the increased volumes of storm waters in that period. Similar result was observed by Abessa (2003) in another river from the MRSP. Anyway, the sediments from SLR presented low levels of OM in all sampling surveys.

The concentrations of ammonia and total kjeldahl nitrogen were relatively low, with lower concentrations in the sediments from JQT008. In comparison to the concentrations detected upstream (in the city of São Lourenço da Serra) by Silva *et al.* (2014), the levels of nitrogen compounds in sediments from SLR in Juquitiba were lower. However, for the phosphorus, the concentrations near Juquitiba were higher, suggesting that in this area the influence of sewage of effluents from WTP/STP may be more intense.

The benthic community was composed by a low number of taxonomic groups. Richness was low in most of the stations, with the exception of JQT007 in March 2006 and JQT006 and JQT008 in September 2006. Still, in September 2006, organisms from the family Tanypodinae

Taxonomic group	Sampling JQT002	station – N JQT003	1arch 2006 JQT004	JQT006	JQT007	JQT008	Total	Sampling JQT002	station – St JQT003	eptember 20 JQT004	06 JQT006	JQT008	Total
	00				00		ç						
Nematoda sp1	33				33		90						0
Curbiculidae			22				22				44	300	344
Pisididae					122		122				22		22
Tubificidae	167	44	144		500	7,088	7.943	389	200	133	22	433	1,177
Glossiphonidae					55	n.	55						0
Hidracaridae				11	11		22					11	11
Trichdactylidae					11		11						0
Chironomidae				11			11	33				311	344
Ortocladinae		22					22	33				44	77
Ceratopogonidae					11		11						0
Chironominae							0				22	78	100
Tanypodinae							0				11		11
Density	200	99	166	22	743	7,088	8,285	455	200	133	88	1,093	1,975
Richness	2	2	2	2	7			က	1	1	2	9	
T/TD	0.83	0.66	0.86	0.50	0.67	1		0.85	1	Ч	0.39	0.36	

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Table VII. Densities of the taxonomic groups of macrobenthos, richness and T/TD (tolerant organisms/ total densities) in sediments from the São Lourenço River (Juquitiba, São Paulo, Brazil)



were found in JQT006. This family normally is not found in polluted sites and is typically found in reference sites (Marques *et al.*, 1999; CETESB, 2007); thus, their presence suggests favorable conditions for benthic species in JQT006 in September 2006. The presence of the invasive bivalve *Corbicula fluminea* in JQT006 and JQT008 (September 2006) is concerning, as this species is invading the Brazilian rivers (Mansur *et al.*, 2004; Castilho, 2007) and is found in the Ribeira de Iguape River basin (Guimarães and Sigolo, 2008).

Changes in the species' composition between campaigns may be explained by the changes in sediment texture related with the rainfall regime, and other factors, such as the extraction of sand and the fact that the WTP sludge started to be transferred to the STP. The concentrations of chlorine in sediments were lower in September 2006, dropping to zero in JQT003, JQT006, JQT007 and JQT008. The presence of individuals from the family Chironomidae, especially in stations located downstream may indicate a better condition as well; although this family is considered tolerant to pollution, hypoxia and organic enrichment, some of its species are considered pollution sensitive (Silva, 2005; Marques *et al.*, 1999).

The family Tubificidae was found in all sampling stations, excepting in JQT006 in March 2006. This family was dominant in most of the stations, and their abundance was very high in JQT008, in March 2006. The dominance of tubificids suggests that the SLR is impacted

near Juquitiba. The densities tended to be higher in September than in March, but as they were strongly influenced by the presence of opportunistic species, this descriptor does not explain well the results. Anyway, as in March some parameters suggested a worse condition (e.g. chlorine in sediments), the lower densities may indicate that benthos is being affected by anthropic activities.

When the taxonomic composition is compared to that found near São Lourenço da Serra by Silva *et al.* (2014), there are more organisms from the families Chironomidae, Ortocladinae, Ceratopogonidae, Tanypodinae and Curbiculidae in Juquitiba, while the tubificids are more abundant in São Lourenço da Serra. Thus, it is possible to infer that the conditions in Juquitiba are more suitable to aquatic life.

When the results are integrated and combined to determine the environmental quality in all the sampling stations from the SLR, it is possible to observe that the benthic community shows signs of degradation in the majority of stations, with exception of JQT006. Toxicities were recurrent in JQT007 and JQT008, while the concentrations of most of substances in sediments were low. However, the levels of P, Fe and Al were eventually above the limits for freshwaters (Brasil – República Federativa, 2005); they could explain partially the benthic alteration, as toxicities did not correlate with the concentrations of metals and other substances. Nipper *et al.* (1998) have discussed that integrated studies in mildly contaminated environments can produce dubious results. In case of the SLR, unmeasured contaminants other than metals may be the cause of toxicity and benthic alterations; thus, further studies should be conducted in order to identify the environmental stressors for the biota of the SLR.

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