TRACE ELEMENTS (Rb, Cs, Sr, Pb, Th, U) BIOAVAILABILITY POTENTIAL AND SPECIATION IN THE PIRACICABA RIVER BOTTOM SEDIMENTS, SÃO PAULO, BRAZIL

Alexandre Martins Fernandes(1), Jefferson Mortatti(1), Jean-Luc Probst(2), Helder de Oliveira(1), João Paulo Rambelli Bibian(1), Graziela Meneghel de Moraes (1)

1Centro de Energia Nuclear na Agricultura (CENA)
Universidade de São Paulo
Av. Centenário, 303
13400-970, CP: 96, Piracicaba, São Paulo.
afernandes@cena.usp.br
jmortatt@cena.usp.br
helder@cena.usp.br
jpbibian@cena.usp.br
gmmoraes@cena.usp.br

2Ecole Nationale Supérieure Agronomique de Toulouse (ENSAT)
Avenue de l'Agrobiopole, BP 107
31326 Castanet Tolosan Cedex, Auzeville Tolosane, France.
jean-luc.probst@ensat.fr

ABSTRACT

It was studied the bioavailability potential of Rb, Cs, Sr, Pb, Th and U and their chemical speciation in Piracicaba river bottom sediments. This river system crosses important agricultural and urban areas of São Paulo state, which groups about 3 million people and receives a large load of agricultural, industrial and domestic wastes. The procedure used to estimate trace elements bioavailability potential was related to a 7-step sequential chemical extraction. This scheme was designed to dissolve and separate sample chemical phases, which can be affected by changes in physical-chemical conditions; in the following order: water soluble, exchangeable, bound to carbonates or acid fraction, bound to Mn-oxides, bound to Fe-oxides and bound to organic matter. Trace element concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) after each extraction step. With the used extraction procedure, it was possible to identify the fraction where some trace elements could be found in order to evaluate their bioavailability potential. Rb and Cs were particularly involved with the organic fraction, while Sr revealed to be associated mainly to the exchangeable fraction (clay minerals). Pb, Th and U were mainly bound to the residual and Fe-oxide fractions.

1. INTRODUCTION

Different forms of trace elements are present in the environment (atmosphere, water, soil, sediments and living organisms). These forms are controlled by the physic and chemical conditions of the environment and in terms of the main elements constituting the ecosystem. The biodisponibility of some trace elements in the fluvial ecosystems is related not only to the observed high concentrations but involved also with the weathering process. In this way, several data focus on trace element concentrations in dissolved and particulate river loads, [1], [2], [3]. However, river suspended matters consist of two major phases: the residual and labile fractions. According to Leleyter & Probst [4] trace elements from labile fractions are participating in liquid-solid adsorption-desorption, surface complexation and co-precipitation
with different solid fractions such as clay minerals, carbonates, oxides and organic matter. Thus, the study in order to quantify the major trace elements partitioned between labile and residual fractions in fluvial sediments is very important for local and regional settings. The aim of this paper is to determine the speciation of some trace elements (Rb, Cs, Sr, Pb, Th and U) in the Piracicaba river bottom sediment, in order to determine their mobility in such a lateritic environment and to determine their distribution among the different labile fractions, in order to assess the factors controlling the biosorptionibility of these chemical species in river waters and sediments.

2. STUDY AREA

The Piracicaba river basin is located in a zone of subtropical climate ranged from 45°51’ to 48°24’ W and a latitudinal extent ranging from 22°05’ to 23°16’ S and drains an area of about 124000 km². The Piracicaba river is formed by the confluence of the Atibaia and Jaguari rivers. Downstream, the Piracicaba river receives the Corumbatai river and discharges into the Tiête river which is a tributary of the Parana river (Fig. 1).

![Figure 1. Location map of the Piracicaba river basin including the sampling stations along of the river.](image)

The eastern headwaters of the Piracicaba river basin are relatively unpolluted, whereas the central and western sub-basins, which have higher population densities, are polluted mainly
for domestic effluents and industrial discharges into the river [5]. In this catchment, two major rock types are outcropping: crystalline rock, in the upper part of the basin, carbonate sedimentary rock in the lower part of the basin. The weathering profiles are mainly represented by red lateritic soils which are composed of kaolinite and iron oxides.

3. METHODOLOGY

The bottom sediments were sampled during January 2005 period, along the Piracicaba river basin, in the sampling stations: Atibaia river (P1A and P2A), Jaguari river (P1J and P2J), Piracicaba river (P1P and P2P) and Corumbataí river (P1C). It was used a classical grab sampler and sediment samples were stored at 4 °C in plastic bags until the chemical analysis. The sediment was sieved (63µm) and the total trace element extraction was carried out using the alkaline fusion procedure with lithium tetraborate and lithium metaborate (2:1) in a platinum crucible under 1000 °C during 30 minutes. The residual phase was taken in 100 mL HNO₃ 2M. The chemical analyses were performed using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) for Rb, Cs, Sr, Pb, Th and U.

3.1 Sequential Extraction Procedure

All the samples (1.0 g of sediment dried at 100 °C) were leached by a sequential extraction procedure (Table 1), according to Leleyter & Probst [4], which allows to dissolve selectively and efficiently all the chemical constituents of the riverine sediments, of which the particulate elements can be released in solution by changes of physico-chemical conditions, in the following order: elements dissolved by water (S1), really exchangeable elements (S2), elements bound to carbonates (S3), manganese oxides (S4), amorphous iron oxides (S5a), crystalline iron oxides (S5b) and organic matter (S6). The total bioavailability fraction of the sample (SB) is the sum of all the previous leached fractions (S1 to S6). The residual fraction results from the difference between the total sample and the sum (SB) of all the labile fractions (S1 to S6).

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Extractor</th>
<th>Time (h)</th>
<th>T (°C)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>dissolved</td>
<td>H₂O Milli-Q</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>S2</td>
<td>exchangeable</td>
<td>1 M Mg(NO₃)₂</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>S3</td>
<td>acid soluble</td>
<td>1 M NaOA c/HOAc</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>S4</td>
<td>Mn oxide</td>
<td>0.1 M NH₂OH HCl</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>S5a</td>
<td>Fe oxide amorph.</td>
<td>0.2 M (NH₄)₂C₂O₄+0.2 M H₂C₂O₄</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>S5b</td>
<td>Fe oxide crystal.</td>
<td>0.2 M (NH₄)₂C₂O₄+0.2 M H₂C₂O₄ + C₆H₈O₆</td>
<td>0.5</td>
<td>85</td>
</tr>
<tr>
<td>S6</td>
<td>organic matter</td>
<td>35% H₂O₂/HNO₃ + 3.2 M NH₄OAc</td>
<td>5</td>
<td>85</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

The total concentration of Rb, Cs, Sr, Pb, Th and U in the bottom sediments of the Piracicaba river basin can be observed in Table 2.

Table 2. Some trace elements observed in the bottom sediments of the Piracicaba river basin during the studied period.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb (mg kg⁻¹)</th>
<th>Sr (mg kg⁻¹)</th>
<th>Cs (mg kg⁻¹)</th>
<th>Pb (mg kg⁻¹)</th>
<th>Th (mg kg⁻¹)</th>
<th>U (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1A</td>
<td>62</td>
<td>40</td>
<td>5</td>
<td>35</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>P2A</td>
<td>80</td>
<td>62</td>
<td>6</td>
<td>40</td>
<td>22</td>
<td>4</td>
</tr>
<tr>
<td>P1J</td>
<td>40</td>
<td>32</td>
<td>3</td>
<td>14</td>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>P2J</td>
<td>45</td>
<td>38</td>
<td>3</td>
<td>15</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>P1P</td>
<td>102</td>
<td>65</td>
<td>6</td>
<td>45</td>
<td>25</td>
<td>6</td>
</tr>
<tr>
<td>P1C</td>
<td>81</td>
<td>54</td>
<td>5</td>
<td>42</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td>P2P</td>
<td>110</td>
<td>72</td>
<td>7</td>
<td>50</td>
<td>22</td>
<td>4</td>
</tr>
</tbody>
</table>

It can be verified the occurrence of significant Rb, Sr, Pb, Th concentrations along the basin, being more important at downstream sampling stations. A maximum concentration for Rb was observed in Piracicaba river station (P2P) after the urban zone of the Piracicaba city. Similar behaviors were observed for Sr, Pb and Th. These results seem to be associated with the agricultural practices that promote constantly soil remobilization.

Fig. 2 shows, in percentual terms, the main results of the sequential extraction used to identify the dominant fraction that the studied trace elements in the bottom sediments. According to Kabata-Pendias & Pendias [6], the alkalines Rb and Cs are mainly associated to the residual phase of the sediments therefore, in the Piracicaba river bottom sediments, these trace elements were verified in the organic matter fraction. This kind of complexation shows that Rb and Cs were not bioavailability in the basin in spite of the high concentrations observed in the sampling station P2P, with 110 and 7 mg kg⁻¹ for Rb and Cs respectively.

In terms of Sr, the extraction process showed a significant presence of this trace element mainly in the exchangeable fraction with values varying between 50 and 90 % and consequently bioavailability in the labile phase. A relative bioavailability (40-60 % in the labile phase) was observed for Pb in the lower sediments of the Piracicaba river basin after the extraction procedure. This Pb shows to be constant along the basin and mainly associated with Fe-oxide and < 10 % with the organic matter fractions.

Both Th and U were found in labile phase (70 and 50 %, respectively) mainly associated with Fe-oxide (particular case for Th) and acid soluble fractions (U). These values are not in
accordance to the established by Kabata-Pendias & Pendias [6] that reports to the organic matter the responsibility for this complexation.

Figure 2. Percentual selective extraction of Rb, Cs, Sr, Pb, Th and U in the bottom sediments of the Piracicaba river basin during the studied period.

5. CONCLUSIONS

With the used extraction procedure it was possible to identify the fraction where some trace elements in bottom sediments like Rb, Cs, Sr, Pb, Th and U could be found in order to evaluate their bioavailability potential along the Piracicaba river basin. This river system crosses important agricultural and urban areas of São Paulo state, which groups about 3 million people and receives a large load of agricultural, industrial and domestic wastes. It was possible to identify Rb and Cs were particularly involved with the organic fraction, while Sr revealed to be associated mainly to the exchangeable fraction (clay minerals). Pb and Th
were mainly bound to the residual phase and Fe-oxide fractions and U was associated in the labile phase with the acid soluble fraction.

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