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Metal concentrations in surface water and sediments from Pardo River, Brazil: Human health risks

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ABSTRACT

Pardo River (Brazil) is suffering from an important anthropogenic impact due to the pressure of highly populated areas and the influence of sugarcane cultivation. The objective of the present study was to determine the levels of 13 trace elements (As, Be, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Tl, Sn, V and Zn) in samples of surface water and sediments from the Pardo River. Furthermore, the human health risks associated with exposure to those metals through oral intake and dermal absorption were also evaluated. Spatial and seasonal trends of the data were closely analyzed from a probabilistic approach. Manganese showed the highest mean concentrations in both water and sediments, remarking the incidence of the agricultural activity and the geological characteristics within the basin. Thallium and arsenic were identified as two priority pollutants, being the most important contributors to the Hazard Index (HI). Since non-carcinogenic risks due to thallium exposure slightly exceeded international guidelines ($HI > 1$), a special effort should be made on this trace element. However, the current concentrations of arsenic, a carcinogenic element, were in accordance to acceptable lifetime risks. Nowadays, there is a clear increasing growth in human population and economic activities in the Pardo River, whose waters have become a serious strategic alternative for the potential supply of drinking water. Therefore, environmental monitoring studies are required not only to assure that the current state of pollution of Pardo River does not mean a risk for the riverside population, but also to assess the potential trends in the environmental levels of those elements.

1. Introduction

Anthropogenic activities may cause the release of large amounts of toxic substances into surface waters. Among these, heavy metals are priority environmental pollutants. Because of their bioaccumulation capacity and environmental persistence, special attention has been paid on toxic trace elements. Although some trace elements (e.g., manganese, copper, chromium, etc.) are essential, they may be also toxic in excess. On the other hand, other elements (e.g., arsenic, cadmium, lead and mercury) may be toxic, even present in very tiny quantities (Domingo, 1994). These chemicals may enter aquatic compartments through a variety of routes, therefore impairing the quality of not only aquatic ecosystems, but also human health (Bao et al., 2012; Furtula et al., 2012; Yi et al., 2011). The analysis of dissolved metals in water is a useful tool for assessing the state of pollution in a particular ecosystem, reflecting its specific degree of contamination (Haloi and Sarma, 2012; Li et al., 2012; Su et al., 2013). In turn, sediments are frequently used to monitor long-term pollution impacts (Tsakovski et al., 2012). The distribution of heavy metals in sediments adjacent to populated areas is also suitable to assist in the evaluation of human health risks associated with water pollution (Bharadwaj and Machibroda, 2008; Ruiz et al., 2006; Zheng et al., 2008).

In recent years, human health risk assessment has become a largely applied methodology to evaluate the potential risks derived from exposure to environmental pollutants, not only contained in water (Ferré-Huguet et al., 2009), but also in other environmental compartments, such as soil or air (Kavcar et al., 2009; Nadal et al., 2011; Schuhmacher et al., 2004; Wu et al., 2010). A number of approaches to handle with uncertainty and variability have been proposed, being Monte-Carlo simulation one of the most recurrent. Monte-Carlo, a numerical technique that integrates different hypotheses linked to probability density functions, has been broadly applied in environmental sciences (Rossi et al., 2013; USEPA, 1997).

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Since 2000, special efforts to protect the environment are being made in emerging countries, whose economic model is based on a quick growth. The ultimate objective of environmental regulatory agencies is to assure that socioeconomic changes do not affect the environmental status of natural resources (Santos and Ranieri, 2013). Specifically for Brazil, and considering the immense natural richness of that country, important pressures have been undertaken to monitor the quality of water bodies, as it is sometimes the only source for human drinking water. Soil quality and climate make the region of Pardo River Watershed one of the major agricultural areas not only in the State of São Paulo, but also in all Brazil. The whole area is characterized by a high productivity, especially of sugarcane, being the largest producer of sugar and alcohol in the world. As a result of the discharge of pesticides and herbicides, which may contain important amounts of arsenic (As) and trace metals, as well as the location of large populated nuclei such as the City of Ribeirão Preto, this area suffers a very severe environmental degradation (Carneseca et al., 2012; Ribeiro, 2008). Agricultural burning of the sugarcane industry, linked to biofuel production, is also notable. In Brazil, 70% of the country's sugarcane plantation is burnt before manual harvesting for biofuel production (Mazzoli-Rocha et al., 2008). Unfortunately, the number of research studies focused on assessing the levels of environmental contaminants in this river is scarce, with only a few investigations reporting data on herbicides and physical–chemical parameters (Jacomini et al., 2011).

The purpose of the present study was to characterize the status of the Pardo River (Brazil) by analyzing the concentration of a number of metals in surface water and sediment samples. A particular study on the seasonal and geographical variations was also performed. Finally, health risks associated with metal exposure were assessed for the population living near the Pardo River.

2. Materials and methods

2.1. Sampling

Pardo River has its headwaters on the south plateau of Minas Gerais. It is the largest tributary in the left margin of the Grande River, which reaches after a course of about 550 km. It has a drainage basin of 10.694 km^2, covering more than one million inhabitants. Between March 2011 and January 2012, samples of surface water and sediments were collected at different sites along the Pardo River. Six campaigns were conducted: 3 of them during the rainy season (March 2011, December 2011, and January 2012), and the remaining 3 during the dry season (June–July 2011, August 2011 and September 2011). Samples were collected in 12 sites, differentiating two areas: upriver and downriver of the Ribeirão Preto City, the most important nucleus of population (Da Silva Alves et al., 2013). The coordinates of the sampling points, which were sequentially numbered along the river, were obtained by GPS. The first point was set at the City of Ipuiúna, while the last one was set at the confluence with the Grande River. The specific location of the sampling points is shown in Fig. 1.

Surface water (100 mL) and riverside sediments (500 g) were collected in polyethylene containers. These had been previously cleaned with a solution of 30% nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) for 24 h to remove any interfering metals, and subsequently they were rinsed with Milli-Q water. Immediately after their collection, water samples were acidified with high purity nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) and preserved at −18 °C until analysis (APHA, 2006). An Ekman Dredge sampler was used in most of the locations, although this tool was replaced by a trowel in those places of difficult access.

2.2. Analytical procedure

Total concentrations of the following 13 trace elements were determined in all samples of water and sediments: arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), thallium (Tl), tin (Sn), vanadium (V) and zinc (Zn). Element concentrations were determined by inductively coupled plasma spectrometry (ICP-MS, PerkinElmer Elan 6000). For surface water analysis, the accuracy of the instrumental methods was checked by triplication of the samples, as well as by using a certificated reference material (River Water Reference Material for Trace Metals, NRC Canada, SLRS-4), which was run after every 5 samples. The limit of detection (LOD) was 0.05 μg/L for Cd, Mn, Pb and Tl; 0.10 μg/L for Sn; 0.20 μg/L for As, Be, Cu, Hg and Ni; and 0.50 μg/L for Cr, V and Zn. With respect to surface sediments, they were dried at room temperature for 30 days. Afterwards, 0.5 g of dried sample was pre-digested with 5 mL of nitric acid (65% Suprapur, E. Merck, Darmstadt, Germany) in hermetic Teflon bombs at room temperature for 8 h. Subsequently, samples were heated at 80 °C for 8 additional hours. After cooling, solutions were filtered and made up to 25.0 mL with ultrapure water (Ocampo-Duque et al., 2008). The accuracy of the results was controlled by digesting duplicate samples and by using blanks as control samples. Furthermore, reference materials (Soil, Loamy clay, Resource Technology Corporation US, CRM 052), which were run every 5 samples, were used to check for drift in the sensitivity of the instruments. For each element, the quantification was based on the most abundant isotope of that element free of analytical interferences. The LOD in sediments was 0.02 mg/kg for Mn; 0.05 mg/kg for Cd, Pb and Tl; 0.10 mg/kg for Sn; 0.20 mg/kg for As, Be, Cu, Hg and Ni; and 0.50 mg/kg for Cr, V and Zn.

2.3. Data analysis

Data were statistically evaluated by using the statistical software package SPSS 14.0. The Levene test was applied to study the equality of variances. Subsequently, Student's *t*-test was executed to detect any significant differences between groups. A probability under 0.05 was considered as statistically significant ($p<0.05$). For calculations, when an element was not detected (ND), the concentration was assumed to be one-half of the respective limit of detection (ND = 1/2 LOD). A probabilistic approach was here followed by applying Monte Carlo simulations (Nadal et al., 2004; Rivera-Velasquez et al., 2013; USEPA, 1997), which were run by means of the Crystal Ball software (Decisioneering, Inc., Denver, CO, USA). The number of simulations was set at 10,000.

2.4. Human health risk assessment

Human health risks associated with the ingestion and dermal absorption of metals through water were assessed under a residential scenario. The daily environmental exposure to metals was estimated, being non-carcinogenic and carcinogenic risks separately assessed. Two main exposure pathways were considered: metal intake through water consumption, and dermal absorption through bath. In turn, calculations, which were based on the USEPA (1996) methodology, were performed for 2 subpopulation groups: adults (as general population) and children (as especially sensitive group), separately.

The expressions (Eqs. (1) and (2)) used to evaluate the exposure through ingestion (Exping) and dermal contact (Expderm) are as follows:

$$\text{Exping} = \frac{C_W \cdot \text{IR} \cdot \text{EF} \cdot \text{ED}}{B_W \cdot \text{AT}} \tag{1}$$

$$\text{Expderm} = \frac{C_W \cdot \text{SA} \cdot K_p \cdot \text{EF} \cdot \text{ED} \cdot \text{ET}}{B_W \cdot \text{AT}} \tag{2}$$

The values and description of the different parameters are summarized in Table 1. Non-carcinogenic risks were assessed by estimating the Hazard Quotient (HQ), calculated as the quotient between the environmental exposure and the reference dose (RfD). HQ values were obtained for each element and exposure pathway. Subsequently, the Hazard Index (HI), which is defined as the total risk through each exposure pathway, was obtained by summing the HQs of each element. Finally, the total HI was calculated by summing the HIs through oral and dermal routes (HI_{ing} and HI_{derm}, respectively) (USEPA, 1989). Values of HI under the unity are considered as safe (USEPA, 1989). Similarly, the excess cancer incidence (ELCR) derived from exposure to carcinogenic elements was also evaluated, considering the same exposure routes. The ELCR was calculated by multiplying the daily exposure and the oral/dermal slope factor (SF) (USEPA, 2002). Cancer risks were assessed for As, the only element for which SF values are available. In order to determine the contribution of each specific pathway, the ELCRs of all elements were summed. Finally, the total excess cancer incidence posed by all chemicals over all routes, which is an estimation of the increased cancer incidence resulting from exposure to all chemicals, was calculated as the sum of all ELCRs (USEPA, 1989).

3. Results and discussion

3.1. Metal concentrations in water and sediments

The concentrations of 13 trace elements in surface water, according to the sampling season (dry/wet), are summarized in Table 2. Manganese and Zn presented the highest mean levels in water, irrespective of the season, while Be, Hg and Sn were not detected in any sample. Manganese may be present in water supplies as a result of natural processes involving both catchment erosion and redox-related