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Health risks of environmental exposure to metals and herbicides in the Pardo River (Brazil) basin

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Abstract

Mixture of metals and herbicides in rivers may pose relevant risks for the health of surrounding communities. Humans may be exposed to river pollution through intake of contaminated water, as well as of fish, seafood and agricultural products. The authorities and regulators of Pardo River (São Paulo, Brazil) has recently proposed to supply river water to some municipalities, whose needs are now covered by groundwater. Unfortunately, the consequences of the shift have not been evaluated yet, not only ecologically but more important, in terms of human health impact. The aim of this study was to determine the distribution and abundance of metals and herbicides in different locations along the Pardo River basin, in the period 2014-2015. Seasonal variances were also studied. Metals were analyzed in total and filtered water fractions, as well as in edible fish. Moreover, the content of herbicides widely used in sugarcane crops (diuron, tebuthiuron, simazine, atrazine, ametryn and hexazinone) was also determined in water samples. Aluminum, Cd, Cu, Mn, Pb and Zn levels in the Pardo River water were higher than USEPA benchmarks. Non-carcinogenic risks due to pollutants mixture exposure were above the threshold, while carcinogenic risks of As exposure were above $>10^{-6}$, in both cases during the rainy season. Metal levels in fish were lower than the maximum allowable concentrations established by Brazilian legislation, and therefore they do not pose a threat for the public health. Herbicides were detected in four of the five sampling points, with atrazine concentrations (range: 0.16-0.32 µg/L) below the Brazilian legal limits (2.0 µg/L), but above the levels allowed by the European Union (0.1 µg/L).

Keywords: Risk assessment; Metals; Pesticides; Tropical ecotoxicology; Surface water quality.

1. Introduction

Contaminated rivers pose a risk to human health, especially when they are used as a public water source, for recreation or/and fishing. São Paulo (SP) state contributes with half of the Brazilian sugarcane production, with around 653 million tons every year (Bargos et al. 2016). In recent years, the application of agricultural chemicals has been intensified (OECD/FAO 2015). These agricultural products, such as pesticides and fertilizers, can be transported to superficial waters by leaching, especially during rainy periods.

The water crisis that occurred in Brazil between 2013-2015 motivated governments to find better alternatives for public water supply (Nobre et al. 2016). Some municipalities that are currently supplied by groundwater, as Ribeirão Preto, SP (Fregonesi et al. 2015), have been considering to be supplied by Pardo River water after proper treatment (ANA 2013). Unfortunately, there is no reliable information on the state of pollution of the Pardo River, as studies about the occurrence of pesticides and fertilizers in Brazilian freshwaters are scarce (Albuquerque et al. 2016).

Bioaccumulative substances, such as metals and herbicides, are able to be transferred through the food chain via water and sediment to zoo-benthos and fishes, until humans (Yi et al. 2011). The major concern about metals and some pesticides in surface water is that the removal of these pollutants by conventional water treatment is limited, and they are not completely removed (Stackelberg et al. 2004; Benner et al. 2013). Thus, in order to reduce the contamination to acceptable levels by advanced water treatment it is necessary to know the levels of pollutants in the water source and also in river water, physical-chemical and environmental influences. Metals can reach the human by ingestion, inhalation and skin-contact (Rovira et al. 2015). Long-term exposure to toxic elements, and high concentrations of essential elements, have been associated with adverse health effects (Domingo et al. 2007; Callan et al. 2015; Kim et al. 2016). Furthermore, estimating the potential risk by considering one chemical at a time might significantly underestimate the risks associated with simultaneous exposures to several substances (Hernández et al. 2013). Health risk assessment of chemical mixtures approach assumes that simultaneous exposures to various pollutants could result in adverse health effects (USEPA 1989).

Herbicides are applied in sugarcane both pre and post-emergence, being most persistent in the environment, (Vonberg et al. 2014; Barchanska et al. 2016). In Brazil, the maximum levels permitted for some herbicides, like atrazine, in surface water and drinking water is 2 µg/L (Conama 2005; BHM 2011), while the same herbicide is prohibited in the European Union and the maximum level allowable in water is 0.1 µg/L (Vonberg et al. 2014). The effects for human health by the long-term exposure to these pollutants are not clear yet (Sass and Colangelo 2006; Machado et al. 2016). Therefore, heath risk assessment of environmental exposure and monitoring of pollutants in river water is thus essential. In this context, the purpose of the present study was to assess the human health risks through river water consumption and fish intake, as well as to determine the distribution and abundance of metals and herbicides in the Pardo River.

2. Materials and Methods

2.1 Sampling site and data collection

Pardo River's headwaters are located on the south plateau of Minas Gerais, Brazil. It is the largest tributary in the left margin of the Grande River, where it arrives after a course of about 550 km. It has a drainage basin of 10,694 km^2, covering more than one million inhabitants (CBH Pardo 2015). Four sampling campaigns were performed and duplicate water samples were collected in five sampling points along the Pardo River (Figure 1).

All the sampling points were located near to sugarcane crops. Sampling point #1 is located before São José do Rio Pardo city (SP, Brazil) where some potential pollutant industries, such as tannery (GEMG 2014), electrical conductors factory (GEMG 2013) and metal foundries (GEMG 2011), are installed nearby. São José do Rio Pardo city uses the Pardo River as a source of public water supply, and six of the Pardo River Basin municipalities require a new source or the expansion of the existing system to supply the water demand (ANA 2016). Sampling point #2 is located after Mococa city (SP, Brazil), a city with a 73% of its surface occupied by agricultural crops. Sugarcane is the main product (53.08%), followed by corn (18.48%), coffee (13.85%) and orange (9.56%) (IPEADATA 2010).

Located in the rural area of Ribeirão Preto city (SP, Brazil), sampling point #3 has been approved as a future water catchment for human supply (ANA 2013). Sampling point #4 is located in the urban area of Ribeirão Preto city (SP, Brazil), in a private recreation club. Above this sampling point there is a municipal station of sewage treatment

(DOSP 2012). Sampling point #5 is located between Pontal city and Cândia city (SP, Brazil) and previously this sampling point there is a sugarcane industry (DOSP 1978).

Considering the rainfall pattern in the sampling area, two sampling campaigns were performed in the dry season (October 2014 and June 2015) and two in the rainy season (January 2015 and March 2015). River water samples were collected in amber glass bottles (1 L) previously cleaned with HNO_3 for metal determination, and with methanol and acetone for herbicide analysis. In order to determine the soluble metal fraction, filtered water (syringe filter 0.45 µm, Whatman) was also collected and quantified. The levels of pH and temperature in water were determined *in situ*. Fish species were acquired with local fishermen in October 2015. The three species evaluated were *Leporellus vittatus* (Valenciennes, 1850), *Leporinus octofasciatus* (Steindachner 1915) and *Pimelodus maculatus* (Lacepède 1803).

2.2 Metal analysis in Pardo River water and fish tissue

The metals evaluated in this study were aluminum (Al), arsenic (As), beryllium (Be), cadmium (Cd), chrome (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), thallium (Tl), tin (Sn), vanadium (V) and zinc (Zn). River water samples collected were acidified with HNO_3 (65% Suprapur, Merck Millipore, Darmstadt, Germany) and preserved at -18 °C until analysis by inductively coupled plasma spectrometry (ICP-MS, Perkin Elmer Elan 6000 (APHA 2006).

Fish species were identified, measured and weighed (Table 1). Muscle tissues were dissected using materials previously immersed in acidic solution overnight, freeze-dried 0.1 g of each sample was digested by microwave. The digestion was conducted with 3 mL of HNO_3 (65% Suprapur, Merck Millipore, Darmstadt, Germany), 3 mL of H_2O_2 and 2 mL of ultrapure water in a Milestone Start D Microwave Digestion System for 5 min at 120 °C, then 10 min from 120 °C to 200 °C, and finally, 15 min at 200 °C. After cooling, extracts were made up to 25 mL with ultrapure water. Extracts were kept frozen at -20 °C until elemental analysis.

The levels of metals in fish muscle were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Blank and control samples, as well as reference materials (TORT-2 Lobster Hepatopancreas Reference Material for Trace Metals), were used to check the accuracy of the instrumental methods. The limits of detection (LODs) for water were the following: 0.05 µg/L for Cd, Pb, Mn and Tl; 0.1 µg/L for Be and Sn; 0.2 µg/L for As, Cu, Hg and Ni; 0.5 µg/L for Cr and Zn; 1.0 µg/L for Al and V. In turn, for fish they were: 0.05 µg/g for Cd; 0.1 µg/g for Be, Cu, Pb, Mn and Tl; 0.2 µg/g for As, Hg, Ni and Sn; 1.0 µg/g for V and Zn; 2.0 µg/g for Cr and 3.0 µg/g for Al.

2.3 Herbicides determination in Pardo River water

The herbicides analyzed in this study were diuron, tebuthiuron, simazine, atrazine, ametryn and hexazinone, all of them widely used in sugarcane crops. The analytes were extracted from river water by Solid Phase Extraction (SPE) using C18 disks (Sigma-Aldrich, USA) and all the used solvents were specific for chromatography (Fluka 99.9 % pure, supplied by Sigma-Aldrich, USA). The extraction was conducted at the temperature of 25°C, pressure of 15 mmHg, methanol was used as filter conditioner and ethyl acetate as elution solvent. The extracts obtained were completely evaporated using a TurboVap LV® evaporator (Zymark, Hopkinton, USA). After the evaporation step, 200 µL of ethyl acetate were added for analytes resuspension and the quantification was conducted by Gas Chromatography with Nitrogen Phosphorous Detector-GC/NPD by means of a CP3800 Varian GC (Agilent Technologies, Santa Clara, USA).

The chromatographic separation was carried out on a DB-5 analytical column (5% Phenyl 95% dimethylpolysiloxane, 60 m × 0.25 mmid; 0.25 µm film thickness) (Agilent Technologies, Santa Clara, USA). For the analysis, a volume of 1 µL of the sample extract was injected in splitless mode, with a column rate of 1 mL/min. The validation was conducted with the quantification of ultrapure water spiked with an herbicides mix solution (six analyzed herbicides in ethyl acetate) and triphenyl phosphate (internal standard - IS) in six different concentrations levels, five replicates. The compounds were quantified by peak area ration (analyte versus IS) and identified by retention times. To calculate extraction recoveries, ultrapure water was spiked with herbicides mix solution, one before and one after the extraction, being afterwards analyzed. The analytical validation details are shown in Table 2.

Recovery percentages next to 100% are the ideal; however, lower values are accepted when the method shows adequate values for precision and accuracy (ANVISA 2003). In all cases, determination coefficients (R^2) were higher than 0.99. The LODs and the limits of quantitation (LOQs) were estimated from the instrumental signal and taking into account extraction recoveries. For LODs, a signal/noise ratio of three was considered, while LOQs were fixed to the lowest instrumental calibration point. Thus, LODs ranged from 0.01 to 0.05 µg/L, while LOQs were 0.1 µg/L.

2.4 Exposure and risk assessment

Human health risks associated with the ingestion of metals through water and fish 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 and fish consumption. In turn, calculations, which were based on the USEPA (1996) methodology, were performed for adults, as general population. The expressions used to evaluate the exposure through ingestion of water (I_w) and fish (I_{Fish}) are as follows:

$$I_w = \frac{CF \times IR_w \times EF_w \times ED}{BW \times AT}$$

$$I_{fish} = \frac{CF \times IR_F \times FI \times EF_F \times ED}{BW \times AT}$$

The values and description of the different parameters used for the calculations are summarized in Table 3. Non-carcinogenic risks were assessed by estimating the Hazard Quotient (HQ), calculated as the quotient between the environmental exposure for each element and the reference dose (RfD). Values of HQ under the unity are considered as safe. Subsequently, the Hazard Index (HI), which is defined as the total risk by the pollutants mixture exposure through each pathway, was obtained by summing the HQs of each element (USEPA 1989).

Similarly, the Excess Lifetime 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 2008). Cancer risks were assessed for As and atrazine, SFs 1.50 and 0.23 $(mg/kg\ day)^{-1}$, respectively (RAIS 2016). Finally, the total excess cancer incidence posed by all chemicals, which is an estimation of the increased cancer incidence resulting from exposure to all substances, was calculated as the sum of all ELCRs (USEPA 1989).

2.5 Statistics

For the calculations, those herbicides and metals presenting levels below the corresponding LOD or LOQ were assumed to have a concentration equal to one half of the LOD or LOQ, respectively. Metal and herbicides levels in water were compared between the two sampling conditions (dry and rainy) by the Mann-Whitney U test. Significant correlations were displayed in scatterplots. The relationships between spatial and seasonal variation trends of related contaminant elements, sampling matrix and physical-chemical parameters in Pardo River were performed based on Pearson's correlation coefficient.

3. Results and discussion

The metals distribution among various fractions of water within the basin is essential to understand their environmental behavior and to improve watershed management plans (Palleiro et al. 2016). Different environmental conditions such as pH, redox potential, organic matter and cation exchange capacity, may influence the form the metal is present in the river water (USEPA 2007). Phenomena such as the increase or decrease of water volume resulting from rainfall regime in tropical countries like Brazil, may promote variations in the physical-chemical water conditions, changes on the concentration of substances and organic matter, affecting the metals mobilization.

3.1 Metal fractions in the Pardo River water

During the sampling periods, river water pH ranged from 5.7 to 8.0, and temperature registered variations from 19.5 °C to 32.4 °C. Metal levels in the Pardo River water and the Freshwater Screening Benchmarks established by the USEPA are shown in Table 4.

Aluminum and Cd levels in the total fraction were significantly higher in the rainy period ($p<0.05$), being above the USEPA threshold values in all sampling points during the rainy period. In turn, during the dry period the benchmark was only exceeded for Al in sampling points #4 and #5Aluminum has generally high background concentrations in soils and sediments (USEPA 2007). A potential increase of Al levels in water may be related to the solubilization of Al present in soils or sediments, and then transported to water. Soil acidification may lead to cation losses typically from tropical soils. Major cations losses, such as Ca, K, and Mg can be significant in sugarcane fields in Brazil (Filoso et al. 2015), where more than 70% of the agricultural soils are acidic (Deus et al. 2014).

Furthermore, water pH variations during rainy periods may contribute to Al mobility from sediments to river water. In our study, water pH in the sampling points #1, #2, #3, #4 and #5, respectively, were 7.3, 6.7, 6.5, 6.7 and 6.6 (rainy period) and 7.4, 7.3, 7.2, 7.1 and 7.2 (dry period), predominating the acidic pH in the rainy period. Study conducted between 2001 and 2004 in the Pardo River indicated elevated Al levels in water (Bonadio et al. 2005). As in the present study, the highest Al concentrations were detected in rainy periods, indicating diffuse contamination associated with the soil of the surrounding region. Several studies points to the Al exposure as an important influence on the excess inflammatory brain activity and neurodegenerative diseases (Ferreira et al. 2008; Bondy 2016).

Values of total and filtered fractions were quite similar, and Al levels on the filtered fraction were also above the USEPA threshold (range: 151.5-251.1 µg/L) during the rainy period for all the sampling points. This result may indicate that metals are soluble and not linked to suspended matter on the river, and may represent more risks related to the bioavailability. Chromium was majority in FW fraction during the dry period (range: 1.1-1.5 µg/L), maybe it was in the chromate/dichromate (Cr VI) form, more soluble and toxic specie that would be present in waters affected by industrial and urban impacts (Roig et al. 2013).

Cadmium, Pb and Cr are undesirable components of the fertilizers raw materials applied in sugarcane crops, in addition to desirable elements as micronutrients supply (Deus et al. 2014; Filoso et al. 2015). Lead levels were higher in the sampling points #1, #3 and #4 during the rainy season, as well as Zn levels that were higher in the sampling point #2 at the same period ($p<0.05$). Considering the increase of the rainfall and the modifications on the permanent preservation areas (PPA) in Pardo River (Machado et al. 2015), these findings indicate that the products applied on the sugarcane crops have undergone surface runoff and leaching to aquatic systems. Besides environmental damage and health risks associated with increased levels of these substances in the river water, this result is an important indicator of investment losses by farmers, with excessive application of fertilizers in the soil, especially during intense rainfall period.

Finally, Mn levels were above the USEPA limits in the sampling point #1 during the rainy season in total metal fraction. High levels of Mn may be related to a natural processes involving both catchment erosion and redox-related dissolution of Mn-containing minerals at/near the sediment water interface (Alves et al. 2014), as well as the presence of effluents (Cardoso-Silva et al 2016; Vymazal and Svehla 2013). In summary, the quantification of metals in the Pardo River water resulted in decreasing concentrations in the order Al > Zn > Mn > Cu > Ni > V > Pb > Cr > Cd > Sn > As > Be > Tl > Hg.

3.2 Metal in the fish muscle

Metal levels in fish muscle are shown in the Table 5. Concentrations in fish samples were converted into wet weight basis by taking into consideration the moisture content (71–83%). Lengths and weights of all fish species varied from 18 to 37 cm and from 141 to 800 g, respectively.

Arsenic, Be, Cd, Cr, Pb, Hg, Ni, Tl, Sn and V concentrations were below their LODs in all the samples. The highest concentration was found for Zn in *L. octofasciatus* (14.68 µg/g), followed by *L. vittatus (13.29* µg/g), while in *P. maculatus* Zn concentration was considerably lower. Fish behavior may impact on the metals accumulation; benthic species are exposed to metals accumulated on sediments, while predatory fish accumulate more metals from water and food (Djikanović et al. 2016). *Leporellus vittatus* feeds on invertebrates (Buckup et al. 2007), *L. octofasciatus* diet is predominantly herbivorous (Duraes et al. 2001) and *P. maculatus* has ontogenetic dietary shifts, i.e. smaller individuals feed on larvae and pupae of Chironomidae, while larger individuals feed mainly on fish (Lima-Junior and Goitein 2003).

Zinc is an essential element important to human nutrition that acts on different biochemical metabolism functions. However, high concentrations may have adverse effects (Medeiros et al. 2012). Aluminum levels varied from 6.72 µg/g in *P. maculatus* to 11.64 µg/g. in *L. vittatus.* Brazilian legislation does not define the maximum Al values in fish tissue, and studies have found high concentrations of Al in salmon (1934.3 µg/g) (Medeiros et al. 2012).

Acidification processes on superficial water associated with acid rain, industrial or urban discharges and atmospheric emissions may contribute to the water pH reduction and Al mobilization from soils and sediments to water, accumulating in fish tissues (Nilsen et al. 2013).

Metal levels in the fish muscles observed in this study were all lower than the maximum allowable concentrations established by Brazilian legislation. Manganese was detected in the Pardo River water, and the highest level in fish muscle was observed in *L. vittatus* (2.36 µg/g), a pelagic fish that that eat invertebrates (Buckup et al. 2007).

3.3 Herbicides in the Pardo River water

Among the herbicides analyzed only atrazine, ametryn and hexazinone exhibited values of concentration above the detection limit in four out of the five sampling points. Sampling point #2 (between the cities of Mococa and Casa Branca, SP, Brazil) was the most impacted by herbicides being atrazine, ametrine and hexazinone detected. Sugarcane crops, chemical industries, tannery and dairy industry are located next to that sampling point. In turn, atrazine was the most ubiquitous herbicide, indicating the wide range of application in Pardo River Basin. Atrazine was detected during the rainy period with concentrations of 0.32, 0.19, 0.16 and 0.18 µg/L in sampling points #2, #3, #4 and #5, respectively. Atrazine is known as one of the most effective and affordable herbicides and river contamination by this herbicide is widespread in several countries, including in Brazil, due to its frequent use in agriculture (Hu et al. 2015). Even ten years after the withdrawal from the use of atrazine in Poland, its degradation products are still present in surface water, sediment and soils (Barchanska et al. 2016). Considering the atrazine removal from superficial water with potable purpose is still a challenge (Ghosh and Philip 2006), the detection of atrazine, mainly on the sampling point #3 (future water catchment) is an important information to the authorities and to the local community, face to human health effects related to this herbicide.

The maximum level permitted by the Brazilian legislation for atrazine in both surface water and drinking water is 2.0 µg/L (Conama 2005; BHM 2011), a high value when compared with European Union (EU) standards (0.1 µg/L). In Germany, for example, atrazine was banned due to its persistence in high concentrations in drinking water (Sass and Colangelo 2006; Vonberg et al. 2014). In the present study, concentrations of atrazine were higher than the EU limit (range: 0.16-0.32 µg/L). The detection of triazine herbicides in the environment has progressively increased in recent years (Fairbairn et al. 2016). These herbicides in can affect animals, as they are toxic to the endocrine system, and they own carcinogenic potential (Carmo et al. 2013).

In the dry period, the herbicides ametrine and hexazinone were detected at the sampling point #2 with concentrations of 0.27 µg/L and 0.21 µg/L, respectively. Ametrine is a selective terrestrial herbicide registered for use in sugarcane, banana, pineapple, citrus, corn, among others. This herbicide is transported from the soil by leaching relatively easy manner and some studies suggest concentrations dangerous to the aquatic biota in Brazilian rivers (Botelho et al. 2015). Hexazinone is a non-selective contact herbicide that acts on the inhibition of photosynthesis, used in sugarcane, pineapple and non-agricultural areas.

3.4 Human health risk assessment

Table 6 shows the metals and herbicides exposure through water consumption. The exposure was only calculated for those elements with values above the LOD.

Aluminum showed the highest exposure for adults in a residential scenario, during the rainy period, for all the sampling points, ranging from $1.5 \cdot 10^{-2}$ to $1.9 \cdot 10^{-2}$ mg/kg day. In the dry period, the highest exposure was found at the sampling points #3, #4 and #5 for Al ($1.0 \cdot 10^{-3}$, $1.4 \cdot 10^{-3}$ and $1.4 \cdot 10^{-3}$ mg/kg day, respectively). Atrazine showed the greatest exposure ($9.2 \cdot 10^{-6}$ mg/kg day) on the sampling point #2 during the rainy period

Non-carcinogenic risk associated with the intake of water was estimated for all sampling points. The results on herbicides indicate that the current exposure to these chemicals through the consumption of Pardo River water do not pose a non-carcinogenic risk for the population living nearby (HQ<1). The HQ was calculated for each metal, and the highest levels during the rainy and dry period are shown in Figures 2 and 3 respectively.

HQ associated to the exposure to all the analyzed metals in water samples was below 1, indicating these elements do not pose non-carcinogenic risks. The only exception was the exposure to Al by the ingestion of water, which showed a HQ higher than 1 in all sampling points. A high exposure to Al may result into neurophysiological damage and Alzheimer's disease (Ferreira et al. 2008). It is known that the Al is present in some foods- However, Al in water is especially bioavailable and it can be easily absorbed by the intestine. Considering that the Pardo River Basin is highly surrounded by sugarcane crops and the PPAs are not in accordance with Brazilian legislation (Government of Brazil 2012; Machado et al. 2015), prevention actions such as restoration of riparian vegetation would be important to prevent soil entrainment from the margins to the river channel and the consequent water contamination. In addition, this contamination evidence (Bonadio et al. 2005) indicates the necessity to adopt and implement measures to control and reduction of Al contamination, especially in the rainy seasons, when pollutant levels are increased.

The HQ was higher than 1 in sampling points #3, #4 and #5 during the dry period. Information about the risks associated with Pardo River water consumption may help to find the better choice about water treatment, especially in the cities that are currently using Pardo River as a water source, São José do Rio Pardo city (point #1) and the future intention for Ribeirao Preto city (point #3). Six of the Pardo River Basin municipalities require a new source or the expansion of the existing system (ANA 2016). To assess the overall potential for non-carcinogenic effects posed by more than one chemical, a hazard index (HI) was calculated by the sum of each substance HQ (Figure 4).

The HI calculated as a sum of HQs for each one of the herbicides and metals within the mixture of pollutants, was above the safety limit (HI>1) for all sampling points, especially during the rainy period. The highest HI levels corresponded to sampling points #4 and #1 (47.1 and 46.6, respectively), and Al was the element that mostly contributed to the risks. In addition to water samples, metals were analyzed in some fish species. The highest exposure was $5.1 \cdot 10^{-4}$ mg/(kg day) for Zn in *Leporinus octofasciatus*, $4.0 \cdot 10^{-4}$ mg/(kg day) for Al and $8.1 \cdot 10^{-4}$ mg/(kg day) for Mn in *Leporellus vittatus*. Hazard Index calculated for fish species indicated that the exposure to the levels determined in this study do not pose non-carcinogenic risk for the population (HI<1). Although the fish consumption is encouraged by the health benefits, knowledge of the effects on human health from exposure to several accumulative substances in fish muscle is still limited (Domingo et al. 2007).

Carcinogenic risks were only calculated for As and atrazine (Table 7), since they were the only detected elements for which an oral SF has been established. Carcinogenic risks associated to As exposure due to water ingestion were above the acceptable ($>10^{-6}$) limits in all the sampling points during the rainy period, according to international standards. Regarding ingestion of fish tissue, risks were below safe limits ($<10^{-6}$) and therefore do not pose a threat to public health.

4. Conclusion

Our finding indicates that the Pardo River has two majority problems: 1) the Al contamination associated to surrounding soils and water acidification, and 2) the anthropogenic contamination as a consequence of wide use of herbicides, such as atrazine, in sugarcane crops. Herbicides were detected in some of the sampling points, with atrazine showing especially high concentrations in comparison to EU standards. Although those levels should not mean a risk for the human health, herbicides detected in the Pardo River water may affect the ecological dynamics and pose a risk to environmental balance. The limitation or ban of atrazine might be a solution to minimize chemical pollution in freshwater and to reduce any potential environmental impacts.

Aluminum, Cd, Cu, Mn, Pb and Zn levels in the Pardo River water were higher than USEPA benchmarks, indicating there exist important anthropogenic pressures that have negative impacts on Pardo River water quality. Diffuse contamination related to fertilizer applications, particularly that based on Cd, Pb, Cr and Zn in sugarcane and herbicides detection in Pardo River water, showed that agriculture is a major contributor to the water pollution, indicating that measures should be adopted by authorities.

Non-carcinogenic risks due to pollutants mixture exposure were above the threshold (HI>1) for all sampling points during the rainy period and for the sampling points #3, #4 and #5 during the dry period, in accordance with the adopted parameters. Carcinogenic risks associated to As exposure were above the acceptable ($>10^{-6}$) limits in all the sampling points during the rainy period. Metal levels in the fish muscles were all lower than the maximum allowable concentrations set by Brazilian legislation and probably they are not a threat to public health (HI<1).

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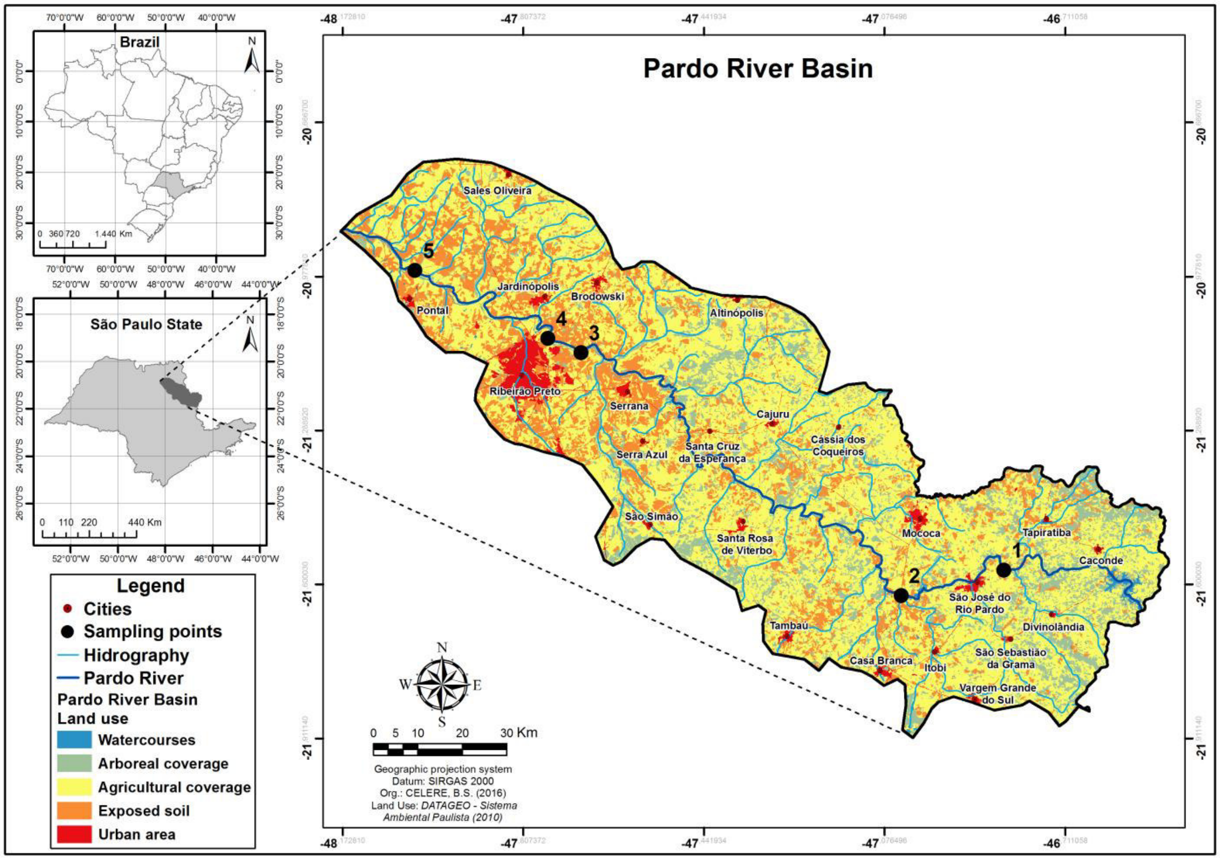

Figure 1. Sampling points and Pardo River Basin land use patterns.

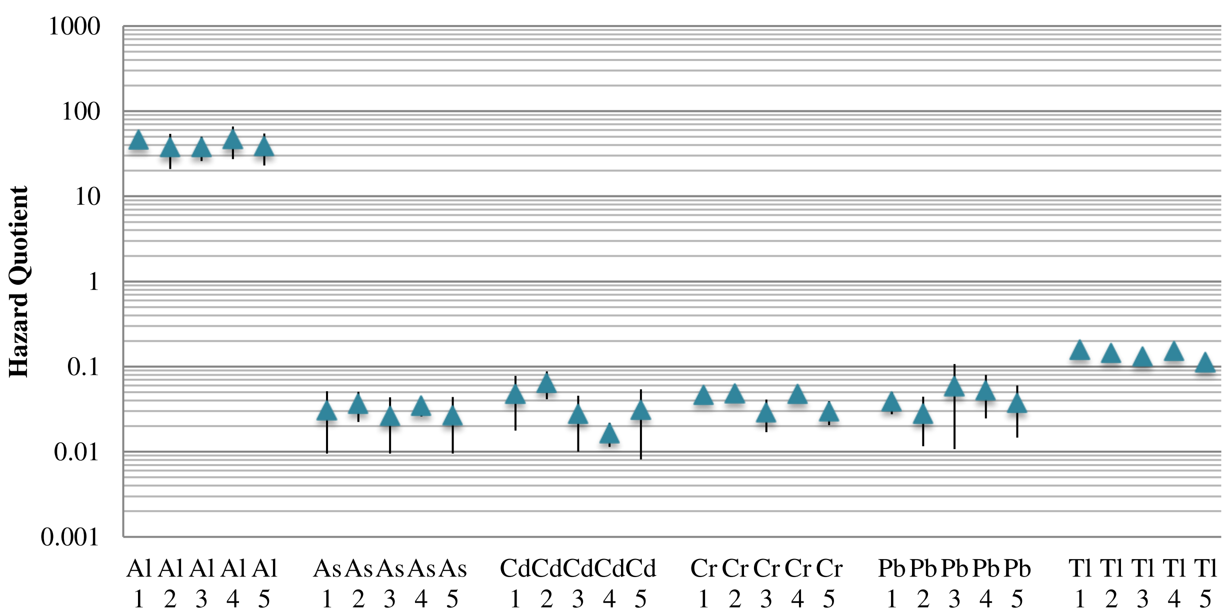

Figure 2. Hazard Quotient for the five sampling points during the rainy period.

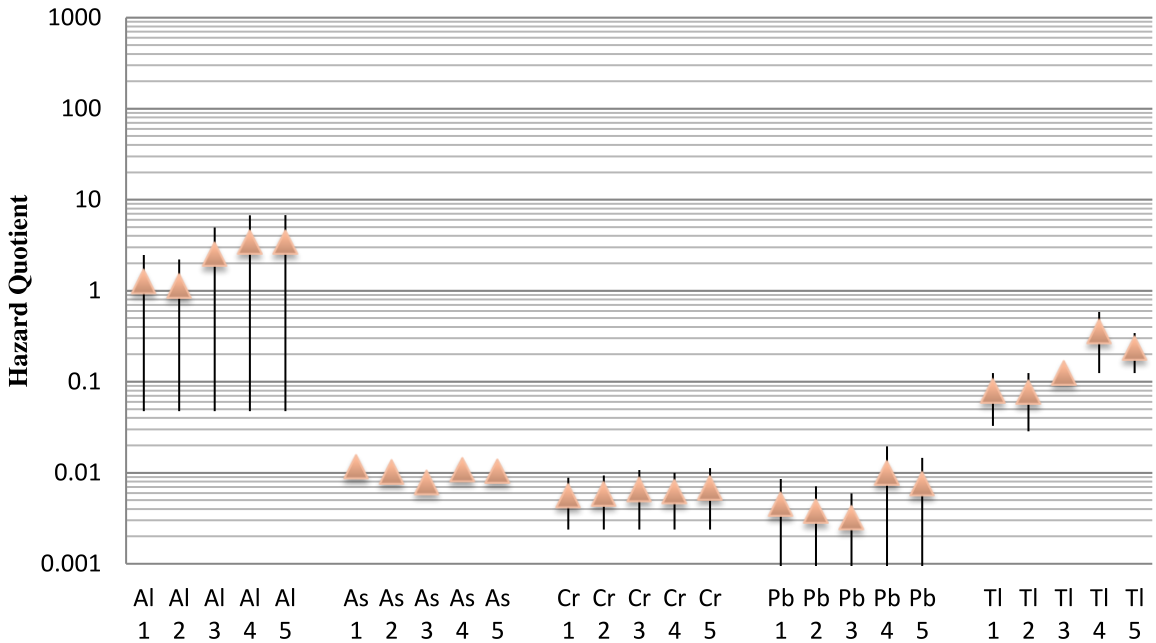

Figure 3. Hazard Quotient for the five sampling points during the dry period.

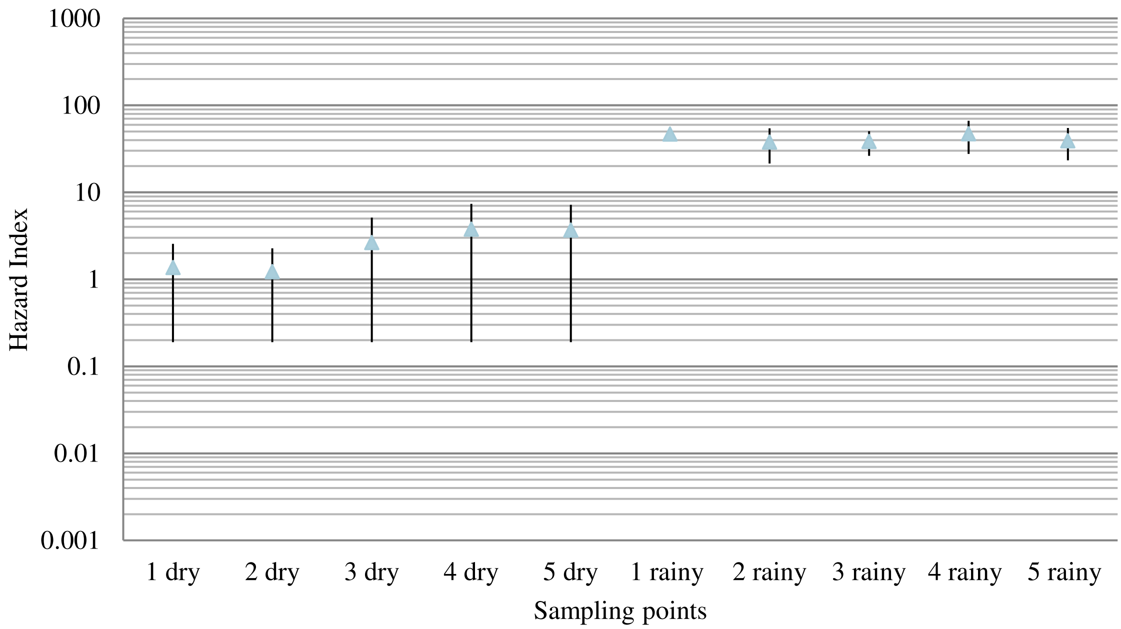

Figure 4. Hazard Index to herbicides and metals mixture on each sampling point for the dry and wet seasons.

Table 1. Fish samples characteristics.

Identification	Length (cm)	Weight (g)	Humidity (%)
Leporellus vittatus	26.0	174.6	76.8
Leporinus octofasciatus	18.0	140.9	71.3
Pimelodus maculatus	37.0	800.0	82.5

Table 2. Validation details of the herbicides quantification method.

Compound	Rt (min)	r^2	Linearity (µg/L)	LOD (µg/L)	LOQ (µg/L)	Recovery
Diuron	10.67	0.994	0.1-2.0	0.05	0.1	91.9
Tebuthiuron	12.67	0.991	0.1-2.2	0.05	0.1	97.6
Simazine	17.76	0.995	0.1-2.5	0.01	0.1	77.4
Atrazine	17.94	0.995	0.1-2.5	0.01	0.1	93.0
Ametryn	20.52	0.991	0.1-2.5	0.01	0.1	98.3
Hexazinone	25.57	0.995	0.1-2.2	0.05	0.1	89.1

Table 3. Parameter values for metal exposure and risk. Input data.

Variable	**Description**	**Value**	**Reference**
CF	Concentration of element in water and fish muscle	Water (mg/L) Fish muscle (µg/kg)	Present study
IR_w	Water ingestion rate	1.26 L/day	USEPA 1996
IR_F	Fish ingestion rate	0.041 kg/day	FAO 2010
FI	Fraction ingestion from source	0.4 (unitless)	Sidhu 2003
EF_w	Exposure frequency of water	345 day/year	Alves et al 2014
EF_F	Exposure frequency of fish	52 meals/year	Sidhu 2003
ED	Exposure duration	70 years	USEPA 1989
BW	Body weight adult	67.6 kg	Alves et al. 2014
AT_c	Averaging time carcinogenic	70 years for carcinogenic effect (25550 days)	USEPA 1989
AT_{nc}	Averaging time non-carcinogenic	11 years for non-carcinogenic effect (4146.4 days)	USEPA 1989

Table 4. Total metal levels on the five sampling points of Pardo River water on dry and rainy periods and threshold values (µg/L).

	Dry					Rainy					USEPA (2006)
	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	
Al	34.6	30.8	69.5	**94.6***	**94.9**	**647.5**	**526.2**	**532.6**	**654.3**	**545.3**	87.0
As	0.1	0.1	0.1	0.1	0.1	0.3	0.4	0.3	0.4	0.3	5.0
Be	0.1	0.1	0.1	<LOD	<LOD	0.2	0.1	0.1	0.2	0.2	0.7
Cd	<LOD	0.1	<LOD	0.1	0.1	**1.0**	**1.1**	**0.5**	**0.3**	**0.5**	0.3
Cr	0.9	1.0	1.1	1.0	1.2	4.9	5.1	3.1	5.0	3.1	85.0
Cu	1.1	1.7	1.7	2.6	1.9	4.2	2.3	2.6	4.1	4.8	9.0
Hg	<LOD	<LOD	0.1	0.1	0.1	<LOD	0.1	0.1	<LOD	0.1	0.3
Mn	26.7	23.5	44.8	20.7	15.7	**147.5**	60.7	55.3	53.6	62.4	120.0
Ni	0.1	0.1	0.1	0.7	0.1	0.1	1.3	1.3	0.1	2.7	52.0
Pb	0.6	0.5	0.4	1.3	0.9	**2.5**	1.8	**3.8**	**3.4**	2.4	2.5
Sn	<LOD	<LOD	<LOD	0.1	0.1	0.2	0.1	0.2	0.7	0.2	73.0
Tl	<LOD	<LOD	<LOD	0.2	0.1	0.1	0.1	<LOD	0.1	<LOD	0.8
V	0.3	0.6	1.4	1.1	1.4	1.3	1.2	2.0	2.2	3.1	20.0
Zn	9.3	12.6	8.9	17.8	14.3	75.0	**126.1**	64.4	108.1	79.7	120.0

*Bold values correspond to the data above the USEPA limits (USEPA 2006).
LOD: limit of detection.

Table 5. Metal levels in the muscle of the three fish species evaluated (µg/g wet weight).

	Al	As	Be	Cd	Cr	Cu	Pb	Mn	Hg	Ni	Tl	Sn	V	Zn
L. vittatus	11.64	<LOD	<LOD	<LOD	<LOD	0.29	<LOD	2.36	<LOD	<LOD	<LOD	<LOD	<LOD	13.29
L. octofasciatus	10.61	<LOD	<LOD	<LOD	<LOD	0.55	<LOD	0.30	<LOD	<LOD	<LOD	<LOD	<LOD	14.68
P. maculatus	6.72	<LOD	<LOD	<LOD	<LOD	0.41	<LOD	0.11	<LOD	<LOD	<LOD	<LOD	<LOD	2.23
Limits (ANVISA, 2013)	-	1.0	-	0.05	-	-	0.3	-	0.05	-	-	-	-	-

LOD: limit of detection.

Table 6. Ingestion exposure (mg/(kg*day)) of metals and herbicides in the Pardo River water.

	Dry					Rainy				
	1	2	3	4	5	1	2	3	4	5
Al	$5.0 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$1.8 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$
As	$3.5 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$	$9.2 \cdot 10^{-6}$	$1.1 \cdot 10^{-5}$	$7.9 \cdot 10^{-6}$	$1.0 \cdot 10^{-5}$	$8.0 \cdot 10^{-6}$
Cr	$1.7 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$8.7 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$	$9.0 \cdot 10^{-5}$
Pb	$8.3 \cdot 10^{-6}$	$7.0 \cdot 10^{-6}$	$5.9 \cdot 10^{-6}$	$1.8 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$7.2 \cdot 10^{-5}$	$5.2 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	$9.6 \cdot 10^{-5}$	$6.9 \cdot 10^{-5}$
Cu	$1.6 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	$3.8 \cdot 10^{-5}$	$2.9 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$6.5 \cdot 10^{-5}$	$7.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$
Mn	$3.8 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$	$6.4 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$4.2 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Ni	$2.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$3.7 \cdot 10^{-5}$	$3.6 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	$7.6 \cdot 10^{-5}$
Zn	$1.4 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$	$2.1 \cdot 10^{-3}$	$3.6 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	$3.1 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
Cd	$9.8 \cdot 10^{-7}$	$1.3 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	$2.4 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$8.3 \cdot 10^{-6}$	$1.6 \cdot 10^{-5}$
Hg	$2.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$	$9.8 \cdot 10^{-7}$	$1.8 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$5.2 \cdot 10^{-7}$	$2.9 \cdot 10^{-6}$
Tl	$7.9 \cdot 10^{-7}$	$7.7 \cdot 10^{-7}$	$1.3 \cdot 10^{-6}$	$3.6 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$
Be	$1.4 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$9.3 \cdot 10^{-7}$	$8.3 \cdot 10^{-7}$	$4.8 \cdot 10^{-6}$	$3.1 \cdot 10^{-6}$	$4.1 \cdot 10^{-6}$	$5.4 \cdot 10^{-6}$	$5.2 \cdot 10^{-6}$
Sn	$9.7 \cdot 10^{-7}$	$1.1 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	$1.8 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	$5.1 \cdot 10^{-6}$	$3.7 \cdot 10^{-6}$	$5.0 \cdot 10^{-6}$	$2.0 \cdot 10^{-5}$	$5.7 \cdot 10^{-6}$
V	$1.1 \cdot 10^{-5}$	$1.5 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$	$3.8 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$	$5.6 \cdot 10^{-5}$	$6.4 \cdot 10^{-5}$	$8.8 \cdot 10^{-5}$
Atrazine	ND	ND	ND	ND	ND	ND	$9.2 \cdot 10^{-6}$	$5.6 \cdot 10^{-6}$	$4.7 \cdot 10^{-6}$	$5.2 \cdot 10^{-6}$
Hexazine	ND	$6.1 \cdot 10^{-6}$	ND	ND	ND	ND	ND	ND	ND	ND
Ametryn	ND	$7.7 \cdot 10^{-6}$	ND	ND	ND	ND	ND	ND	ND	ND

ND: not detected.

Table 7. Cancer risk distribution of As and atrazine through water for adults living in the Pardo River Basin.

Sampling point	Period	Carcinogenic risk for Arsenic	Carcinogenic risk for Atrazine
1	Rainy	$2.3.10^{-5}$	ND
2	Rainy	$2.3.10^{-5}$	$2.1.10^{-6}$
3	Rainy	$1.9.10^{-5}$	$1.3.10^{-6}$
4	Rainy	$1.9.10^{-5}$	$1.1.10^{-6}$
5	Rainy	$1.9.10^{-5}$	$1.2.10^{-6}$
1	Dry	$5.2.10^{-6}$	ND
2	Dry	$4.6.10^{-6}$	ND
3	Dry	$3.5.10^{-6}$	ND
4	Dry	$4.9.10^{-6}$	ND
5	Dry	$4.7.10^{-6}$	ND

ND: not detected.