

Keywords: Heavy metals; Sediment record; Enrichment factors; Environmental pollution

Introduction

Chemical pollution of aquatic systems has already become a major public concern in almost all parts of the world. It occurs because of the constant release of pollutants and the intense development of several activities that lead into aquatic systems a large variety of synthetic and geogenic compounds [1,2]. Among the released pollutants, heavy metals are frequently found in environmental samples (sediments, water, organisms and etc.) and its presence is mainly correlated with anthropogenic activities [3].

Heavy metals are commonly found in urban and industrial sewage, coming from geochemical and anthropogenic sources. Soil represents a major sink for heavy metal ions, which may then enter the food chain via plants or leaching into ground water [1]. Also, fertilizers, inks, pharmaceutical and cosmetic products and a large amount of synthetic products contribute to the environmental contamination by heavy metal, as well as their manufacturing processes [3,4]. These hazardous pollutants can enter into the aquatic systems through irregular discharge of urban wastewater, superficial drainage, agricultural activities and atmospheric deposition [5-7].

After to be released and through the processes of chemical adsorption and physical precipitation, metals can remain accumulated in the sediment for a long period [8]. Besides readily accumulate, the sediments also could serve as repository of these and other pollutants in aquatic environments when disturbing events occur [9].

Studies developed to evaluate heavy metals concentrations in the aquatic systems should consider the lithogenic/geogenic origin of these compounds. Lithogenic micro pollutants, as selenium, arsenium, chromium and cobalt, can be found in increased concentrations because the elevation of their content in geological formations or because reactions responsible to transform environmental conditions and consequently change the partitioning behavior on the aquatic system [1,2,10]. Therefore,

high heavy metal concentrations might also result from natural processes and the presence of these compounds cannot be only from anthropogenic pollution [5]. These geochemical and background reference values are very important in environmental studies of the pollution and may be used to assess the natural source of trace elements [11].

Metal accumulations in sediments have been frequently investigated in urban rivers. Some elements are commonly found in specific sources, for example, cadmium and chromium are mainly present in domestic sewage [4], lead is mainly linked to traffic activities, cadmium to application of fertilizers, while copper, manganese, mercury and zinc are often associated with street dust samples from different urban and industrial areas [12,13]. The metals such as arsenic, vanadium, lead and cobalt were already related to mixed natural and anthropogenic sources. Nevertheless, different parts of the world can present different natural sources due the diversity of soil compositions [12].

The history of the adjacent environment can be reflected in the presence of metals accumulated in sediments from lakes and rivers. Sediment cores can be used to reconstruct the scenario of land use, growing of urban cities and industrial activities, correlating with levels of these chemical pollutants, since remote decades [10,14,15]. These cores are useful for this purpose, once it can present data from up to thousands of years ago [16].

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sample, i.e., the background sample. Based on the radiometric age modelling, this bottom most sample is previous to human influence in the area.

Moreover, to further evaluate the contamination of heavy metals in the Barigui River, the metals concentrations of the three cores were compared to ISQG (interim sediment quality guideline) and PEL (probable effect level) reference values for superficial freshwater sediments [24], to evaluate the contamination of heavy metals in the Barigui River.

The statistical data analysis involved ANOVA to check the existence of statistically significant differences among data variables variance (heavy metals, TOC, granulometry) variance for the cores and Pearson correlation analysis to assess the presence of relationships among the data variables for each sediment profile.

Discussion

Sediment composition

Particle size has a profound influence on the accumulation of heavy metals in sediments. Fine-grained sediments frequently present higher levels of heavy metals due to its higher grain superficial area when compared to the grain volume, in addition to its enrichment in organic matter enrichment and Fe-Mn oxides [25].

Being so, significant vertical granulometric variations can lead to characteristics in the heavy metals distribution that do not represent the real changes on its concentrations. In this study, the granulometric analysis (Table 1 and Figure 3) showed that sand (90-2360 μm) and silt (3-64 μm) are the dominant fractions in all three cores. This dominance can be related to hydrological factors of the region, such as intensity of water currents and water column depth. Heavier particles (such as sand) tend to deposit, whereas lighter ones (such as silt and clay) tend to be transported by the riverine flux [26]. The observed tendency of both silt and clay (<3 μm) distributions are similar and inverse to the sand distribution (Figure 3). All cores presented some level of vertical variation in the granulometric distribution; however, there is no statistically significant difference (p>0.05) in the cores' particle size composition.

Regarding TOC, cores F-0 and G-0 presented a vertical reduction in TOC content. For core E-0, it was observed a statistically significant difference (p<0.05) in the TOC content. The TOC content in core E-0 was significantly higher (p<0.05) than in cores F-0 and G-0 (Table 2).

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the choice of the background values is of utmost importance. Even though many studies use predefined mean values or Earth's crust mean abundance, the best alternative is the comparison with uncontaminated sediment of similar mineralogy and texture [23]. In this study, the concentration of the core's bottom most samples was used as background value, which is considered to be previous to the human influence in the region. The evaluation of contamination intensity was assessed with the enrichment factor (EF) [15], calculated with Equation 1.

$$EF = [(C_m/C_n)_{sample}] / [(C_m/C_n)_{background}]$$

Where $(C_m/C_n)_{sample}$ is the concentration of the element of interest (m) normalized with the reference element (n) in the sample, and $(C_m/C_n)_{background}$ is the concentration of the element of interest (m) normalized with the reference element (n) in the core's bottom most

Canadian quality guidelines showed that, in all sampled cores, the maximum values of Cd, Cr, Cu, Pb and Zn (Table 1) were above the ISQG threshold and below the PEL values [24], being just Pb in the core E-0 as exception for this statement. This range of values is typical for regions with considerable levels of human pollution. The observed mean values in all three cores are characteristic of recent sediment from urban areas, according the comparison with other literature reports on heavy metals contamination [15,27-29].

As reported in Table 1, there is little variation of the heavy metal content among the cores. The highest values of Cu were observed in core E-0, Pb, Zn in core F-0 and Cd, Cr in core G-0. This distribution can be due to the specific features of each sample site and the geographic distribution of the main pollution sources, discussed below in the text.

These observations are corroborated by the ANOVA performed with the data from Table 2, showing that there is no statistically significant

difference ($p>0.05$) of the heavy metals levels among the cores (the only exception is Cr on core G-0, $p<0.05$).

Enrichment factors of the heavy metals

The study of sediment vertical profiles can be an important source

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The area of core G-0 is the most impacted region by the local industries, as it is in a downstream area and receives part of the urbanization impacts. Another aggravating factor is the occurrence of an oil spill in 2000 [56], which are probably responsible for the peaks in Cd, Cr, Cu and Pb levels in that year (Figures 4 and 5). Levels between 100 and 2,000 mg kg⁻¹ of those elements can be found in unprocessed crude oil [57].

Conclusion

The results of this study reflect the evolution of the anthropogenic impact in the aquatic system of Barigui River in the last centuries. Sediments accumulated during the 19th century were already affected by a moderate heavy metal contamination, mainly in the central and

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