CONCENTRAÇÃO DE ALUMÍNIO, FERRO E MANGANÊS EM RIOS URBANOS LOCALIZADOS EM ÁREA DE ABRANGÊNCIA DO AQUIFERO GUARANI EM LAGES - SC

CONCENTRATION OF ALUMINUM, IRON AND MANGANESE IN URBAN RIVERS LOCATED IN A COVERAGE AREA OF THE GUARANI AQUIFER IN LAGES - SC

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RESUMO

O objetivo do presente estudo foi avaliar a concentração de alumínio (Al), ferro (Fe) e manganês (Mn) na água e no sedimento de rios urbanos (Carahá, Caveiras e Ponte Grande) da serra, na cidade de Lages, Santa Catarina, localizada em área de abrangência do Aquífero Guarani. As amostras de água e sedimento foram coletadas entre maio e outubro de 2016 em três rios urbanos, seguindo um gradiente de perturbação ambiental. Para a extração dos metais presentes na amostra, foram utilizados os métodos 3030 - *Standard Methods of Water and Wastewater* (2005) para as amostras de água e ISO 11.466 (1995) para as amostras de sedimento. A quantificação dos metais foi realizada através de um espectrômetro de alta resolução de absorção atômica, com automação de chama (acetileno-ar ou óxido nitroso-ar). Para avaliar a quantificação, utilizou-se um material certificado (SRM 2709a - San Joaquin Soil - NIST). Nas amostras de água foram encontradas concentrações de Mn acima da classe III, definidas pela Resolução 357/05 do Conselho Nacional do Meio Ambiente - Brasil. A matriz de correlação de Pearson mostrou correlação positiva entre as variáveis Al/Fe, Fe/Mn e Al/Mn no sedimento e Fe/Mn na água. Para o sedimento, foram encontradas altas concentrações de Al, Fe e Mn em algumas das amostras. Pelos resultados encontrados, evidencia-se aumento na concentração de Al e Fe no sedimento do rio Carahá, e concentrações de Al, Fe e Mn no sedimento do rio Ponte Grande, nos pontos localizados em Lages - SC.

Palavras-chave: *água, sedimento, metais, meio-ambiente.*

ABSTRACT

The objective of the current study was to evaluate the concentration of aluminum (Al), iron (Fe) and manganese (Mn) on water and on the sediment of urban rivers (Carahá, Caveiras and Ponte Grande) in Lages, located on the mountain region of Santa Catarina, placed in a coverage area of the Guarani Aquifer. The water and sediment samples were collected between May and October of 2016 in three urban rivers, following an environmental disturbance gradient. For the extraction of the metals present on the sample, it was used the methods 3030 - *Standard Methods of Water and Wastewater* (2005) for the water samples and ISO 11,466 (1995)

for the sediment samples. The quantification of metals was performed through a high-resolution spectrometer with atomic absorption, with a flame automation (acetylene-air or nitrous oxide-air). To evaluate the quantification, it was used a certified material (SRM 2709a - San Joaquin Soil - NIST). On the water samples were found concentrations of Mn above of class III, defined by the Resolution 357/05 of the Environment National Board-Brazil. The Pearson correlation matrix showed a positive correlation between the variables Al/Fe, Fe/Mn e Al/Mn on sediment and Fe/Mn on water. For the sediment, it was found high concentrations of Al, Fe, and Mn in some of the samples. By the results found, it is evinced an increase in the concentration of Al and Fe on the Carahá river sediment, and concentrations of Al, Fe, and Mn on the Ponte Grande river sediment, on the spots located at Lages - SC.

Keywords: *water; sediment, metals, environmental.*

INTRODUCTION

The Guarani Aquifer constitutes one of the most important hydrostratigraphic unities of the meridional portion of the South-American continent. The unity occupies an area superior to 1.000.000 Km² that extends itself through Argentina, Brazil, Uruguay, and Paraguay. In its northerly portion, it presents a great relevance for the public and private supplying.

At the mountain plateau, there are several upwelling areas and a direct recharge from the Guarani Aquifer, an important reserve of fresh water for Santa Catarina state. However, at the city of Lages, this water resource is at the risk of contamination by the productive processes, irregular occupation, the outflow of not-treated effluents and improper disposal of residues on the outflow areas (Mazzolli and Ehrhardt-Brocardo, 2013) and it might contain metallic pollutants.

The metallic pollutants have been receiving considerable attention because they have a low biodegradability, they're transported by the rivers and they are absorbed with the capacity of sediments to associate themselves to the geological materials of the original draining bay (Bordon *et al.*, 2011; Paula Filho *et al.*, 2014).

In Brazil, due to the several existing geological formations, studies about the accumulation of metals have been aiming to establish the geochemical basis to evaluate if the origin is anthropogenic or natural. Determine the natural levels of metals is essential for the precise evaluation of the degree in which a certain metal has been enriched on the environment. Evaluations like this provide an objective basis for the decision taking from the public departments and for the proper use of natural resources (Reimann *et al.*, 2005; Paula Filho *et al.*, 2014). The analysis of metals in sediments deposited on the course of aquatic systems is an important

environmental tool to evaluate and monitor the water quality because the sediment can accumulate higher concentrations of toxic metals than the ones at the water column. The metals present on the sediments and on the water, can occur on the form of solutions, mineral compounds, adsorbed in inorganic and organic particles or even accumulated in aquatic organisms (Semensatto-Jr. *et al.*, 2007), which makes a persistent contamination. This way, the practices to monitor sediments are essential to protect the aquatic ecosystems (Bordon *et al.*, 2011, Yuan *et al.*, 2014, Coringa *et al.*, 2016).

Metals such as Al, Fe, and Mn are found in significant concentrations in superficial waters according to the abundance of the origin material. This way, the levels of these elements in superficial waters can increase during raining periods due to the erosion on the rivers' margins. The concentration of iron on the environment can also increase with the metallurgical industrial effluents and coagulants made on iron basis, used at water and effluents treatment plants. The aluminum and its salts are used on the water treatment, such as food additives, manufacturing of cans, tiles, aluminum foil, on the pharmaceutical industry, among others. The manganese and its compounds are used on the steel industry, metal alloys, glasses, cleanliness oxidants, fertilizers, varnishes and veterinary supplements (CETESB, 2017).

The manganese is an essential element found on the land crust and on the locations where the oxygen is dissolved and the potential redox is low, where lower levels of Mn can be found on its reduced dissolved state (Mn(II)). The higher concentrations of Mn are found on the underground waters, while the superficial water rarely presents high concentrations. Higher concentrations of Mn on the potable water that exceed the value of 0,4 mg L⁻¹ were reported in several studies (Joode *et al.*, 2016). The excess of

Mn can cause talking and memory disorders and degenerative diseases (Riguetti *et al.*, 2015).

The metallic ions can be bio-accumulated by aquatic organisms, such as invertebrate and fishes, presenting a threat to the human health because of the food chain or by the own ingestion of water. The accumulation of these elements over time causes damages to the kidneys, liver and to the nervous system when they're found above the tolerance levels (Goher *et al.*, 2015).

In face of what's exposed, the goal of the current study was to determine the concentration of three metals, Al, Fe, and Mn, in superficial waters and sediments of rivers in the Caveiras river bay, located in an urban area in the city of Lages-SC.

MATERIAL AND METHODS

2.1. Study region

The Caveiras river bay is in Santa Catarina state, with the nascent above of 1.300 m on the general mountain region. The study region was Lages-SC (latitude: -27° 48' 58" S, Longitude: -50° 19' 34" W, altitude: 916M), which has nearly 158.000 inhabitants, the average temperature of 16°C and an annual average precipitation of 1.236,2mm, well distributed over the year.

The city of Lages is located at the mountain plateau of Santa Catarina. In this region, especially on the cities of Urubici, Painele, Lages, São José do Cerrito, Correia Pinto and Ponte Alta, there were upwelling areas and direct recharge from the Guarani Aquifer, representing, thus, a strategical reserve for the water supply for Santa Catarina state. Scheibe and Hirata (2008) emphasize the occurrence of an indent upwelling of sandstones from the Botucatu Formation (Matrix of the Guarani Aquifer), occasioned by the over-elevation of the Lages Dome, where volcanic rocks from the General Mountain recovers sandstones at the west of Lages.

For this study, it was selected nine sampling points located at the Caveiras river bay (affluent of the Canoas river), located in areas covered by the Guarani Aquifer in urban areas of Lages (Figure 1).

Figure 1. Localization of the sampling points (P1 to P9), where it was collected the samples of superficial water and sediment to determine the physicochemical characteristics and aluminum, iron and manganese levels.

From these, three points (P1, P2, and P3) were collected at Carahá river, being, respectively, a point near the nascent (upstream), one in the central passage and another on the river mouth (downstream). Equally, three points (P4, P5, and P6) were sampled in Caveiras river, being one point to the upstream, one point after receiving the contribution from the Carahá river (center) and other at the downstream at Lages. The points (P7, P8, and P9) represent the samples collected in the Ponte Grande river (upstream, center and downstream). From these, the points (P1 and P7) are in a permanent preservation area and were used as a control.

2.2. Collection and extraction of the elements on the water and sediment samples

The water and sediment samples were collected in a period where there were not rains (at minimum five days before the collection) between April and October of 2016. In each point, it was

collected 0.5L of water in backwater passages, with the support of a polyethylene bottle containing one millimeter of nitric acid to preserve the sample. It was also collected sediments samples with the support of a stainless-steel drag at the depth of 0-0.1m. In each river, it was collected three sediment samples with a distance among each other of about 50m, and they were wrapped in plastic bags. After the collection, the water and sediment samples were transported to the lab in a thermal box. In each point was also determined the pH, dissolved oxygen (DO) and the electrical conductivity (EC) of the water with a multi-parameter probe and the texture of sediments by the pipette method.

For the extraction of elements on the water samples, it was used the procedure 3030 - Standard Methods of Water and Wastewater (2005). It was transferred a volume of 100 mL of the water sample to an Erlenmeyer, being added 5 mL of nitric acid, covering it with a clock glass to minimize the losses. After that, the sample was heated until a boiling state in a heating plate and was kept until the acquisition of the lowest volume possible (10-20 mL), avoiding that the sample was precipitated or became dry. Up next, it was heated with the addition of nitric acid until the acquisition of a clear solution. Finally, the solution was filtered and enlarged to 50 mL.

For the extraction of the sediment elements, it was adopted procedures described in ISO 11466:1995. Initially, the material was dried in a study at 60°C for five days and it then it was pulverized. A sub-sample of 0.75g was placed in a digestion tube. Up next, it was added to the tube with 0.05g of water followed by 7 mL of Aqua Regia. After that, the digestion tube was left to rest for 16 hours at the environment temperature and, next, it was heated at 90°C during 2 h. Finally, the solution was filtered at the environmental temperature and enlarged to 50 mL with an ultra-pure water, type 1 by ASTM D1193-06 standard.

2.3. Quantification of Al, Fe, and Mn

The quantification of the Al, Fe and Mn elements was performed in a high-resolution spectrometer with atomic absorption, with a flame automation (acetylene-air or nitrous oxide-air) from the model AA-6300 - Shimadzu.

As a minimal parameter for the detection limit, it was considered the first spot on the calibration curve. The efficient of quantification was verified through the analysis of a certified material, whose values can be verified in Table 1,

where it was obtained values within the tracks established.

Table 1. *Quantification of Certified Material - Nist San Joaquin Soil 2709*

	Al (%)	Fe (%)	Mn (mg/kg)
Quantified	1.9 ±1.23	2.8 ±4.63	480 ±1.82
Total certificate material	7.5 ±0.06	3.5 ±0.05	538 ±17
Certified material leached	2 – 3.1	2.5 – 3.3	300–600

2.4. References values of Al, Fe, and Mn

In Brazil, the Resolution 357 of 2005 of CONAMA (National Board of the Environment-Brazil) dispose about the classification of the water bodies and environmental guidelines for its framework, as well as it established the conditions and standards for the release of effluents. The framework of fresh water is done through four classes by several organic and inorganic parameters. For a possible framework on the classes I, II, III and IV of CONAMA, the parameter of elements below must be within what was specified, including the other inorganic and organic parameters previewed by the Resolution (BRASIL, 2005). Article 15 establishes that it must be applied to the class II fresh water the conditions and standards of class I for the inorganic parameters (with an exception for the phosphorus). Due to this reason, classes I and II have the same concentration limits for Al, Fe, and Mn, as shown in Table 2.

The reference values for the contamination levels in sediments was proposed by Thomas (1987). The author established contamination levels for Fe and Mn, ranking the levels of these elements in pollution categories, being: non-polluted, moderately polluted and highly polluted, as it can be seen in Table 3.

Table 3: *Pollution categories for the Fe and Mn parameters established by Thomas (1987) in (mg/kg)*

Metal	Not polluted	Moderately polluted	Highly polluted
Fe	<17,000	17,000-25,000	>25,000
Mn	<300	300-500	>500

2.5. Results analysis

The results obtained on the water and sediment analysis were compared with the reference values, proposed by the Resolution 357 of CONAMA for the classification of water and by Thomas (1987) for the pollution levels on the sediment. The results were evaluated through a descriptive statistic and analysis of tendencies in column graphics to evaluate the concentration gradient of the parameters on the sense from the amount to the downstream. It was made Pearson correlations between the variables and a t-test to verify which correlations were significant among the level 5 elements and 1% with the support from the Assistant 7.7 Program.

RESULTS AND DISCUSSION

3.1. Water's physicochemical properties

It is found, in Table 4, the results of the pH, dissolved oxygen (DO) and electrical conductivity (EC) for the water of the points P1 to P9 over the evaluated rivers.

The points P3, P8 and P9 presented DO levels inferior to 4 mg/L, which makes these points fit on class IV (Table 2) of the Resolution 357 of CONAMA (BRASIL, 2005). The same Resolution established that the pH must be between 6 and 9 for fresh waters of all classes and it is verified that, for all points, this value was within or near the recommended track. For the EC, the P3 points of Carahá river and the points P7, P8 and P9 of the Ponte Grande river presented a conductivity above 250 $\mu\text{S}/\text{cm}$, indicating a significant presence of ions on the water. Although Resolution 357 does not specify the maximum values for the conductivity for the water ranking, the high EC values observed in these points indicate that there are contributing factors for an increase in these passages of the water resource. According to Gasparotto (2011), for the river that is highly contaminated by sewers, the water EC can vary from 100 to 10.000 $\mu\text{S}/\text{cm}$. Therefore, having as maximum limit 100 $\mu\text{S}/\text{cm}$ for a good quality water, it is possible to say that on the passages quoted above and constant on Table 4, the water presents itself with a bad quality.

Table 4: pH, dissolved oxygen and electrical conductivity of Lages urban river waters between May and October of 2016

River	Point	pH	OD (mg/L)	EC ($\mu\text{S}/\text{cm}$) (25°C)
Carahá	P1	6.34	8.26	129
	P2	6.87	4.51	119
	P3	7.51	2.88	310
Caveiras	P4	6.25	6.54	35
	P5	7.06	4.86	92
	P6	5.88	9.1	55
Ponte Grande	P7	5.99	10.4	300
	P8	7.11	1.34	265
	P9	7.13	3.54	258

3.2 Concentration of Al, Fe, and Mn on the water of urban rivers

Table 5 shows the results of the average concentration (mg/L) of Al, Fe, and Mn on the waters of nine points (P1 to P9) of the urban rivers in Lages.

Comparing the results from the Al, Fe and Mn concentrations presented in Table 5 with the reference values established by Resolution 357 (Table 2). This resolution establishes values of dissolved Al and Fe and values of the total Mn; due the fact the samples were collected in a dry period, the extraction method of the elements was total, therefore, it is hoped a minimal difference between the dissolved and the total, because the concentration of these elements is directly connected to the transportation of sediments from the rivers' margins. It is verified that for the Al element all points presented values that classify the water as a class IV, but the reference values refer themselves to a soluble Al. Thus, the water from the sampling points of this study can be destined for the navigation and landscaping harmony (BRASIL, 2005).

Table 5: Concentration (mg/L) and variation coefficient (vc %) of Al, Fe, and Mn on the waters of nine points (P1 to P9) of the urban rivers in Lages

	Al		Fe		Mn	
	mg/L	vc%	mg/L	vc%	mg/L	vc%
P1	0.23	7.00	0.61	3.22	0.01	3.79
P2	1.37	3.60	1.03	2.61	0.01	0.96
P3	4.86	2.56	1.94	0.50	0.26	3.31
P4	0.96	2.01	1.29	0.84	0.04	4.00
P5	1.85	1.49	1.37	1.48	0.10	3.07
P6	1.37	3.60	0.76	2.61	0.03	0.96
P7	0.42	5.41	0.62	2.93	0.01	2.71
P8	1.50	4.06	2.29	1.16	0.95	1.97
P9	2.71	2.90	1.98	0.97	0.69	3.20

For Fe, all points presented concentrations that fit them on class III. The waters of class III rivers can be aimed to the supply for the human consumption after the conventional or advanced treatment, to the irrigation of arboreal, crops and forage cultures, to the amateur fishing, the recreation of secondary contacts and to a reliable place to drink water for the animals.

For the Mn, the P8 and P9 of the Ponte Grande river presented a concentration above 0.5 mg/L, which ranks it as a class IV, while P3 presented a concentration for the class III and the points P2, P4, P5, P6, and P7 stayed at classes I and II. It is noticed that the points P3, P8 and P9 coincide with higher EC values, confirming the hypothesis of a higher concentration of an ion in these points. Waters from class I rivers can be destined to the supply for human consumption after the simplified treatment, protection of the water communities, recreation of primary contact, irrigation of greeneries that are not eaten raw and of fruits that grow near the soil and that are eaten raw without removing the layer and protection from the water communities in indigenous lands (Brasil, 2005).

At Figure 2 it is shown the behavior profiles of Al, Fe, and Mn on water over the rivers (from the amount to the downstream). The metal levels in the waters of Carahá river presented a positive tendency line and a positive concentration gradient for Fe and Al, on the direction from the amount to the downstream.

Figure 2. Aluminum, iron and manganese profiles obtained for the waters of Carahá, Caveiras and Ponte Grande rivers from the city of Lages.

The Mn presented low concentration on points P1 and P2, presenting a significantly higher level on point P3. On Caveiras river, the levels of Al, Fe, and Mn on water basically presented themselves as constants from the amount to the downstream, but they presented significantly higher levels than the nascent used as a control. On Ponte Grande river, the Al followed a positive tendency line and a growing gradient

concentration over the sampled points. For the Fe and Mn elements, it occurred a reduction on the concentration from the center to the downstream. Therefore, on the points where it was observed a positive tendency line and a positive concentration gradient on the direction amount to downstream, it is evinced the anthropic contribution over the city of Lages.

3.3. The concentration of Al, Fe, and Mn on the sediment of urban rivers

The sediments' texture is a factor that interferes on the concentration of metals. On the evaluated points, the texture varied between sand and blunts (P1 - sand, P2 - sand blunt, P3 - sand, P4 - sand blunt, P5 - silty blunt, P6 - sand blunt, P7 - sand blunt, P8 - silty blunt and P9 - sand blunt). This property interferes on the capacity to retain ions by the sediment, because higher the specific surface area of the sedimentary material, higher the adsorption and retention of substances, including the toxic contaminants. It is expected a higher retention of metals on the sediments with a silty characteristic because it has a higher surface area than the sandy sediments. The metals associated with the sediments can be released on the water column and bio-accumulate itself in plants and animals, entering, thus, on the food chain (Jesus *et al.*, 2004). However, environmental factors such as pH variations, redox potential, and presence of organic matter can influence on the stocking capacity on the sediments or on the bio-availability of the stocked elements, moving them on the environment, especially during flooding periods (Loureiro *et al.*, 2012).

In Table 6, it is presented the average concentration levels of Al, Fe, and Mn on the sediments of the points P1 to P9. On the central passage of the Caveiras river, there was a reduction of 40% on the concentration of Al and Fe, and there was a multiplication on the concentration of the downstream passage (exit from the urban area) in relation to the point to the amount. The Mn reduced 70% on the central passage and it had a new increase of 20% on the passage to the downstream in relation to the amount point. However, the Al, Fe and Mn levels on sediment in all the points were of 6 to 12 times superior to the sediments from the control stream (P1 and P7), what evince a significant degree of urban contamination.

Table 6: Concentration (mg/L) of Al, Fe, and Mn on the sediments of nine points (P1 to P9) of the urban rivers in Lages.

	Al		Fe		Mn	
	mg/L	vc%	mg/L	vc%	mg/L	vc%
P1	3,438	3.19	4,400	1.76	69	0.87
P2	18,142	2.40	10,035	0.33	83	1.03
P3	23,330	1.29	20,173	3.58	297	1.90
P4	19,915	1.58	27,865	3.50	525	1.70
P5	12,037	1.61	15,500	4.66	216	1.90
P6	39,693	1.70	44,179	2.56	621	1.77
P7	4,051	4.2	6,013	0.88	94	2.44
P8	23,784	3.77	30,362	4.60	355	1.03
P9	21,635	1.20	24,208	4.12	368	1.82

According with Thomas (1987) (Table 3), it is verified that the sediments from the points P1 and P2 (Carahá), P5 (intermediary point of Caveiras river) and P7 (intermediary point from the Rio Grande river) are classified as not-polluted by Fe, and, in the same way, these points added to the point P3 of Carahá river also did not present contamination by Mn. The sediments from points P3 of Carahá river and P9 of the Rio Grande river presented themselves as moderately polluted by Fe, while the sediments from the points P8 and P9 of Rio Grande river presented themselves as moderately polluted by the Mn element. The points P4 and P6 of the Caveiras river and P8 of the Rio Grande river presented themselves as highly polluted by Fe, and the points P4 and P6 of Caveiras river presented themselves as moderately polluted by Mn.

Figure 3 presents the behavior profiles from the Al, Fe and Mn parameters on the sediments of the three studied rivers.

On Carahá river, it was observed a positive tendency line and a growing concentration gradient, from the amount to the downstream, for the three parameters (Al, Fe, and Mn), evincing an increase of urban pollutants over the passage until the downstream. Caveiras river also presented a positive tendency line for the parameters that were monitored on the sediments, but it was not observed a growing gradient concentration, because there was a reduction of concentration on the central passage and an increase on the downstream.

Figure 3. Aluminum, iron and manganese profiles obtained for the sediments of Carahá, Caveiras, and Ponte Grande rivers from the city of Lages.

The concentrations of Al, Fe, and Mn over the Caveiras river presented themselves significantly above the control streams. The Al, Fe and Mn levels for the sediment of the Ponte Grande river presented positive tendency lines, but it did not occur a growing concentration gradient from the center to the downstream. Several factors might have influenced this

behavior besides the volume of pollution sources over the urban passage, the texture and pH, that might influence the results found. It was observed that the central point of the Ponte Grande river presented a silty blunt texture, while the other points have a sandy characteristic, which might have contributed for a higher adsorption of metals in the sediment. Besides, the pH in this point was around 7, what might have contributed to keeping the metals precipitated or strongly connected to their solid phase, as the central point of Caveiras river.

3.4. Pearson correlation between Al, Fe, and Mn on water and on sediment

On Table 7 there's the matrix of Pearson correlation, which shows the results of the t-test on the significant levels of 5% and 1% for the concentrations of Al, Fe, and Mn on sediment and on water.

It is noticed that there's a positive correlation between the variables Al and Fe, Fe and Mn and Al and Mn on the sediment, indicating a strong association between these variables. It is also noticed a positive correlation between the variables Fe and Mn on water, indicating that the Fe variable is strongly related to the Mn variable. It was not expected positive correlations from the pH with Al and Fe on water, this behavior can be influenced by several factors, such as solid, dissolved gases, hardness, alkalinity, temperature, biotic factors, among others (Fritzons *et al.*, 2003). According to Coringa *et al.* (2016), the precipitation of oxides hydrated with iron is associated with the transportation and availability of metals that influence the exchanges on the water-sediment interface. The high correlation between Fe and Mn on the sediment can be explained through the adsorption of manganese on the way of precipitated of iron oxides and hydroxides.

CONCLUSIONS

The concentrations of Al, Fe, and Mn deferred between the water and sediment samples and over the disturbance gradient analyzed. The water from the sampled points presented an elevated conductivity, indicating the significant presence of metals on its ionic form. In all of the sampled points, it was obtained Al values equivalent to the class IV of the Resolution 357 from the Environment National Board. On the sediment, it was observed concentrations of Al, Fe, and Mn much superior to the ones observed

on both nascent from the Carahá and Ponte Grande rivers (P1 and P2 points) in a magnitude from 6 to 12 times. The levels of these elements on the sediment, according to the references for the pollution levels, fit the studied rivers in moderately or highly polluted in their central passages and to the downstream (river mouth or on the exit from the urban area). It occurred an increase in the concentration of some major elements, such as Al, Fe and Mn, when compared with the control points that might result on the significant increase of other elements, which are more toxic than the ones evaluated as Cd, Cr, Cu, Zn and Pb, since they can be retained by oxides of Fe, Al, and Mn, turning the monitoring of these urban rivers into an important preservation tool from this water resource, which is so important for the city of Lages-SC-Brazil.

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Table 2. Concentration limits for the Al, Fe and Mn parameters on the different classes established by the Resolution 357 of CONAMA of 2005

	Class I	Class II	Class II	Class IV
Al dissolved	0.1 mg/L	0.1 mg/L	0.2 mg/L	>0.2 mg/L
Fe dissolved	0.3 mg/L	0.3 mg/L	5 mg/L	>5 mg/L
Mn total	0.1 mg/L	0.1 mg/L	0.5 mg/L	>0.5/mg/L
pH	6 – 9	6 - 9	6 – 9	6 – 9
Dissolved oxygen	>6	> 5	> 4	> 2

Table 7: Pearson correlation matrix with significance levels for the t-test for the concentrations of Al, Fe, and Mn on sediment and on water.

	Al _{sediment}	Mn _{sediment}	Mn _{sediment}	Al _{water}	Fe _{water}	Mn _{water}	pH
Mn _{sediment}	0.93**	1.00					
Mn _{sediment}	0.84**	0.96**	1.00				
Al _{water}	0.39ns	0.22ns	0.20ns	1.00			
Fe _{water}	0.34ns	0.35ns	0.28ns	0.67ns	1.00		
Mn _{water}	0.27ns	0.35ns	0.22ns	0.33ns	0.86**	1.00	
pH	0.05ns	-0.08ns	-0.17ns	0.77	0.82**	0.57ns	1.00
EC	-0.20ns	-0.26ns	-0.34ns	0.45ns	0.46ns	0.53ns	0.47ns

* Significant test at the 5% level of significance; ** Significant test at the 1% level; ns Test not significant to the 5% levels of significance.