LEAD DISTRIBUTION BY URBAN SEDIMENTS ON IMPERMEABLE AREAS OF PORTO ALEGRE – RS, BRAZIL

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Received 23 April 2009; received in revised form 15 June 2010; accepted 18 June 2010

Abstract: Heavy metals, like lead (Pb), are subproducts of industrial activities; however, in recent years, studies have shown that even in non-industrial areas, elevated concentrations of this element have been found. In this study, Pb concentrations were measured in 20 composite samples of urban sediments collected in an urban watershed of 4.85 km² with three types of soil use (commercial/residential, commercial and industrial) in the city of Porto Alegre, RS, Brazil. Concentrations were determined by acid digestion (EPA 3050) of the 209 µm, 150 µm, 90 µm, 63 µm and 45 µm fractions followed by atomic emission spectrophotometry with inductively coupled plasma. Average values of 178.1 µg.g⁻¹ (± 332); 226.5 µg.g⁻¹ (± 500); 245.2 µg.g⁻¹ (± 454.1); 272.4 µg.g⁻¹ (± 497.3) and 251.5 µg.g⁻¹ (± 322.6) were obtained in the 209, 150, 90, 63 and 45 µm fractions, respectively. Concentrations of the metals studied were interpolated and represented geographically using Idrisi© Andes. Results show that the greatest concentrations are located in the commercial part of the study area, characterized as presenting high vehicle flow most of the day, with this being considered a potential source of lead. All concentrations were above that of the local background. Studies of this type are important because they make the establishment of control targets possible within sustainable management of water resources, allowing inferences regarding future pollution scenarios of local water resources.

Keywords: Urban sediment; diffuse pollution; GIS; lead

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INTRODUCTION

Most South American cities present accelerated growth trends; however, they are disorganized, generating negative impacts especially on bodies of water (Poleto et al., 2009a; Deletic et al., 1997), principally due to the increase of impermeable surfaces like roadways, roofs, parking lots, among other things, which reduce the rate of infiltration and increase surface runoff, thus increasing transport of urban sediment and pollutant loads to watercourses (Poleto et al., 2009b; Taylor 2007; Charlesworth et al., 2003; Deletic et al., 1997). Urban drainage networks are responsible for conveying these loads and it is now known that they constitute important sources of degradation of rivers, lakes and estuaries (Horowitz, 2009), (Deletic et al., 1997).

Sediments in urban areas are submitted to man-made alterations from different sources, as for example, the input of organic matter coming from discarding sewage in a clandestine manner, in the same way as particles of human origin present in large quantities in urban environments, such as glass particles, metallic particles, residues from industrial processes and civil construction, which present chemical and mineralogical properties different from sediment particles from natural sources, which results in these sediments interacting in a different way within the environment (Poleto & Martínez, 2009); Taylor (2007). Sediments deposited in roadways have become, through time, an important means for determining the human contribution of pollutants, especially that of heavy metals. The ubiquitous nature of road deposited sediments, their ease of sampling, their strong association with automobile emissions, and their relationship with nonpoint source pollution make them a valuable archive of environmental information (Sutherland 2003).

More precisely, one of the chemical characteristics of vital importance in the study of urban sediments is adsorption of heavy metals. Banerjee (2003) defines the behavior of heavy metals in terms of the most common different solid phases found in urban sediments in Table 1.

Affinity of heavy metals by sediments is strongly influenced by particle size (Deletic et al., 1997; Charlesworth et al., 2003; Sutherland, 2003; Taylor, 2007; Poleto et al., 2009a). There is sufficient evidence that shows the fact that sediments are enriched with heavy metals, above all in the fine particle fraction. In a similar way to sediments in other environments, increase in the pollutant load in finer sized particles is generally associated with the increase of surface area in smaller sized particles, providing greater space for adsorption of metals in clay minerals or in organic matter present in sediment particles. Understanding that heavy metal loads are heterogeneously distributed is important in the formulation of pollution management and control strategies (Horowitz, 2009; Poleto et al., 2009b; Taylor, 2007). Fergusson & Ryan (1984) studied the composition of particles deposited in urban areas, specifically particle size and the sediment source; they found that many of the elements analyzed increased with reduction in particle size, a result corroborated by Al-Rajhi et al. (1996).

In urban environments, heavy metals are part of our daily activities and many of them enter in the urban environment as subproducts of economic activities which are considered typical in urbanizing watersheds (Poleto & Charlesworth, 2010; Poleto et al., 2009a; Poleto & Martínez 2009; Irvine et al., 2009); in the case of lead, it frequently appears as a subproduct from petroleum and coal combustion; tire, oil, paint and welded part residues (Horowitz, 2009; Poleto & Merten, 2008; Charlesworth & Lees 1999). Lead concentration values are variable and depend in large part on surrounding local conditions; Sutherland (2003) found that 51% (221 µg.g⁻¹) of the lead load present in sediments deposited in urban roadways in Hawaii were found in the < 63 µm fraction; Robertson et al. (2003) found concentrations of 354 µg.g⁻¹ within the city of Manchester (United Kingdom); Charlesworth et al. (2003) found average values of 48 and 47.1 µg.g⁻¹ in the cities of Birmingham and Coventry (United Kingdom), respectively; Irvine et al. (2009) reported values of 276 µg.g⁻¹ in the city of Hamilton, Ontario (Canada); an average value of 230.52 µg.g⁻¹ with a maximum of 3060 µg.g⁻¹ were found by Yongming et al. (2006) in the province of Xi’an in China; McAlister et al. (2005) reported concentrations from 200 to 700 µg.g⁻¹ in areas with diverse soil uses in the city of Rio de Janeiro (Brazil) and Poleto et al. (2009) found concentrations from 16 to 110 µg.g⁻¹ in 20 cities in the South of Brazil.

Sediments deposited in roadways are commonly associated with risks to the environment and to human health, mainly in children (Taylor, 2007; Charlesworth et al., 2003; Al-Rajhi et al., 1996). Environmental and health effects initially depend on the mobility and availability of the elements, and the mobility and availability in terms of their chemical speciation and fractionation within or on particles (Banerjee, 2003). In the case of lead, there is evidence that indicates that exposure to this metal (inhalation or through consumption of contaminated foods) can trigger problems in the central nervous system, as well as having carcinogenic effects (Wang et al., 2005).

<table>
<thead>
<tr>
<th>Solid phase fraction</th>
<th>Affinity of heavy metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>Cd &gt; Pb &gt; N i &gt; Zn &gt; Cu &gt; Cr</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Cd &gt; Zn &gt; Pb &gt; Ni &gt; Cu &gt; Cr</td>
</tr>
<tr>
<td>Fe-Mn oxide bonding</td>
<td>Zn &gt; Pb &gt; Ni = Cu &gt; Cd &gt; Cr</td>
</tr>
<tr>
<td>Organic matter</td>
<td>Cu &gt; Pb &gt; Zn &gt; Ni &gt; Cd &gt; Cr</td>
</tr>
<tr>
<td>Residual</td>
<td>Cr &gt; Ni &gt; Cu &gt; Cd &gt; Pb &gt; Zn</td>
</tr>
</tbody>
</table>

Adapted from: Banerjee (2003).
In the present study, the lead concentration present in 20 composite samples of urban sediments collected at different points of the Tamandaré Basin (which drains into Guaíba Lake) and which present different soil uses was evaluated. Lead (Pb) concentrations were determined in different granulometric fractions of the sediments for the purpose of establishing a correlation; afterwards they were geographically represented through the use of a GIS, with values corresponding to the < 63 µm fraction, considered by diverse studies as that which presents the greatest heavy metal adsorption capacity.

**MATERIAL AND METHODS**

**Study area**

The study area chosen is located between the center downtown area and the northern part of the city of Porto Alegre, capital of the state of Rio Grande do Sul, in the South of Brazil (Fig. 1).

In accordance with the Koppen (1936) classification, the climate in the region is temperate, subtropical and humid. The study area is inserted within the urban Almirante Tamandaré sub-basin, which drains into Lake Guaíba and is georeferenced between the coordinates 476 561.77 E; 6 676 956.05 S and 481 482.71 E; 6 682 109.55 S. Within the study area, three areas representative of predominant soil uses in the city were chosen: industrial (3.0 km²), commercial (1.02 km²) and residential/commercial (0.83 km²), as represented in Fig. 2. The limits of the study area represent avenues of high vehicular traffic volume.

**Sediment monitoring**

During the month of June, composite samples of sediments accumulated from the streets of the study area were collected. The samples were the result of the composition of various sub-samples of dry sediment collected in an area of approximately 200 m² for each point chosen (thus reducing the influence of point source pollution, making the samples more representative), as represented in Fig. 3 and following a methodology similar to that used by Poleto et al. (2009), Krčmová et al. (2009), Yetimoğlu et al. (2008), Banerjee (2003), Charlesworth et al. (2003), Charlesworth & Lees (1999) and Deletic et al. (1997).

Approximately 500 g of dry sediment were collected for each point (Poleto et al., 2009; Sutherland, 2003).

Samples were collected using a portable vacuum without metallic parts and which facilitated the collection of samples without direct manual contact and which lead to sampling of finer particle fractions. Collected samples were deposited in plastic bags and refrigerated for later performance of physical and chemical analyses.
Lead analyses by granulometric fraction

Each sample collected was submitted to sieving (polyethylene sieves – without metallic parts), using screens or openings of 45 µm, 63 µm, 90 µm, 150 µm and 209 µm, following the methodology used by Banerjee (2003) and Charlesworth et al. (2003) and which shows the separation of the most important granulometric fractions for urban sediment quality studies.

Granulometric analysis was made by a laser particle analyzer Cilas® 1180 located at the Laboratory of the UFRGS Density Currents Study Center – Núcleo de Estudos de Correntes de Densidade da UFRGS. This piece of equipment allows one to differentiate particles from 0.04 to 2500 µm. The methodology used is described by Poleto et al. (2009a).

Samples were submitted to acid digestion (HCl, HF, HClO4, HNO3), in accordance with methodology from the U. S. Environmental Protection Agency (EPA 3050). These analyses were duplicated and two USGS reference materials (SGR-1b and SCO-1) for quality control were used. Afterwards, total metal concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Perkin Elmer brand piece of equipment by the UFRGS Soil Laboratory.

All equipment and glass items used in the sample collection procedure and sample treatments were washed with distilled water, remained soaking in a 14% (v/v) nitric acid solution for 24 hours and once more rinsed with distilled water.

Interpretation of results

Descriptive statistics of the concentration data obtained from chemical analyses were calculated and, afterwards, linear regression of the concentrations was applied in terms of particle size for the purpose of establishing a correlation between these two variables, widely mentioned in studies of this type. In the event that the adjusted model presents poor correlation, the best adjustment would be applied with the averages from the data of each fraction studied, in accordance with that suggested by Al-Rajhi et al. (1996).

After this process, the non parametric Kruskall-Wallis Test was undertaken, followed by the Bonferroni test for the purpose of analyzing the significance of the sample collection location in respect to the Pb concentrations found, in accordance with that suggested by Irvine et al. (2009), Norra et al. (2006) and Kuang et al. (2004). The statistical analyses were undertaken using the software XLSTAT© v. 2009.

The lead values of the < 63 µm fraction were interpolated through the IDW (Inverse Distance Weight) method and the result was represented on a thematic map using the SIG Idrisi© Andes, which allowed visualization of the greatest lead concentration areas within the study area, as well as allowing inferences regarding the factors which had an influence on these results.

RESULTS AND DISCUSSIONS

Granulometry of urban sediments

The results of granulometric analysis undertaken in the samples collected in the study area are presented in Fig. 4. The < 63 µm fraction, which according to Poleto et al. (2009a), Poleto et al. (2009b), Irvine et al. (2009), Charlesworth et al. (1999; 2003), Robertson et al. (2003) and Sutherland (2003) is strongly correlated with the greatest concentrations of heavy metals, represents approximately 40% of the sediments collected in the area with commercial/residential soil use and 60% for the two other sampled areas. Sutherland (2003) found that the dominant fraction was the < 63 µm one with 38% of the total of analyzed fractions.

Descriptive statistics

The values of Pb concentrations obtained in the 20 sediment samples are presented in Table 2. The fact of the median being greater than the average of the data says that the data distribution is asymmetrical to the right, which is corroborated by the Fisher coefficient ($\alpha = 0.05$). This asymmetry obeys the peaks of concentration found in some sampling points, which generates a considerable standard deviation for the data. Yonming et al. (2006) found values from 29 to 3060 µg.g$^{-1}$ and a Fisher coefficient of 5.34 in samples of urban sediments collected in the Xi’an province in Central China, showing the same trend of the values found in this study.

Fig. 4 Granulometric analyses of the urban sediment samples.
Table 2 Descriptive statistics of lead concentrations (µg.g⁻¹)

<table>
<thead>
<tr>
<th>Descriptive Statistic</th>
<th>209</th>
<th>150</th>
<th>90</th>
<th>63</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>22</td>
<td>39</td>
<td>58</td>
<td>76</td>
<td>86</td>
</tr>
<tr>
<td>Maximum</td>
<td>1500</td>
<td>2300</td>
<td>121.00</td>
<td>123.50</td>
<td>147.00</td>
</tr>
<tr>
<td>Median</td>
<td>91.00</td>
<td>93.00</td>
<td>121.00</td>
<td>123.50</td>
<td>147.00</td>
</tr>
<tr>
<td>Mean</td>
<td>178.10</td>
<td>226.45</td>
<td>245.20</td>
<td>272.35</td>
<td>251.54</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>331.99</td>
<td>499.99</td>
<td>454.15</td>
<td>497.29</td>
<td>322.59</td>
</tr>
<tr>
<td>Skewness (Fisher)</td>
<td>1.82</td>
<td>2.15</td>
<td>1.81</td>
<td>1.78</td>
<td>1.23</td>
</tr>
</tbody>
</table>

In the minimum values, one may observe the increase in lead concentration with reduction in particle size, which is corroborated by Poleto et al. (2009a), Irvine et al. (2009), Norra et al. (2006), Kuang et al. (2004), Charlesworth et al. (2003), Charlesworth & Lees (1999). Maximum values are commonly found in this type of study and were cited by Charlesworth et al. (2003) who found lead concentrations of 2 582.5 µg.g⁻¹ for New York and 2241 µg.g⁻¹ for London. Al-Rahji et al. (1996) perceived that these maximum values increase the standard deviation of the data and usually alter the correlations between particle diameter and concentrations of heavy metals.

Lead concentration values were correlated (α = 0.05) with the opening of the mesh through a linear model; however, the results showed poor correlation, established by the value of the regression coefficient (R² = 0.005). This is explained by the fact that most of the values are outside the statistical confidence interval (95%), above all in the 63 to 150 µm fractions. Linear regression may be observed in Fig. 5.

To correct this, the average of the values of the concentrations in each one of the fractions was calculated and regression models were once more calculated. Of all the models tested, the exponential model presented the best correlation (R² = 0.87) at the same level of significance. This result is similar to that reported by Al-Rahji et al. (1996), who found correlations above 80%. Figure 6 presents the result of the exponential adjustment of the data obtained.

The mathematical model obtained in this regression is presented in Eq. (1).

\[ Y = 298.4e^{-0.002x} \]  

where \( x \) represents the particle diameter (µm) and \( Y \) the Pb concentration (µg.g⁻¹).

Results demonstrate that urban sediments are enriched with Pb, above all in the fine fraction of the particles. In a similar way to sediments in other environments, the increase in pollution load in finer sized particles is generally associated with the increase in surface area in smaller sized particles, supplying a greater space for adsorption of metals in clay minerals or in the organic matter present in sediment particles. Robertson et al. (2003) suggested that the particles generated by automotive vehicles present a high Fe/Pb ratio and concluded that in their case the principal source of lead in urban areas was vehicular traffic.

Understanding that heavy metal loads are heterogeneously distributed is important in the formulation of pollution management and control strategies (Poleto et al., 2009a; Irvine et al., 2009; Taylor, 2007; Charlesworth et al., 2003; Sutherland, 2003).

Spatial distribution of lead in the study area

Studies of lead associated with urban sediment particles were the first to be performed for the purpose of
establishing the risk to human health generated by vehicle traffic, which in the past used lead in gasoline in abundance (Taylor, 2007; Robertson et al., 2003). The results obtained were important in the decision to reduce lead concentration in gasoline in many countries.

To determine what the increase of Pb concentrations due to human activity is, there is the need to verify the value of the local background. As the study area is densely urbanized, it was not possible to find a naturally preserved area (without any human interference); for that reason we took into consideration the data obtained in the studies of Poleto & Merten (2005) and Poleto et al. (2008) which were obtained for the same watershed, which is a sub-watershed in the Porto Alegre metropolitan area. The value found by the authors is 31.30 µg.g⁻¹, thus, configuring elevated human enrichment in the study area.

Distribution of concentrations by soil use, represented in Fig. 7, shows how the lead concentration is greater in the commercial area, even greater than in the industrial area where gasoline selling stations and industries that use metals as raw material predominate. Nevertheless, most of the points sampled in the industrial area present a traffic volume in a lower proportion than in the two other areas studied. In this commercial area, two of the points sampled presented values above the average of the rest of the data and these points coincide precisely with a street of high city bus traffic. At this point, the presence of vehicle oil and tire particles on the surface was observed, indicating that this potential source would be the main lead potential in this area.

The result of the Kruskall-Wallis Test showed that the data is derived from the same population; whereas the Bonferroni Test showed that there is no significant relationship between the lead concentrations and the respective area of sample collection, to a 5% level of significance, similar to the results found by Charlesworth et al. (2003) in the city of Birmingham. The fact that soil use is not correlated with the lead concentration may indicate that there is an external factor that influences this behavior, which is probably the chemical composition of the sediment particles, which influences the rate of lead adsorption, in accordance with results presented by Banerjee (2003) and Robertson et al. (2003) who define that lead is associated with the residual fraction > Fe/Mn oxides > organic matter > exchangeable fraction > carbonates. According to Krčmová, et al. (2009) and Charlesworth et al. (2003), it is still difficult to establish the main source of lead in urban sediments; nevertheless, some studies suggest that the presence of this metal together with zinc is associated with tire residues, which is directly associated with vehicular traffic volume.

**Figure 8** presents the spatial distribution of Pb in the study area.

It is fitting to highlight that the commercial area of Porto Alegre presents a high volume of people and that high metal concentrations like the lead adsorbed in the finer particles may present health risks since this finer range is breathable. Likewise, the nearness of these areas to Guaíba Lake (main local body of water) may be contributing in a significant way to the increase of heavy metals in these ecosystems since the Lake is the final point in the urban drainage systems of this watershed.

![Fig. 8 Spatial distribution of Pb (µg.g⁻¹) in urban sediments in the study area.](image-url)
CONCLUSIONS

- Pb is a heavy metal which is closely associated with urban sediment particles;

- Samples are composed of large percentages of fine particles (< 63 µm) in the three areas monitored;

- Maximum values of concentration were found in the finest particles of the collected sediment samples, regardless of the point of origin of the sample;

- The mathematical model which best explained the regression between the Pb concentration and the particle size was based on an exponential adjustment of the variables;

- The highest Pb values were found in commercial areas, a situation that may be explained in terms of vehicular traffic volume and this coincides with other studies in different cities in the world;

- Lead concentrations in urban sediments of the three areas went far beyond the local background concentration which was adopted;

- Research should be increased in regard to how to make urban systems more sustainable, reducing their pollution potential and minimizing the entrance of potentially polluting particles into bodies of water that pass through these urbanized areas.

Acknowledgments The Authors would like to thank CAPES, CNPq and Soils Analysis Laboratory of UFRGS.

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