Environ Monit Assess (2018) 190: 243
https://doi.org/10.1007/s10661-018-6611-9

Contamination by lead in sediments at Toledo River, hydrographic basin of PARANÁ III

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Received: 14 January 2018 / Accepted: 8 March 2018 / Published online: 23 March 2018

Abstract Due to intense agricultural and industrial activities, the environment has been affected by increasing amounts of pollutants, such as lead, a toxic heavy metal. When introduced to the environment, toxic metals are distributed and incorporated into the liquid medium, sediments, and aquatic biota; bioaccumulating. This research aimed to identify and quantify the levels of toxic metals present in the waters and sediments of Toledo River, compare the obtained results with legislation and other studies, as well as to evaluate the possible pollutant sources of the water body. Six water and sediment samples were taken at seven strategic sites. The concentrations of Cu, Zn, Fe, Mn, Cd, Pb, and Cr in water were compared to the maximum limits established by Brazilian legislation IN CONAMA No. 357/05, for class II fresh waters. The sediment samples were submitted to nitroperchloric digestion, and then the total concentrations of the metals were determined by flame atomic absorption spectrometry (FAAS). The toxicological quality of the Toledo River has been considerably affected by the activities carried out in its surroundings, such as extensive areas of agriculture, pig farming and industrial areas, causing concentrations of Cd, Fe, and mainly Pb, which is observed at concentrations higher than value allowed by the legislation.

Keywords Water contamination · Toxic metals · Aquatic pollution · Diffuse pollution · Bioaccumulation

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Introduction

The quality of the water resources can be compromised due to the by-products of anthropic activities that have been deposited over time in the water bodies. The existence of possibly toxic products and elements may be responsible for adverse effects on the environment.

Natural reservoirs are the repository of a variety of by-products from anthropogenic activity; in addition, the presence of toxic elements is responsible for harmful effects on the environment, generating effects on public health and economy, because the waste from the most diverse activities has organic and inorganic contaminants, which can cause significant changes to ecosystems (Silva et al. 2010, 2013).

The insertion of metals into aquatic systems may occur naturally in the environment as a result of geochemical processes, weathering of rocks, leaching and discharging of material disassociated by fluvial and wind media, and atmospheric precipitation, or may occur by anthropic way, through waste from human activities, such as industrial and agricultural activities, disposal of urban effluent, electroplating and metalworking industry, tanneries or mineral fertilizers from dubious sources, among others. The insertions occurring by the anthropic actions are reflections of their wide use by the industry and the agricultural activities, which contain high concentrations of metals like chromium (Cr), zinc (Zn), iron (Fe), lead (Pb), copper (Cu), mercury (Hg), among others (Espinoza-Quiñones et al. 2010; Loureiro et al. 2012).

The growth of industrial and agricultural activities, added with the unbridled growth of urbanization, has increased the risks of contamination of soils and water resources by metals (Gonçalves Jr et al. 2014). The presence of toxic metals in the environmental compartments, as well as in the soil, sediment, and water systems has been treated with priority in many studies, since the most varied life forms can be directly or indirectly affected by their presence (Fortunato et al. 2012).

Agricultural activities are responsible for the release of pesticides and fertilizers into the water bodies. In their compositions, these compounds contain toxic, carcinogenic, mutagenic, and recalcitrant elements. The livestock, mainly characterized by the production of pigs, is present in the region of Toledo, and the problem of the exploitation of this activity is the vast production of organic waste, responsible for the generation of a great environmental problem (Masomboon et al. 2010).

The environmental impacts caused by the anthropic release of toxic metals have caused great concern. Due to this aspect, water, sediment, particulate materials, among others, have been presented as indicators for the evaluation of the dimensions and characterization of the impacts. According to Souza et al. (2014), the sediments and particulate matter deposited in the riverbed are excellent indicators of pollution, since they have a high capacity for the accumulation of toxic pollutants.

The evaluation of metals in sediments makes it possible to identify the main sources of pollution of a given water body, because the aquatic sediments have been considered as a compartment of accumulation of several pollutants from water, and this accumulation is due to the fact that sediments present high sorption capacity and accumulation, allowing the concentration of pollutants in the sediments to be higher than in the corresponding waters, thus, the sediment of a given water resource becomes an indicator of environmental pollution (Santiago and Cunha-Santino 2014).

There is no legislation in Brazil regulating the accumulation of metals in sediments, and since other countries have such regulations (USA, Canada, among others), the present study aimed to evaluate the presence of toxic metals in the waters and sediments of Toledo River, compare the obtained results in water to the maximum values established by IN CONAMA No. 357/2005 (BRAZIL 2005) and other studies, as well as to verify the possible sources of insertion of these contaminants in different sites of sampling, in order to generate information that proves the need for environmental regulations for this environmental compartment.

Material and methods

Sampling sites

The water and sediment sample sites were determined at Toledo River (Fig. 1), under the geographical coordinates shown in Table 1, and were named as follows: site 1 (R1), site 2 (R2), site 3 (R3), site 4 (R4), site 5 (R5), site 6 (R6), and site 7 (R7). The sampling sites were also classified according to the influences received by each of them, being R1, agriculture influenced area (RI); R2, mixed influenced area (IM); and R3, R4, R5, R6, R7, of urban influenced area (UI).

Analytical determinations

Water samples were taken according to the methodology described by APHA (2012), and the sediments were collected in the 0–20-cm layer of the river bed with sterilized glass vials with cleaning solution 2% HCl (*v*/*v*). All samples were stored under a temperature of

Source: Google Earth, 2017.

Fig. 1 Location of water and sediment sampling points at Toledo River in the municipality of Toledo/PR/Brazil

4 °C until Cu, Zn, Fe, Mn, Cd, Pb, and Cr metals were measured by means of flame atomic absorption spectrometry (FAAS), at the State University of the West of Paraná (UNIOESTE), Campus Marechal Cândido Rondon.

After being sampled, the sediments were dried in a forced ventilation oven at 45 °C for 48 h, for later milling and nitroperchloric digestion, according to the methodology of the Association of Official Analytical Chemists (AOAC 2012).

From the obtained results for waters, a comparison was made with the maximum permitted values (MPV) by the environmental legislation, IN CONAMA No. 357 of March 17, 2005, for water bodies of class II, presented in Table 2. The obtained results for sediments were compared to the standards established by CETESB (2015) and to international legislations.

Experimental design and statistical treatments of the data

The data were analyzed using a completely randomized design (DIC), in a 6 × 7 double factorial scheme,

Table 1 Geographic coordinates of the water and sediment sampling sites at Toledo River

Sampling site	Geographic coordinates
R1	24° 45′ 02.43″ S 53° 39′ 51.86″ O
R2	24° 43′ 50.39″ S 53° 42′ 12.55″ O
R3	24° 43′ 56.18″ S 53° 43′ 13.14″ O
R4	24° 43′ 59.52″ S 53° 43′ 44.77″ O
R5	24°44′ 27.58″ S 53° 44′ 3.67″ O
R6	24° 44′ 40.92″ S 53° 44′ 12.89″ O
R7	24° 45′ 11.75″ S 53° 46′ 36.69″ O

Table 2 Maximum permitted values (MPV) of toxic metals for class II water bodies, established by IN CONAMA No. 357 of March 2005

Metal	Unit	MPV (mg L^{-1})
Cu	mg L^{-1}	0.009
Zn	mg L^{-1}	0.180
Fe	mg L^{-1}	0.300
Mn	mg L^{-1}	0.100
Cd	mg L^{-1}	0.001
Pb	mg L^{-1}	0.010
Cr	mg L^{-1}	0.050

Source: Brazil 2005

consisting of a microbasin (Toledo River), six sampling periods (September, October, and December of 2015, March, May, and June of 2016) and seven sampling points.

The results were submitted to analysis of variance, and, when found significant, submitted to Tukey test at the 5% probability level. All statistical treatment was performed using the Sisvar Software (Ferreira 2003).

Statistical analysis of canonical correspondence was also carried out, in order to verify the relation of concentrations of toxic metals to sampling points.

Results and discussion

Characterization of sampling sites

From the macroscopic environmental assessment carried out at the sampling sites, the characterization was performed as shown in Table 3.

Table 3 Characterization of the sampling sites at Toledo River, municipality of Toledo/PR, after macroscopic environmental assessment performed in loco

Sampling sites	Description
R1	• Located near the headwaters, countryside • Preserved riparian forest • Direct influence of agricultural activities
R2	• Located after rural region (agricultural activities) • Near to the highway BR-467 • Beginning of the urban area of Toledo City • Degraded riparian forest • Presence of municipal solid waste
R3	• Located in the urban area, near the fish farming industry • Degraded riparian forest
R4	• Located in urban area, close to public parks • Degraded riparian forest • Presence of urban solid waste
R5	• Located in the urban area, with a high concentration of population • Located before the release of domestic and industrial effluents • No riparian forest • Presence of municipal solid waste
R6	• Located in the urban area, with a high concentration of population • Located after the release of domestic and industrial effluents • Preserved riparian forest
R7	• Located near the mouth of the river, rural area with urban influences • Presence of municipal solid waste • Preserved riparain forest

Results of analytical determinations

The mean concentrations of metals in water, when compared to the limits established by the Brazilian legislation (Table 2), exhibit parameters above the MPV for class II freshwater (Fig. 2).

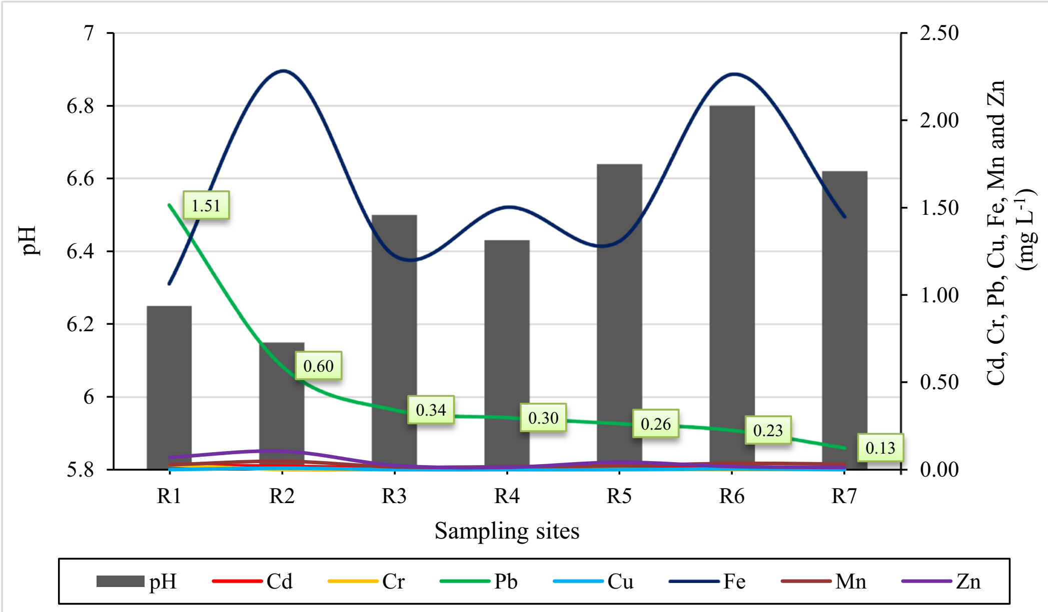
The Cr and Mn are the only ones that show complete framing; Cu and Zn exhibited only higher than those established by the legislation once.

The parameters Cd, Fe, and Pb, for the most part, exhibit values higher than the values established by Brazilian legislation. These results may be related to the land use and occupation format in the vicinity of the sampling sites, since according to Fig. 1, there are several activities being carried out in their proximity directly affecting the water quality.

Espinoza-Quiñones et al. (2005), also studied the Toledo River, identifying the presence of the elements Cr, Mn, Ni, Cu, and Zn, with high concentrations of Cu and Mn along the river. The authors attributed the presence of the metals and the high concentrations to the erosion from agricultural areas that surround the River, and also the very intense swine activity. The municipality of Toledo has the largest herd of swine in Paraná State and the second largest in Brazil, and it also has the largest poultry slaughter in the State of Paraná and the largest pig slaughterhouse in Latin America (Guilland and Cruz 2017; Strassburg et al. 2016).

Rocha et al. (2014), obtained concentrations of Pb ranging from 0.2132 to 0.2377 mg L^{-1}, and attributed the high values found to the activities carried out around the water body, such as the discharge of urban and industrial effluents, to intensive agricultural activity and the residues of insecticides, herbicides, fungicides, and fertilizers used in this activity.

The levels of Fe, also presented high concentrations in all the sampled sites, mainly in the months of October 2015 and May and June 2016. According to CETESB (2009), their contents may increase in surface waters in rainy periods and also due to the occurrence of erosion in the water body margins, a factor that is routinely visualized in the sampled sites, because although some points have an area of riparian forest, it is not dense and properly isolated.



Note: LQ (limit of quantification in mg L^{-1}): Cd = 0.005; Cr = 0.010; Pb = 0.010; Cu = 0.005; Fe = 0.010; Mn = 0.010; Zn = 0.005. Lead concentration is highlighted in the green box.

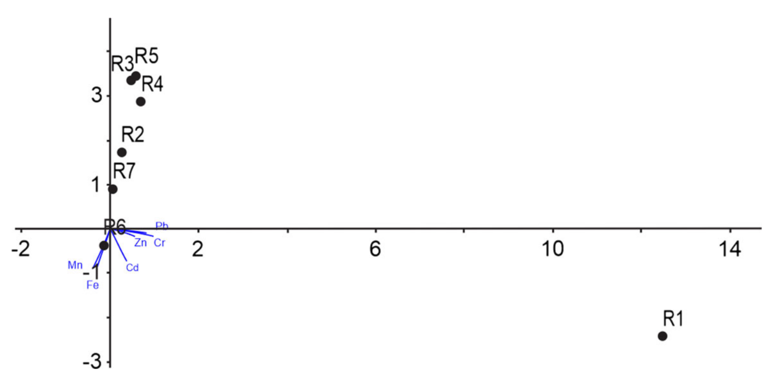
Fig. 2 Means of total concentrations of metals in the waters at Toledo River - Toledo/PR, determined through samples at seven sampling points

The canonical correspondence analysis, carried out to evaluate the relationship between the toxic metals concentrations and the sampling sites (Fig. 3), suggests that the concentrations of metals have a greater relationship with the R6 and R1 points. Possibly, this association with R6 was established by the characterization of the site, already the relations with the R1, probably occur by this site is located in an agricultural area with the use of agrochemicals and fertilizers in the cultivation of plants, with the possibility of leaching metals into the river.

According to Nacke et al. (2013), toxic metals have been identified in considerable concentrations in mineral fertilizers and acidity correction products of agricultural soils; in addition, the application of animal biofertilizer, depending on the additives and the feed offered to the animals, can also increase the concentrations of toxic metals into the soil. In this sense, the region located near the R1 may present toxicological quality compromised due to the transportation of these products into the water body.

There is still another factor that can directly contribute to the toxicological quality of the waters of the Toledo River, the pH, because this influences the availability of the chemical elements in the water medium, thus, depending on the pH values, the chemical forms of metals may change, presenting in ionic form (cations or

Fig. 3 Canonical correspondence analysis relating the sampling sites to the toxic elements evaluated in the Toledo River



anions), or in complex forms (insoluble), causing its precipitation and this will become a constituent part of the sediments.

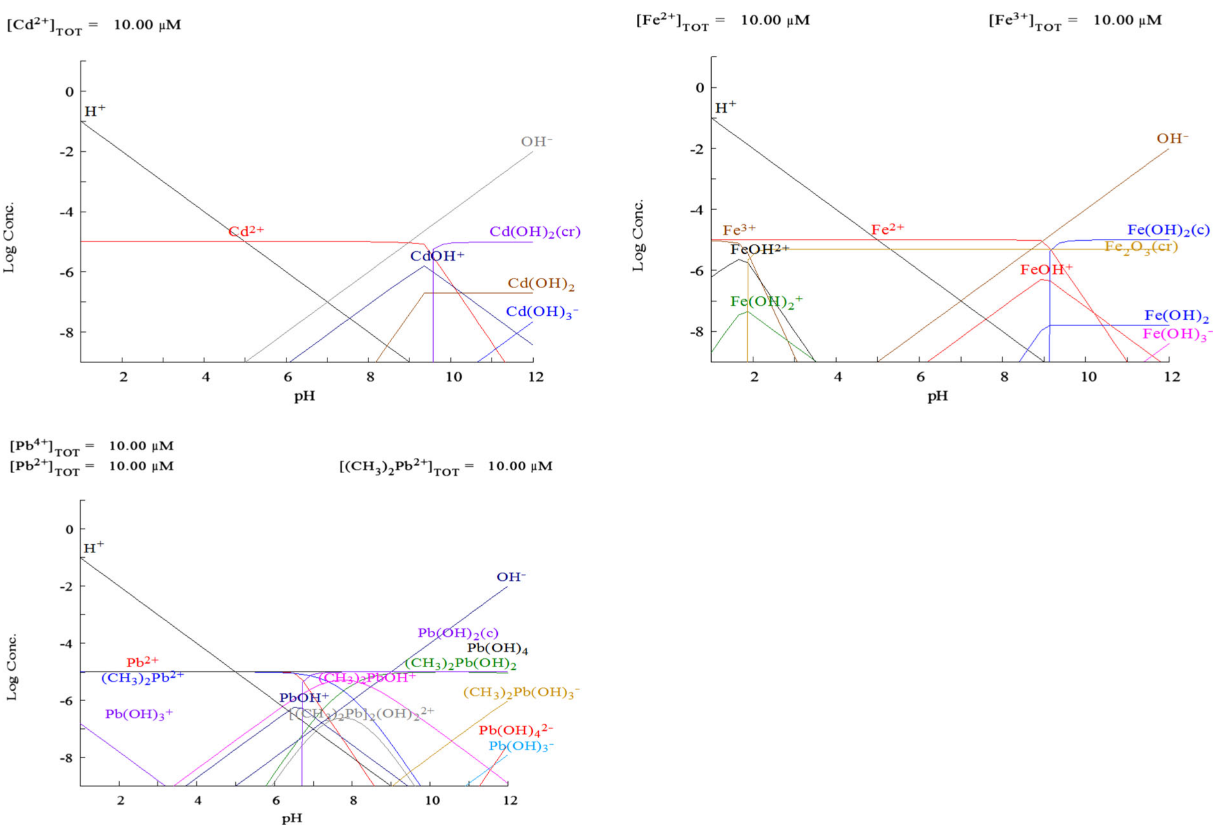
Considering the theoretical diagram (Fig. 4), it is observed that at pH ≥ 9.0, the predominance of poorly soluble forms of Cd, in the form $Cd(OH)_2$, while Fe, at pH = 2.0, precipitation predominates in the form Fe_2O_3, and at pH 9.0, occur the predominance of $FeOH^+$. At pH above 7.0, there is predominance of poorly soluble Pb molecules in $Pb(OH)_4$, $(CH_3)_2Pb(OH)_2$, and e $Pb(OH)_2$ forms.

Considering that the pH values found in the Toledo River are concentrated between 5.82 and 7.10, also considering the diagrams shown in Fig. 4, the high concentrations of Cd, Fe, and Pb metals (Fig. 2), can be explained by the predominance of the soluble forms of these compounds in the waters.

The Toledo River basin is also responsible for the drainage of an area of approximately 97 km^2 and is characterized by the intense anthropic activities carried out in its surroundings, such as discharge of urban wastewater, effluent from large food industry, and drainage of agricultural areas, because the region had large areas of natural vegetation replaced by agricultural plantations (Espinoza-Quiñones et al. 2005, 2010).

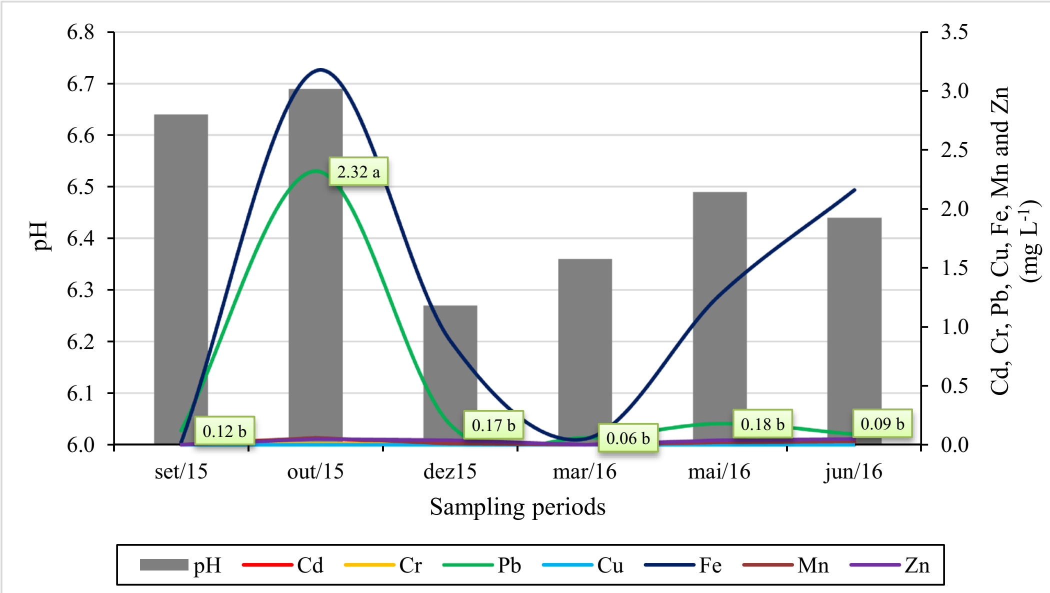
A statistic difference was found at 1% probability level ($P \leq 0.01$) for the source of variation "Sampling periods," which refers to the months in which the water samples were taken, for the concentrations of Fe, Mn, Cd, and Pb.

The Tukey test was performed at 5% probability ($P \leq 0.05$) (Fig. 5) (Table 4), where it was observed that the Pb concentrations in October were higher than the other months. The observed differences for Fe were confirmed by CETESB (2009) during the sampling in months with greater intensity of rain.



Source: Hydra-medusa Software, Puigdomenech (2015).

Fig. 4 Theoretical diagrams for speciation of the Cd, Fe, and Pb metals



N = 7; Different lowercase letters represent difference by Tukey test at 5% probability.

Fig. 5 Tukey's test at 5% for chemical parameters in waters of Toledo River, PR, during the period from September 2015 to June 2016

In this sense, it is possible to observe that the toxicological quality of the waters of the Toledo River is being compromised by the use of the soil and occupation format, as well as the anthropic and agricultural activities carried out around its microbasin.

The analysis of the sediments of the water bodies has been of great importance and relevance, because this compartment has been recognized as a repository of large amount of pollutants present in the aquatic environment, regardless of the low concentrations of metals in the liquid phase (Hortellani et al. 2008).

It is worth noting that metals found in water bodies may originate from natural sources, such as the natural composition of the local soil, as well as from the anthropic actions carried out around the hydrographic basin (Silva and Dantas 2014).

The concentrations of Pb in the liquid medium follow the increase of Fe concentration in October, 1 month of intense rainfall, suggesting that these elements must be carried by diffuse pollution of the agricultural environment and in livestock.

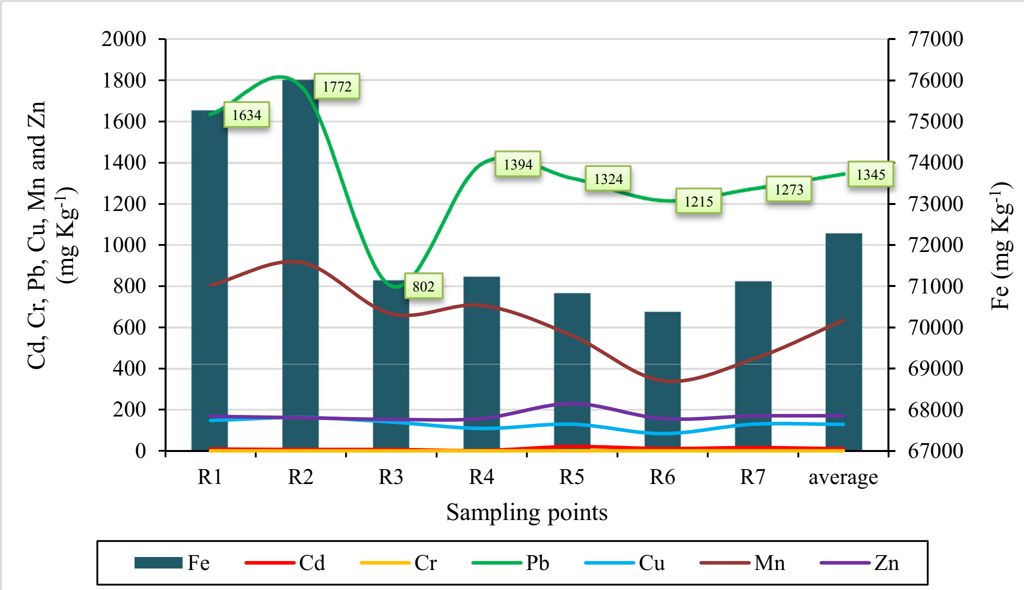
The accumulation of toxic metals in the sediments of Toledo River (Fig. 6) is possibly associated with anthropic occurrences during decades, and according to CETESB (2015), the results in sediments are a reflection of the influence of human activities on aquatic ecosystems for long time, since these influences are not always detectable by physical and chemical parameters in waters—analyzes usually conducted by sanitation agencies.

Table 4 Mean squares for sampling periods in relation to the evaluated parameters in waters of Toledo River, PR

FV	pH	Cu	Zn	Fe	Mn	Cd	Pb	Cr
Sampling periods	0.179004^{ns}	0.000005^{ns}	0.001717^{ns}	1.594363**	0.002022**	0.000562**	0.509012**	0.000028^{ns}
Error	0.147051	0.000006	0.001340	0.081865	0.000141	0.000077	0.076845	0.000028
CV	5.92	0.34	5.03	23.37	1.64	0.87	23.74	0.75

CV, coefficient of variation; *FV*, font of variation; *ns*, non significative

**Significant at the 1% by the Fisher test



Note: LQ (limit of quantification in mg L^{-1}): Cd = 0.005; Cr = 0.010; Pb = 0.01; Cu = 0.005; Fe = 0.01; Mn = 0.01; Zn = 0.005.

Fig. 6 Mean of total metals concentration in sediment of Toledo River during the sampling period

Considering the averages of the concentrations of metals in sediments at Toledo River sampling sites (Fig. 6), it was observed that there was variation between the maximum concentrations, so that not only one site exhibited high levels. It is observed that R5 exhibited the highest concentrations of the metals Cd and Zn, and R2 show the highest concentrations of Cu, Fe, Mn, and Pb.

When the relationship between metals and living organisms is observed, it is possible to verify that few concentrations of certain metals, such as Cu, Mn, and Zn, are necessary for the development of the vital functions of the organisms. In that sense, when at high levels, these can be highly toxic and harmful. Other metals, such as Cd and Pb, do not play any role in living organisms, so when introduced into the environment and inserted by organisms, they present high toxicity, leading to bioaccumulation (Pereira and Ebecken 2009; Ferreira et al. 2010).

A difference was found at the 1% probability level ($P \leq 0.01$), as for the "sampling sites" variation, which refers to the points where the sediment samples were taken, only for the concentration of Mn (Table 5).

The Tukey test at 5% probability ($P \leq 0.05$) (Fig. 7) shows that the concentration of Mn in R2 presented the highest mean concentration, while the R6 point had the lowest mean value.

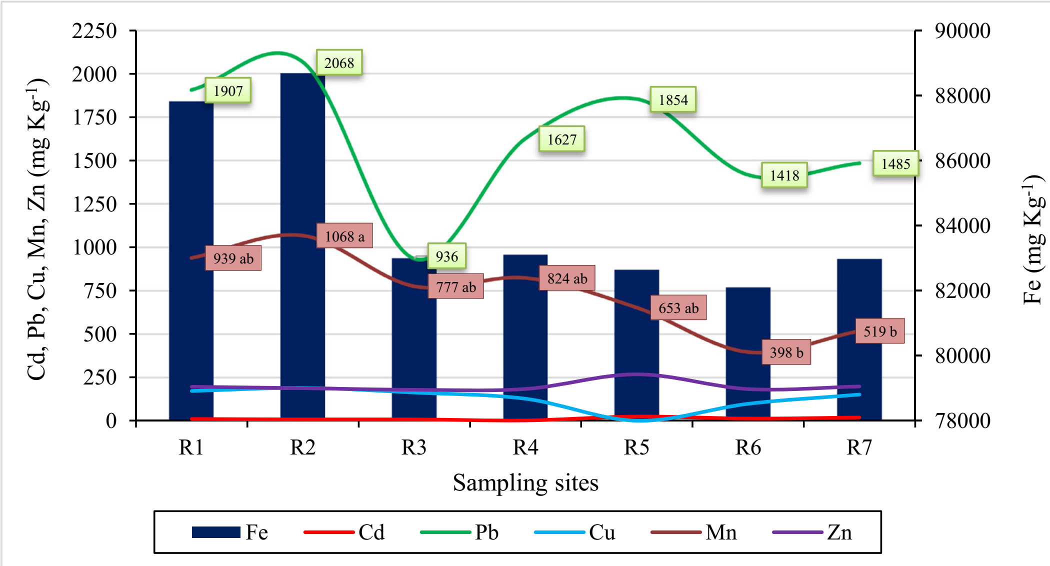
The R2 point, located in a sparsely inhabited urban area, is located after the highway BR 467, which can cause an increase in metal concentrations due to the

Table 5 Mean squares for sampling sites with respect to the parameters evaluated in the sediments of Toledo River, PR

FV	Cu	Zn	Fe	Mn	Cd	Pb
Sampling site	5483.33^{ns}	5781.55^{ns}	43,979,922.34^{ns}	329,482.94**	5.46^{ns}	797,330.56^{ns}
Error	3998.57	5649.64	19,463,207.43	95,747.14	5.39	1,400,026.07
CV	42.16	37.78	5.23	41.83	88.48	75.40

CV, coefficient of variation; *FV*, font of variation; *ns*, non significative

**Significant at the 1% by the Fisher test



N = 7; Different lowercase letters represent difference by Tukey test at 5% probability.

Fig. 7 Tukey's test at 5% for the chemical parameters evaluated in sediments of Toledo River, PR, during the period from September 2015 to June 2016

intense flow of vehicles and the release of pollutants; in addition, R2 was characterized for being located at the beginning of the urban area and after agricultural areas with intense activities. In this way, R2 site receives all cumulative loads from the agricultural area introduced to the water body. Gonçalves (2012), evaluates the concentrations of the heavy metals Cu, Pb, and Zn in soils adjacent to the SP-310 highway, and observes that the sampling sites located closer to the highway present higher levels of metals, which should be related to the release of heavy metals from the burning of fuel. Considering the characteristics presented by site R2, the possibility that the highway is also helping to increase the metal content is valid.

In a study conducted by Trindade et al. (2012), the authors found lower concentrations than the values obtained in Toledo River for Pb and Cu (Fig. 7), and for the Cd, Zn, and Cr, the values were higher than Toledo River. The authors attribute to the high rates found in the study the presence of agricultural area in the hydrographic basin under study.

Among the analyzed elements, the Fe presented very high concentrations when compared to the other metals. Similarly, Mn element also presented considerable concentrations; these results possibly reflecting its abundance in various soil types (CETESB 2015). In addition, the Red Latosols predominate in the studied municipality, whose most common composition includes Fe and Mn oxides and hydroxides (EMBRAPA 2013).

In this sense, the concentrations of Fe in sediments can be associated to the high concentrations in the waters of Toledo River, a relation cited by CETESB (2015), as the landings and erosion of the river banks occur, which justifies the high concentrations of these elements. CETESB (2015) also points out that Mn also occurs naturally in surface waters, and consequently in sediments; however, anthropic activities, mainly the use of fertilizers in areas destined to agriculture and erosion/silting of rivers, may be responsible for the increase of these concentrations, which may justify the high Mn contents at the R1 and R2 points of Toledo River, since the R1 point is characterized mainly by agricultural neighborhood; and R2, consequently, receives the impacts suffered by the flow upstream.

As already mentioned, there are no criteria in the Brazilian environmental legislation for sediment quality, making it a gap in the evaluation of this compartment. Considering its importance within the environmental context, therefore, the results found in this study were compared with the criteria of sediment quality established by CETESB (2015). Under this evaluation, the sediment is classified into five categories, being excellent, good, regular, bad, and very bad, according

Table 6 Limits TEL and PEL for toxic metals with sediment quality classification according to CETESB

Element	Excellent mg kg^{-1}	Good	Regular	Bad	Very bad
Cd	< 0.6	≥ 0.6 to 2.1	> 2.1 to 3.5	3.5 to 5.3	> 5.3
Cu	< 35.7	≥ 35.7 to 116.4	> 116.4 to < 197.0	197.0 to 295.5	> 295.5
Cr	< 37.3	≥ 37.3 to 63.7	> 63.7 to < 90.0	90.0 to 135.0	> 135.0
Pb	< 35.0	≥ 35.0 to 63.2	> 63.2 to < 91.3	91.3 to 137.0	> 137.0
Zn	< 123.0	≥ 123.0 to 219.0	> 219.0 to < 315.0	315.0 to 473.0	> 473.0

Source: adapted from CETESB (2015)

to the limits of TEL and PEL. The TEL represents that there is a low probability of occurrence of adverse effects to the aquatic biota, and the PEL represents conditions in which there is a high probability of adverse effects occurring in the same group of organisms.

It can be observed (Table 6) that for the toxic metals Cd (10.0 mg kg^{-1}) and Pb (1345.0 mg kg^{-1}) was classified as very bad, i.e, the results indicate that these two metals in these proportions may cause adverse effects on the aquatic life of the Toledo River, whereas Cu (128.6 mg kg^{-1}), Zn (170.5 mg kg^{-1}), and Cr (≤ 0.010 mg kg^{-1}) presented regular, good, and optimal quality, respectively. While the results obtained for Fe and Mn do not have established limits of TEL and PEL.

Legislation and guidelines developed by environmental agencies in other countries, such as Canada, Australia, New Zealand and the USA, establish maximum levels of toxic metals in sediments, and are presented in Table 7.

The limits established by other countries (Table 7) are similar to those established by CETESB (2015) (Table 6), which is based on the limits used by Canadian legislation, however, has more flexible limits.

Thus, if the obtained results in this study were compared to the international limits, the result observed for Cu (128.5714 mg kg^{-1}) considered regular by CETESB, are higher than the international standards, and Zn (170.5 mg kg^{-1}) only fits under the laws of Australia and New Zealand. Therefore, the discussion and understanding of the importance of sediment should be carried out effectively by the regulatory agencies due to the importance of this environmental compartment.

Table 7 Sediment quality guidelines developed by several countries establishing maximum permissible concentration limits for toxic metals

Country	Cd mg kg^{-1}	Cu	Cr	Pb	Zn
Canada	0.6	35.7	37.3	35.0	123.0
USA	1.2	34.0	81.0	46.7	150.0
Australia	1.5	65.0	80.0	50.0	200.0
New Zealand	1.5	65.0	80.0	50.0	200.0

Source: adapted from Burton Jr (2002)

Despite the increase in Pb concentrations in waters and sediments of the Toledo River, it is possible that this can be recovered, but for that, environmental measures should be urgently adopted in the region, such as the treatment of domestic and industrial sewage before its release into the river, or the re-dimensioning of existing treatment plants that are undersized, reconstruction of riparian forest along the river inside the city and in agricultural areas, and also environmental education projects that raise awareness of the region's population for the preservation of Toledo River.

Conclusion

From the toxicological analyzes carried out on the Toledo River, it is possible to observe that the water quality is being affected by the activities carried out in the Toledo River watershed, since the concentrations of toxic elements such as Cd, Fe, and Pb are above the maximum values established by CONAMA No. 357/2005, for Class 2 freshwaters.

In addition to the presence of metal content in water, there were also worrying concentrations of toxic metals in sediments. These concentrations have probably been accumulated in this compartment for a long time, due to the activities carried out around the water body, mainly agricultural and urban activities, and consequently being incorporated by the aquatic biota, causing bioaccumulation.

When the sediments are analyzed, high concentrations of Fe are observed. This element is part of the soil constitution of the western region of Paraná, where the Toledo River is inserted, which justifies the high levels. However, the high anthropic levels of Pb, according to the limits established by CETESB (2015), suggest that the quality of the sediments of the Toledo River is very bad. In addition, when comparing the results to international parameters, the only metal that meets the maximum limits allowed is chromium.

It is important to emphasize that the Toledo River is responsible for a percentage of population water supply, which generates a great concern, considering that the contents of toxic metals can be accumulated both in sediments and in living beings, causing serious impacts.

Acknowledgments The authors are thankful to National Counsel of Technological and Scientific Development (CNPq) for financial support of this research.

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