Phosphate and arsenate retention in sediments of the Anllóns river (northwest Spain)

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Abstract We have studied the distribution and sorption behavior of phosphate and arsenate in bed-sediments of the Anllóns river (NW Spain). As a consequence of the intense gold-mining activity in the past, substantial amounts of arsenic were found in the river sediments. For phosphorus, higher concentrations were found near two sources of P pollution. Sorption isotherms were described by the Freundlich, Langmuir and Tempkin equations. In general, the sediments sorbed more P than As. The equilibrium P concentration (EPC) reveals that sediments act as a scavenger for soluble P; by contrast, equilibrium As concentration (EAC) values were high for the As-rich sediments and correlates well with total arsenic content. Amorphous Fe oxides content, organic matter and fraction of clay plus silt were the main properties of the sediments related with the sorption of arsenate and phosphate. The results obtained provide a first estimate of the sorption behavior and availability of the phosphate and arsenate anions in the sediments of the Anllóns river.

Keywords Arsenate; basin; phosphate; sediments; sorption

Introduction
Arsenic and phosphorus are chemically similar elements. Arsenic in surface river waters is present primarily as an inorganic ion, arsenate (Mok and Wai, 1994). Phosphate is an essential nutrient for organisms, whereas arsenate is toxic to both plants and animals. The presence of As in the environment can be attributed both to the parent materials and to anthropogenic activities, especially mining and smelting (Bhumbla and Keefer, 1994; Liu et al., 2001). Two of the key processes involved in P and As retention by the sediments are adsorption and desorption. Several studies have focused on the sorption processes of P on sediments (Taylor and Kunishi, 1971) and sediment components (Lijklema, 1980). Similarly, in a river As is predominantly bound to sediments, as a consequence, in a contaminated river, sediments can contain substantial (100–300 µg/g, or even higher) amounts of arsenic that are potentially mobile during water-sediment interactions (Brannon and Patrick, 1987; Mok and Wai, 1994). Arsenic species interact mainly with iron, manganese and aluminum compounds (Brannon and Patrick, 1987; Mok and Wai, 1994; Roussel et al., 2000), although the organic matter and humic acids may also play an important role (Thanabalasingam and Pickering, 1986). In addition, the concentration of phosphate present in the system is a significant factor in the uptake and release of As from the solid phases (Liu et al., 2001). Input of phosphate to a river contaminated with As can promote greater mobility or reduce the sorption of As (Mok and Wai, 1994).

In the past the area studied underwent intense gold-mining activity. The gold in this area is associated with pyrite and arsenopyrite (Nespereira, 1978). The problems caused by the arsenic contamination as a consequence of gold-mining activities are well known (United Nations, WHO, 2001). In addition, at the present moment there are two important sources of P pollution near Carballo (Figure 2): a wastewater treatment plant and a food-packing factory.

In this paper we describe first the distribution of As and P in the sediments along the course of the Anllóns river. Then, we investigated the sorption of added arsenate and
phosphate by selected sediments of the river, because it may give information about potential fixation or release in the environment. Also, the equilibrium phosphate concentration (EPC) and the equilibrium arsenate concentration (EAC) were determined for the sediments studied.

The aims of this work are: (i) to describe the distribution of total concentrations of As and P in the sediments of the Anllóns river, (ii) to provide data on phosphate and arsenate sorption behavior for the sediments of the Anllóns river, (iii) to estimate the EPC and the EAC for the sediments studied, and (iv) to determine the relationship between sediment properties and P or As(V) sorption data.

**Materials and methods**

**The study basin**

The Anllóns river basin (Figure 1) is located in Galicia, Northwest of Spain. The river mainly runs through Bergantiños county, from East to West, emptying into the sea at the Ría of Corme and Laxe. The river is 71 km long, with a mean slope of 7.6‰, and the river basin covers an area of 516 km². The Anllóns is a river of great regularity, its average annual flow is 10.77 m³ s⁻¹. Most of the river basin is dedicated to agriculture and cattle raising. From a geological point of view, the river basin is divided into three well differentiated areas: (i) the Malpica-Tui unit, in which schists and paragneisses predominate, (ii) the Ordes domain, with basic and ultrabasic rocks and schists, and (iii) the schistic domain of Central Galicia. Finally, in the last stretch of the river we find alluvial deposits (Figure 2).

**Sampling**

Five points were selected for sediment sampling (Figure 2). Point 1 (Tuixe) is located near the source of the river. Point 2 (Carballo) is near the two sources of P pollution. Point 3 is located at Verdes. Point 4 (Xavarido-Cabana) is located in the gold-mining area. Point 5 (Ponteceso) is located at the mouth of the river, near the town of Ponteceso. Samples of surface sediments (0–5 cm) were taken at the five points, and except at Point 1, sediment cores were collected reaching a depth of 20–30 cm.

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**Figure 1** The Anllóns river basin
Sample preparation and characterization

The surface sediment samples were centrifuged (2,000 rpm, 10 min) to separate the interstitial water. The sediments were then dried at 40°C and sieved (2 mm-sieve). pH, particle size distribution, mineralogical analysis, total organic carbon, total N, P and As, and metals (Fe, Al, Mn) were determined for the fraction <2 mm (representing >99% of the sediment). The sediment core samples were divided into 2-cm layers, dried, ground and stored in sterile flasks. Total organic carbon, total N, S, P and total As were determined for these samples. Total P and total As were determined after acid digestion by the molybdenum blue method (Murphy and Riley, 1962) and by the hydride generation technique (HGAAS), respectively. The amorphous or poor crystallines Fe oxide content was determined by extraction with ammonium oxalate pH 3 (Schwertmann, 1964). The crystallines Fe oxide content was determined by means of extraction with ammonium oxalate pH 3 + ascorbic acid (Shuman, 1982).

Sorption studies

Batch sorption studies with the surface sediments were conducted at room temperature (20 ± 2°C). Identical methodology and treatments were used to obtain data for each oxyanion. Phosphate or arsenate sorption curves were determined by shaking 2 g of sediment with 40 ml of 0.01 M CaCl₂ solutions containing P, as Ca(H₂PO₄)₂, or As, as AsO₄⁻Na₂·7H₂O. The range of concentrations studied for both P and As was from 1.60 to 160 µM. After 18 hour of shaking, the suspensions were centrifuged and filtered (Whatman 540 filter papers). The filtrates were analysed for P (by the molybdenum blue method) or As (HGAAS). The difference between P or As concentration before and after equilibration with the sediment was considered to represent the quantity of P or As sorbed to the sediment.

Equilibrium phosphate concentration (EPC) and equilibrium arsenate concentration (EAC)

EPC and EAC values were determined for the surface sediments. The experimental procedure used to determine EPC and EAC was described by Reddy et al. (1980). The EPC or the EAC is the concentration of P or As that is supported by the solid sample when in contact with an ambient solution such that no phosphate or arsenate is either gained or lost by the solid. The method used to estimate the EPC and EAC of the sediments studied was the method of Taylor and Kunishi (1971). The initial concentrations of P or As used to determine EPC and EAC ranged from 0 to 3.23 µM P or As in 0.01 M CaCl₂.
Results and discussion
Sediment properties
Table 1 presents selected properties of the surface sediments employed in this study. Particle size distribution (PSD) analysis shows that the sand fraction dominates, especially for Points 1 and 3. XRD analysis showed that the clay fraction was mainly made up of chlorite, and to a lesser degree, by mica and quartz. Selective extractions showed that the Fe_{ox/asc} ranges from 5.4% (Point 5) to 25.8% (Point 4) of total iron content. Poorly crystalline Fe oxide content was small, with values ranging from 0.4% (Point 1) to 4.3% (Point 2).

Distribution of total arsenic and phosphorus in the sediment
The concentrations of total As found were markedly different depending on the point of sampling. In the surface sediments, the highest value was found at Point 4 (137.2 mg/kg) (Table 1). This point corresponds to the gold-mining activity area in the past. At Point 5 the As concentration was also high (69.4 mg/kg). The vertical distribution of the As concentrations (Figure 3) shows that for Point 4 the maximum is located in the top 10 cm layer. However, the highest As contents were found at depth of about 20–30 cm for Point 5 (maximum As content of 235.1 mg/kg). As a reference, a world average arsenic content of 5 mg/kg has been estimated for river sediments. Similar average As concentrations have also been found in river sediments where groundwater-arsenic concentrations are high: 2 mg/kg for sediments from the River Ganges and 2.8 mg/kg for sediments from the Brahmmaputra river (United Nations, WHO, 2001). However, arsenic concentrations much higher (up to 1,000 mg/kg) than baseline values have been found in sediments contaminated by the products of mining activity. Phytotoxic critical contents ranging from 10 to 51 mg/kg have been reported for arsenic (Huang, 1994).

Regarding the distribution of total P, the values found were much higher than those of total As, as we expected (Table 1). The highest values were found for the surface sediments and for Point 2, where the discharges from the two sources of P pollution, a wastewater treatment plant and a food-packing factory, are located. Phosphorus concentrations in the sediment decrease with depth for all of the sampled points.

Phosphate and arsenate sorption data and fitting
Data obtained were described by the Freundlich (Eq. (1)), Langmuir (Eq. (2)) and Tempkin (Eq. (3)) models:

\[
Q = K_f C^n
\]

\[
Q = \left( \frac{K_L C Q_{\text{max}}}{1 + K_L C} \right)
\]

Table 1  Selected properties of the surface sediments

<table>
<thead>
<tr>
<th>Point</th>
<th>PSD (%)</th>
<th>pH</th>
<th>OM*</th>
<th>N*</th>
<th>Total content(g/kg)</th>
<th>g/kg</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sand</td>
<td>Silt</td>
<td>Clay</td>
<td></td>
<td>Fe</td>
<td>Al</td>
<td>Mn</td>
</tr>
<tr>
<td>1</td>
<td>81.7</td>
<td>2.5</td>
<td>7.9</td>
<td>5.5</td>
<td>3.0</td>
<td>0.14</td>
<td>30.8</td>
</tr>
<tr>
<td>2</td>
<td>62.1</td>
<td>25.4</td>
<td>12.5</td>
<td>7.0</td>
<td>11.6</td>
<td>0.19</td>
<td>54.3</td>
</tr>
<tr>
<td>3</td>
<td>86.6</td>
<td>8.7</td>
<td>4.7</td>
<td>6.9</td>
<td>1.5</td>
<td>0.07</td>
<td>52.9</td>
</tr>
<tr>
<td>4</td>
<td>78.3</td>
<td>12.9</td>
<td>8.8</td>
<td>5.8</td>
<td>4.5</td>
<td>0.15</td>
<td>50.1</td>
</tr>
<tr>
<td>5</td>
<td>73.6</td>
<td>15.1</td>
<td>11.3</td>
<td>5.7</td>
<td>7.5</td>
<td>0.32</td>
<td>72.0</td>
</tr>
</tbody>
</table>

*Fe_{asc} is Fe extracted by oxalate-ascorbic acid. Fe_{ox} is Fe extracted by oxalate pH 3

*OM is organic matter content, determined by the wet oxidation method

*N is Kjeldahl nitrogen
\[ Q = K_\alpha + K_\beta \ln C \]  

(Eq. 3)

where \( Q \) is the amount of P or As sorbed by unit weight of the sediment (\( \mu \text{mol/g} \)), \( C \) is the equilibrium P or As concentration (\( \mu \text{M} \)); \( K_f (\text{L/g}) \), \( n, K_L, Q_{\text{max}} (\mu \text{mol/g}) \), \( K_\alpha \) and \( K_\beta \) are constants. The Tempkin equation (Eq. (3)) was tested because it has been used earlier to describe the sorption of both arsenate and phosphate (Raven et al., 1998; Dubus and Becquer, 2001) and it is useful to represent a large range of concentrations.

The maximum sorption capacity (\( Q_{\text{max}} \)) of the surface sediments for P and As(V) was estimated by the application of the Langmuir equation (Figure 4), despite its limitations. In general, the sediments sorbed more phosphate than arsenate (Tables 2 and 3), except for Point 4, for which the amounts of P and As sorbed were the same (4.0 \( \mu \text{mol/g} \)). Several studies have shown that the relative affinity of these oxyanions for the surfaces is higher for phosphate than for arsenate (Melamed et al., 1995).

**Equilibrium phosphate concentration (EPC) and equilibrium arsenate concentration (EAC)**

EPC and EAC values for the surface sediments studied are shown in Table 4. EPC values obtained ranged from 31 \( \mu \text{g/L} \) (Point 3) to 72 \( \mu \text{g/L} \) (Point 5). These values, when compared

<table>
<thead>
<tr>
<th>Sample</th>
<th>Freundlich</th>
<th></th>
<th>Langmuir</th>
<th></th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_f )</td>
<td>( n )</td>
<td>( r^2 )</td>
<td>( Q_{\text{max}} )</td>
<td>( K_L )</td>
</tr>
<tr>
<td>Point 1</td>
<td>0.311</td>
<td>0.599</td>
<td>0.999</td>
<td>3.520</td>
<td>0.073</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.364</td>
<td>0.857</td>
<td>0.990</td>
<td>8.496</td>
<td>0.044</td>
</tr>
<tr>
<td>Point 3</td>
<td>0.304</td>
<td>0.527</td>
<td>0.926</td>
<td>2.732</td>
<td>0.086</td>
</tr>
<tr>
<td>Point 4</td>
<td>0.338</td>
<td>0.665</td>
<td>0.875</td>
<td>3.998</td>
<td>0.078</td>
</tr>
<tr>
<td>Point 5</td>
<td>0.207</td>
<td>0.747</td>
<td>0.902</td>
<td>4.288</td>
<td>0.043</td>
</tr>
</tbody>
</table>

\( K_f (\text{L/g}); Q_{\text{max}} (\mu \text{mol/g}) \)

**Table 3** Arsenate sorption parameters for the Freundlich, Langmuir and Tempkin equations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Freundlich</th>
<th></th>
<th>Langmuir</th>
<th></th>
<th>Tempkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_f )</td>
<td>( n )</td>
<td>( r^2 )</td>
<td>( Q_{\text{max}} )</td>
<td>( K_L )</td>
</tr>
<tr>
<td>Point 1</td>
<td>0.176</td>
<td>0.618</td>
<td>0.977</td>
<td>2.016</td>
<td>0.111</td>
</tr>
<tr>
<td>Point 2</td>
<td>0.071</td>
<td>0.902</td>
<td>0.990</td>
<td>5.500</td>
<td>0.013</td>
</tr>
<tr>
<td>Point 3</td>
<td>0.161</td>
<td>0.562</td>
<td>0.967</td>
<td>1.493</td>
<td>0.142</td>
</tr>
<tr>
<td>Point 4</td>
<td>0.217</td>
<td>0.802</td>
<td>0.933</td>
<td>4.006</td>
<td>0.059</td>
</tr>
<tr>
<td>Point 5</td>
<td>0.215</td>
<td>0.781</td>
<td>0.961</td>
<td>3.519</td>
<td>0.071</td>
</tr>
</tbody>
</table>

\( K_f (\text{L/g}); Q_{\text{max}} (\mu \text{mol/g}) \)
with soluble P concentrations in water indicate that the P moves from the water to the sediment. Thus, the sediments act as a scavenger for soluble P. For arsenate, EAC values ranged from 0.6 (Point 3) to 19.8 µg/L (Point 4), which is the sediment that contains the maximum concentration of total As. EAC values correlate well ($r^2 = 0.989$) to the total As in the sediments, however EPC values don’t correlate well to total P. EAC values obtained were clearly less than EPC values for all sediments studied, except for Point 4, for which EPC was only 2.3 times larger than EAC, even when the sediment contained 12 times more P than As. EAC values for Points 4 and 5 were high, which means that, when compared with soluble As concentrations in water, these sediments release As.

**Correlation between arsenate and phosphate sorption and soil properties**

Correlation between soil properties and pollutant sorption has been widely used in recent years to determine the soil components involved (Vo Dinh Quang et al., 1996; Yin et al.,

**Table 4** EPC and EAC values for the surface sediments

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPC (µg/L)</th>
<th>EAC (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>38</td>
<td>1.2</td>
</tr>
<tr>
<td>Point 2</td>
<td>51</td>
<td>3.6</td>
</tr>
<tr>
<td>Point 3</td>
<td>31</td>
<td>0.6</td>
</tr>
<tr>
<td>Point 4</td>
<td>46</td>
<td>19.8</td>
</tr>
<tr>
<td>Point 5</td>
<td>72</td>
<td>18.8</td>
</tr>
</tbody>
</table>
1996; Dubus and Becquer, 2001). We plotted the Langmuir constants $Q_{\text{max}}$ for P or As(V) sorption vs. various sediment properties, including pH, Fe, Al and Mn oxides, total As or P, organic matter content and particle size distribution. Positive correlations were found between arsenate or phosphate sorption maximum and amorphous Fe oxides content, clay plus silt fraction and organic matter content. The $r^2$ was 0.906, 0.884 and 0.833 between As(V) sorption maximum and percentage of amorphous Fe oxides; percentage of clay plus silt, and organic matter content, respectively. For phosphate sorption, the highest $r^2$ values were obtained for the same properties, and were 0.714, 0.818 and 0.881. Because all these parameters affected sorption, a multiple regression analysis relating P or As(V) sorption maximum and other independent sediment variables was performed. The multiple regression equations were, for arsenate and phosphate, respectively:

\[
Q_{\text{As max}} = 4.848 - 0.586(\text{Clay+Silt}) + 0.831(\text{OM}) + 56.049(\text{Fe}_{\text{am}}) \quad (r^2 = 0.998)
\]

\[
Q_{\text{P max}} = 2.385 - 0.119(\text{Clay+Silt}) + 0.656(\text{OM}) + 9.695(\text{Fe}_{\text{am}}) \quad (r^2 = 0.882)
\]

Since the percentages of clay plus silt were related to amorphous Fe oxides content ($r^2 = 0.956$), the regression equations can be simplified. The multiple regression equations obtained when only two variables were included were:

\[
Q_{\text{As max}} = 1.119 + 0.124(\text{OM}) + 12.531(\text{Fe}_{\text{am}}) \quad (r^2 = 0.925)
\]

\[
Q_{\text{P max}} = 1.623 + 0.512(\text{OM}) + 0.838(\text{Fe}_{\text{am}}) \quad (r^2 = 0.881)
\]

The equation terms can be easily determined by routine chemical analyses, so these equations may be useful for estimating the phosphate and arsenate behaviour of sediments of the Anllöns river.

**Conclusions**

Substantial amounts of total As were found in sediments of the Anllöns river in samples taken near an ancient gold-mining area and in the mouth of the river. The highest As contents (>200 mg/kg) were found in sediments from the mouth of the river at a depth of about 20–30 cm. For the P, the highest concentrations were found for surface sediments at Point 2, near the wastewater treatment plant and the food-packing factory. Phosphate and arsenate sorption studies performed with surface sediments showed that the Anllöns river sediments displayed similar behavior for As(V) and P sorption, although the river sediments sorb more P than As(V). The EPC values obtained reveal that sediments act as a scavenger for soluble phosphate. For arsenate, EAC values were higher for the As-rich sediments. Amorphous Fe oxides content, organic matter and fraction of clay plus silt were the main properties of the sediments related with the sorption of As(V) and P.

**References**


