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FULL PAPER

Current State of Contamination by Persistent Organic Pollutants and Trace Elements on Piabanha River Basin - Rio de Janeiro, Brazil

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Abstract:

Water bodies can be considered the ultimate receptor of pollutants produced or remobilized as a result of anthropogenic activities. Whereas diffuse pollution occurs throughout the Piabanha river basin, the aim of this work was to evaluate the distribution of trace elements and persistent organic pollutants in its sediments over time and space, gathering information to assess the risks to the ecosystem and the population. And also to provide data to orient governmental institutions management of water resources in this region. The levels of organic pollutants highlight the influence of the historical use of pesticides in farming and industrial activities, mainly for Posse (203.36 ng/g dry weight) and Fagundes river (198.33 ng/g d.w) during the dry season and Moura Brazil (77.50 ng/g d.w) and Garagem (77.06 ng/g d.w) in the rainy season. In relation to available trace elements, the most contaminated locations were within and around Petrópolis center, possibly by industrial and domestic effluents, where Liceu (44-245 µg/g d.w) and Garagem (15-189 µg/g d.w) showed the highest concentrations of zinc. Furthermore, Liceu (5-58 µg/g d.w) also excelled in concentrations of lead. Cadmium was the element with major contribution to the contamination of the locations studied (Geoaccumulation index from 3 to 5 in all collected points), mainly because of its high mobility and the river flow. In addition, Poço do Ferreira river presented trace elements levels that exceeds the level 2 of the National Environment Council (CONAMA) classification. The authors highlight the need for a monitoring program on this region for the contaminants analyzed.

Keywords: anthropic activities; geoaccumulation index; organochlorine pesticides; polychlorinated biphenyls; trace elements

1. Introduction

Water bodies, including rivers, are susceptible to processes of eutrophication and exogenous contamination, mostly from domestic and industrial sewage discharges in urban centers and rural regions [1]. In this way, water bodies constitute the ultimate fate of pollutants produced or remobilized as a result of anthropogenic activities. From there it can either be deposited in the sediment or accumulate in the resident biota [2]

Trace elements and persistent organic pollutants (POPs) are present in various abiotic compartments of the ecosystem. Trace elements may either come from natural sources or human disposal and remobilization. While the anthropogenic POPs are mainly from industrial or agricultural sources [3]. These compounds in high concentrations can be responsible for

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harmful effects in a wide range of organisms. Therefore, aquatic environment monitoring is an essential tool to assess the issues required for the implementation of mitigation measures.

Sediments can act as carriers and potential sources of contaminants to the aquatic systems [2]. Some of these pollutants can be adsorbed on the organic matter, suspended material or finer particles associated with bottom sediments [4]. This compartment can become the temporary or final destination of many contaminants.

The Piabanha river basin is one of the most important sub-basins that form the Paraíba do Sul river in the Rio de Janeiro state and is a system that suffer an intense anthropic action [5]. The river has high social and economic importance for the region. Diffuse pollution in this basin includes rainwater drainage of urban and rural areas, as well as atmospheric transport, which bring pollutants emitted from densely populated or high industrialized areas, such as Rio de Janeiro (South), Juiz de Fora (North) and Volta Redonda (East) cities [6]. The disordered urbanization in the region contributes to the indiscriminate disposal of domestic and industrial sewage (more than 50 industries with high potential of pollution) in this basin [6]. In addition, historical rural development can also contribute to accelerate erosive processes.

This work aims to evaluate the distribution of trace elements and persistent organic pollutants in Piabanha river basin sediments to test the hypothesis that there are differences in the contamination profiles over time and space, assessing the associated risks to the population and ecosystems. The data generate on this study will benefit governmental institutions, such as the Basin Committee of the Piabanha river, member of the State System of Management and Water Resources (SEGRHI), which is responsible for promoting decentralized and participatory management of water resources in this region

2. Results and Discussion

Trace elements in the sediment

The contribution of each metal varied across the river points. Concentrations of the available elements determined in the sediment (partial fraction) can be observed in Figure 1. The nickel was not included in the statistics because more than 75% of the concentrations were below the limit of quantification. There was no significant difference between any sample point for the elements analyzed (Kruskall-Wallis, $p > 0.05$; Fe- $p=0.828$; Zn- $p=0.051$; Cu- $p=0.446$; Mn- $p=0.133$; Cr- $p=0.477$; Cd- $p=0.896$; Pb- $p=0.501$). Notwithstanding, the higher concentration of Fe observed in the point 4 river is probably due to leaching of this metal, which is abundant in the lithosphere. In addition, Fe can easily form complexes and adsorb with organic matter and it becomes more conducive because this sample had lentic waters (well). Zn and Cu presented the highest concentrations in points 2 (243 µg/g and 66 µg/g, respectively) and 3 (189 µg/g and 47 µg/g) during the rainy season of 2014. Cu was more available at these locations and also at point 5 (98 µg/g) during the same period. These three points are the most degraded in our study, which could be related to populational and industrial concentrations at Piabanha river banks releasing large volumes of effluents into the river.

Mn is one of the most abundant metals in the Earth's crust and can be found in all kinds of rocks. It is used for making steel and metallic alloys, and it also can be present in pesticides used on farms. The point 9 during the dry season (2013/2), followed by point 6 in dry season (2012/2), presented the highest concentrations of Mn: 1,046 and 937 µg/g, respectively. The lower flow during this period may be allowing the precipitation of these metals in the sediment. There is an intense presence of agricultural activity at sampling point 9. Additionally, the extraction of sand is a strong activity in the region and it can remobilize the sediment, affecting the bioavailability of Mn, for example, which presents a high factor of individual mobility [7]. In relation to Cr, the higher availability observed in points 3 and 7 may be associated with the industry center of this region, since this element is one of the industrial contaminants most released in water bodies.

Considering the National Environment Council (CONAMA) Resolution No. 454/2012 [8], which provides sediment quality criteria, where level 1 is the threshold below which a low probability of adverse effects to biota is foreseen and level 2 is the threshold above which a probable adverse effect is foreseen for the biota (Table 1). Six localities (2, 3, 4, 6, 7 and 8) showed concentrations between the level 1 and 2 for cadmium (0.6 µg/g), while only the point 4 presented values above the level 2 (3.5 µg/g), indicating possible adverse effects on biota.

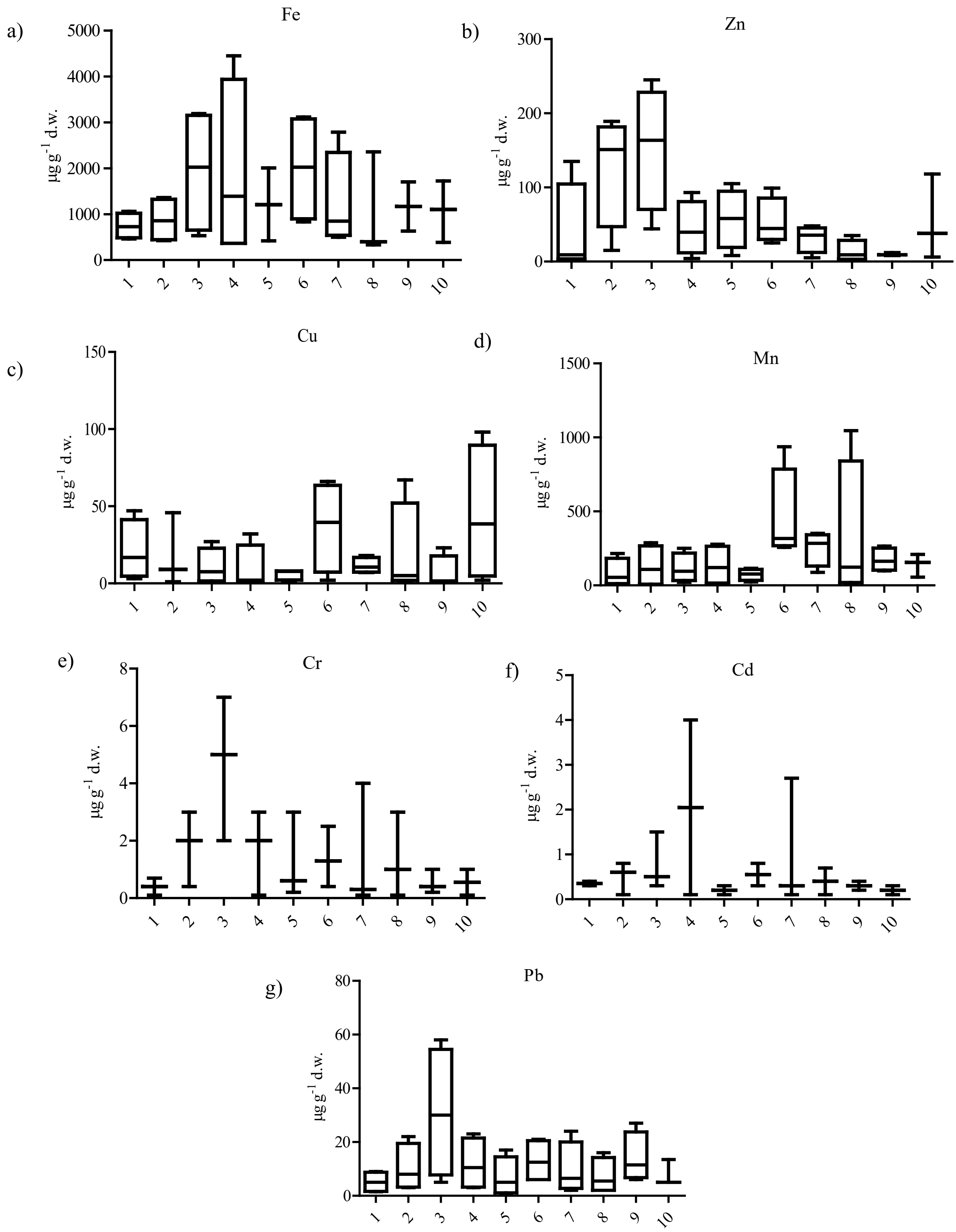

Figure 1. Total levels of the available trace elements in the sediment at the sampling points: a) iron; b) zinc; c) cupper; d) manganese; e) chrome; f) cadmium; g) lead. Points: 1- Levalon; 2- Garagem; 3 - Liceu; 4 – Poço do Ferreira river; 5 – Itaipava Municipal Park; 6- Pedro do Rio; 7-Posse; 8- Fagundes river; 9- Preto river; 10- Moura Brazil.

A larger attention should be given to these locations, since the Cd is not an essential metal. In addition, they may be suffering influence of textile and paint factories in the region, as well as the use of fertilizers. The latter can be a source of cadmium on agriculture, through its impurities. Regarding Pb, the points 3 and 5 showed concentrations above the level 1 (35μg/g dry weight). These locations, including points 2 and 10, presented higher concentrations of Cu (> 35.7 μg/g). Points 2 and 3 had their sediments with Zn levels higher than the level 1 (123 μg/g) in both dry and rainy periods. These locations have a dense population in Petrópolis. It needs to be highlighted that values found in the partial fraction (available) are even larger than the considered safe for the total fraction.

Table 1. Sediment classification levels to be dredged, considering the likelihood of harmful effects to biota according to CONAMA.

SEDIMENT CLASSIFICATION LEVELS (in unit of dry material)				THIS STUDY
		Level 1	**Level 2**	
Heavy Metals (mg/Kg)	Cadmium	0.6	3.5	0.1-4
	Lead	35	91.3	<LOQ-58
	Copper	35.7	197	1-98
	Chrome	37.3	90	<LOQ-7
	Nickel	18	35.9	<LOQ-8
	Zinc	123	315	1-245

Linear regressions did not show influence of pH or percentage of organic matter on the available metals levels in the sediment of Piabanha basin ($p > 0.05$ for all metals), although these parameters affect the distribution of the elements between the sediment and the water column.

Despite no observed differences in the concentrations of trace elements in the sediment between sampling periods ($p > 0.05$, Mann-Whitney; Fe- $p = 0.144$; Zn- $p = 0.088$; Cu- $p = 0.465$; Mn- $p = 0.182$; Cr- $p = 0.419$; Cd- $p = 0.131$; Pb- $p = 0.103$), the majority of the points in the rainy season (March) had greater concentrations than in dry period (September). As the region drained by the Piabanha basin has a high incidence of flooding, especially in the summer, it is likely that the leaching of metals from the soil and the consequent increased organic matter are contributing to this increase in the rainy season. In addition, it was observed an increasing trend of metals concentrations over time ($p < 0.0373$, Mann-Whitney; Fe- $p = 0.007$; Zn- $p = 0.016$; Cu- $p = 0.045$; Mn- $p = 0.018$; Cr- $p = 0.012$; Cd- $p = 0.008$; Pb- $p = 0.015$; Figure 2). It can be associated not only with the leaching that occurs, but mainly with the increase of constructions in the margins closer than 50m from the river, which are illegal accordingly to Brazilian Forest Code (updated by Brazilian law Nº. 12.727/12) [9].

Geo-accumulation index (Igeo) classes observed in the dry season of 2013 are shown in Table 2. As can be observed, for most metals, the samples collected do not present a pollution degree above moderate, except for Cd in all localities and Zn at the point 6. Cadmium, had concentrations above thresholds 1 and 2, with a degree of contamination from moderate to extremely polluted in all localities (Table 2). It is a relatively rare element in the Earth's crust (0.1-0.5 ppm) [10] and its increase along the basin could be influenced by the anthropogenic activities. This element is naturally found associated with sulfites of Zn, Pb and Cu ores, which could explain the highest Igeo of Cd in the localities with higher Igeo of Zn and Pb. In addition, the different applications of this metal, transport and entry forms in aquatic systems indicates that contamination of the sampling points can be diffuse, not necessarily local. However, the main activities of Petrópolis, involving textile and furniture industries, frequently discharge their effluents into the river - a fact observed several times during the field work.

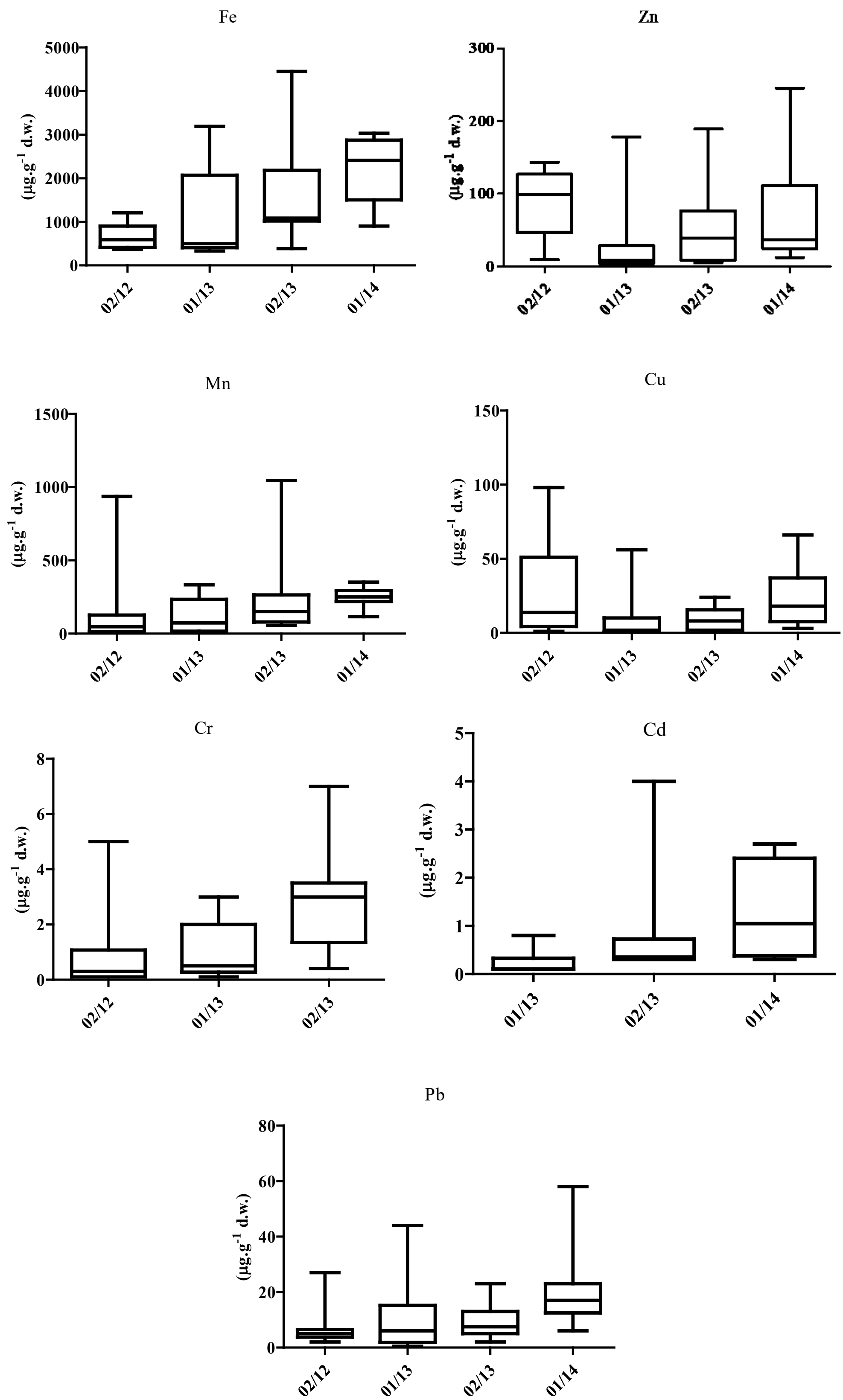

Figure 2. Total dry weight of each element in the different collections: 02 / 12- second half (dry period-September) of 2012; 01 / 13- first half (wet period-March) of 2013; 02 / 13- second half (September) of 2013; 01 / 2014- first half (March) of 2014.

This could be responsible for the enrichment of cadmium in sediment located at the city center and downstream the industries center. In the point 9, the levels found could be associated with agricultural activities in the region, since cadmium is present in pesticides [10]. In the location of the point 10 (Três Rios city), the main industrial activities are in the rail business, food and automotive sectors, which can contribute with cadmium contamination that are present in metal alloys, steel and iron coating, plastics and glass pigments.

POPs in the sediment

The highest total POPs concentrations in the sediment were observed in the dry period for points 7 (203.4 ng/g) and 8 (198.3 ng/g) (Table 3). During the dry period, the flow of the river decreases and there is an increase in the precipitated material. The downstream locality 7 is under direct influence of the urban perimeter of Petrópolis. In this region, there are several breweries and other industries that can contribute to the overwhelming majority of the PCBs (87%). The point 8 is a tributary that drains three cities (Paty de Alferes, Petrópolis and Paraíba do Sul) until reaching Areal, where it was sampled. In these cities there is a mix of industries and farming activities, which can be contributing to the concentration of organochlorine pesticides. Kruskal-Wallis test indicated that there were significant differences among localities ($p < 0.0001$) and Dunn test showed that the point 8 presented significantly higher concentrations than points 3, 5, 6, 9 and 10 ($p < 0.05$).

Table 2. Geoaccumulation index (IGEO) during September 2013 (dry season). 0-Unpolluted; 1-Little to moderately polluted; 2-Moderately polluted; 3-Moderately to heavily polluted; 4-Strongly polluted; 5-Strongly polluted; 6-Extremely polluted.

Sept/2013	Fe	Zn	Mn	Cr	Cd	Pb	Ni
Point 1	0	0	0	0	3	0	0
Point 2	0	0	0	0	3	0	0
Point 3	0	2	0	0	4	2	1
Point 4	0	0	0	0	3	0	0
Point 5	0	0	0	0	3	0	0
Point 6	0	4	0	0	5	1	0
Point 7	0	0	0	0	4	0	0
Point 8	0	0	0	0	3	0	0
Point 9	1	1	0	0	4	1	0
Point 10	0	2	0	0	5	0	0

Table 3. Total concentrations ($ng.g^{-1}$ dry weight) of the different groups of POPs during the dry and rainy seasons in the 10 studied localities. Dry and rainy seasons include two periods each.

Points	Σ PCB ($ng.g^{-1}$)		Σ DDT($ng.g^{-1}$)		Σ OCP ($ng.g^{-1}$)		Σ POPs ($ng.g^{-1}$)	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
1	2.84	1.04	0.21	0.17	0.86	0.72	3.69	1.76
2	2.14	31.96	0.22	5.20	1.58	45.10	3.72	77.06
3	6.19	-	0.23	-	1.68	-	7.88	-
4	4.36	3.88	0.19	0.22	1.09	0.50	5.45	4.38
5	20.49	1.73	1.74	0.13	7.83	0.71	28.32	2.44
6	1.56	-	0.22	-	1.56	-	3.12	-
7	175.95	3.42	6.51	0.22	27.42	3.30	203.36	6.72
8	173.93	1.04	9.13	0.15	24.40	1.30	198.33	2.33
9	0.68	-	0.02	-	0.74	-	1.42	0.00
10	20.05	67.99	0.91	1.99	5.48	9.51	25.52	77.50

The lowest concentrations of POPs have been found at point 1, at the Piabanha river source, where there is almost none direct anthropogenic influence. Considering the organochlorine pesticides, the highest levels were found during the drought at points 7 and 8 and during the rainy period at points 2 and 10 (Telemetric Station). Total DDTs (*o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE and *p,p'*-DDE) were markedly higher in points 7 and 8. Regarding sediments, *p,p'*-DDE and HeptaEpoxi were the most abundant pesticides for both

Piabanha river and its tributaries, while the most abundant PCBs were -77, -66 and -123. The HeptaEpoxi is a relatively stable Heptachlor byproduct of metabolism in soils, plants and animals. The latter was one of the most active POPs in Brazil [11].

Differences in contamination profile for POPs on dry period ($p<0.05$; Dunn test) among localities can be observed in Table 4. In rainy period, significant differences were only observed between the point 5 in relation to localities 7 and 10. Considering sampling periods (dry and rainy) in each locality, there were significant differences ($p < 0.05$; Dunn test) among points 1, 5, 7 and 8. The lowest concentrations observed in the rainy period for these locations may be influenced by the increased flow and consequent dilution of contaminants and by the higher temperatures during the period. Notwithstanding the leaching effect after the occurrence of a flood event, this study observed, in several localities, decreasing concentrations during these periods. Additionally, the high population density living on the Piabanha river banks, as well as the industrial and agricultural activities, could be responsible for the highest POPs levels in the sediment.

Table 4. Results of the Dunn test, showing for which points there was a significant difference in the concentrations of POPs (contamination profile). The X signals $p <0.05$.

Points (dry)	1	2	3	4	5	6	7	8	9	10
1	-					X			X	
2		-		X			X	X		
3			-	X			X	X		
4		X	X	-		X			X	
5					-	X	X	X	X	
6	X			X	X	-	X			X
7		X	X		X	X	-		X	
8		X	X		X			-	X	
9	X			X	X		X	X	-	X
10							X	X	X	-

Piabanha river is one of the main tributaries of Paraíba do Sul river, which is the main source of drinking water supply for the metropolitan region. Torres et al. [12] found a mean concentration of 225 ng/g for ΣDDT (2-3 orders of magnitude higher than found on this present study) in the sediment of the Paraíba do Sul river, in the State of Rio de Janeiro.

3. Material and Methods

The Piabanha river has 80 km of extension, with its source at the Serra do Mar, it flows into the Paraíba do Sul river, which is the most important river of Rio de Janeiro state. The main sub-basins of the Piabanha River are: Quitandinha, Itamarati, Poço do Ferreira, Santo Antônio and Preto rivers (on the right bank of the river); and Araras and Fagundes rivers (on the left bank of the river) [13]. Therefore, it has influence of its tributary rivers, which drain large areas, where rural activities are prevalent. The natural slow river flow is another variable influencing the dilution of released loads. Furthermore, factors such as low temperatures, high altitudes and dynamic mechanisms of polar air masses can impact the transport of organic pollutants to this region.

In this study, ten points of the basin were sampled: 3 points in tributaries (Poço do Ferreira, Preto and Fagundes rivers) and 7 points distributed along the Piabanha river, as shown in Figure 3 and Table 5.

Sediments were collected at 10 different points distributed along the basin, encompassing four expeditions: two in the rainy season (September/2012 and 2013) and two in dry season (March/2013 and 2014). Temperatures at the collection points ranged from 20 to 30 °C and 17.7 to 33 °C, respectively. Surface sediment samples (15 cm) were obtained with the aid of a sediment collector in points with low depth and a dredge Ekman when depth permitted, both stored in glass jars afterwards.

For sediment analysis, all materials were dried in an oven (maximum of 40 °C) and sifted to obtain the fraction smaller than 70 µm. Iron (Fe), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr), manganese (Mn) were quantified in replicas for each sample by Flames Atomic Absorption Spectrometry (FAAS) (Varian Spectra AA240FS). To assess the available portion of trace elements in the sediment, a partial extraction method was used. The methodology adopted was previously described by Fizmam et al. [14]. Firstly, the sediment was dried in an oven for 24-48 hours according to the amount of water present in the sample. Then, 2g were used and added 10 mL of 0.1N HCl, which was evaporated on a hot plate.

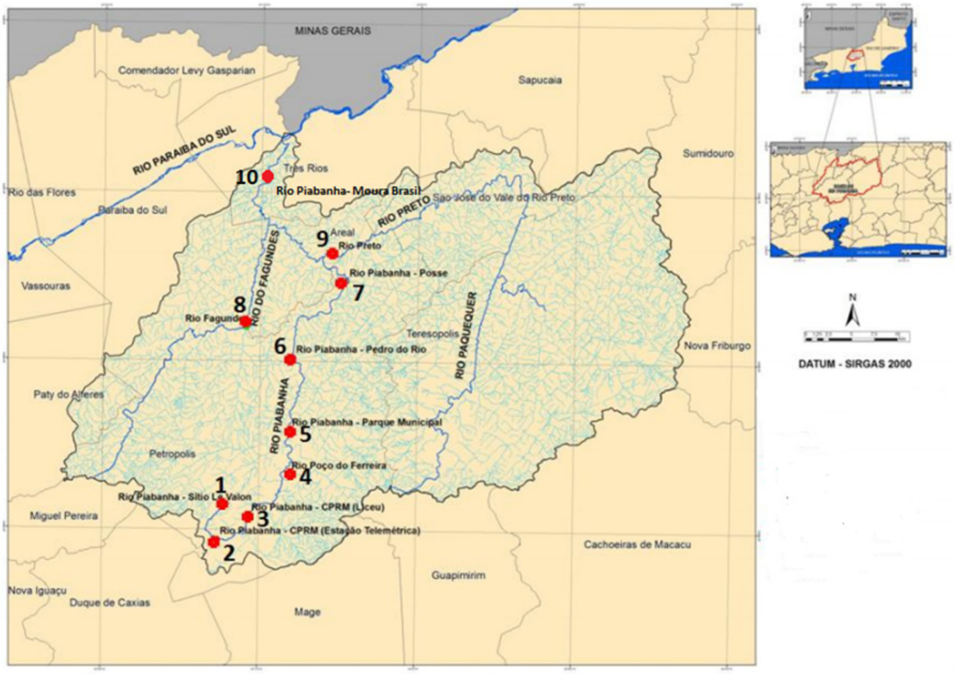

Figure 3. Map of the Piabanha River basin with the marking of collecting points distributed along the Piabanha River and some of its tributaries.

Table 5. Sample points, location and coordinates.

Collecting points	Location	Coordinates
1- Levalon (Piabanha river)	Petrópolis (Moinho Preto)	22°28’39”S; 43°12’15”W
2- Garagem (Piabanha river)	Petrópolis downtown	22°30’38”S; 43°12’37”W
3- Liceu (Piabanha river)	Petrópolis downtown	22°29’13”S; 43°10’37”W
4- Poço do Ferreira river	Petrópolis (District of Correias)	22°26’43”S; 43°08’07”W
5- Itaipava Municipal Park (Piabanha river)	Petrópolis (District of Itaipava)	22°24’9,9”S; 43°08’5,5”W
6- Pedro do Rio (Piabanha river)	Petrópolis (District of Pedro do Rio)	22°19’51”S; 43°07’55”W
7- Posse (Piabanha river)	Petrópolis (District of Posse)	22°16’17”S; 43°05’07”W
8- Fagundes river	Três Rios	22°18’02”S; 43°10’53”W
9- Preto river	Petrópolis/Areal	22°13’40,6”S; 43°05’18,1”W
10- Moura Brazil (Piabanha river)	Três Rios	22°07'36,2"S; 43°08'35,7"W

Finally, 15 mL of 0.1 N HCl was added and the solution was filtered on Whatman type filters. The final volume of the solution was 20 mL using 0.1N HCl to achieve the desired volume. Concentrations of the available elements analyzed in the sediment (partial fraction) were presented in µg/g dry weight. Mean limits of quantification (LOQs) for trace elements in sediments were: Pb- 1.51µg/g; Zn- 0.36µg/g; Fe-6.62µg/g; Cd-0.17µg/g; Cd-0.17µg/g; Cu-0.07µg/g; Cr- 0,63µg/g; Mn- 0.12µg/g; Ni-0,27µg/g.

The method for POP analysis was adapted from Meire et al. [15]. Briefly, six grams of <70 µm fraction was spiked with PCB103 and 198 standards for recovery analysis. The extraction was performed using dichloromethane in an ultrasonic bath at 90 °C for 20 minutes, followed by a cleanup step in columns with alumina, desulfurizing agent and sodium sulphate eluted with hexane. The POPs were quantified using a conventional gas chromatography coupled to electron capture detector (GC-ECD Shimatzu 2010). The average concentrations found were presented in ng/g (ppb) of dry weight (Table 2). LOQs for organochlorine pesticides and polychlorinated biphenyls (PCBs) ranged from 0.34 to 32.9 ng/g lipid weight (l.w) and mean recoveries for internal standards were within 75-113% range. Geoaccumulation index (Igeo) was used to quantify the degree of pollution for each sampling point [16]. This index is widely used in works for geochemical evaluation of impacted environments [17] and is obtained according to the formula:

$$Igeo = \log_2 [C_n (1.5 B_n) -1],$$

where C_n is the measured concentration of the metal n on fine sediment fraction (< 63 μm) and B_n is the value of geochemical background of this metal based on average composition of shales. The 1.5 factor of the equation is used to compensate possible variations of the "background data" due to lithogenic effects [18]. The use of the average composition of shales as a global reference ("background") allows the contamination degree of different areas to be comparable. In this study, the background used was regional referring to the average concentration of metals in river sediments in control areas of the same region [19]. The Igeo consists of seven levels: Unpolluted (Igeo < 0 – class 0), Not polluted to moderately polluted (0 < Igeo < 1 – class 1), Moderately polluted (1 < Igeo < 2 – class 2), Moderately to strongly polluted (2 < Igeo < 3 - class 3), Strongly polluted (3 < Igeo < 4 – class 4), Strongly to Extremely polluted (4 < Igeo < 5 – class 5) and Extremely polluted (Igeo > 5 – class 6). The class 6 reflects an enrichment of 100 times above the average values of the background values.

Statistical analysis was performed in GraphPad Prism 5.0 (license GPW6-207405-UFM4-5D5E4). Shapiro-Wilk test was used to check the data normality. Due to no data normality ($p > 0.05$), nonparametric tests were applied. Kruskal-Wallis and the post-hoc Dunn tests were applied to compare metal and POPs concentrations among different sampling points, while Mann-Whitney was used to compare sampling periods. In addition, linear regressions were carried to verify the influence of the pH and organic matter (%) on metals concentrations. These data were obtained by the group of the Laboratory of Limnology, who also participated in the same project. Nickel was not included in the statistics because more than 75% of the concentrations were below the limit of quantification. The adopted significance level was 5% for all tests.

4. Conclusions

The levels of organic pollutants highlight the influence of industrial activities and the historical use of pesticides in farming, especially in the Fagundes river (point 8) and Posse region (point 7), respectively. The high levels of metals in the sediment represent the greatest potential for bioaccumulation and, therefore, special attention should be given to any activity that interferes the sediment dynamics. A significant temporal variation was only observed among years and not between dry and rainy seasons, showing an increment of metals over time and confirming the importance of long-term monitoring. Furthermore, diverse sources of metals along the Piabanha river basin have been identified, such as industrial, agricultural and domestic sources. The most contaminated locations were within and around Petrópolis city center, being Garagem (point 2) and Liceu (point 3) the most degraded mainly by industrial and domestic effluents. Cadmium was the element with major contribution to the contamination of the locations studied, probably because of its high mobility and the river flow. Considering that, this element deserves greater attention regarding its sediment concentration. Additionally, point 4 had the highest available metal concentrations and should have a long-term monitoring program for sediment and water levels, as well as investigate potential damage to organisms.

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References and Notes

[1] Tundisi, J. G.; Matsamura, T. T. *São Paulo: Oficina de Textos* **2008,** 632.

[2] Murray, K. S.; Cauvet. D.; Lybeer. M.; Thomas. J. C. *Environ. Sci. Technol.* **1999**, *33*, 987. [Crossref]

[3] Nriagu, J. O. *Nature* **1989**. *338,* 47. [Crossref]

[4] Forstner. U.; Wittmann. G. T. W. Metal pollution in the aquatic environment. New York: Springer-Verlag. 1979.

[5] Morais, A.; Villas-Boas, M. D.; Monteiro, A. E. G. C.; Araujo, L. M. N. *Anais II Seminário de Recursos Hídricos da Bacia Hidrográfica do Paraíba do Sul* **2009**,173. [Crossref]

[6] Cesar, R.; Colonese, J.; Silva, M.; Egler, S.; Bidone, E.; Castilhos, Z.; Polinavov, H. *Geoquímica* **2011**, *25*, 35.

[7] Coringa, J. E. S.; Pezza, L.; Coringa, E. A. O.; Weber, O. L. S. *Acta Amazonica* **2016**, *46*, 161. [Crossref]

[8] Conselho Nacional de Meio Ambiente (CONAMA). Resolução 404. 2012. [Link]

[9] Brasil. Lei nº 12.727. 2012. [Link]

[10] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Cadmium. 2012. [Link]

[11] Almeida, F. V.; Centeno, A.; Bisinoti, M. C.; Jardim, W. F. *Quim. Nova* **2007,** *30*, 1976**.** [Crossref]

[12] Torres, J. P. M.; Malm, O.; Vieira, E. D. F.; Japenga, J.; Koopmans, G. F. *Cadernos de Saúde Pública* **2002**, *18*, 488. [Crossref]

[13] De Paula, T. P. Dissertação de Mestrado, Programa de Pós-graduação em Engenharia Civil, COPPE, Universidade Federal do Rio de Janeiro. 2011.

[14] Fiszman, M.; Pfeiffer, W. C.; Lacerda, L. D. *Environ. Technol. Lett.* **1984***, 5,* 567.

[15] Meire, R. O.; Azeredo, A.; Pereira, M. S.; Torres, J. P. M.; Malm, O. *Chemosphere* **2008,** *73,* 180**.** [Crossref]

[16] Muller, P. J.; Suess, E. *Deep-Sea Res.* **1979**, *26*, 1347. [Crossref]

[17] Luiz-Silva, W.; Matos, R. H. R.; Kristoch, G. C. *Quim. Nova* **2002**, *25,* 753. [Crossref]

[18] Forstner, U. In: Metal pollution in the Aquatic Environments. Forstner. U.; Whitman. G. T. eds. New York: Springer verlag. 1983.

[19] Torres, J. P. M. Dissertação de Mestrado, Ciências Biológicas/ Biofísica, Instituto de Biofísica, Universidade Federal do Rio de Janeiro.1992.