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Spatial Evolution of Phosphorus Fractionation in the Sediments of Rhumel River in the Northeast Algeria

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Abstract

The objective of the present study is the characterization of the spatial evolution of phosphorus forms in sediments of Rhumel River located in northeast Algeria during winter conditions. Sediments samples were collected along the river in Constantine city during the year 2012. The samples were subjected to physicochemical characterization and metals analysis. Phosphorus was fractionated by sequential extractions procedure in exchangeable, oxyhydroxides bound; calcium bound; organic and residual fractions.

The distribution of the different forms of phosphorus in the sediments appears to be influenced by the physicochemical characteristics, which depend on the sampling location. Phosphorus speciation along the river is characterized by the predominance of inorganic phosphorus forms. The exchangeable fraction is the lowest. Phosphorus concentration in this fraction does not exceed 20 mg/kg. The fraction bound to calcium is the most important in retaining inorganic phosphorus with concentrations varying from 328 to 490 mg/kg. Phosphorus bound to oxyhydroxides represents an average of 172 mg/kg. Along the river, the contribution of the different fractions in the phosphorus retention follows the order: exchangeable < bound to oxyhydroxides ~ organic < bound to calcium < residual. As estimated by the sum of exchangeable, bound to oxyhydroxides and bound to organic matter, an average of about 28% of the total phosphorus can become bioavailable. The predominant fraction in the Rhumel sediments changes from residual at upstream Constantine city to bound to calcium at downstream from it.

Keywords: phosphorus, fractionation, mobility, sediment, Rhumel

1. Introduction

Phosphorus is an essential element in the functioning of aquatic ecosystems, it is considered as one of the major nutrients required by primary producers (Liu et al., 2012). However, it is also identified as a key nutrient responsible for eutrophication of aquatic environments which has become a serious environmental problem. Phosphorus is naturally present in the aquatic environment. It has various natural sources including leaching from rocks, drainage of forests and soil erosion. During the last century, the amount of phosphorus in freshwater has been greatly increased and amplified by human influence through industrial, agricultural and domestic activities. Sediments play an important role in the phosphorus cycle; they can adsorb large quantities of it and can also release it into the overlying water column when the concentration in water decreases and/or under the conditions of strong water dynamic or change of redox potential (Yang & He, 2010). The nature of the chemical and physical links of phosphorus with sediments is the most important factor that governs its release. The mechanisms involved can be of chemical or biological nature or a combination of both (Slomp, Van Raaphorst, Malschaert, Kok, & Sandee, 1993). Generally, phosphorus in sediments can be adsorbed by Fe, Al and Mn oxihydroxides, tied in organic substances and bound to calcium (Balzer, 1986). The mobilization of phosphorus can be affected by many factors such as temperature, dissolved oxygen, pH and the nature of the sediments (Hasnaoui et al., 2001). Under anoxic conditions, the release of the chemically bound phosphorus is due to

reduction of iron oxides (Sallade & Sims, 1997), mineralization of organic matter (Golterman, 1995) and acidification of sediments (Golterman, 1998).

The main objective of the present work is the evaluation of phosphorus mobility in the sediments of Rhumel River which traverses Constantine city in eastern Algeria. In our knowledge no such study has been undertaken in the area.

2. Material and Methods

2.1 Study Site

Rhumel River is located in the northeastern Algeria (Figure 1). It originates from the northwestern Bellaa in Setif. It traverses the high plains of Constantine, with an orientation southwest - northeast until Constantine city. Then, it suddenly changes the direction and turns to the right and flows obliquely towards the northwest (Mébarki, 1984), it confluences with the Oued Endja around Sidi Merouene in Mila town. The main tributary of the river is Oued Boumerzoug which drains industrial and urban zones.

The climate of the area is a semiarid type; characterized by wet winters and dry and hot summers. The quality of the river water is characterized by neutral to alkaline pH and high electrical conductivity.

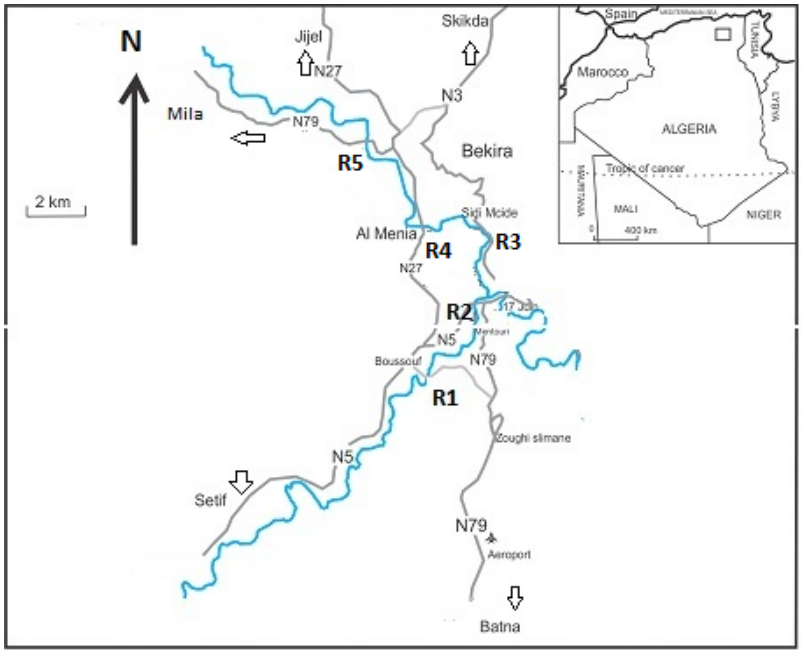

Figure 1. Localization of the Rhumel River and the sampling stations

2.2 Samples Collection and Pretreatment

The studied sediments were collected at five stations along the river (Figure 1, Table 1) in January 2012. Samples were placed in plastic bags and transported to the laboratory where they were dried at 40 °C then ground and sieved using a 0.215 mm sieve and conserved in polyethylene bottles until use.

Table1. Localization of the sampling stations

Location	Latitude	Longitude
R1	36°19'37.15"N	6°35'37.65"E
R2	36°20'53.45"N	6°36'49.61"E
R3	36°22'22.80"N	6°36'41.47"E
R4	36°22'22.90"N	6°35'32.63"E
R5	36°23'57.79"N	6°34'15.50"E

2.3 Physicochemical Characterization

Measurements of pH and electrical conductivity were performed in suspensions formed with distilled water. Organic matter was determined by loss on ignition at 550 °C. The total phosphorus was extracted with HCl (3.5 M) after calcination. Phosphorus was measured in extracts by UV-visible spectrophotometry using the method of Murphy and Riley (1962). In this method, orthophosphate ions react with molybdate to form a yellow phosphomolybdic complex. Ascorbic acid specifically reduced the phosphomolybdic complex to give a blue color. The absorbance was measured at 700 nm with a spectrophotometer Shimadzu UV-1650PC. The metals were determined after calcination and acid digestion by flame atomic absorption using an atomic absorption spectrometer Varian AA140.

2.4 Fractionation of Phosphorus in Sediments

The different forms of phosphorus were extracted using the fractionation procedure described by Hieltjes and Lijklema (1980). The target phases and the reagents used are illustrated in Table 2. Phosphorus in all extracts was determined by the method described above. All results are average values of triplicate determinations.

Table 2. Sequential extractions procedure

Target fraction	Extraction reagent
Exchangeable	NH_4Cl (1 M) 2 h shaking
Bound to oxyhydroxides	NaOH (1 M) 16 h shaking
Bound to calcium	HCl (0.5 M) 16 h shaking
Organic	Calcination at 550 °C 3 h,
	HCl (1 M) 16h shaking

3. Results and Discussion

3.1 Physicochemical Characterization

The physicochemical results are presented in Table 3. The sampled sediments have an alkaline pH reflecting the dominance of limestone and clay and the buffering capacity associated with these sedimentary materials (Nassali, Ben bouih, & Srhiri, 2002). At the first sampling station (R1), the lowest pH and the highest electrical conductivity are observed, showing the effect of the industrial zone located upstream. Generally, high values of electrical conductivity of the sediments are due to the enrichment by monovalent and divalent ions (Nassali et al., 2002). The low water contents reflect a low fluidity of these sediments (Abdallaoui, Derraz, Bhenabdallah, & Lek, 1998). The important organic matter contents ranging from 4% to 6% are probably due to the degradation of dead cells of the fauna and flora within the River and leaching of surrounding soils (Abdellaoui, 1998).

Calcium is the most abundant element in the studied sediments. The measured concentrations of this metal ranged from 134.48 g/kg to 182.35 g/kg. The Rhumel sediments are quite rich in iron and aluminum. The concentrations of the two metals vary between 15 g/kg – 20 g/kg and 13 g/kg – 18 g/kg respectively. Generally, the metals concentrations in the Rhumel sediments follow the order Mn < Al < Fe < Ca. Along the river, only calcium and manganese show a linear correlation in their spatial evolution (R: 0.86). Concentrations of total phosphorus vary from one site to another. The higher contents are observed at the two stations R1 and R4 located downstream the industrial zone and Constantine city respectively. Along the river, phosphorus is correlated with organic matter. The spatial evolution of its total concentration shows a decrease downstream. Phosphorus concentrations found in this study are similar to those measured in Oued D'Kor (1287 mg/kg) and Oued Beht (1343 mg/kg) in Morocco (Abdallaoui, 1998).

Table 3. Physicochemical analysis of sediments of Rhumel River

Sample	R1	R2	R3	R4	R5
pH	7.75	8.34	8.11	8.00	8.01
Electrical Conductivity(µs/cm)	1703	482	488	786	792
Water content (%)	3.25	2.61	2.05	1.31	0.89
Loss on ignition (%)	8.76	6.84	7.23	7.48	5.23
Total phosphorus (mg/kg)	1568	1140.29	1337.74	1547.98	1115.13
Ca (g/kg)	146.01	182.35	134.48	143.77	141.86
Fe (g/kg)	15.66	16.97	17.95	19.61	20.77
Al (g/kg)	18.43	15.66	12.95	14.58	13.70
Mn (mg/kg)	324.50	367.34	245.28	261.04	234.38

3.2 Fractionation of Phosphorus in Sediments

The used sequential fractionation scheme (Hieltjes & Lijklema, 1980) allowed us to distinguish five fractions: soluble phosphorus; phosphorus bound to iron, aluminum and manganese oxyhydroxides; phosphorus bound to calcium; organic phosphorus and residual fraction. The last fraction is calculated as the difference between total phosphorus and the sum of the four other fractions.

3.2.1 Spatial Evolution of Soluble Fraction

The exchangeable fraction represents mineral fraction adsorbed on exchange sites (Hieltjes & Lijklema, 1980), directly assimilated by algae. It is the most available fraction. In the Rhumel sediments (Figure 2), the soluble phosphorus does not exceed 20 mg/kg. The highest value is observed at the sampling station R4 and can be attributed to the settlement of finer particles due to slower water flow (Yang, He, Lin, & Stoffella, 2010). Low values of soluble phosphorus concentration have also been found in other studies (Salvia-Castellvi, Scholer, &Hoffmann, 2002; Taoufik & Dafir, 2002; Taoufik, Kemmou, Loukili Idrissi, & Dafir, 2004; Kemmou, Dafir, Wartiti, & Taoufik, 2006).

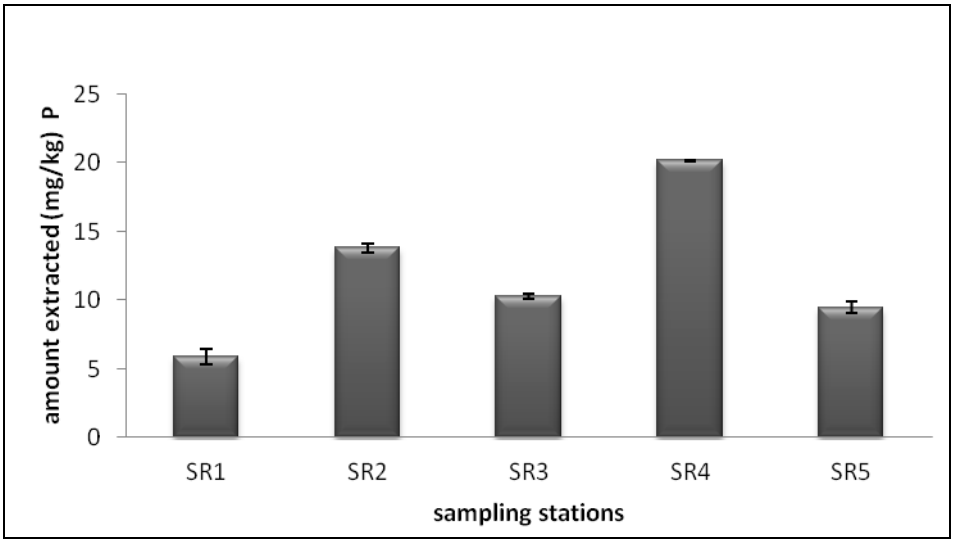

Figure 2. Spatial evolution of the exchangeable fraction

3.2.2 Spatial Evolution of the Fraction Bound to Oxyhydroxides

In the sediments, phosphorus is frequently associated with Fe, Al and Mn oxides and hydroxides (Pardo, Lopez-Sanchez, & Rauret, 2003). This fraction plays an important role in phosphorus exchange at the sediment-water interface (Kemmou et al., 2006). It is easily mobilized and is responsible for an increase of eutrophication (Zhou, Gibson, & Zhu, 2001). In the Rhumel sediments, concentrations of phosphorus extracted by NaOH ranged from 130 mg/kg to 221 mg/kg (Figure 3). The spatial evolution of this fraction shows that phosphorus is more closely related to Fe than Al and Mn. Consequently, anoxic conditions mediated by bacteria result in the release of sorbed phosphorus from iron oxyhydroxides. The Fe/P ratio of 2 has been regarded as a threshold of phosphorus saturation in soil or sediments (Blomqvist, Gunnars, & Elmgren, 2004). Elsewhere, the molar ratio P/(Fe+Al) has been considered as a better indicator of the potential availability of phosphorus in river sediments (Nair, Portier, Graetz, & Walker, 2004). In the present study, Fe/P ratios are above 2; the highest calculated value concern the sediments collected downstream from Constantine city. The calculated P/(Fe+Al) molar ratios vary around 0.05 implying the importance of phosphorus immobilization along the river.

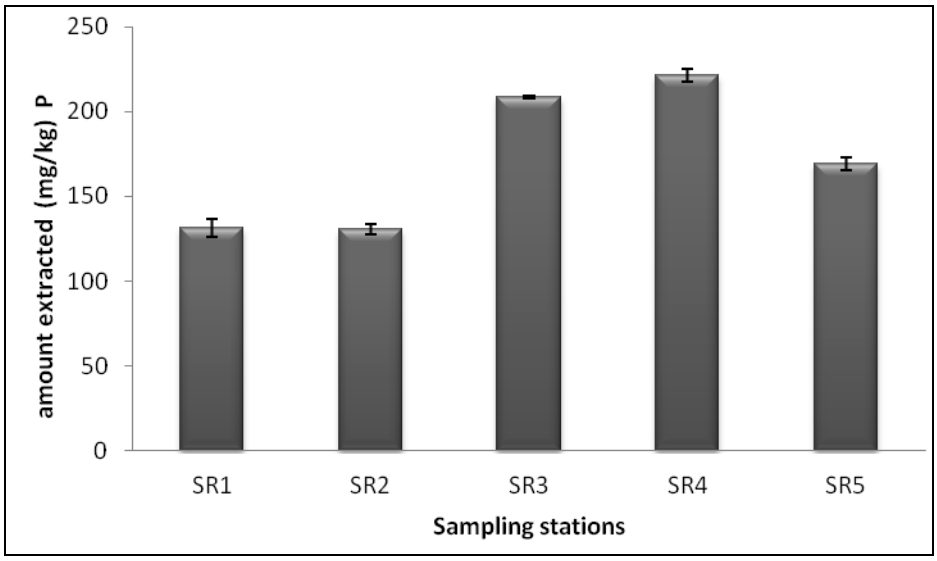

Figure 3. Spatial evolution of oxyhydroxides bound fraction

3.2.3 Spatial Evolution of the Fraction Bound to Calcium

This fraction is sensitive to low pH. It is assumed to be composed mainly of calcium bound phosphorus as apatite such as $Ca_5(PO_4)_3(OH, F, Cl)$ and phosphorus bound to calcium carbonate. The first fraction is highly insoluble and redox-insensitive; it can only be attacked by strong acids (Smolders et al., 2006). The Rhumel sediments are characterized by high concentrations of phosphorus bound to calcium varying from 328.35 mg/kg to 490.79 mg/kg (Figure 4). This is related to the significant calcium contents (Table 2). According to Golterman (1995), when sediments are acidified a part of the phosphorus bound to calcium carbonate might be solubilized. In the present study, pH does not vary significantly. Consequently, this fraction is the most uniform along the river. Generally, phosphorus bound to calcium is considered as the main route of permanent storage of phosphorus in sediments and soils (Gonsiorczyk, Casper, & Koschel, 1998). This fraction is released from sediments with difficulty. Consequently, it is not easily used by algae (Kozerski & Kleeberg, 1998; Kaiserli, Voutsa, & Samara, 2002).

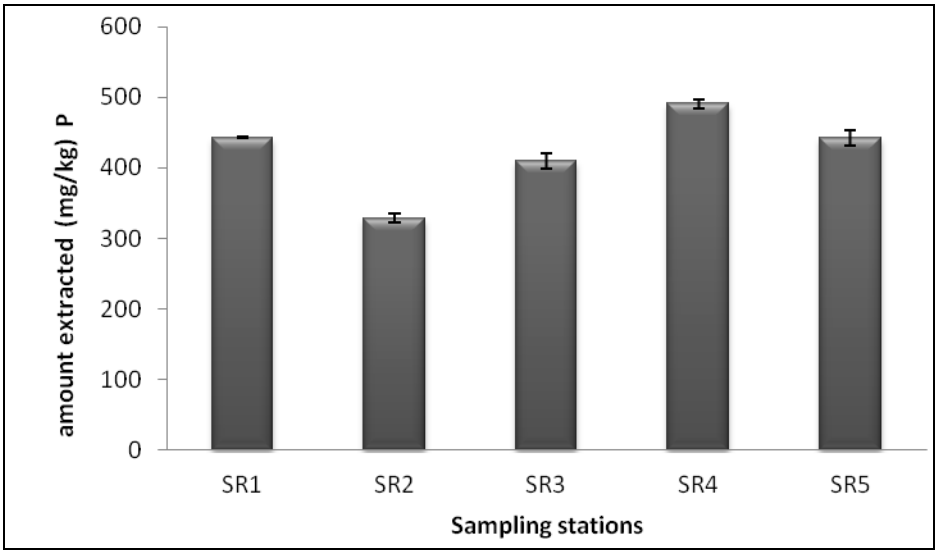

Figure 4. Spatial evolution of calcium bound fraction

3.2.4 Spatial Evolution of Organic Fraction

In the studied sediments, concentrations of organic phosphorus are lower than those of inorganic phosphorus (Figure 5). The spatial distribution of this fraction is generally similar to that of the organic matter. At the sampling stations located in the urban area (R2, R3, R4), a marked increase in organic phosphorus is observed. An increase in the organic matter amount of the sediment leads to an increase in the amount of associated phosphorus. It has been suggested that organic phosphorus in sediments is predominantly associated with humic material by complexation and chelation reactions involving metallic cations (Garcia & de Iorio, 2003). The complexes of organic matter with iron can also adsorb phosphorus (Kemmou et al., 2006). Under anoxic conditions, the organic fraction can become bioavailable after sediments mineralization.

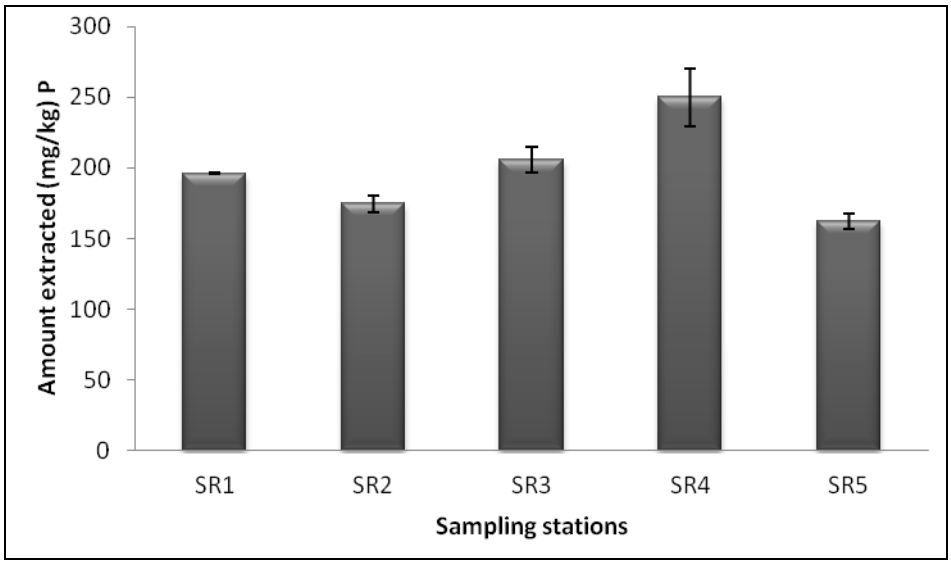

Figure 5. Spatial evolution of organic fraction

3.2.5 Distribution of Phosphorus in the Sediments

The speciation of sedimentary phosphorus in Rhumel River (Figure 6), show that it is mostly in inorganic forms. Along the river, the exchangeable form is the lowest compared to the other fractions. Phosphorus availability in the Rhumel sediments appeared to be related to phosphorus sorption by oxyhydroxides and complexation with organic material. Upstream the confluence with Boumerzoug tributary (R1, R2), the contribution of the organic

fraction is more important than the one of the oxyhydroxides. However at downstream, the two fractions are closer. The fraction related to calcium is the most important part of the inorganic phosphorus. It has been suggested that the high phosphorus contents of this fraction could be also explained by the fact that a part of phosphorus extracted with NaOH is readsorbed on calcium (De Groot, & Golterman, 1990). In addition, a part of the organic fraction can be solubilized by acid extraction resulting in an overestimation of the phosphorus amount extracted during this step. The contribution of the residual fraction decreases along the river. In this fraction, phosphorus can be associated to crystalline iron oxides, silicates (Buffle, de Vitre, Perret, & Leppard, 1989) and crystalline aluminum-silicate species (Jonsson, 1997). The predominant phosphorus fraction in the Rhumel sediments changes from residual at upstream of Constantine city to bound to calcium downstream from it.

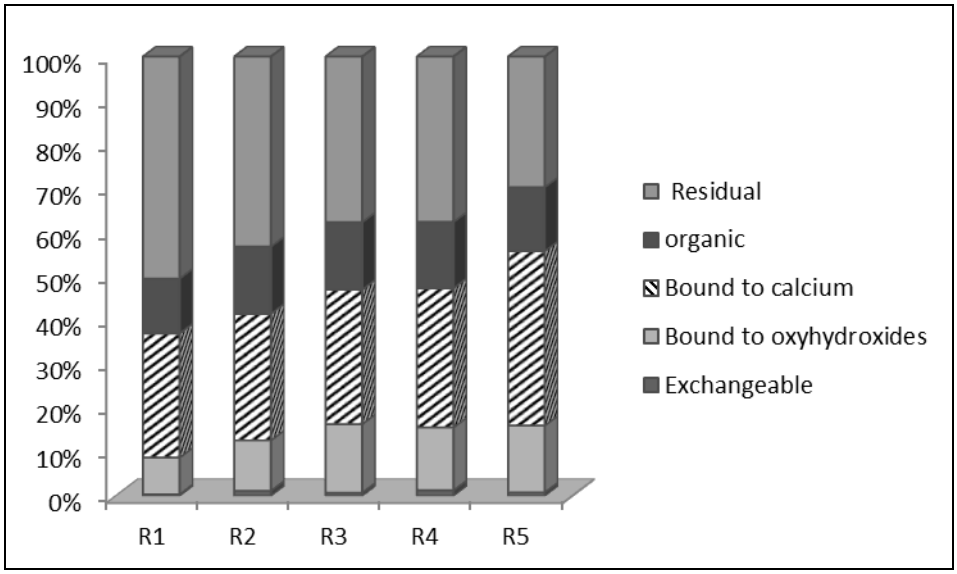

Figure 6. Spatial evolution of phosphorus distribution in Rhumel sediments

4. Conclusion

Sedimentary phosphorus in Rhumel River is mainly inorganic. The fraction directly available is the lowest. The two fractions, residual and bound to calcium considered as permanents, are the most important. As estimated by the sum of exchangeable, bound to oxyhydroxides and bound to organic matter, about 28% of the total phosphorus in Rhumel sediments can become bioavailable.

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