MINERALOGICAL AND CHEMICAL CHARACTERIZATION OF SEDIMENTS FROM IMPERVIOUS URBAN STREETS

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Abstract: This study aimed to determine the granulometric and mineralogical composition and the Cr, Ni and Pb trace element content in sediments collected from impermeable streets located in the urban perimeter of Toledo, PR, Brazil. The mineralogical analyses were performed by a diffractometer, the granulometric analyses by integrated sieving methods and laser diffraction, and the analyses of the trace elements in quartered fractions of the sediments were carried out by optical emission spectrometry with inductively coupled plasma (ICP-OES). It was concluded that the sediments had an average granulometry greater than 0.09 mm, with finer fractions represented by clay. The mineralogy identified ferruginous substances characteristic of Distroferric Red Latosol DRL, with a high presence of quartz and diopside. Statistically, it was shown that the sediment samples were significantly enriched with the trace elements Chromium and Nickel in the central area streets and with Lead in lower concentrations in the streets in the peripheral areas. The sediments have an average particle diameter greater than 0.09 mm, represented by sand, with fine sediments representing 2 to 6% of the samples. The software indicated that the sediments are from different anthropogenic sources. The diffractograms show peaks for quartz and diopside. Enrichment by trace elements was significant for chromium and nickel in the downtown area streets.

Keywords: Sediments; diffraction; granulometry

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INTRODUCTION

One particularity of urbanization is related to total waterproofing of the urban perimeter of cities, which results in a decrease in soil infiltration by rainwater and the dissolution and disposal of pollutants into the rivers which drain these sites. Martinez and Poleto (2014) reported that urbanization considerably increases the amount of pollutants in watersheds due to the fact that urban sediments can easily adsorb trace elements from precipitation and complexation reactions, and from humic substances (Oliveira & Marins, 2011).

Sediments accumulate in impervious areas of urban environments, where they are constantly enriched by trace elements derived from human activities carried out in these locations. Finer fractions of these sediments are responsible for adsorbing these trace elements, and it is because of this that Sutherland (2003) states that fractions greater than 2 mm are of limited importance for the transport and adsorption of metals in urban systems, finding the highest concentrations of lead in particles of clay, silt and sand (64%) and concluding that particles smaller than 0.063 mm accounted for 51% of the total load of stored lead. Also, the study by Zhao et al. (2011), in Beijing, China, concluded that heavy metals are mostly deposited in particles smaller than 0.250 mm, while in Queensland, Australia, the study by Gunawardana et al. (2012) observed that 70% of the particles were smaller than 0.150 mm, and of these approximately 60% were loaded with heavy metals.

Another important feature in urban sediments relates to their geochemical characteristics (geochemical substrate), due to the presence of carbonates, clay minerals, organic matter, oxides and hydroxides of iron and manganese, and the retention of metal cations in these particles is often due to cation exchange capacity (CEC), metal selectivity, concentration of other cations, pH and ion activity in the solution (Hvitved-Jacobsen et al., 2010).

A characterization of sediments produced in urban centers and accumulated in their impermeable surfaces can create prospects for new methods of retaining or removing pollutants before they are carried away by rainwater and end up in the rivers that drain these cities, thus minimizing the harmful effects to things living in this habitat. Thus, this case study aimed to determine the granulometric and mineralogical composition, and concentrations of Cr, Ni and Pb trace elements in sediments strategically collected from five impermeable streets in Toledo, PR.

MATERIAL AND METHODS

The city of Toledo is located at 24° 45′ 50″ South latitude and 53° 44′ 34″ West longitude, in the Western region of the state of Paraná, in Southern Brazil (Fig. 1). The urban area has an almost symmetrical ground. The agroindustrial base is favoured by the Humid Subtropical Mesothermal – Cfa (Köppen) climate and Distroferric Red Latosol - DRL (EMBRAPA, 2013).

Samples of sediment were taken monthly from March 2012 to April 2013. They were extracted with the aid of a portable vacuum cleaner and stored directly, without filtering, in the plastic collector - cleaner machine. The sites for the sampling consisted of main streets and peripheral streets, characterized by light and heavy vehicles, respectively.

Each sample for a month and location was composed of 10 sub-samples collected from an impervious area of
approximately 100 m², resulting in approximately 500g of dried sediment (Poleto et al., 2009), wherein the analytical determinations were performed after the sediments were dried in circulating air ovens in which major constituents were discarded, such as cuttings, leaves, and pieces of glass, etc.

In the case of the granulometric and mineralogical analyzes, it was necessary to take a mixture of 6 samplings carried out from July to December 2013, which after being duly quartered (Jones) were analyzed at the Analysis Laboratory for Minerals and Rocks – LAMIR, of the Federal University of Paraná – UFPR. Specifically, the mineralogical (total dust) analyzes were performed by a diffractometer (EMPYREAN) with an X Celerator detector which operated with a copper pipe and 40 kV and 40 mA setting. The minerals were identified with the help of High Score software, using the PDF-2 mineralogical database. The granulometric analyzes were performed using two methods: integrated sieving and laser diffraction (CILAS, Model 1064) using the theoretical foundations for diffraction from Fraunhofer to separate the sediments smaller than 60 mesh into 100 classes.

The results of granulometry of the sediment fractions smaller than 0.063 mm were subjected to statistical analysis using the SYSGRAN (System of Granulometric Analysis) program from UFPR, in which the McCammon – b standard method was used for 97% efficiency (Camargo, 2006).

Regarding enrichment by trace elements in the sediments in this study, analytical determinations for trace elements Cr, Ni and Pb were performed monthly in urban sediment quartered fractions smaller than 0.063 mm, which after being subjected to total content extraction by acid attack, were analyzed via inductively coupled plasma optical emission spectrometry (ICP-OES) using Optima 8000 ICP equipment from Perkin Elmer. Statistical correlation techniques were applied to the data obtained in the laboratory analyzes for easy interpretation of this information.

RESULTS AND DISCUSSION

The results presented in Table 1 are total mass of sediments, distributed according to the Wentworth granulometric scale.

The sediment samples collected over the year of research presented, higher percentages for their granulometric composition distributed between particles with diameters greater than 0.09 mm (thick sand to fine sand), with rates of approximately 62 and 82%, respectively, for streets 5 and 3. One of the assumptions behind this rate may be related to population growth and demand for housing, since according to the Brazilian Institute of Geography and Statistics - IBGE (2014), Toledo had an increase of 32,000 people in the last decade, which generated intense traffic of material for the construction industry.

Larger proportions of silt and clay were found in the sediments from streets 4 (26.6% and 3.5%, respectively) and 5 (33.3% and 4.4%, respectively), which according to Horowitz et al. (2001) can adsorb trace-elements in greater capacities as particle size decreases (Table 5). Another factor to consider is related to the geography of this urban area, where there is a slope which rises from street 4 to street 5, and because of this, suspension of sediments occurring at rainy times can induce the release of metals, nutrients and other unwanted components of the sediments into the water column (Gibson et al., 2015), thus increasing the environmental risks to rivers, which are the sites of final disposal of the sludge.

Zafra et al. (2007) also state that sediments classified as thin are likely to present the highest concentrations of metals, and thus can start to provide information on pollution distribution levels and support environmental management of watersheds. Table 2 shows the granulometric percentage distribution of sediments with granulometry inferior to 0.250 mm from the bottom of the analyzed rivers.

This fraction covers medium sand to clay, according to the Wentworth granulometric scale (<0.250 mm). The major parameters D10 and D90 shown by street 1 represent the diameters of the section of the cumulative distribution curve at 10% and 90%, respectively, whereas the highest mean diameter D50 of the sediment was found in street 1, and the smaller percentages for street 5are the median distribution and correspond to the average particle diameter (Dm).

### Table 1. Granulometric composition of sediments

<table>
<thead>
<tr>
<th>Street</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vsf</td>
<td>cs</td>
<td>as</td>
</tr>
<tr>
<td>1</td>
<td>12.9</td>
<td>14.3</td>
<td>21.4</td>
</tr>
<tr>
<td>2</td>
<td>4.8</td>
<td>23.8</td>
<td>30.1</td>
</tr>
<tr>
<td>3</td>
<td>30.6</td>
<td>16.6</td>
<td>22.8</td>
</tr>
<tr>
<td>4</td>
<td>8.5</td>
<td>21.8</td>
<td>31.8</td>
</tr>
<tr>
<td>5</td>
<td>11.1</td>
<td>21.8</td>
<td>19.6</td>
</tr>
</tbody>
</table>

Note: vsf: very coarse sand (> 2 mm); cs: coarse sand (0.5 mm); as: average sand (0.25 mm); fs: fine sand (0.18 mm); vsf: very fine sand (0.09 mm)
Table 2. Granulometry of sediments (< 0.250 mm)

<table>
<thead>
<tr>
<th>Street</th>
<th>D_{10}</th>
<th>D_{50}</th>
<th>D_{90}</th>
<th>Average diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μm)</td>
<td>(μm)</td>
<td>(μm)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5.46</td>
<td>70.59</td>
<td>164.56</td>
<td>79.08</td>
</tr>
<tr>
<td>2</td>
<td>5.37</td>
<td>65.52</td>
<td>142.75</td>
<td>67.36</td>
</tr>
<tr>
<td>3</td>
<td>5.28</td>
<td>65.15</td>
<td>160.18</td>
<td>75.62</td>
</tr>
<tr>
<td>4</td>
<td>3.84</td>
<td>46.79</td>
<td>150.24</td>
<td>64.79</td>
</tr>
<tr>
<td>5</td>
<td>3.32</td>
<td>35.96</td>
<td>126.53</td>
<td>52.55</td>
</tr>
</tbody>
</table>

Note: Results of laser granulometry.

Thus, these results show that the peripheral areas of the city accumulate coarser sediments and the central regions accumulate finer sediments and are more likely to contain higher proportions of trace elements, as in the study from Charlesworth (2003), which showed that in the urban surfaces of Coventry (UK), a dominant fraction smaller than 0.063 mm is responsible for the transport of trace elements.

For the remaining collection sites, it was found that about 50% of the granulometric fractions have a particle size ranging from 0.047 to 0.056 mm. This result reflects data from collection points where every day there is a similar flow of vehicles, due to the fact that these sites are located in central areas of the city, leading to a similar distribution of sediments.

Using the SYSGRAN software, Table 3 presents for fractions smaller than 0.063 mm the average results (average diameter), selection (degree of selection or standard deviation), asymmetry, kurtosis, and also the calculation of the percentage (%) of granulometric parameters for each of the points investigated. In this analysis, the software requires conversion of the particle diameters in millimeters (mm) into $\phi$ (phi), in accordance with the following equation:

$$\phi = -\log_2 \text{d} \text{ (mm)}$$

Table 3. Results obtained by SYSGRAN software

<table>
<thead>
<tr>
<th>Street</th>
<th>Average</th>
<th>Median</th>
<th>Selection</th>
<th>Kurtosis</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μm)</td>
<td>(μm)</td>
<td>(°)</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.14</td>
<td>3.89</td>
<td>2.46</td>
<td>1.15</td>
<td>53.4</td>
<td>35.2</td>
<td>11.4</td>
</tr>
<tr>
<td>2</td>
<td>4.39</td>
<td>4.23</td>
<td>2.24</td>
<td>1.60</td>
<td>43.3</td>
<td>45.5</td>
<td>11.2</td>
</tr>
<tr>
<td>3</td>
<td>4.26</td>
<td>4.09</td>
<td>2.42</td>
<td>1.19</td>
<td>47.9</td>
<td>40.5</td>
<td>11.6</td>
</tr>
<tr>
<td>4</td>
<td>5.05</td>
<td>4.86</td>
<td>2.36</td>
<td>1.37</td>
<td>30.1</td>
<td>54.4</td>
<td>15.6</td>
</tr>
<tr>
<td>5</td>
<td>5.05</td>
<td>4.86</td>
<td>2.36</td>
<td>1.37</td>
<td>30.1</td>
<td>54.4</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Note: *$\phi = -\log_2 \text{d} \text{ (mm)}$; ** Standard deviation range (σ): well selected (0.35 e 0.5); moderately (0.5 e 1.0 poorly (1.0 e 2.0); very poorly (2.0 e 4.0); extreme very poorly selected (>3)

For this granulometric fraction of urban sediments (< 0.063 mm), streets 4 and 5, which are more centrally located, have a higher percentage of clay and silts, probably due to the smaller intensity of heavy traffic and construction in the locations, which result in an increase in the specific surface area (SSA) of the sediments and thus increase the adsorption of trace elements, as can be observed in Table 5.

SSA is inversely proportional to particle diameter, thus it mainly depends on the texture and mineralogy of thinner fractions (silt and clay), which have higher reactivity (Souza Jr. et al., 2007).

Selection or degree of selection is a measure of sample dispersion, or standard deviation in size distribution. Well selected sediments imply grains with little dispersion in granulometric values, while poorly selected sediments indicate the opposite.

This sediment fraction was given a “very poorly selected” classification by the software for all sampling sites, as the standard deviation (σ) was between 2.0 and 4.0 and indicates that the contributions to these sediments come from multiple and diverse anthropogenic sources. On the other hand, well selected sediments imply grains with little dispersion in their granulometric values, or central tendency measure values; however, with increasing transport or stirring up of the medium, different sized particles tend to be separated by size (Nichols, 2009).

Asymmetry represents the degree of deformation of the single frequency curve to the right of left in order to analyze the relationship between mode, mean and median. Thus, it can be said that the streets have a positive asymmetry, which occurs when the mean value is greater than the median value, which in turn is greater than the mode value, and thus the tail of the distribution curve is higher for the thinner grains, since no symmetry occurs when the mean value is lower than the median value, which in turn is inferior to the mode value (Dias, 2004).

Kurtosis is the degree of flattening of a curve relative to a curve representing normal distribution, in which a distribution curve can be classified as: platykurtic (flattened), mesokurtic (normal) or leptokurtic (elongated). Thus, streets 1 and 3 have more mesokurtic curves than the other streets, presenting kurtosis values closer to 1, and therefore a normal distribution curve. However, it is necessary to remember that the sediments were considered poorly selected and can present a wide
variation of classifications of their particles in this fraction of sediments.

The Shepard diagram shown in Fig. 2 is also used as a way to present the results of a classification obtained for the granulometric fractions of the thin sediments from the city streets.

According to the diagram, the fine sediments from the streets are mainly formed of clayey silt or sandy silt with fractions of granules greater than 3%. Also, these particles (silt + clay) represent, on average, 38% and 30% of the fractions from streets 5 and 4, respectively. This fine sediment rate could be caused by the fact that occasional sweeping procedures performed by the government hardly remove these granules and these fine particles are almost entirely removed by heavier rain, whereas with low pluviometric intensities, this fraction tends to remain on the surface of impermeable areas.

The use of mineralogical techniques in sediment mineral determination gives an understanding of the chemical and physical interactions that occur in adsorption processes and sorption of pollutants in urban areas. Thus, Table 4 shows the results of the qualitative determination of the minerals identified in the analysis of the "Total dust" fraction of sediments and therefore these results mainly express minerals found in Latosols and over time suffer from the action of atmospheric elements, leaching, and especially, the effects of pollution.

In the diffractogrphy analyzes, the sediments, when reduced to total dust, acquired colors that tended to range from orange to yellow tones, due to a greater presence of ferruginous substances, present in abundance in the Distroferric Red Latosol (DRL), characteristic of the river basin in the study. According to Mineropar (2005), the geological substratum of the region consists of conglomeratic sandstone, sandstone and siltstone, interspersed with thick strokes of basic effusive rocks in the middle, displaying different acids (dacites, rhyodacites and rhyolites) from the Paraná Basin.

Table 4 shows the presence of the minerals quartz, andesine and kaolinite in all sediment samples and the absence of rutile. Hematite, except for street 2, requires specific treatment for its confirmation. According to Anthony et al. (2010), the mineral andesine consists mainly of Silicon and Aluminum, belonging to the feldspar group and widely occurring in igneous rocks with intermediate silica content. They may also be associated with quartz and ceramic materials, thus a high residue present in civil buildings and the sediments present in the streets characterized in this work.

The diffractogram for street 4 is shown in Fig. 3. The results for the other streets studied revealed a behavior very similar to this street. Thus, the mineralogical compositions of the urban sediments in this paper can be analyzed.

The diffractograms for the samples studied show a high number of peaks for the minerals quartz and diopside. By definition, quartz is a silicone oxide, is constituted of the most common of all minerals, is abundant in all kinds of rocks, and is therefore found in large proportions in these sediments, due to extensive use in construction, electronics, optics, ceramics, glass, abrasives and as a gem (Mineropar, 2005).
As mineralogical distribution is strongly influenced by the geology of the region, the clay and silt fractions are therefore formed of clay minerals, quartz and a multitude of oxides and hydroxides. In the samples, larger particles from anthropogenic origins were also found, such as glass particles, metal particles, and industrial and construction process waste, and because they present chemical and mineralogical properties different from natural source particles, they can interact in a different manner within the environment (Poleto & Merten, 2007; Taylor, 2007).

This paper also shows, in Table 5, monthly quantitative calculations and correlations between percentages of fine sediments and concentrations of these trace elements in granulometric fractions inferior to 0.063 mm, in levels of trace elements such as chromium, lead and nickel, presenting characteristics that are toxic to aquatic ecosystems and that are potentially found in urban runoff water (Gunawardana et al., 2012).

Cr, Ni and Pb contents in these sediments are determined by the daily activities of any urban environment. Thus, according to Horowitz et al. (2001), Chromium may result from metal galvanizing processes, engine and brake parts, Nickel is present in diesel fuel, lubricating oil, galvanized metals, brakes and asphalt pavements, and Lead may be present in vehicle exhausts, tires, lubricating oil, welded parts and paints.

Statistically, the results in Table 5 show that there is not enough evidence to support the existence of a significant linear or exponential correlation between the amount of fine sediment from each sampling site, and the concentrations of certain trace elements. Therefore, it was possible to conclude that these concentrations are exclusively caused by larger or smaller anthropogenic contributions occurring and discarded in each one of the streets.

The quantities of trace elements in sediments calculated in this study corroborate the results described by Covelo et al. (2007), who studied the sorption of heavy metals, and claim that chromium is preferred for adsorption by kaolinite and mica, while iron oxides and manganese adsorb lead. Also, the study from Gunawardana et al. (2012) states that the granulometric composition of urban sediments and their pollutants varies with a range of factors, such as geographical location (soil characteristics), soil use, and traffic conditions.

Finally, the enrichment of these trace elements in sediments was measured by comparing the average values in sediments to the background values established by Juchen (2014) for this area of study. So, it can be stated that Cr (background: 52.4 mg kg⁻¹) presents enrichment on street 4, in the center of the city, and Ni (background: 26 mg kg⁻¹) enriches streets 3, 4 and 5.

As for the Pb enrichment occurring in streets 3 and 4 (background: 17.5 mg kg⁻¹), although according to Kremová et al. (2009) it is still difficult to establish the main source of lead in urban sediment, some studies suggest that the presence of this metal with zinc is associated with tire waste, which is directly associated with vehicle traffic volumes. Thus, it is considered that the Pb level results were much lower than in the study from Yongming et al. (2006), which found lead levels between 29 and 3060 mg kg⁻¹ in urban sediment samples collected in the province of Xi’an in Central China.

Systematic monitoring of concentrations and the mobility of trace elements in urban environment sediments is considered important, as it can provide data for establishing public health strategies and contamination control, thus making it necessary to introduce continuous research programs regarding the dynamics of pollutants associated with sediment, with the aim of increasing knowledge in this area.

**CONCLUSION**

The sediments collected over a year from impermeable urban areas of Toledo, PR, had their granulometric composition distributed among particles with diameters superiors to 0.09 mm, and were thus mostly classified as sand, due to this material being transported for construction.
On the other hand, sediments classified as fine and clay are mainly represented by 2 to 6% of the total weight of the sediments.

The SYSGRAN software used for this paper showed a selection model that indicated an injection of sediments from multiple and different anthropogenic sources.

The sediments when reduced to total dust, acquiring colors tending to range from orange to yellow in tone, due to the greater presence of ferruginous substances, characteristic of the Eutroferric Red Latosol (ERL) present in this watershed study.

Also, the diffractograms showed similarities between these total dust samples and presented peaks of intensity, especially for the minerals quartz and diopside.

Statistical analysis of the percentage of fine sediment and concentrations of the trace elements Cr, Ni and Pb showed that there was not sufficient evidence to support the existence of a significant linear or exponential correlation, therefore it may be concluded that the concentrations of these elements are exclusively caused by larger or smaller anthropogenic contributions occurring in each of the streets studied.

Also, enrichment of the sediments by these trace elements was significant for Chromium and Nickel in the streets that make up the central area of the city. However, the Lead element was present in less significant concentrations in streets in the peripheral area.

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Beijing and its Potential Contribution to Runoff Pollution. 