Water Air Soil Pollut (2009) 200:341–352
DOI 10.1007/s11270-008-9917-3

Total Phosphorous Distribution and Bioavailability in the Bed Sediments of an Atlantic Basin (Galicia, NW Spain): Spatial Distribution and Vertical Profiles

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Received: 16 August 2008 / Accepted: 3 November 2008 / Published online: 26 November 2008

Abstract The Anllóns basin (NW Spain) has been included in the Natura 2000 Network and declared as Site of Community Importance. The main contamination problems of the basin come from a former gold mine and from agricultural activities, which influence the quality of the sediment–water system. Phosphorus (P) enrichment in the bed sediments was evaluated by analyzing P in the pore waters, in the surface bed sediments, and in the vertical sediment profiles, including both total and bioavailable forms. Two granulometric fractions (<2 mm and <63 μm) were evaluated. Pore waters, bed sediments, and vertical profiles showed high percentages of the bioavailable P fraction with respect to the total P content, which evidences the potential risk of pollution which suppose the bed sediments of the Anllóns River. The vertical profiles showed P enrichment in the superficial layers, which could be the consequence of the increased use of fertilizers in the last decades. With regards to the granulometric distributions, the <63 μm showed, in general, higher P concentrations than the <2 mm fraction. However, at the sampling points most heavily contaminated, the concentration of both fractions becomes similar, thus indicating that, at these sites, the coatings formed over sands can retain important P concentrations in the bed sediments.

Keywords Phosphorus · Bioavailability · Pore water · Sediments · Cores

1 Introduction

In general terms, P in river bed sediments comes from several sources: from natural processes, such as erosive processes or lixiviation (Nash and Halliwell 2000), to anthropogenic inputs to the river waters such as sewage sludges, wastewater treatment plants, detergent effluents with high contents of polyphosphates (García-Rodeja 1994; Maidment 1992), organic fertilizers (García-Rodeja 1994), manures and other wastes originated from animals (Cooke and Williams 1973), and food industry (Tusseau-Vuillemin 2001).

P is incorporated to sediments through the deposition of the suspended solids or by direct contact with the waters through mechanisms such as adsorption, precipitation, isomorphic substitution in minerals, or by anionic exchange (Gunatilaka et al. 1988). As a general rule, bed sediments play an important role in the P equilibrium in riverine ecosystems. In this sense, Bowes and House (2001) have shown that, as a function of the P gradient between sediment and water, high P concentrations can be adsorbed onto fluvial sediments or, as a contrary, be released to the

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water column. On the other hand, the capacity of the sediments to retain or release P to the water column is highly conditioned by their composition as well as the oxidation–reduction potential, temperature, and bioturbation (Holdren and Armstrong 1980). So, inorganic solids like Fe oxihydroxides (goethite and lepidrocrocite), Al hydroxides, and Ca minerals show high affinity by P. In general, an inverse correlation has been observed between the contaminant concentrations and the >63 μm fraction content, due to the diluting effect of this fraction, because of its higher content in quartz and feldspars (Horowitz 1991). However, the role of the coarse particles within the watercourse must be taken into account, as they can retain considerable amounts of pollutants over the coatings formed onto these coarse particles (Chen et al. 2000).

Traditionally, only the fine fraction of the sediments (<63 μm) is analyzed because it is considered to be more representative of the fraction that can be eroded from the soils of the basin and transported as suspended soils. This fraction presents higher adsorption capacity and cationic exchange, and so therefore numerous studies realized in sediments have focused on the <63 μm fraction. However, the <2 mm fraction can have importance in the P retention of sediments, related to the coatings over the sand fraction (Chen et al. 2000). These coatings, formed by Fe and Mn oxides as well as organic matter, can suppose until 50% of the total superficial area of the sediments (Turner et al. 2004). The importance of coatings is also important due of the fact that, in many rivers, a high percentage of the contaminants are associated to the organic matter (Förstner and Wittmann 1983; Mendiguchía et al. 2005).

In the particular case of marine sediments, it has been observed that P introduced in the marine system will follow two opposite tendencies. On the one hand, an increase in the P concentrations in sediments is due to the gathered contributions of P coming from atmosphere, marine biota decomposition, and the contribution of P coming from the rivers. On the other hand, a release of P associated to sediments is because of a decrease in the P in equilibrium, due to the increase in the salinity and the decrease in the oxygen concentration (Caraco et al. 1990; House et al. 1998; Gardolinski et al. 2004).

The Anllóns basin (Galicia, NW Spain) was declared in 2004 an Area of Special Protection of the Natural Resources by the Galician regulation (Decree 72/2004), and was also declared as a Special Area of Conservation and Site of Community Importance included in the Natura 2000 Network. Among its uniqueness, it can be found a vast population of *Omphalodes littoralis* subsp. *gallaecica*, an endangered species of the Boragineaceae family, protected by the Spanish government (RD 439/1990) and by the Berna Convention (RCL 1986/3023). In spite of the special conservation of the area, the basin has some special features which may favor the contamination of the basin. There is located in the basin an antique gold mine—where Au mineralizations are associated to As—which was in operation in the area since the Roman times, and that was again exploited from 1895 to 1910, with intermittent extractions after this period. The mine areas, together with agricultural activities and urban areas, are the main contamination sources in the basin which influence the quality of the sediment–water system.

Phosphorus (P) has been identified as a major pollutant of the basin (Devesa-Rey et al. 2008). This excessive P, either in total or bioavailable forms, may have a negative influence in the river system, favoring the growth of phytoplankton which ultimately would be the cause of eutrophication. On the other hand, an increase in P concentrations in the bed sediments can exert an important influence in the As geochemistry, because P competes with As in the adsorption sites favoring the release of As from the bed sediments to the water column (Rubinos et al. 2003), which can cause problems of toxicity to the biota (Devesa-Rey et al. 2008b). These high total As concentrations in the Anllóns River sediments are attributed to natural geogenic As enrichment due to arsenopyrite (AsFeS) mineralizations associated with the gold ores in hydrothermal quartz veins (Boixet et al. 2007).

The present study aims at researching the environmental phosphorus availability in the Anllóns system. For that purpose, P concentration will be analyzed in three compartments: pore waters, bed sediments, and sediment vertical profiles. The risk of eutrophication due to phosphorus will be analyzed as a function of the sediment grain size and will be also evaluated the influence of salinity gradient towards the mouth of the river.

2 Materials and Methods

2.1 Study Area

The Anllóns River is located in the NW of Spain. The basin drains a rural catchment of 516 km^2 with a history of agricultural, forestry, and cattle-raising activities (Fig. 1). Two main human settlements are located in the basin: Carballo, with a population of over 25,000 and a sea food canning industry, and Ponteceso, with a population of about 7,000. The climate is wet (1,200 mm on average), with a mean temperature of 9°C in winter and a mean summer temperature of 20°C. The river runs over schists in the upper area, turning into a smooth profile in the middle area of the river, characterized by basic rocks (gabbros and amphibolites). Finally, the lower stretch of the river runs over granite of two micas, followed by biotitic gneiss at the mouth. The land use of the area is a mixed forest of *Eucalyptus globulus*, *Eucalyptus alba*, and *Pinus pinaster* (60% of the total cover), cultivated lands (18%), pastures (12%), scrublands (9%), and urban uses (1%). The sampling areas were mostly shaded by trees and the riparian vegetation is characterized by *Alnus glutinosa* and *Fraxinus excelsior*.

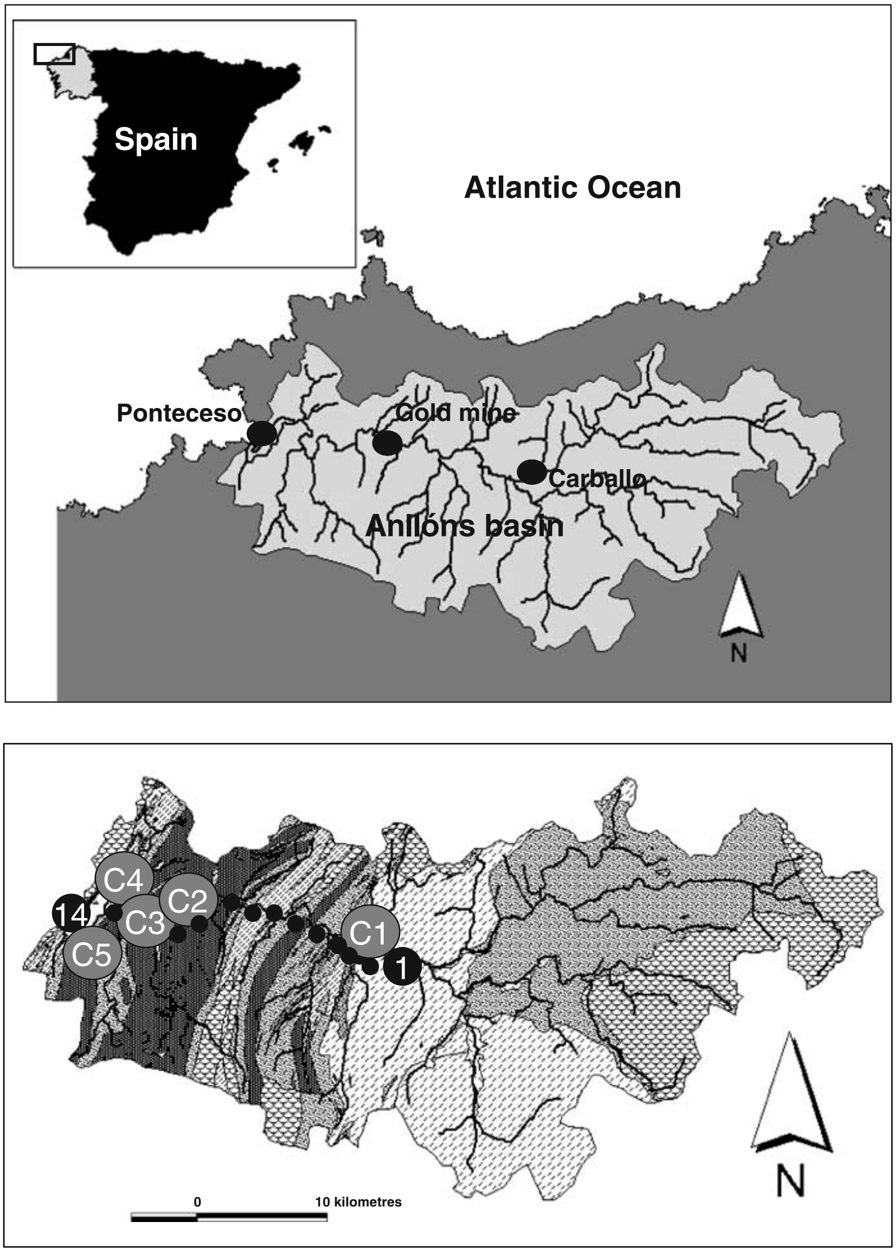

Fig. 1 Anllóns basin localization and geologic map. Surface samples were numbered consecutively from 1 to 14. Core samples were numbered from C1 to C5

The lengthwise profile of the river showed three low slope areas, which are favorable for the sediment deposition. In these depositional areas, 14 superficial samples and five cores were taken, between the locality of Carballo and the river mouth, covering a distance of approximately 30 km (Table 1).

2.2 Methods

Superficial sediment samples were collected from the top 5 cm with a small plastic shovel and taken to the laboratory in hermetic plastic containers. Samples were in a sub-oxic state, with a mean Eh value of 31.5 mV, with the exception of the sample 14, located at the mouth of the river, with a value of −42 mV. Pore waters were separated by centrifugation, and total phosphorus ($P_{T\text{-}PW}$) was determined. Soluble phosphorus ($P_{SOL\text{-}PW}$) was also determined in filtered samples (<0.45 µm). Solid samples were freeze dried, sieved by 2 mm or 63 µm, and analyzed to determine the percentage of fine fraction (FF), total organic carbon (C), nitrogen (N), total phosphorus (P_T), and bioavailable phosphorus (P_{BIO}). Vertical profiles were taken with a Van der Grab corer, split in 2-cm sections, placed into plastic bags, and taken to the laboratory in a fridge. Once in the laboratory, samples were freeze dried and sieved by 2 mm or 63 µm. In these samples were determined total phosphorus (P_T), bioavailable phosphorus (P_{BIO}), percentage of fine fraction (FF), total organic carbon (C), and nitrogen (N).

$P_{T\text{-}PW}$ was determined by means of an acid digestion of the samples with 1 ml H_2SO_4 31% and 0.1 g $(NH_4)_2S_2O_8$ at 120°C during 30 min. P in the extracts was determined by the phosphomolybdenum blue method described by Murphy and Riley (1962). $P_{SOL\text{-}PW}$ was filtered by 0.45 µm and it was colorimetrically determined by following the method described by Murphy and Riley (1962).

With regards to surface sediments, C and the percentage of fine fraction were determined as per Guitián and Carballas (1976). N was determined by wet digestion with H_2SO_4, by using the Kjeldhal method as described in Guitián and Carballas (1976). P_T in surface sediments was determined by means of an acid digestion (HF, H_2SO_4, HCl, 10:1:10) followed by colorimetric determination with molybdenum blue, as described by Murphy and Riley (1962). In relation to the vertical profiles, C and N were determined in an element analyzer (LECO-SC32), based on an infrared detection after combustion of the samples at 1,100°C.

Table 1 List of sampling sites, including surface sediments and vertical profiles (C)

Sites	Distance[a] (km)	Special feature
SED-1	3.19	Close to a wastewater treatment plant upstream
C-1	3.19	Close to a wastewater treatment plant upstream
SED-2	4.11	Proximity of a wastewater treatment plant upstream
SED-3	5.75	Proximity of a wastewater treatment plant upstream
SED-4	7.48	Possible non-point sources coming from domestic drainages
SED-5	8.23	Possible non-point sources coming from domestic drainages
SED-6	9.39	Clean area. Fishing reserve
SED-7	9.71	Clean area. Fishing reserve
SED-8	10.03	Clean area. Fishing reserve
SED-9	10.96	Clean area. Fishing reserve
SED-10	15.49	Past Au mining activities which remobilized As mineralizations
SED-11	16.02	Past Au mining activities which remobilized As mineralizations
SED-12	16.85	Cattle-raising activities. Intensive agricultural area
C-2	27.75	Tidal influence
SED-13	27.75	Tidal influence
C-3	29.50	Estuary. Industrial and urban environment
C-4	29.71	Estuary. Industrial and urban environment
SED-14	29.71	Estuary. Industrial and urban environment
C-5	35.20	Coastline. Shellfish-gathering activities

[a] From the town of Carballo, the nearest settlement upstream

P_T was determined by means of an acid digestion (HNO_3, HF, HCl, 5:1:5) followed by determination with ICP-OES (PerkinElmer, Optima 4300DV). P_{BIO} was determined in surface sediments and vertical profiles by extracting the sediment with NaOH 0.1 M in a 1:1,000 sediment:solution ratio (Wolf et al. 1985).

3 Results

3.1 Pore Waters

$P_{T\text{-}PW}$ showed a mean value of 0.40 mg l^{-1}, with two maxima at sites 3 (0.67 mg l^{-1}) and 6 (0.92 mg l^{-1}) (Table 2). $P_{SOL\text{-}PW}$ showed an average value of 0.06 mg l^{-1} and accounted for 16% to 62% of $P_{T\text{-}PW}$.

3.2 Surface Sediments

With regards to the general properties analyzed, according to the particle size distribution, the samples were classified as very coarse sand. The finest texture corresponded to points 14 and 3 although, even in these sediments, the fine fraction represented only 2.01% and 4.39% of the total sediment. The C concentrations vary between 10.6% at site 1 and 0.6% at site 8. Finally, N varies between 0.84% at sampling site 1 and 0.06% at sampling site 7.

P_T was measured in the whole sediment (<2 mm) ($P_{T\ <2\ mm}$) and in the <63 μm ($P_{T\ <63\ \mu m}$) fraction (Table 3). Comparing both fractions, it can be observed that they follow the same pattern along the basin, with higher P values at point 1 (which receives the effluents of a wastewater treatment plant), followed by a decrease in P values from points 3 to 9, due to the confluence with Vao and Rosende tributaries, which provide clean waters and increase significantly the river flow. Next, another increase at sampling points 10 and 11 puts in manifest the importance of non-point sources of contamination in the basin associated with agricultural activities. However, higher values were obtained in all cases for the $P_{T\ <63\ \mu m}$ fraction, which supposes, on average, twice as much of $P_{T\ <2\ mm}$.

Table 2 Total P concentrations ($P_{T\text{-}PW}$) and soluble P in the pore waters ($P_{SOL\text{-}PW}$)

	$P_{T\text{-}PW}$ (mg l^{-1})	$P_{SOL\text{-}PW}$ (mg l^{-1})
1	0.31	0.01
2	0.51	0.08
3	0.67	0.08
4	0.23	0.05
5	0.37	0.01
6	0.92	0.10
7	0.27	0.08
8	0.21	0.03
9	0.24	0.03
10	0.33	0.04
11	0.41	0.04
12	0.43	0.06
13	0.38	0.07
14	0.31	0.08

On the other hand, P_{BIO} was measured in the <2 mm ($P_{BIO\ <2\ mm}$) and <63 μm ($P_{BIO\ <63<\ \mu m}$) fractions (Table 3). P_{BIO} in bulk and fine fractions showed two maxima at sites 1 and 10. $P_{BIO\ <63\ \mu m}$ concentrations were, in average, twice as much the $P_{BIO\ <2\ mm}$. In addition, P_{BIO} represented between 25% (sampling site 11) and 88% (sampling site 10) of the P_T for the <2 mm fraction, whereas $P_{BIO\ <63\ \mu m}$ represented between 43% (sampling site 3) and 66% (sampling site 11) of the P_T for the <63 μm fraction. This high P bioavailability evidences the risk of pollution which supposes the bed sediments of the Anllóns River.

3.3 Vertical Profiles

P_T was measured in the <2 mm ($P_{T\ <2\ mm}$) and <63 μm ($P_{T\ <63\ \mu m}$) fractions (Fig. 2). $P_{T\ <2\ mm}$ showed a decreasing tendency towards the mouth, with a maxima at site 1, located downstream of the wastewater treatment plant of Carballo. The same behavior was observed for $P_{T\ <63\ \mu m}$ and $P_{BIO\ <2\ mm}$ (Table 4). With regards to each sampling site, vertical profiles C1 to C4 showed the highest values near the surface, with a slight decrease downwards in the top 10 cm, followed by a stabilization of the values from this depth to the end of the core. On the other hand, in C5 was observed an inverse tendency when compared with the other cores analyzed, characterized by a P increase with depth, especially from 40 cm depth to the end of the core. The same pattern was observed for C and N, whereas FF showed the inverse tendency (Fig. 3).

3.4 Statistical Analysis

Statistical analyses were performed by using SPSS v15.0 for Windows (Table 5). On the one hand,

Table 3 Bed sediments total P concentrations in the <2 mm ($P_{T\ <2\ mm}$) and <63 µm ($P_{T\ <63\ \mu m}$) fractions, and bioavailable P in the <2 mm ($P_{BIO\ <2\ mm}$) and <63 µm ($P_{BIO\ <63\ \mu m}$) fractions

Samples	FF (%)	C (%)	N (%)	$P_{T\ <2\ mm}$ (mg kg^{-1})	$P_{BIO\ <2\ mm}$ (mg kg^{-1})	% $P_{BIO\ <2\ mm}$/ $P_{T\ <2\ mm}$	$P_{T\ <63\ \mu m}$ (mg kg^{-1})	$P_{BIO\ <63\ \mu m}$ (mg kg^{-1})	% $P_{BIO\ <63\ \mu m}$/ $P_{T\ <63\ \mu m}$
1	0.45	10.6	0.84	2,324	877	38	2,079	1,221	59
2	0.56	0.9	0.07	611	321	53	1,721	848	50
3	2.01	3.4	0.22	731	494	68	2,296	980	43
4	0.57	1.0	0.06	685	302	44	1,653	870	53
5	0.24	1.0	0.06	588	287	49	1,783	1,005	56
6	0.49	3.7	0.28	804	512	64	1,677	791	47
7	0.22	0.3	0.06	435	212	49	1,140	672	59
8	0.23	0.6	0.11	604	289	48	1,123	669	60
9	0.24	2.0	0.16	394	205	52	941	500	53
10	0.68	4.0	0.31	434	382	88	2,527	1,377	55
11	0.24	3.3	0.09	1,122	284	25	1,505	988	66
12	0.54	3.3	0.21	676	350	52	1,492	733	49
13	0.46	2.2	0.33	933	403	43	1,402	696	50
14	4.39	1.7	0.33	965	520	54	1,034	535	52

Table shows also the concentrations of total organic carbon (*C*), nitrogen (*N*), and percentage of fine fraction (*FF*)

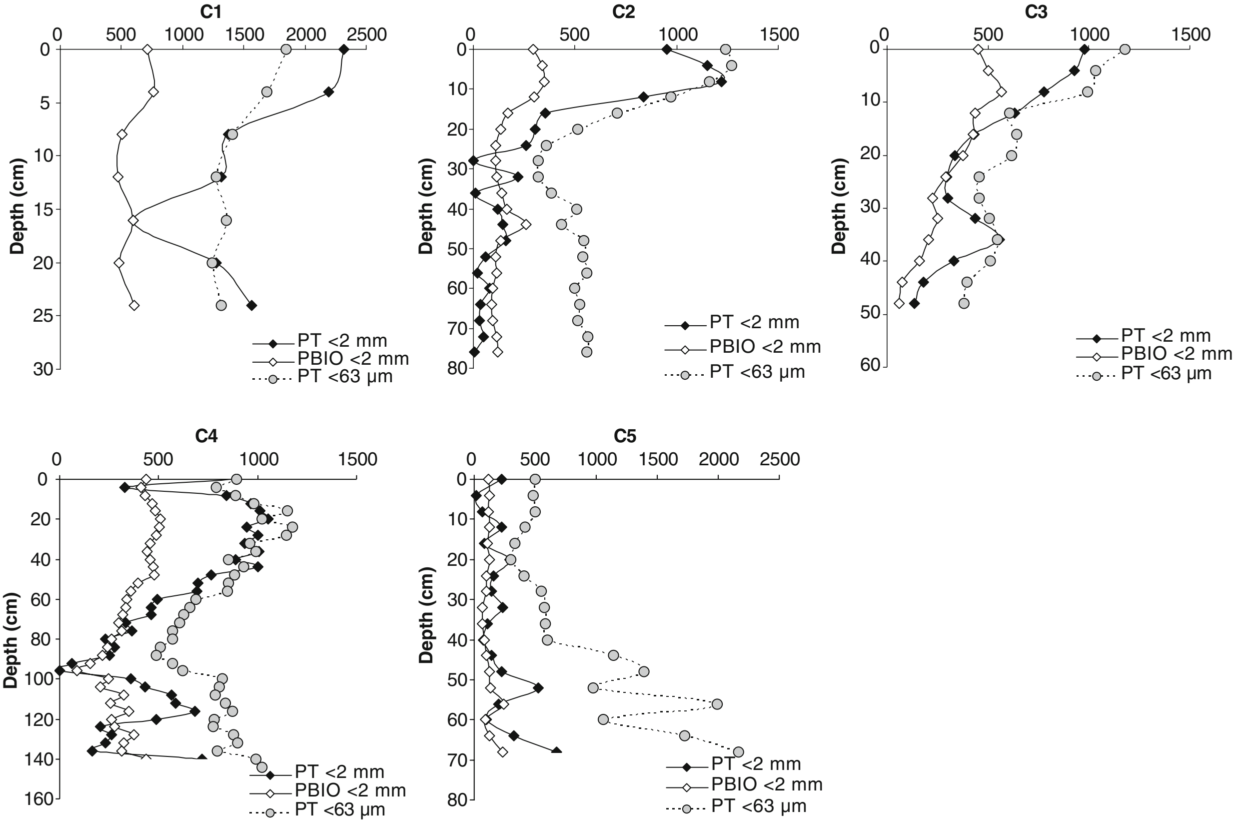

Fig. 2 Vertical distributions of total P along the cores in the <2 mm ($P_{T\ <2\ mm}$) and <63 µm ($P_{T\ <63\ \mu m}$) fractions, and bioavailable P in the <2 mm fraction ($P_{BIO\ <63\ \mu m}$)

Table 4 Summary of the main properties analyzed

	$P_{T\ <2\ mm}$	$P_{T\ <63\ \mu m}$	$P_{BIO\ <2\ mm}$	C	N	FF
C1	1,520 [2,316–600]	1,447 [1,845–1,241]	589 [763–475]	7.9 [11.9–5.8]	0.5 [0.8–0.4]	39 [47–30]
C2	315 [1,220–5]	624 [1,272–319]	168 [350–89]	3.2 [6.0–2.2]	0.2 [0.4–0.1]	63 [75–16]
C3	486 [979–135]	642 [1,181–381]	310 [569–59]	4.3 [5.5–3.3]	4.3 [0.4–0.2]	77 [86–44]
C4	580 [1,055–n.d.]	826 [1,175–486]	355 [507–89]	4.8 [6.7–0.9]	0.3 [0.5–0.03]	57 [83–10]
C5	212 [678–17]	873 [2,167–304]	122 [240–64]	1.8 [3.5–0.3]	0.1 [0.1–n.d.]	12 [28–3]

For each vertical profile are shown the average value and the maximum and minimum values (in square brackets)

n.d. not detected

significant statistical correlation was found between $P_{T\text{-}PW}$ and $P_{SOL\text{-}PW}$ ($r^2=0.615$; $p<0.05$). However, no significant correlation was found between $P_{T\text{-}PW}$ and P_T, neither in the <2 mm fraction nor in the <63 µm fraction.

With regards to the surface sediments, $P_{T\ <2\ mm}$ showed significant correlations with C ($r^2=0.850$; $p<0.01$) and N ($r^2=0.838$; $p<0.01$), whereas no correlation was found between $P_{T\ <63\ \mu m}$ and C or N, which suggests that these components of the organic matter of the sediment favor the P accumulation in the <2 mm fraction acting as coatings formed onto the coarser particles. Also, the bioavailable fraction is positively correlated ($r^2=0.859$; $p<0.05$) with the total P fractions. Nevertheless, the percentage of FF did not show significant effects in the P distribution along the watercourse.

In relation to the vertical profiles, positive significant correlations were found in all the cores between $P_{T\ <2\ mm}$ and $P_{T\ <63\ \mu m}$. From C1 to C4, C and N are positively correlated with the P content of the sediments. In contrast, C5 showed a negative correlation between P content and C and N. In this core (C5), approximately the top 30 cm are regularly submitted to shellfish-gathering activities which produce an increase and homogenization in the organic matter. Significant negative correlations were found between P concentrations in both size fractions and the percentage of FF in C2, C3, and C5. Finally, C4 and C5 have in common a great variability in the bottom layers (below 100 cm in C4 and 40 cm in C5). In fact, a C/N ratio=31 is found at this depth in C4. This C/N ratio is a typical value of organic matter with cellulosic structure, coming from terrestrial plants (Zepp 1987; Lamb et al. 2006).With regards to the carbon and nitrogen content, Moreira et al. (2004) explained this high variability at 90 cm in lake sediments due to the presence of vegetal fragments and charcoal particles.

4 Discussion

In this study, no significant correlation was found between $P_{T\text{-}PW}$ and P_T in surface sediments, which can be attributed to the concentration of P in equilibrium

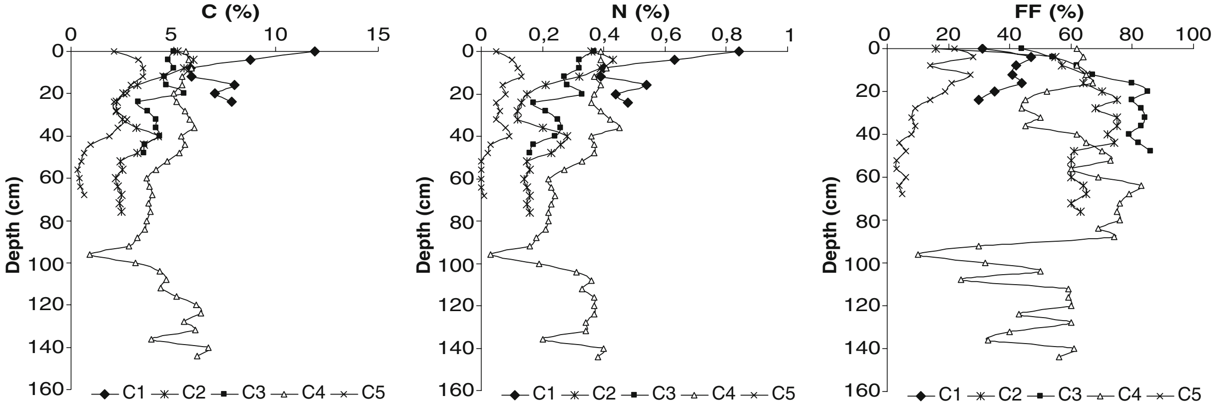

Fig. 3 Vertical distribution of C, N, and fine fraction (*FF*) in the <2 mm fraction

Table 5 Correlation coefficients for pore water, surface sediments, and vertical profiles

	$P_{\mathrm{SOL\text{-}PW}}$	$P_{\mathrm{T}\ <2\ \mathrm{mm}}$	$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$	$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$	$P_{\mathrm{BIO}\ <63\ \mu\mathrm{m}}$	C	N	FF
Pore waters								
$P_{\mathrm{T\text{-}PW}}$	0.615*							
Surface sediments								
$P_{\mathrm{T}\ <2\ \mathrm{mm}}$		1.000		0.704**		0.850**	0.838**	
$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$			1.000	0.634*	0.914**			
$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$				1.000	0.614*	0.850**	0.902**	
$P_{\mathrm{BIO}\ <63\ \mu\mathrm{m}}$					1.000	0.575**		
C						1.000	0.907**	
N							1.000	
FF								1.000
Vertical profiles								
C1								
$P_{\mathrm{T}\ <2\ \mathrm{mm}}$		1.000	0.800*					
$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$			1.000	0.859*		0.844*	0.916**	
$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$				1.000		0.798*	0.835*	
C						1.000	0.984**	
N							1.000	
FF								1.000
C2								
$P_{\mathrm{T}\ <2\ \mathrm{mm}}$		1.000	0.917**	0.911**		0.892**	0.872**	−0.509*
$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$			1.000	0.854**		0.873**	0.882**	
$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$				1.000		0.945**	0.947**	
C						1.000	0.992**	−0.465*
N							1.000	−0.478*
FF								1.000
C3								
$P_{\mathrm{T}\ <2\ \mathrm{mm}}$		1.000	0.938**	0.807**		0.621*	0.824**	−0.901**
$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$			1.000	0.820**		0.701**	0.862**	−0.920**
$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$				1.000		0.736**	0.813**	−0.738**
C						1.000	0.936**	−0.554*
N							1.000	−0.716**
FF								1.000
C4								
$P_{\mathrm{T}\ <2\ \mathrm{mm}}$		1.000	0.786**	0.868**		0.594**	0.748**	
$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$			1.000	0.781**		0.685**	0.762**	
$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$				1.000		0.714**	0.782**	
C						1.000	0.945**	
N							1.000	
FF								1.000
C5								
$P_{\mathrm{T}\ <2\ \mathrm{mm}}$		1.000	0.570*	0.564*		−0.478*	−0.513*	
$P_{\mathrm{T}\ <63\ \mu\mathrm{m}}$			1.000	0.716**		−0.821**	−0.753**	−0.679**
$P_{\mathrm{BIO}\ <2\ \mathrm{mm}}$				1.000				
C						1.000	0.934**	0.811**
N							1.000	0.748**
FF								1.000

Table displays only significant correlations. *Significant correlations at 0.05 level (bilateral); **significant correlations at 0.01 level (bilateral)

(EPC) (Taylor and Kunishi 1971). $P_{T\text{-}PW}$ obtained in the present study exceeds the EPC values obtained in a previous study by Rubinos et al. (2003) (0.032–0.072 mg l^{-1}), thus indicating that the bed sediments may be actively adsorbing P from the pore waters. Consequently, as the adsorbing capacity of the sediments was not reached, $P_{T\text{-}PW}$ concentrations were low and almost negligible in the case of $P_{SOL\text{-}PW}$.

In this study, superficial samples (0–5 cm) were taken as it is considered the active layer under the water–sediment interface, which takes part in adsorption/desorption reactions and that can be easily resuspended. Wang et al. (2003) define this active layer as the depth of the sediment affected by bioturbation and potential to the flux towards the water column. This active layer takes part in P interchange between sediments and water. Additionally, sampling of surface sediments supposes an approximation of the sediments which could be resuspended.

Taking this into account, for surface sediments, an average value of 808 mg kg^{-1} was found for $P_{T\ <2\ mm}$, and an average value of 1,600 mg kg^{-1} was found for $P_{T\ <63\ \mu m}$. These concentrations can be compared with those found by Owens and Walling (2002) in the <63 µm fractions which oscillate between 500 and 1,500 mg kg^{-1} for bed sediments in the Swale River. In the Catatumbo River (Venezuela), bulk bed river sediments had P concentrations ranging between 64 and 1,305 mg kg^{-1} (Rivas et al. 2000).

An attempt to evaluate sediment quality can be made by examining the Canadian Quality Sediment Guidelines which consider that a sediment is contaminated if P_T is equal or higher than 2,000 mg kg^{-1} (severe effect) and that can affect the health of the digger organisms (Persaud et al. 1993), whereas values up to 600 mg kg^{-1} are considered to exert lowest effects, and no effects related to the health of the digger organisms are considered below this value. This value was established for bulk sediments, and the Guidelines include a factor to correct P content according to different fractions. According to this value, in the $P_{T\ <2\ mm}$ fraction, sampling site 1 shows a severe concentration level, whereas sampling sites 2, 3, 4, 6, and 11–14 reached the lowest effect level. With regards to the $P_{T\ <63\ \mu m}$ fraction, sampling sites 1, 3, and 10 show severe concentration level, whereas sampling sites 2–14 show lowest effect level. In what concerns the sediment cores, only superficial layers of C1 reach the severe concentration level, whereas most of the samples of the vertical profiles showed moderate P concentration levels.

In relation to the spatial distribution, P_T presents two maxima across the river. The first, at sampling site 1, is located downstream of a wastewater treatment plant, which provides effluents rich in detergents and other sewage sludge. The second maximum corresponds to sampling sites 10 and 11, located near an agricultural area and cattle-raising activities. With regards to P variation along the watercourse, Owens and Walling (2002) studied the P contamination in a rural basin and in an industrialized basin. Similarly to the present study, in the rural basin no increase in P was observed across the basin, whereas Owens and Walling (2002) found that, in the industrialized basin, P_T increased downstream.

In this study, the bioavailable P was also analyzed by extracting it with a low sediment:solution ratio (Sagher 1976; Dorich et al. 1980; Dorich et al. 1985) which is supposed to be an adequate estimation of the bioavailable P to algae. This bioavailable P can be defined as the sum of the P immediately bioavailable and the P that can be transformed into a bioavailable form by natural chemical (e.g., dissolution and desorption) and biological processes (e.g., enzymatic degradation) (Boström et al. 1988). The high percentages of P_{BIO} with respect to P_T evidence the risk of pollution which supposes the bed sediments of the Anllóns River. The percentage of P_{BIO} with respect to P_T stays relatively stable throughout the river, with little variations at points affected by non-point (sampling sites 3 and 6) and by point sources of contamination (sampling sites 10 and 11). In this sense, Mainstone and Parr (2002) found that point sources usually contain highly bioavailable P derived from sewage treatment works, whereas diffuse sources of contamination are highly delivered from surface run-off, whose bioavailability is more complicated and highly seasonal.

Finally, the vertical profiles analyzed showed, from C1 to C4, an increase of P in the surface layers. This pattern has been observed also by Wu et al. (2008) which attribute this superficial P increase to the higher human impact over the zone in the last century, due to the generalized use of artificial fertilizers, especially since the 1950s. This fact was observed also by Zhang and Shan (2008) in sediments of an agricultural watershed, with superficial P values up to

400 mg kg^{-1}, which stated that this increased surface P concentrations could reach the maximum sorption capacity of the sediments, thus leading to a water deterioration in the watershed and downstream. On the other hand, Vaalgamaa and Conley (2008) which studied sediment cores in estuaries, detected P concentrations around 4,000 mg kg^{-1}, and related this P enrichment not only to the use of artificial fertilizers, but also to the changes in the land use. These authors studied that the new forestry practices introduced in Finland in the 1960s such as extensive draining, clear cutting, and forest fertilization contributed significantly to the P transfer from terrestrial to aquatic ecosystems. In the Anllóns River, it was determined that the suspended and bed sediments showed an enrichment in relation to the soils of the basin. Also, the soils which contributed with the highest P concentrations were those allocated to cultivation and pasture, related to the amendments and fertilizer contribution (Iglesias et al. 2008).

As an exception for the P general increase in surface layers, C5, collected in the estuary, showed the inverse tendency. This behavior was observed also by Sahu et al. (2007), who explained that the P decrease in the upper layers could be associated with the phosphatase activity related to the presence of actinomycetes in surface, which produced an appreciable quantity of P to be leached into the medium in estuarine environments. Also, bioturbation by digger organisms was identified by Holdren and Armstrong (1980) as the parameter having the greatest effect on P release rates, which may be sufficient to perpetuate a eutrophic condition if the P loading from external sources is significantly reduced. An additional parameter controlling P release in estuaries is the local shellfish production, which was identified by Schmidt et al. (2007) as the key parameter that influences bioturbation through biodeposition. In this sense, Pennifold and Davis (2001) found significant correlations between the macrofaunal biomass and the nutrient fluxes in the Swan River Estuary, the macrofauna that most affected the nutrient cycling being polychaetes and molluscs. This may happen preferentially in summer, where the pore system formed because of the burrows of the macrofauna favors the penetration of oxygen to deeper layers and the flux of nutrients therein. Garmendia et al. (2003) found in other Galician Rias (Ares and Betanzos) a predominance of polychaetes mainly near the surface, whereas molluscs, crustaceans, and echinoderms become important with depth.

5 Conclusions

In this study, spatial and temporal P variations were evaluated along the Anllóns River (NW Spain). In the samples, total and bioavailable P was analyzed in the pore waters, surface sediments, and in the vertical profiles. In the case of the solid samples, the <2 mm and the <63 μm fractions were analyzed. Low concentrations of P in the pore waters were observed along the watercourse. Instead, the bed sediments showed high P concentrations which reach the Severe Effect threshold at site 1 (in the <2 mm fraction) and sites 1, 3, and 10 (in the <63 μm fraction). This Severe Effect was defined by the Canadian Quality Sediment Guidelines as P concentrations over 2,000 mg kg^{-1}, which can affect the health of the digger organisms. In the samples analyzed, the <63 μm showed approximately twice as much the concentrations of the <2 mm fraction. However, at the sampling points most heavily contaminated, the concentration of both fractions becomes similar, thus indicating that, at these sites, the coatings formed over sands can retain important P concentrations in the bed sediments. The percentage of bioavailable P with respect to total P stays relatively stable throughout the River, with little variations at points affected by non-point (sites 3 and 6) and by point sources of contamination (sites 10 and 11). However, the high bioavailable to total P ratios evidences the potential risk of pollution which supposes the sediments of the Anllóns River. With regards to the vertical profiles C1 to C4, an increase of P was observed in the surface layers, which could be attributed to the increased use of fertilizers in the last decades. As a contrary, P concentration in C5 (estuary) showed a homogenization in P values in the surface values which was tentatively attributed to bioturbation.

Acknowledgements The present study was financed by the Science and Education Ministry of Spain (MEC, REN 2003-08673/BES-2004-5894). Rosa Devesa-Rey was granted with a FPI grant.

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