Abstract

Concentrations of metallic elements in sediment from Aurá River basin between 2008 and 2012 were checked, with implementation of two environmental quality criteria for sediments: enrichment factor and degree of chemical and biological contamination. The results showed that the metals Al, Fe, Mn, Cr, Cu, Ni, Pb and Cd had concentrations very close to the limit safe for aquatic biota, and despite of seasonal fluctuations, some metals reached worrying levels with contamination risk for quality of life human resident near the basin. Near the Aurá River mouth there is a pipeline company's state waters, pumping water for Metropolitan Region of Belém. The environmental assessment criteria applied indicated geological enrichment for Fe, Mn, Cr, Ni and Cu, and enrichment of Pb and Cd by the leachate from the landfill closed to drainage basin. According to the criteria of sediments quality used in this study, there is the presence of anthropogenic contamination and impairment of sediments by Pb and Cd.

Keywords: trace metals, environmental assessment criteria, public health, metallic pollution, contamination risk, metallic flow.

1. Introduction

Sediments have been widely used as environmental indicators because they have great ability to merge and accumulate contaminants. Generally, the space-temporal analysis of sediments at various sampling sites of interest region is used to track sources of contamination, or check the behavior of contaminants. Sediments pollution is linked to water pollution, and come from the domestic and industrial effluents, urban sewage and agricultural activities. The situation is more critical in regions where there are waste activities from open dumps, where the sedimentary environments can store historical records on origin of sedimentary material, transportation and deposition characteristics of the environment.

Contaminants accumulation in sediments tends to occur by physicochemical mechanisms, e.g. flocculation, direct precipitation and by adsorption to particulate matter with later deposition in the background. Therefore, sediment contamination is used as an important indicator of environmental pollution, serving to map, delineate and watch anthropogenic sources of contamination and/or geochemical anomalies caused by natural processes (Carmo et al., 2011).

With respect to environmental management of contaminated sediments, the choice of remediation measures must take into account the impact on human health, aquatic biota to make sure the continuity of the dynamic equilibrium of an ecosystem. In this sense, the technical guide for remediation of contaminated sediments, titled Sediment Remediation Guidance - Guidance for Hazardous Waste Sites (US. EPA, 2005), is a reference for the study of the impact caused by contamination of sediments, as well as for a responsible and safe decision-making on environmental management of contamination diagnosed. The environmental quality of a given region can be assessed indirectly from chemical analyzes of the sources of contamination.

The flooded areas and rivers of the Amazon region are environments sensitive to environmental pollution, since its waters are crowded with less energy by tidal streams, making these natural ecosystems to become natural accumulators of wastes of inorganic and organic origin. The local geomorphology, with sinuous features associated with the tremendous amount of sedimentary material transported by the flood pulse, further contributes to the residual accumulation process in the region (Siqueira and Aprile, 2013). The Metropolitan Region of Belém (MRB) has rivers, channels, streams and lakes present in diverse sizes and shapes. In this huge mosaic, of aquatic ecosystems, there is a constant anthropogenic pressure by inserting the urban environment in the surrounding environmental limits, causing pollution and contamination of surface water bodies. Among the pressures on the environment, the Aurá landfill is considered uncontrolled by Ferreira and Costa (2006), and it contributes with countless sewage arising from lack of an adequate sanitation program to communities on the periphery of MRB.

This study aimed to check on the aspect space-temporal the concentrations of trace elements Al, Fe, Mn, Cr, Ni, Cu, Pb and Cd in fractionated sediments, sampled between 2008 and 2012 in Aurá River basin, at the Metropolitan Region of Belém - MRB, Pará State (Amazonian, Brazil), applying environmental quality criteria of sediments to offer conditions for an environmental management program in the region, which comprises an area of springs for water supply for the MRB. A flow model to trace metals also was proposed to assist in the regional environmental management program.
2. Materials and Methods

2.1 Study area

The MRB is situated in a geological province of Cenozoic cover on the lower level of land Quaternary Amazonia, lying 120 km from the ocean and sitting on terraces resulting from the process of local drainage. The result is a sedimentary cover easily erodible. Gradations of relief demonstrate the presence of streams, marshy, floodplains and upland areas, demonstrating that the wetland is a feature of the MRB. The Aurá and Guamá rivers communicate themselves at the E-SE of MRB, under a plain fluviatile accumulation Holocene-Pleistocene, forming a micro-basin drainages with little extension, which includes the forest-streams Santo Antônio do Aurá, Pescada, Juvêncio, Jarucu and Santana do Aurá. The Aurá River basin has a total length of 10,400m, making the western boundary with the springs Bologna and Agua Preta (Fig 1), which supply the MRB. In the northern part of the basin is a landfill of irregular maintenance (9842700-9844720N and 790510-792180E; Fig 1), showing characteristics of open dump with numerous sewers, which contaminate soil and part of the springs with leachate leaked, threatening the water quality for public supply, the target of this study.

![Fig 1: Aurá River basin indicating the sampling sites, the area of solid waste disposal, water abstraction points for State Supply Co., and the springs used for water supply for the MRB (Source: Siqueira and Aprile, 2013).](image)

2.2 Analytical procedures

Surface sediments and field measurements were performed at 30 sampling sites in the Aurá River basin (Fig 1), between the isobaths 0.5 to 8.5 meters, with collections in January and September in the period between 2008 and 2012. The samplings were standardized considering the first hour of the ebb tide, during which there was greater influence of leaching in the region. In January, rains were detected large volume over the sample period, which was not observed in the months of September and October. At each sampling site was sampled 1000g of sediment at an average depth of 0.15 m with Van-Veen sampler, and each sample were sub-sampled with polyethylene spatula, and placed in a cold chamber at -20 ºC, according to international recommendations (Loring and Rantala, 1992; APHA/AWWA/WEF, 2005). Field was also performed measurements of transparency with Secchi disc; temperature (ºC), dissolved oxygen (mg L-1), content of oxygen saturation (%), electrical conductivity (µS cm-1) and pH by direct reading by YSI multiparameter probe electrodes model 550A.

Sediments were dried in an oven air circulation 40±5 ºC for 48h. After drying, the sediments were broken, pulverized, homogenized and fractionated. For geochemical analysis was selected fraction of silt-clay (≤ 63 µm), following recommendations of Förstner and Wittmann (1983) and Siqueira and Aprile (2013). Before each analysis, all glassware was washed with HNO3 solution at 10% (v/v) for 24h and then dried at 105 ºC. The digestion was done with a microwave, aiming to do total extraction of trace metals, and to make sure a high recovery (near 100%) of Al element used as normalizer. For extraction was added 0.100 g (dw) of sediment in a Teflon vial with a mixture of 10 mL of Milli-Q H2O, 5 mL of HNO3, 4 mL HF and 1 mL of HClO4. Trace metals concentrations were determined by Atomic Emission Spectrometry coupled with Induced Coupled Plasma. For analytical quality control, the recovery levels of acid digestion and determination of metals by ICP were tested using certified reference material (SRM 2710) analyzed in triplicate. The recovery for most metals was >90%, illustrating that certified material exhibited an excellent solubilizing complete digestion by microwave. Operational conditions were adjusted by the manufacturer’s guidelines to yield optimal determination, and quantification of trace metals was based upon calibration curves of standard solutions of metals.
Once defined the levels of trace metals, the intensity of the anomalies was expressed through the technical standards for enrichment factor (EF) (Woitke et al., 2003; Selvaraj et al., 2004), and a flow model to trace metals was proposed from the results.

\[ EF = \frac{[\text{metal}]_{\text{sample}}}{[\text{Al}]_{\text{sample}}} / \frac{[\text{metal}]_{\text{background}}}{[\text{Al}]_{\text{background}}} \]  

(Equation 1)

Where: background values from sediment samples determined by Turekian and Wedepohl (1961) and Bowen (1979).

2.3 Environmental Assessment Criteria of Sediment

The environmental interpretation of the levels of metallic elements in sediments and their possible relationships with adverse effects to biota (risk of contamination) were obtained by comparison with reference values of environmental contamination, defined as ‘Values Guide of Sediment Quality’ (VGSQ). The VGSQ have been used in many applications, including the development of monitoring programs contamination, interpretation of historical data, quality assessment of dredged materials, studies on remediation and environmental hazards, and to establish classification of areas of environmental risk (Long and Macdonald, 1998; Long et al., 1998; Macdonald et al., 2000). In this study we established two criteria for evaluation. The first criterion refers to the values reported by the Canadian Council of Ministers of the Environment (CCME, 2003) for trace metals (Table 1). The values of TEL (Threshold Effect Level) and PEL (Probable Effect Level) were developed by the Great Lakes National Program Office (GLNPO), linked to the US. EPA, and adapted and adopted as guide values by the Canadian Council of Ministries of the Environment and by the U.S. states of Florida and Alaska. The TEL and PEL values were calculated from statistical treatment of pre-existing data, taking into account values of effect and non-effect for analysis. This criterion was adopted by the Brazilian Ministry of Environment, through Resolution CONAMA 344/04 (CONAMA, 2004), which establishes a minimum guidance and rules for dredged material evaluation. Based on total concentrations and in the occurrence chance of deleterious effects on the biota, the lowest limit TEL (Level 1) is the concentration below which adverse effects are rarely expected to organisms, while the higher limit PEL (Level 2) represents the concentration above which is often expected an adverse effect on organisms. In the range between TEL (Level 1) and PEL (Level 2) are located the values that are expected to occasionally varied adverse effects on organisms. The adoption of these values allowed searching for evidence of contaminants in concentrations that cause deleterious effects, especially with respect to toxicity to biota.

Table 1: Values guide (in µg g\(^{-1}\)) of quality established by the CCME (2003) and adopted by CONAMA Resolution 344/04 (CONAMA, 2004).

<table>
<thead>
<tr>
<th>Metals</th>
<th>TEL(^a) (Level 1)</th>
<th>PEL(^b) (Level 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>5.9</td>
<td>17.0</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.6</td>
<td>3.5</td>
</tr>
<tr>
<td>Lead</td>
<td>35.0</td>
<td>91.3</td>
</tr>
<tr>
<td>Copper</td>
<td>35.7</td>
<td>197.0</td>
</tr>
<tr>
<td>Chromium</td>
<td>37.3</td>
<td>90.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.170</td>
<td>0.486</td>
</tr>
<tr>
<td>Nickel</td>
<td>18.0</td>
<td>35.9</td>
</tr>
<tr>
<td>Zinc</td>
<td>123</td>
<td>315</td>
</tr>
</tbody>
</table>

\(^a\) lowest limit TEL - adverse effects are rarely expected to organisms

\(^b\) higher limit PEL - often expected an adverse effect on organisms

The second evaluation criterion adopted in this study was the American criterion (Long et al., 1998), where the author used chemical and biological data and conducted field studies in marine and estuarine sediments, defining two boundaries and three ranges to define the sediments quality: the ERL (Effects Range Low), which indicates the concentration limit below which sediments are rarely toxic; ERM (Effects Range Medium), indicating that the sediments are probably toxic when some metallic element exceeds this value, and the intermediate range between ERL and ERM, which indicates that the sediments are potentially toxic. The values of ERL and ERM were originally developed as quality informal sediments of estuaries and marine by the U.S. National Oceanic and Atmospheric Administration (NOAA), based on its database named NOAA’s Biological Effects Database for Sediments (BEDS). Using the same database, the Great Lakes National Program Office (GLNPO), linked to the U.S. Environmental Protection Agency (US. EPA, 2005), and estimated values of ERL and ERM for freshwater sediments, with good agreement with the values originally established by WDESMU (2002). These values are used as a quality criterion of sediment by various environmental agencies in several countries, e.g. the United States - California and New York, Australia and New Zealand. The levels established by this criterion and applied in this study are showed in Table 2.

Table 2: Limits values (in µg g\(^{-1}\)) established for ERL and ERM for trace metals in marine and estuarine sediments (Hortellani et al., 2008).

<table>
<thead>
<tr>
<th>Metals</th>
<th>ERL</th>
<th>ERM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>1.2</td>
<td>9.6</td>
</tr>
<tr>
<td>Lead</td>
<td>46.7</td>
<td>218.0</td>
</tr>
<tr>
<td>Chromium</td>
<td>81.0</td>
<td>370.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>20.9</td>
<td>51.6</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Seasonal analysis and evaluation of the metallic charge

The maximum, minimum and average±SD determined in sediments of the Aurá River basin (PA) were showed in Table 3. Al content varied between 2.61 and 8.65% with average of 4.81±1.25% (Table 3) for the entire study period, and specifically to the year 2012, the average was of 7.54±0.86%, indicating an increase of Al in sediments to determinations obtained in 2010 by Siqueira and Aprile (2013). Analyzing the spatial distribution of Al along the Aurá River basin (isovalues in Fig 2A), it was observed that concentrations remained constant throughout the environment. However, on temporal aspect was found Al enrichment in the sediments of the river in the order of 1.7 times. Possibly, this may be due to the leached material associated with an increased discharge of solid material from plume of effluents leachate from the landfill. In the Guamá River were obtained average contents of Al ranging from 4.40 to 4.45% in sediment samples collected near the river banks (Santos et al., 2011).

Al is a chemical element somewhat mobile in aquatic ecosystems (Yun et al., 2000; Selvaraj et al., 2004), and generally enriched in sediment leaches. Al is the main and not reactive constituent of the clay minerals, which are the major part of the suspended solids and sediments (Sholkovitz and Price, 1980). Al in solution can be stabilized in organic complexes, which may precipitate in the form of hydrated oxides, especially in estuarine environment, whose pH tends to be higher. The Al may also react with silicon to form hydrated aluminosilicates (Coutinho, 1979).

The total Fe content had varying between 1.35 and 3.46% with average of 2.33±0.45% (Table 3). The average concentrations of total Fe over the sampling sites showed a decline from 2008 to 2012 (Fig 4). Following the same trend of the Al concentrations of total Fe remained constant throughout the environment. The authors believe that the processes of weathering are releasing iron of the original rocks, and introducing in geochemical cycle in this system. In the Guamá River were obtained average levels of Fe ranging between 0.34 and 0.35% in sediment samples near the river banks (Santos et al., 2011). These average levels of Fe are very similar to the average content of total Fe obtained for this study (see isovalues in Fig 2B).

The Mn presented contents ranging from 120 to 1050 μg g⁻¹ with mean 821±188 μg g⁻¹ (Table 3). Following the same trend observed for Fe, Mn also showed an average reduction of their concentrations in the sediment compared to the years 2008 and 2010 (Fig 4). This reduction, however, does not necessarily mean an improvement in environmental conditions, and by coating the grains by oxides Fe and Mn, the Mn was a decrease in their concentrations in the upstream direction of the basin. The sediment generally have their values on the order of 690 μg g⁻¹ of Mn (Forstner and Muller 1974), while the average levels found in this study were, in general, below the mentioned by the authors. According to Barcellos et al. (1988) and Fernandes et al. (1994) is a pattern for explaining Mn sediment enrichment, compared with the levels of the metal in the continental rocks or estuarine sediments. This pattern of behavior can be understood by reduction of Mn³⁺ to Mn²⁺ and Fe³⁺ to Fe²⁺ in sediment with reducing characteristics, with process being more efficient for Mn than for Fe. These ionic forms when reduced migrating through sediment by the water interstitial, returning the water column. If the conditions of the water column are reducing the metals stay in solution, otherwise the metals return the upper layer of the sediment. There is also possibility of trace metals remain associated with suspended colloidal particles, mainly in the fractions corresponding to the oxo-hydroxides of Fe and Mn. A flow model of the metal ions Fe and Mn between the water and sediment compartments was proposed by Siqueira and Aprile (2013), depending on the flow of oxygen in the hypolimnion. The map of the Mn isovalues throughout the study region was showed in Fig 2C.

Cr showed levels ranging between 17.4 and 74.2 μg g⁻¹ with an average of 45.5±10.1 μg g⁻¹ (Table 3). Again was observed reduction of trace element in 2012 compared to earlier years (Fig 4). In 2012, the levels of Cr ranged from 29.7 to 53.5 μg g⁻¹, average 39.5±6.2 μg g⁻¹. In seasonal studies in the Guajará Bay and Guamá River, Aviz et al. (2012) obtained Cr contents between 28.0±17.5 μg g⁻¹ and 76.0±5.0 μg g⁻¹ in superficial sediments, during the rainiest season. These levels of Cr are very similar to the average content of Cr obtained for the current study (see isovalues in Fig 2D). In the last sampling there was an increase in the levels of Cr punctually in the most central region of the basin (between sampling sites 15 and 23). In general, the Cr is transported to sediments by organic matter (OM), especially of terrestrial origin, and by coating the grains by oxo-hydroxides of Fe and Mn. The Cr⁶⁺ (hexavalent chromium) tends to be reduced to Cr³⁺ (trivalent chromium), cushioning the impact of trace metal on the aquatic environment (Moore and Ramamoorthy, 1984).

Table 3: Average levels of trace metals in of the Aurá River basin for the period 2008 to 2012 (n= 103).

<table>
<thead>
<tr>
<th></th>
<th>Al (%)</th>
<th>Fe (%)</th>
<th>Mn</th>
<th>Cr</th>
<th>Cu (µg g⁻¹)</th>
<th>Ni</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max</td>
<td>8.6</td>
<td>3.5</td>
<td>1050.3</td>
<td>74.2</td>
<td>32.7</td>
<td>48.8</td>
<td>99.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Min</td>
<td>2.6</td>
<td>1.3</td>
<td>120.9</td>
<td>17.4</td>
<td>10.5</td>
<td>0.9</td>
<td>64.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Average</td>
<td>4.8</td>
<td>2.3</td>
<td>421.6</td>
<td>45.5</td>
<td>20.4</td>
<td>27.2</td>
<td>80.7</td>
<td>1.1</td>
</tr>
<tr>
<td>SD</td>
<td>1.2</td>
<td>0.4</td>
<td>188.5</td>
<td>10.1</td>
<td>4.9</td>
<td>9.9</td>
<td>10.8</td>
<td>0.0</td>
</tr>
<tr>
<td>SRM 2710</td>
<td>12000</td>
<td>22000</td>
<td>7700</td>
<td>23</td>
<td>2400</td>
<td>8.8</td>
<td>4300</td>
<td>20</td>
</tr>
<tr>
<td>Recuperation</td>
<td>98.2</td>
<td>118.2</td>
<td>98.3</td>
<td>113.1</td>
<td>93.5</td>
<td>91.8</td>
<td>98.1</td>
<td>107.7</td>
</tr>
</tbody>
</table>
porated into insoluble particulate material or as ion adsorbed to the sediment determined in samples collected in 2012 (Fig 4), so it is not possible to analyze the temporal distribution of Pb throughout the study environment (Fig 3A). In studies conducted seasonality in the Guajarã Bay and Guamá River, Aviz et al. (2012) obtained Cu in sediments ranging between 8.0±0.5 μg g⁻¹ and 35.5±6.5 μg g⁻¹ at rainiest season. The average of Cu obtained in this study approaches the values cited by Aviz et al. (2012), confirming the trend for the region, once time that Cu is an element quickly adsorbed by the sediments (Moore and Ramamoorthy, 1984).

Ni varied during the study period between 0.92 and 48.82 μg g⁻¹, with average of 27.24±9.91 μg g⁻¹. Of all the trace metals studied within the space-time perception, Ni was the metal with the highest reduction in concentrations in 2012 (Fig 4; average 8.15±4.15 μg g⁻¹). Comparing our results with the recent research in Guamá River (Aviz et al., 2012), river that receiving water from the Aurá River, was noted that the authors obtained an average content of Ni in sediments of 50.0±9.0 μg g⁻¹, a value close to the maximum determined by this study in the Aurá River basin. This is explained because the main condition to fix Ni in sediment is determined mainly by oxy-hydroxides of Fe and Mn (Moore and Ramamoorthy, 1984), very common in the region. The map of isovalue Ni throughout the study region was showed in Fig 3B.

The Pb concentration determined in this study ranged from 64.24 to 99.13 μg g⁻¹ with average 80.75±10.83 μg g⁻¹, and this average was 4.2 times higher than the value of 19 μg g⁻¹ estimated as background to sediment world (Bowen, 1979). The Pb was only determined in samples collected in 2012 (Fig 4), so it is not possible to analyze the temporal distribution of Pb in the Aurá River basin. However, there are other studies in the region that can serve as a reference. The variation of trace metals in sediments of the Guajará River was studied by Santos et al. (2011), founding an average content of 38 μg g⁻¹ of Pb. The importance of the Guajará River for this comparison is the fact that on the right bank of the river is the border town of Belém, where there is evidence of large anthropogenic activity, which could be contributing to the local pollution of waters and sediments. According to Santos et al. (2011), in the Guamá River were observed sign of variations in Pb levels associated to anthropogenic isotopic compositions (206Pb/207Pb ≈ 1.186–1.192), indicating a strong influence of Aurá River discharge on your receptor river, especially by the fact that Aurá River is affected by effluents from the dump. Studies developed on the edge of Belém by Corrêa and Pereira (2002) showed high values of Pb in the environment, with average 54.5 μg g⁻¹ in fine fraction of sediments, near Cumbu Island. Pb presence in Aurá River sediment is a sobering fact, and may indicate waters and sediments contamination by metal transport from the landfill installed in the northern part of the drainage basin (Fig 1). The areas surrounding the landfill, occupied by irregular housing, may also be contributing to the contamination by wastewater discharges.

The distribution of Pb in sediments of the Aurá River could be explained by pH variation along the river. Leach released by the landfill has a pH around 8.11, which favors complexation of Pb in the presence of high levels of organic matter (Santos et al., 2011; Siqueira and Apriile, 2013). The Pb mobility is strongly pH dependent, so in sediments with high content of OM and pH (6 to 8), Pb can form insoluble organic complexes. However, if the pH decreases to values between 4 and 6, it can destabilize the complex, freeing Pb for the water column. Some authors state that the Pb has a tendency to form compounds with anions which have a low solubility, such as hydroxides, carbonates and phosphates. Therefore, the amount of Pb remaining in solution depends on mainly the pH, which is often low. Furthermore, a significant fraction of Pb can be incorporated into insoluble particulate material or as ion adsorbed to the sediment (Moore and Ramamoorthy, 1984). Since the waters of the Guamá River have acidic characteristics (Santos et al., 2011), it contributes to destabilize the organic complexes containing Pb, formed by the high concentration of organic matter and alkaline pH of the leachate. Thus, near the mouth of the Aurá River, possibly the waters are more acidic, and this

![Fig 2: Map of isovalues for trace metals Al, Fe, Mn and Cr to the spatial and temporal distribution in the Aurá River basin.](Image 134x534 to 476x798)
acidity is likely to vary with the ebb and flow of the tides. These pH values are responsible for the destabilization of the organic complexes containing Pb, reducing its concentration, however without deleting the ‘anthropogenic subscription’ linked to the deposit of solid residues in the region.

The Pb is incorporated into the outer layers in the structure of the hydroxides, with exchange of hydrogen ions, and thus the Pb displays a strong affinity with the hydroxyl groups of crystals FeOOH (Förstner and Wittmann, 1983). Experiments showed that the accumulation of Pb in fish occurs through the food chain, and Pb in the alimentary tract of the fish is released more slowly than that absorbed by the gills (Moore and Ramamoorthy, 1984). According to the authors, Pb is an element non-essential whose acute lethal dose (LD50) is 8x10^{-3} mol kg^{-1} in rats from laboratory. When Pb is released into the environment, it has a long residence time compared to most other pollutants. As a result, Pb tends to accumulate in soils and sediments where, due to low solubility, can stay accessible to the food chain, affecting human metabolism (Sauve et al., 1997). In general, Pb^{2+} ion is more toxic than inorganic complexes and, therefore, any factor which increases and decreases the complexation of the free ion concentration can affect the Pb toxicity in the system (Moore and Ramamoorthy, 1984). It is known that Pb is an extremely toxic metal, which tends to accumulate in tissues of man and other animals, having no demonstrably beneficial effects or nutritional. The map of isovalues Pb throughout the study region was showed in Fig 3C.

Cd ranged in this study from 1.12 to 1.15 μg g^{-1} with average 1.14±0.01 μg g^{-1}. This mean value was 3.8 times higher than the value of 0.3 μg g^{-1} Cd amount considered as background to sediment estimated by Turekian and Wedepohl (1961). Cd also was determined only in samples from 2012 (Fig 4), and its trend was showed in the map of the isovalues (Fig 3D). The Cd is very similar to Zn atomic structure and chemical behavior, both metals usually occur together. The main difference is that Zn is an essential element, since the Cd has no biological function defined. The Cd competes with other metals for binding sites on cells. Due to its similarity in chemical structure and behavior with Zn, competition with this metal is great. The Cd tends, such as, to take the place Zn in a series of enzymes, whose operation depends on the same. The Cd is one of the most toxic metals to living organisms. In rats, the acute lethal dose (LD50) is 6.3x10^{-4} mol kg^{-1} (Moore and Ramamoorthy, 1984).

The main anthropogenic sources of Cd to the environment come from of tailings fungicides, batteries, rubber processing, production of pigments, electroplating and mining, may still be environmental pollution through emissions of industrial iron and steel, fossil fuels (coal, gas, oil, peat and wood), cement and phosphate fertilizers (Moore and Ramamoorthy, 1984; WHO, 1992). Urban waste has Cd from various sources that contaminate the organic compound, including leachate, which end up being discarded in receiving bodies (rivers and lakes) and percolate into the soil reaching groundwater and surface water (Teves, 2001). In this study, was consider that the main sediment contamination by cadmium can be generated through waste deposited at the landfill located upstream of the Aurá River basin. Waste may be being formed from irregular disposal of Ni-Cd and packaging, which in a controlled environment were being stored in suitable places with high security.

Fig 3: Map of isovalues for trace metals Cu, Ni, Pb and Cd to the spatial and temporal distribution in the Aurá River basin.

According to ATSDR (1997), the form as Cd is sediment is very important to find their availability and remobilization. The Cd is less liable to be mobilized by re-suspension of sediment or biological activities when the metal is associated with carbonates precipitated as stable solid compounds or co-precipitated with iron-hydrated oxides. Moreover, Cd adsorbed to the surface of minerals such as clay or organic matter is more easily bio-accumulated or released when there are environmental disturbances.
3.2 Standardization of Data

To check changes in the concentrations of metal ions studied in sediments of the Aurá River, the enrichment factor (EF) was calculated. In order to reduce the effects mineralogical and grain size the data were normalized using Al as conservative element (Bowen, 1979; Woitke et al., 2003; Selvaraj et al., 2004). The enrichment factors (EF) determined for each trace metal for the year 2012 was showed in Table 4. A pre-test of cluster allowed us to separate sampling sites in five sub-areas of study: upstream, upper-middle, middle-stream, lower middle and downstream.

Table 4: Enrichments factors calculated from equation 1 for the trace metals in the Aurá River basin for the period 2008 to 2012.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Area</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>Us</td>
<td>0.9</td>
<td>0.7</td>
<td>1.1</td>
<td>0.9</td>
<td>0.8</td>
<td>3.3</td>
<td>4.0</td>
</tr>
<tr>
<td>5-9</td>
<td>Um</td>
<td>0.8</td>
<td>0.6</td>
<td>1.0</td>
<td>0.9</td>
<td>0.7</td>
<td>3.4</td>
<td>4.2</td>
</tr>
<tr>
<td>10-19</td>
<td>Ms</td>
<td>0.9</td>
<td>1.2</td>
<td>0.9</td>
<td>1.0</td>
<td>0.8</td>
<td>3.8</td>
<td>4.2</td>
</tr>
<tr>
<td>20-26</td>
<td>Lm</td>
<td>0.9</td>
<td>1.3</td>
<td>1.0</td>
<td>1.0</td>
<td>0.7</td>
<td>4.3</td>
<td>4.8</td>
</tr>
<tr>
<td>27-30</td>
<td>Ds</td>
<td>0.9</td>
<td>1.1</td>
<td>0.9</td>
<td>1.1</td>
<td>0.8</td>
<td>4.9</td>
<td>5.1</td>
</tr>
</tbody>
</table>

**Bold:** EF > 1; Us= upstream, Um= upper-middle, M= middle-stream, Lm= lower middle and Ds= downstream.

EF values calculated for the metals which were in the range of 0.1 ≤ EF ≤ 1.0 suggests that trace metals present in sediments may come from the geological composition or of the influence of natural climatic processes. The points presented EF > 1.0 indicates evidence that a significant proportion of the metallic element is from other sources, suggesting environmental contamination. However, that various indices of enrichment factor were very close to the limit established by Woitke et al. (2003) and Selvaraj et al. (2004). So that the level of environmental contamination can be even greater than that calculated. It believes that the sources of enrichment of trace metals studied are beyond the landfill contributions, originating from soil erosion, leaching and domestic sewage in the region.

Thus, was hypothesizing that the plume of leachate from the landfill is contributing to trace metals enrichment in all sections of the Aurá River, but especially in the middle-stream of the basin (Table 4). Studies conducted in the area of the Aurá River basin and surrounding, revealed that there is great possibility of metal contamination in the forest-rivers close, by the leachate produced and disposed from the landfill (Bahia et al., 2004; Siqueira and Aprile, 2013).

3.3 Environmental assessment criteria of sediment quality

For Cr, Cu and Ni, all the sampling sites were below the lower limit TEL, which represents the concentration below which are rarely expected adverse effects on aquatic organisms, and were below the limit ERL, indicating the threshold concentration below which the sediments are rarely toxic. However, as the enrichment factor especially Cr and Cu were both close to the limit equal to 1, was considered the results as a ‘state of alert’ requiring periodic monitoring to better assess the issue.

Pb was the only element among all analyzed trace metals in sediments that had values above the PEL. The above values or the values below, but very close to the limit set by the evaluation criterion, show concentrations where it is often expected some adverse effect on biota associated. When analyzing the values of Pb to the second criterion of quality of sediment, it is found that they are all the sampling sites ranging from ERL and ERM, possibly indicating that the sediments are toxic to the Pb. Considering the two criteria applied in this study and the geographical localization, the data suggest that Pb is one of the most worrisome contaminants to the Aurá and Guamá rivers, since the determined values were considered, by both criteria, harmful to local biota, especially for middle and lower middle river. It is know very well that the deleterious effects of lead in biota, especially in humans, are extremely serious. So far any biological function attributed to Pb is unknown, since this metal does not take part in physiological processes in aquatic organisms, and is considered a potentially toxic element. Contamination of soils and sediments by Pb is irreversible (Cunha et al., 1993), which generates a process of accumulative character, even when small amounts are added to the environment.
For the cadmium, the analysis showed that all sampling sites are ranging between the limits of TEL (Level 1) and PEL (Level 2). However, when was analyzed the results by ERL criteria (Long et al., 1998) for 2008 and 2012, it was noted that the concentrations of trace metal fall under the concentration limit below which the sediments are rarely toxic (Table 5).

Table 5: Environmental risk assessment ERL-ERM for Aurá River basin.

<table>
<thead>
<tr>
<th>Area</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Us</td>
<td>36.2</td>
<td>27.4</td>
<td>8.1</td>
<td>72.4</td>
<td>1.1</td>
<td>53.2</td>
<td>19.9</td>
<td>33.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Um</td>
<td>34.3</td>
<td>28.4</td>
<td>9.9</td>
<td>81.6</td>
<td>1.1</td>
<td>50.0</td>
<td>18.9</td>
<td>31.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ms</td>
<td>43.5</td>
<td>27.8</td>
<td>5.3</td>
<td>86.4</td>
<td>1.1</td>
<td>43.8</td>
<td>23.7</td>
<td>39.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lm</td>
<td>45.1</td>
<td>28.2</td>
<td>10.7</td>
<td>79.9</td>
<td>1.1</td>
<td>43.9</td>
<td>18.8</td>
<td>29.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ds</td>
<td>35.6</td>
<td>25.8</td>
<td>3.8</td>
<td>88.7</td>
<td>1.1</td>
<td>36.0</td>
<td>16.5</td>
<td>23.7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Us= upstream, Um= upper-middle, M= middle-stream, Lm= lower middle, and Ds= downstream.

Based on the results was proposed a flow model for trace elements (Fig 5), which takes into account the importance of uncontrolled landfill as a source of metals, and the influence of hydrogen potential in the precipitation and maintenance of the metals in sediment surface layer. The return of these metals to the water column is due not only to decreased pH in the springs, but also due the physical action of water pumping (re-suspension), which can alter the patterns of oxygen in the hypolimnion, interfering in the process of fixing metal of sediments. Since the waters of the springs have slightly lower pH (pH ≤ 6.0) that the Guamá and Aurá rivers (mean pH=7.5), the metals associated with sediments can return to the water column, making it is available for bioaccumulation, remembering that the waters of the springs are distributed to MRB for human consumption. Within the conditions in the study area, it is estimated that the trivalent forms of trace elements Fe³⁺, Al³⁺, Cu³⁺ and Ni³⁺ remain associated with the sediments. However, the bivalent forms of the Pb²⁺, Cd²⁺, Ni²⁺ and Mn²⁺, and also Zn²⁺ and Hg²⁺ not monitored in this study, may be being released to the water column (see Fig 5), with high potential for risk of contamination.

4. Conclusion

Based on the results obtained it was clear seasonal analysis importance, showing that recommended continuous monitoring of the study area in order to make sure that contamination levels do not exceed safe limits for aquatic biota site. In general, the trace metals analyzed were concentrated mostly in the middle part of the Aurá River basin. It should be understood that even complexed and precipitated sediment to the river, the trace metals may continue to show a strong potential for contaminating the water column, since the sediments may function as ‘pool’ of toxic substances introduced into the aquatic environment, with potential for release to the water column at any time, extremely toxic chemicals accumulated for decades or hundreds of years, which will be incorporated into the food chain in the region.

The hydrological cycle in Amazonia has strong influence on the redox potential variation in the hypolimnion of river basins, and thus influence the precipitation rate and release of metal ions into the sediment. Perhaps this fact helps explain the levels of metal ions found along course of the Aurá River.

The data normalization with Al content, and the use of two different criteria for environmental assessment, both demonstrated their usefulness in assessing contamination by metallic elements of the sediments in the study area, and showed results consistent with the criteria applied. However, sediment quality criteria adopted for classifying the environmental compartment are not definitive. Many of data will allow improved assessment criteria, enabling a quality index to sediment, adapted to the geoclimatic conditions in the Amazon.

According to the criteria of sediments quality used in this study, there is the presence of anthropogenic contamination and impairment of sediments, with a possible influence of the water column, since Pb and Cd have no biological function and defined and have effects cumulative.
References


