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Influence of the hyporheic zone on the phosphorus dynamics of a large gravel-bed river, Garonne River, France

Philippe Vervier,[1,2] Sonia Bonvallet-Garay,[1,2] Sabine Sauvage,[1,2]*, H. Maurice Valett[3] and José-Miguel Sanchez-Perez[1,2]

[1] CNRS, Laboratoire d'Ecologie Fonctionnelle (ECOLAB), Ecole Nationale Supérieure Agronomique de Toulouse (ENSAT), Avenue de l'Agrobiopole BP 32607, Auzeville Tolosane 31326, Castanet-Tolosan Cedex, France
[2] Université de Toulouse, INP, UPS, ECOLAB (Laboratoire d'Ecologie Fonctionnelle), Ecole Nationale Supérieure Agronomique de Toulouse (ENSAT), Avenue de l'Agrobiopole BP 32607, Auzeville Tolosane 31326, Castanet-Tolosan Cedex, France
[3] Department of Biological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

Abstract:

Phosphorus (P) concentrations in sediments and in surface and interstitial water from three gravel bars in a large river (Garonne River, southern France) were measured daily, downstream of a wastewater treatment plant for a city of 740 000 inhabitants (Toulouse). Measurements were made of vertical hydraulic gradient (VHG), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP) and total phosphorus (TP) in water and of three extractable forms of phosphorus (water extractable, NaOH extractable and H_2SO_4 extractable) in hyporheic sediments from the gravel bars. Dissolved phosphorus was the major contributor to TP (74–79%) in both interstitial and surface waters on all sampling dates, and in most cases surface water P concentrations were significantly higher than interstitial concentrations. Hyporheic sediment TP concentrations ranged between 269 and 465 $\mu g\ g^{-1}$ and were highest in fine sediment fractions. Acid-extractable P, a non-bioavailable form, represented at least 95% of sediment TP. A positive relationship was observed between VHG and TP in two of the gravel bars, with wells that were strongly downwelling having lower TP concentrations. These results suggest that in downwelling zones, hyporheic sediments can trap surface-derived dissolved P, and that much of this P becomes stored in refractory particulate forms. Bioavailable P is mainly present in dissolved form and only occupies a small fraction of total P, with particulate P comprising the majority of total P.

KEY WORDS   large river; phosphorus; hyporheic zone; sediments; interstitial water

INTRODUCTION

Phosphorus (P) is generally an important limiting nutrient in temperate oligotrophic freshwaters. Human activities such as sewage and industrial waste disposal and runoff from urban areas and from agricultural land add excessive amounts of P to receiving waters. Enrichment of surface water with P can lead to eutrophication (Vollenweider, 1968), which is associated with excessive aquatic plant growth that can lead to a reduction in aesthetic quality and water quality, deoxygenation and interference with recreational activities.

Management of aquatic ecosystems requires knowledge about their natural P retention capacity, P budget and P mobility (Némery et al., 2005; Némery and Garnier, 2007). Retention can be defined as the capacity of aquatic systems to remove P from the water and to retain it in a form not readily released under normal conditions (Reddy et al., 1999). Retention processes are linked to abiotic processes (sedimentation, adsorption by sediments and precipitation) and biotic processes (assimilation by vegetation, plankton, periphyton and microorganisms). Therefore, the stability and chemical form of particulate P (1) regulate its retention and release from the sediment phase and (2) determine the level of dissolved P in the water column (House, 2003; Jarvie et al., 2005; Ballantine et al., 2006; Katsaounos et al., 2007).

The amount, composition and temporal variation of P fluxes within streams are strongly regulated by retention and release processes (Harms et al., 1978; Froelich, 1988; Fox et al., 1989; Triska et al., 1989; D'Angelo et al., 1991; Stone et al., 1991; Pelton et al., 1998; Dorioz et al., 1998). A few investigations of P retention have been conducted on small rivers (Svendsen et al., 1995) and small watersheds (Dorioz et al., 1989). However, less attention has been paid to P retention in large rivers with highly variable flow. The study zone in the present investigation was the Garonne River, downstream of Toulouse in southwestern France. This river receives P from its tributaries and from the output of a sewage treatment plant for the 740 000 inhabitants of Toulouse. The Garonne River flows in a large alluvial valley and has an active hyporheic zone (Vervier et al., 1993; Bernard et al., 1994). This hyporheic zone is the subsurface zone composed of riverbed sediments (Triska et al., 1989; Findlay, 1995; Bencala, 2000).

The continuous hydrological exchange of hyporheic and surface water (SW), which is well documented (Hynes, 1983; Bencala, 1993; Stanford and Ward, 1993; Valett, 1994; Findlay, 1995; Tockner *et al.*, 1999), is the most obvious link between the surface stream and the hyporheic zone. This hydrological connectivity results in nutrient exchange between SW and hyporheic zone (Grimm and Fisher, 1984; Triska *et al.*, 1993; Campbell *et al.*, 1995; Dahm *et al.*, 1998).

Active exchanges can occur between SW and hyporheic zone, with extensive transformation of nutrients and organic matter fluxes (Hynes, 1983; Gibert *et al.*, 1990; Vervier *et al.*, 1992; Findlay, 1995; Brunke and Gonser, 1997; Boulton *et al.*, 1998; Flipo *et al.*, 2004). Most of the previous studies focus on organic matter and nitrogen cycling (Rutherford and Hynes, 1987; Findlay *et al.*, 1993; Vervier *et al.*, 1993; Gunatilaka *et al.*, 1994; Fischer *et al.*, 1996; Pusch, 1996; Schindler and Krabbenhoft, 1998), whereas only a few investigations have examined the role of subsurface water on P cycling in streams (Dorioz *et al.*, 1989; Valett *et al.*, 1990; Campbell *et al.*, 1995; Mulholland *et al.*, 1997).

The objective of the present study was to examine whether the hyporheic zone can play an important role in P dynamics within the active channel of a large gravel-bed river with high flow dynamics. Our starting hypothesis was that P retention within the hyporheic zone is controlled by the grain size distribution of sediments and by the dynamics of hydrological exchanges between surface water and riverbed sediments.

METHODS

Study sites

The Garonne River is the largest river in southwestern France (8th Stralher order at its mouth), with a watershed area of 60 000 km^2 and a length of 600 km. The region has a general temperate oceanic climate, but two climatic influences prevail, one coming from the Atlantic Ocean and the other from the Mediterranean. Annual rainfall is about 900 mm and can reach 2000 mm in the upper parts of the basin.

Our study site was located downstream of Toulouse in the sector Toulouse—Verdun sur Garonne (Figure 1), which has three tributaries: the Aussonnelle, Hers and Save rivers. In this sector, the flow regime of the Garonne is characterized by two hydrological maxima, one in February and one in May, and a low-flow period from August to September. At Verdun sur Garonne, 30 km south of Toulouse, the mean annual discharge is 200 m^3 s^{-1} and ranges between 17 and 8000 m^3 s^{-1} (Table I). The study site is downstream of the Toulouse sewage treatment plant.

The study was carried out in three gravel bars (GB1, GB2 and GB3) from 30 September 1997 to 17 October 1997, with a three-day interruption between 10 and 12 October (Figure 1). Discharge was low and steady during the first 10 days of the study, with a minimum of 43 m^3 s^{-1} and a maximum of 51 m^3 s^{-1}. During the last five days, discharge increased rapidly from 42 to 76 m^3 s^{-1}.

Sampling strategy in the field

Three piezometers were located in each gravel bar and these piezometers were considered to be replicates. They were located 10 m apart in downwelling zones (Figure 1). Piezometer diameter was 6 cm and the piezometers were fully slotted along their length. The piezometers were bored deep enough to sample a minimum of 50 cm under the watertable.

Vertical hydraulic gradient (VHG). Before sample collection, the hydraulic head of water inside and outside
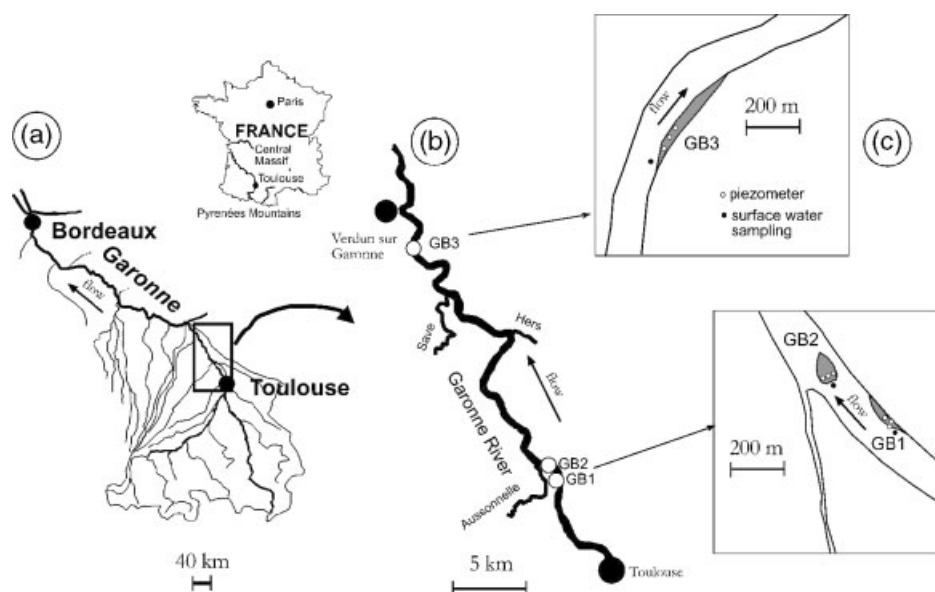

Figure 1. Map of the study site at (a) catchment scale, (b) reach scale and (c) gravel bar scale. GB = gravel bar. In each gravel bar, the sampling points for interstitial water (blank circles) and surface water (white circles) are represented

Table I. Monthly mean discharge ($m^3 s^{-1}$) over 30 years (1972–2001) at Verdun sur Garonne, 30 km downstream of Toulouse

Month	Discharge ($m^3 s^{-1}$)	Month	Discharge ($m^3 s^{-1}$)
January	209	July	130
February	251	August	82
March	242	September	86
April	302	October	126
Mai	351	November	157
June	266	December	200

Data from the French hydrobank (http://hydro.rnde.tm.fr).

the piezometer was measured daily over the full depth of each piezometer for 15 days, yielding 45 measurements from each gravel bar. The VHG is a unitless ratio of the difference in hydraulic head between water inside and outside the piezometer to the depth of the piezometer. A positive VHG indicates hyporheic discharge, or upwelling, where interstitial water (IW) enters the surface stream. Negative VHG values denote recharge, or downwelling, where SW infiltrates the hyporheic zones (Lee and Cherry, 1978; Valett *et al.*, 1994). The greater the difference between the heights of the two waters, the stronger the hydraulic exchange.

Surface and interstitial water (SW and IW). One litre of IW was collected daily by a peristaltic pump with a discharge of 2 l min^{-1}, after pumping for 10 min from the three piezometers in each gravel bar (45 measurements per gravel bar). Once each day for 15 days, SW was simultaneously sampled upstream of the gravel bars. Dissolved oxygen, temperature, pH and electrical conductivity were measured using a specific probe (WTW Multiline P4). The samples for P analysis were stored at 4 °C before analysis.

Subsurface sediments. Sediments were collected on the first day of the study period in each piezometer (nine samples during the study period) to measure their phosphorus content. Sediments were sampled through piezometers with a vacuum pump and frozen in the laboratory until analysed.

Laboratory analyses

Surface and interstitial water. Water samples for the measurement of total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) were filtered through Whatman GF/F filter paper (0·7 μm) before analysis. Total phosphorus (TP) was measured on unfiltered water. SRP was determined directly on the filtrate by molybdate-antimony analysis according to Murphy and Riley (1962), whereas TP and TDP were measured using colorimetry (Murphy and Riley, 1962) after persulphate digestion of organic phosphorus and acid hydrolysis at 105 °C.

Subsurface sediments. Frozen samples were freeze-dried to eliminate IW of sediments before mechanical dry sieving. Four fractions were obtained: gravel (>2000 μm), coarse and medium sand (200–2000 μm), fine and very fine sand (50–200 μm) and silt and clay (<50 μm). Phosphorus was measured on the three smallest size fractions. Each size fraction was analysed for P by sequential extraction. Extraction was based on conversion of different forms of P into soluble orthophosphate, which can be measured using the colorimetric method of Murphy and Riley (1962). It should be pointed out that the percentages of each fraction do not represent the composition of the whole porous medium, as the vacuum pump method only allows small particles to be collected. However, particles that have a role in P dynamics (in our case particles <2000 μm) were collected in abundance. For each size fraction, 0·5 g was successively mixed with extractants of increasing strengths. All the different forms of P were defined by the way in which they were extracted: water-extractable P (sediments shaken with 40 ml of water for 4 h), NaOH-extractable P (sediments shaken with 40 ml of 0·1 N NaOH for 17 h) and H_2SO_4-extractable P (5 ml of 36 N H_2SO_4 and 0·75 g of persulphate added to sediments for hot acid hydrolysis). These three fractions are considered to, respectively, represent the loosely bound and exchangeable fraction (Psenner *et al.*, 1984; Bonzongo *et al.*, 1989), the fraction bound by iron and aluminium oxides (Hieltjes and Lijklema, 1980; Sharpley *et al.*, 1991) and the P fraction not extracted in the two first steps, which consists of Ca-bound P and organic P (Golterman and De Groot, 1994). We did not distinguish between the Ca-bound P fraction and the organic P fraction because our objective was to analyse the dynamics of biologically available and non-available fractions and not to analyse all the different forms of P within the sediment.

The three forms of P analysed here were named P_{H_2O}, P_{NaOH} and $P_{H_2SO_4}$. Only P_{H_2O} and P_{NaOH} are considered to be biologically available fractions of P in sediments (Hieltjes and Lijklema, 1980; Psenner *et al.*, 1984; Fabre *et al.*, 1996), whereas $P_{H_2SO_4}$ is not available to plants or microorganisms. TP in the sediment represented the sum of the P concentration in each of the three fractions multiplied by the percentage of that fraction. Concentrations were expressed in micrograms of P per gram of dry weight sediment.

Calculations

Phosphorus uptake rate. Phosphorus uptake rate was calculated from all forms of P. Uptake rate represented the difference between the P flux measured in the upstream part of the gravel bar (surface water) and the flux measured in the gravel bar, divided by the distance between the two measurement points. Water velocity, which was measured in one of the gravel bars during low water period using a tracer test by Vervier *et al.* (1993), was on average 45 m day^{-1} with a range from 35 to 70 m day^{-1}, whereas the porosity of the gravel bar was 0·15. In the absence of any other data, the same mean velocity value was used for all three gravel bars.

Statistical methods. Repeated analysis of variance (ANOVA) was chosen to test for differences between the different compartments (interstitial water and surface water) and the three sites for each parameter. In all statistical methods, differences were considered significant at $p < 0.05$. Multiple linear regression was used to assess the hydrological parameters that best predicted measured P forms in surface water and interstitial water. All statistical calculations were made using the MINITAB computer package (Minitab, Inc., USA), version 13 for personal computer.

zone within the gravel bed was more frequent than upwelling. VHG measured in piezometers was different in the three gravel bars. In GB1 and GB3, the temporal variation in VHG was weak (range from -0.09 to -0.01 cm cm^{-1} for GB1 and from -0.13 to 0.01 cm cm^{-1} for GB3) but in GB2, the fluctuations were very large (from -0.24 to 0.04 cm cm^{-1}; Table II).

Table II. Measured VHG at each gravel bar

| Site | VHG (cm cm^{-1}) | | | |
	Mean	SD	Min.	Max.
GB1	-0.04	0.02	-0.09	-0.01
GB2	-0.09	0.08	-0.24	0.04
GB3	-0.05	0.04	-0.13	0.01

$N = 45$, SD = standard deviation, Min. = minimum, Max. = maximum. Negative VHG indicates downwelling, that is, surface water infiltrating the hyporheic zone.

RESULTS

Hydrological connection between the surface water body and the hyporheic zone

During the study, VHG indicated that downwelling of the water from the surface water body to the hyporheic

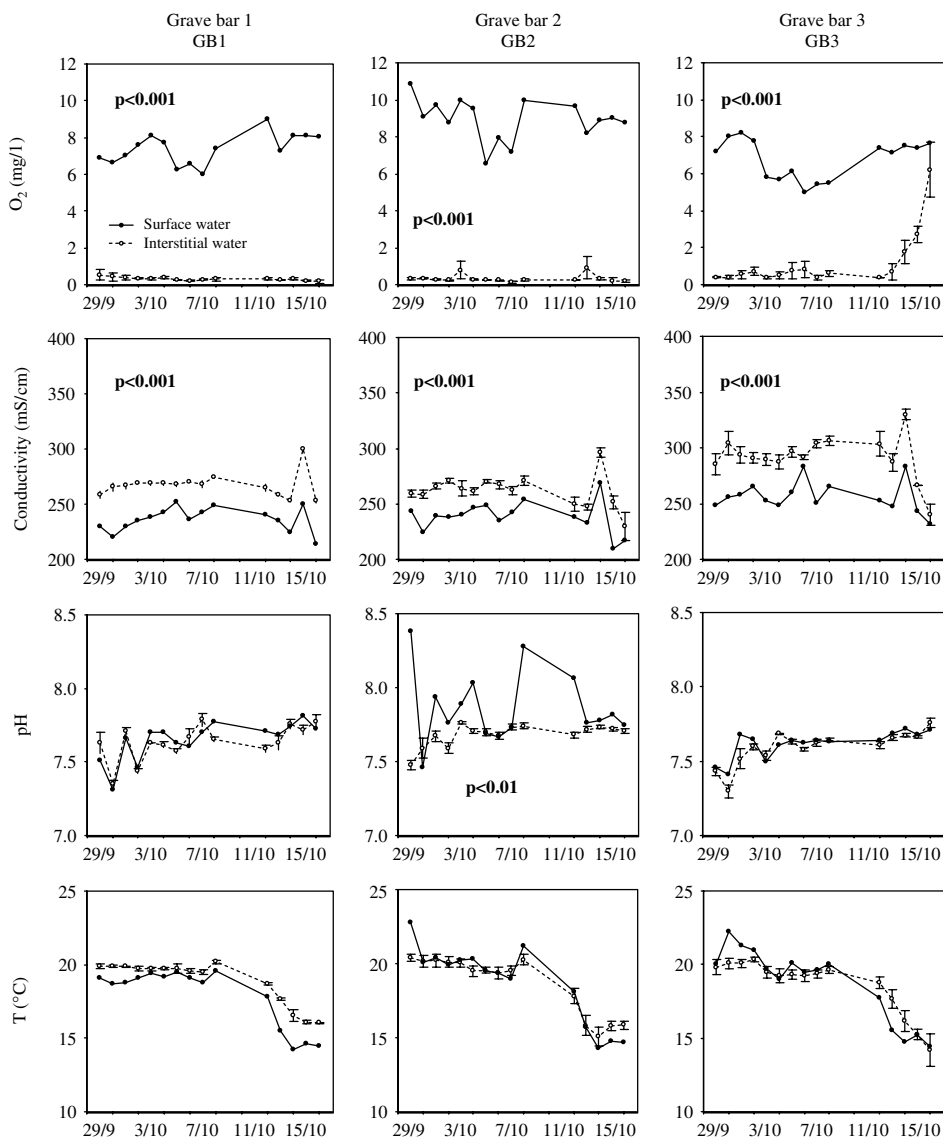

Figure 2. Temporal variation in dissolved oxygen, electrical conductivity, pH and temperature in interstitial water (mean ± standard error) and surface water from 30 September 1997 to 17 October 1997. The *p* values represent the significance of the difference between interstitial water and surface water

The mean electrical conductivity values ranged from 262 to 292 μS cm^{-1} in IW but were significantly weaker in SW (range from 236 to 256 μS cm^{-1}). IW was significantly lower in dissolved O$_2$ than SW, with mean O$_2$ saturation varying between 0·31 and 1·15 mg l^{-1} for IW, whereas for SW it varied between 6·8 and 8·9 mg l^{-1}. Mean pH ranged from 7·59 to 7·68 in IW and from 7·62 to 7·87 in SW, whereas mean temperature ranged from 18·6 to 18·9 °C in IW and from 17·9 to 18·6 °C in (Figure 2).

SW and IW showed the same temporal variations for pH, electrical conductivity and temperature (except pH at GB2). Towards the end of the study, the O$_2$ concentration increased in IW at GB3.

It was possible to indirectly estimate the hydrological connection between the surface water and the porous bed of the river by the temporal variations in dissolved oxygen, conductivity, pH and temperature (Figure 2).

Phosphorus dynamics in SW and IW

Mean concentrations. Mean TP concentrations ranged from 0·16 to 0·18 mg l^{-1} in IW and from 0·16 to 0·22 mg l^{-1} in SW. Mean SRP concentrations (measured as P–PO$_4$) varied from 0·07 to 0·08 mg l^{-1} in IW and from 0·07 to 0·12 mg l^{-1} in SW. Mean TDP concentrations ranged from 0·12 to 0·13 mg l^{-1} in IW and from 0·12 to 0·17 mg l^{-1} in SW (Figure 3).

Phosphorus forms. In IW and SW, TP was essentially represented by dissolved forms of P (74–79% TDP). SRP represented on average 47% of TP. There was no difference between SW and IW except at GB3, where SW contained more TDP than interstitial water.

Concentration differences between SW and IW. In GB1 and GB3, phosphorus concentrations (TP, TDP and SRP) were significantly higher ($p < 0.05$) in SW than in IW, whereas in GB2, phosphorus concentrations in SW did not differ from those in IW.

Phosphorus uptake rate. Phosphorus uptake rate (μg m^{-1} day^{-1}) showed significant differences between the three gravel bars for the three forms of P (SRP, TP and TDP). SRP uptake rate varied from -0.034 μg m^{-1}
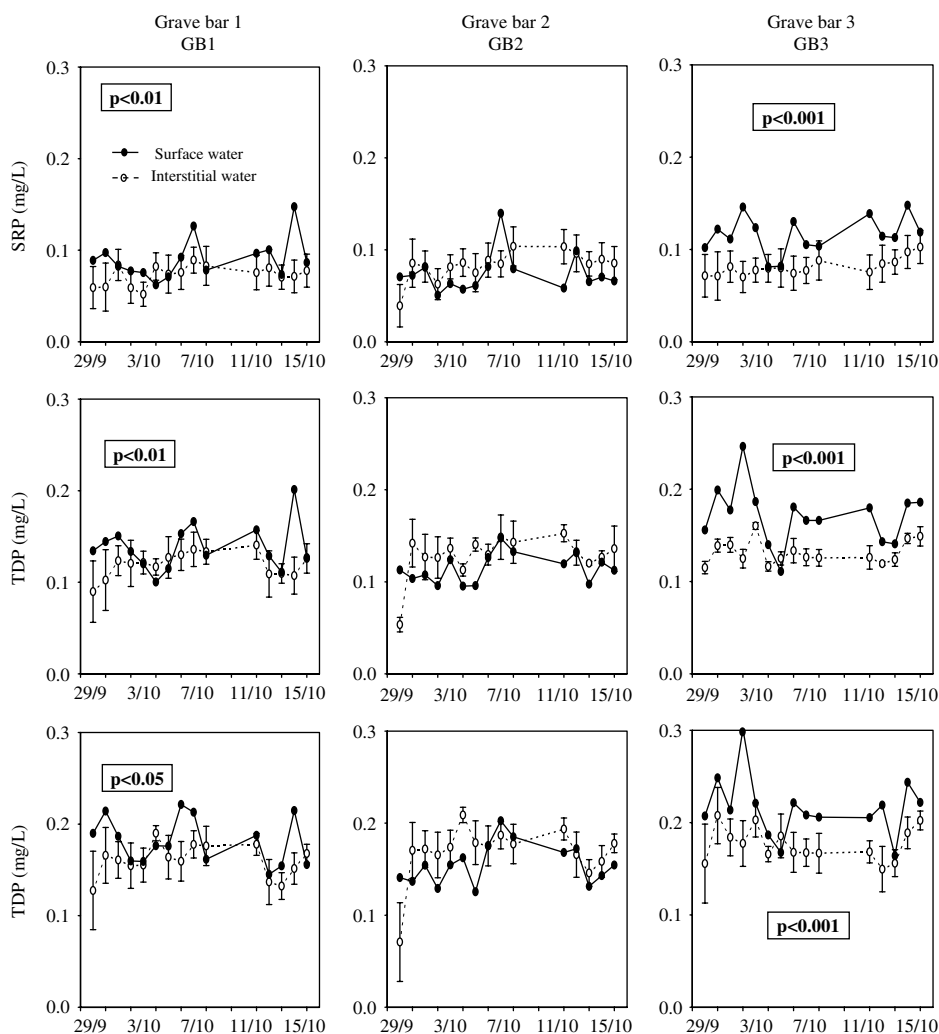

Figure 3. Temporal variation in soluble reactive phosphorus (SRP), total phosphorus (TP) and total dissolved phosphorus (TDP) in interstitial water (mean ± standard error) and surface water from 30 September 1997 to 17 October 1997. The *p* values represent the significance of the difference between interstitial water and surface water

day^{-1} in GB2 to 0·148 μg m^{-1} day^{-1} in GB3, TP from −0·050 μg m^{-1} day^{-1} in GB2 to 0·147 μg m^{-1} day^{-1} in GB3 and TDP from −0·058 μg m^{-1} day^{-1} in GB2 to 0·148 μg m^{-1} day^{-1} in GB3 (Table III).

Sediment characteristics

Grain size composition. Grain size fractions were not distributed in the same way for all three gravel bars (Table IV). GB2 and GB3 were essentially composed of coarse sand (mean content 72–74%) and were relatively

Table III. Phosphorus uptake rate (U, μg m^{-1} day^{-1}) of P forms

Gravel bar	N	Mean	SD
Soluble reactive phosphorus (SRP), μg m^{-1} day^{-1}			
GB1	15	0·069	0·024
GB2	15	−0·034[a]	0·025
GB3	15	0·148	0·021
Total phosphorus (TP), μg m^{-1} day^{-1}			
GB1	15	0·079	0·027
GB2	15	−0·050[a]	0·031
GB3	15	0·147	0·031
Total dissolved phosphorus (TDP), μg m^{-1} day^{-1}			
GB1	15	0·074	0·028
GB2	15	−0·058[a]	0·027
GB3	15	0·148	0·028

N = number of values, SD = standard deviation.
[a] Significant difference at 0·05 level.

poor in the silty fraction (mean content 8–9%). Sediments of GB1 were characterized by a predominance of coarse and fine sand (mean contents 54 and 31%, respectively) and the silty fraction represented 11% of the sediments collected. These results show that gravel bar GB1 was more heterogeneous than the others.

Sediment P distribution. Sediment mean TP concentrations varied between 268·7 and 464·5 μg g^{-1}. The H_2SO_4-extractable form of P represented at least 95% of TP (Table V).

Relationship between phosphorus concentrations and grain size composition

TP concentration varied according to the grain size fraction. The P concentration was low in the coarse sandy fraction (with a mean of 275 μg g^{-1}) but high in the two finest fractions (with a mean of 583 μg g^{-1} for silty sand and a mean of 524 μg g^{-1} for fine sand; Figure 4). These are called fine–very fine sand and silt–clay in Materials section.

This relationship between P concentration within the sediment and grain size composition was also controlled by the proportion of the finest grain size fractions within the sediment. The greater the proportion of silt or fine sand, the higher the TP concentration within the silty or sandy fraction (Table VI).
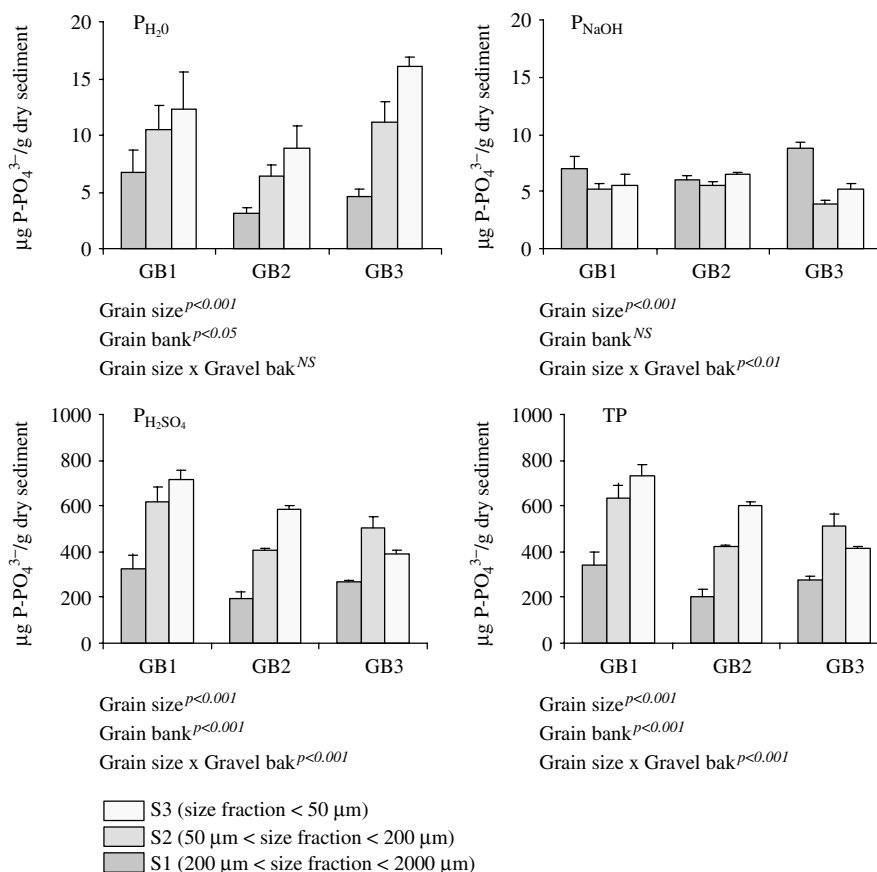

Figure 4. Concentrations of extracted forms of P in the sediment of the three gravel bars in each fraction size. The p values represent the significance of the difference between the three size fractions at all sites, the three gravel bars and the combination of the effect of grain size and gravel bar

Table IV. Percentage of each size fraction in the hyporheic sediments of the three gravel bars

Gravel bar	Fraction size (μm)	N	Mean	SD	Min.	Max.
GB1	<50	3	11·4	7·9	6·4	20·5
	50–200	3	31·2	8·8	21·6	38·7
	200–2000	3	54·0	12·1	42·7	66·8
	>2000	3	3·4	0·9	2·5	4·3
GB2	<50	3	8·3	1·5	7·0	9·9
	50–200	3	15·8	2·2	14·1	18·3
	200–2000	3	73·8	3·7	70·6	77·8
	>2000	3	2·1	2·4	0·3	4·8
GB3	<50	3	9·1	1·8	7·0	10·5
	50–200	3	13·7	3·9	9·9	17·6
	200–2000	3	71·8	3·8	67·9	75·5
	>2000	3	5·5	1·9	4·0	7·6

N = number of samples, SD = standard deviation, Min. = minimum, Max. = maximum.

Table V. Concentrations of extracted forms of P and total P in the complete sediments (all fractions) of the three gravel bars

Gravel bar	N	Mean	SD	Min.	Max.
Water-extractable phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)					
GB1	3	8·4	4·3	3·9	12·5
GB2	3	4·1	1·0	2·9	4·9
GB3	3	6·3	1·5	4·8	7·9
NaOH-extractable phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)					
GB1	3	6·0	1·3	4·5	6·9
GB2	3	5·8	0·3	5·5	6·1
GB3	3	7·4	0·9	6·4	8·2
H$_2$SO$_4$-extractable phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)					
GB1	3	450·0	126·7	308·6	553·2
GB2	3	258·8	45·2	210·6	300·3
GB3	3	295·7	30·1	267·9	327·7
Total phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)					
GB1	3	464·5	130·4	319·5	572·2
GB2	3	268·7	46·6	219·0	311·3
GB3	3	309·4	32·1	280·2	343·7

N = number of samples, SD = standard deviation, Min. = minimum, Max. = maximum.

The influence of a given proportion of a grain size fraction in sediment on its P concentration was observed for P_{H_2O} and $P_{H_2SO_4}$ too. The more abundant the finest grains, the more P_{H_2O} and $P_{H_2SO_4}$ occurred in this fraction. The coarse grain size fraction also showed a negative relationship between its proportion and its richness in P_{H_2O} and $P_{H_2SO_4}$ forms (Table VI).

However, the P_{NaOH} concentrations in grain size fractions were not affected by the percentages of different grain size fractions in the sediment (Table VI). P_{NaOH} appeared to be a buffer form of phosphorus between the most bioavailable P form (P_{H_2O}) and the non-available P form ($P_{H_2SO_4}$).

Relationship between hydrological parameters and phosphorus content

The intensity of the hydrological connection between surface water and the hyporheic zone appeared to influence the P concentration in IW. Gravel bars GB1 and GB3, which had a weaker hydrological connection with surface water than gravel bar GB2, showed a significant relationship between TP concentrations of IW and VHG magnitude, whereas this process did not take place within gravel bar GB2. For GB3, the magnitude of downwelling and TP concentration in interstitial water were positively correlated (Figure 5). This trend reflects the fact that the biotic and abiotic processes that control P uptake from interstitial water by sediments seem to be controlled by hydrodynamics.

Hydrodynamics also played a role in the P content of the riverbed sediments. The hydrodynamic factor with the greatest influence on sediment P concentrations was the intensity of the variation in hydrological connection over time at a given location. This influence can be demonstrated using the 'ΔVHG' parameter, which is derived from the difference between the highest and the lowest values of the VHG measured within a piezometer. For the nine piezometers in this study, we obtained a ΔVHG that was compared with the P content of the sediments. Plotting the total P concentration of the sediments sampled at each piezometer location against the ΔVHG (Figure 6) showed that the mean P concentration of the sediments decreased with increasing ΔVHG.

It can be estimated that for ΔVHG above 0·1 cm cm^{-1}, sediment retention capacity cannot exceed 278 μg g^{-1} sediment (mean calculated with sediment total P concentrations corresponding to ΔVHG above 0·1 cm cm^{-1}).

Concerning the different forms of P, the most bioavailable and non-bioavailable forms (P_{H_2O} and $P_{H_2SO_4}$, respectively) showed similar behaviour (Figure 6). In contrast, no relationship was found between P_{NaOH} and ΔVHG, confirming that this form of phosphorus seems to play a buffer role between the most bioavailable form of P and the non-available form. Sediments seemed to retain interstitial water phosphorus in P_{H_2O} form and store it in

Table VI. Pearson correlation coefficients and p values for relationship between sediment P concentration and grain size

	<50 μm	50–200 μm	200–2000 μm
Water-extractable phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)	0·628 (0·070)	0·351 (0·354)	**−0·663 (0·010)**
NaOH-extractable phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)	0·116 (0·767)	−0·043 (0·913)	0·401 (0·155)
H$_2$SO$_4$-extractable phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)	0·440 (0·237)	**0·682 (0·043)**	**−0·925 (0·000)**
Total phosphorus (μg P–PO$_4^{3-}$ g^{-1} dry sediment)	0·463 (0·210)	**0·677 (0·045)**	**−0·928 (0·000)**

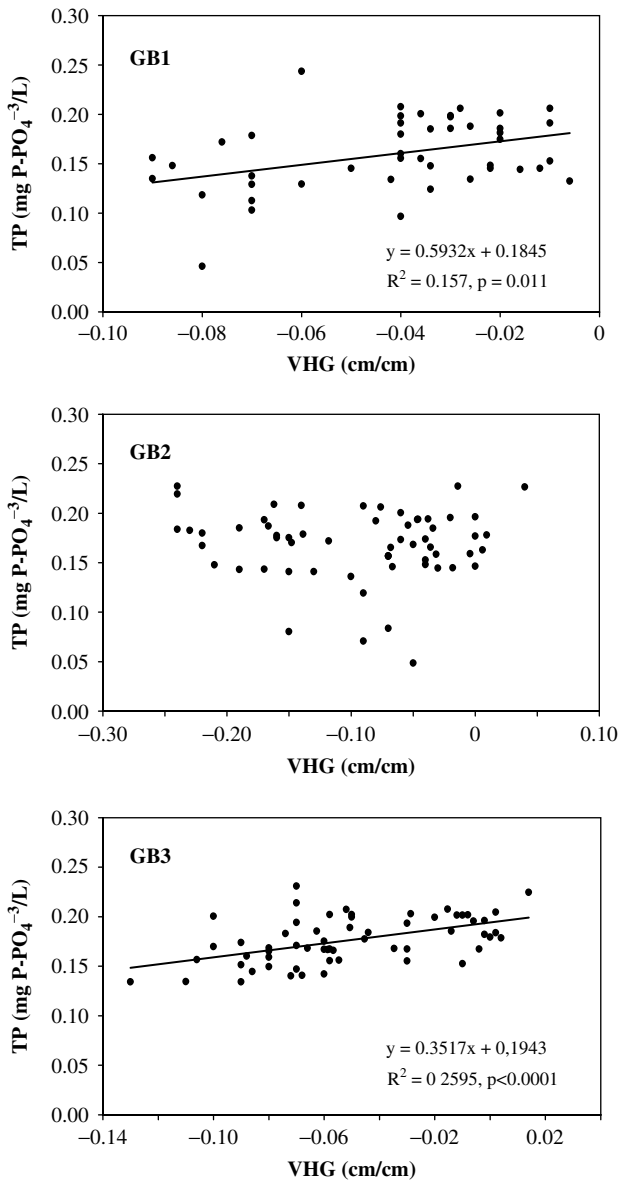Statistically significant correlations indicated by bold font.

Figure 5. Relationships between interstitial total phosphorus (TP) concentrations and vertical hydraulic gradient (VHG) in each gravel bar. p = probability value

$P_{H_2SO_4}$ form, with the P_{NaOH} form intermediate between P_{H_2O} and $P_{H_2SO_4}$.

DISCUSSION

Hydrological connection between the surface water body and the hyporheic zone

It proved possible to indirectly determine the hydrological connection between the surface water (SW) and the porous bed of the river by measurement of dissolved oxygen, conductivity, pH and temperature. The quantity of dissolved oxygen measured in the SW and in the gravel bar indicated two types of water: SW rich in oxygen and hyporheic (interstitial) water poor in oxygen.

SW and IW underwent the same temporal variations in pH, electrical conductivity and temperature (except pH

at GB2), indicating that the two waters are very closely connected hydrologically, as reported by Edwardson *et al.*, (2003) for other hyporheic and parafluvial zones.

In the same way, towards the end of the study, the oxygen concentration increased markedly in IW in GB3. This increase was due to the Hers flood, which occurred during the last days of the study and which most likely increased the hydrological exchanges between surface and interstitial water, providing more oxygen to the downwelling zone.

Phosphorus dynamics in SW and IW

The SRP concentrations in IW were close to values found by Chambers *et al.* (1992) in the Pembina River (Canada), which varied between 0·07 and 0·44 mg l⁻¹, by Takatert *et al.* (1999) in the Ill floodplain groundwater in France, which varied between 0·01 and 0·18 mg l⁻¹, and those reported by Valett *et al.* (1990) in the hyporheic water of Sycamore Creek (Arizona; mean of 0·06 mg l⁻¹). However, the SRP values in IW were higher than values reported by Hendricks and White (1991) for the hyporheic zone of a small stream system (between 0·004 and 0·007 mg l⁻¹).

Surface and interstitial water TP concentrations were significantly higher ($p < 0.05$) at GB3 because of the phosphorus-rich (around 0·6 mg l⁻¹) Hers tributary situated upstream of this gravel bar.

At GB1 and GB3, concentrations of TP and dissolved forms of phosphorus (TDP) were significantly higher ($p < 0.05$) in SW than in IW, whereas at GB2 phosphorus concentrations were similar in SW and IW. This trend has been observed by other authors such as Valett *et al.* (1996) and Takatert *et al.* (1999), but IW P concentrations are generally higher than SW concentrations (Valett *et al.*, 1990; Chambers *et al.*, 1992; White *et al.*, 1992; Hendricks and White, 1995). GB2 showed such a trend, although it was not statistically significant. This demonstrates that relationships between SW and IW can vary spatially between gravel bars of the same ecosystem.

The trends in P concentrations observed here indicate that hyporheic sediments in GB1 and GB3, but not GB2, retained P from the IW. Measurements of the P uptake rate confirmed this result in that the GB2 uptake rates were significantly different from those of the other two gravel bars. GB2 showed a negative uptake rate for SRP, TP and TDP and a high value for the TP uptake rate. It can be postulated that this difference in functioning of GB2 is linked to its geomorphologic location, because it lies in the middle of the riverbed whereas GB1 and GB3 are located at the sides of the river. This might entail differences in water exchange dynamics between surface water and riverbed sediments, because exchanged water fluxes proved to be more important within GB2, as shown by the higher values of VHG (Table II).

The concentrations of TP in the finest-grained sediments, which ranged from 391 to 817 μg g⁻¹, are within the 50–1500 μg g⁻¹ range found by Owens *et al.* (2002)
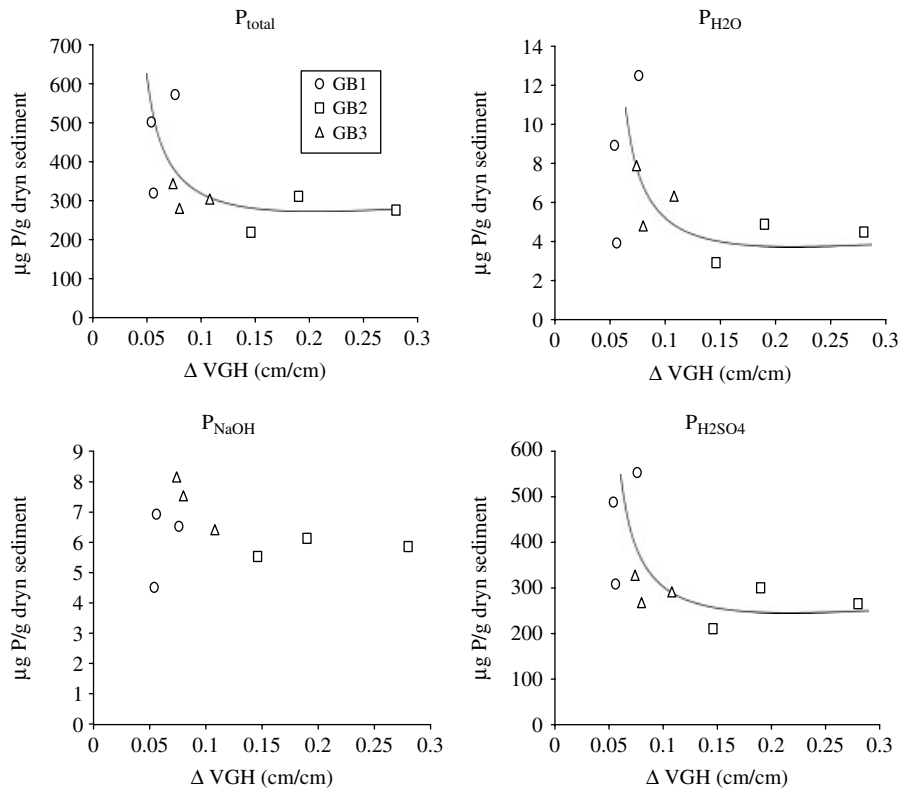
Figure 6. Concentrations of total P and extracted forms of phosphorus (P_{H_2O} = extracted by water, P_{NaOH} = extracted by NaOH, $P_{H_2SO_4}$ = extracted by H_2SO_4) in the total sediment of the three gravel bars as a function of the variation in vertical hydraulic gradient. The fifth line represents the trends in the data

for a fluvial sediment in a rural and industrialized river in the United Kingdom and by House and Denison (2002) for surface-bed sediments taken from rivers in the Thames catchment, and are close to the $700–3000 \; \mu g \; g^{-1}$ range reported by Ballantine *et al.* (2006) for fine sediments on channel beds. House and Denison (2002) also found a relationship between TP content in the sediments and organic matter. Datta *et al.* (1999) showed the TP concentrations to be twofold to fivefold greater in suspended matter than in any particle size fraction of sediment. This has also been observed for the Garonne River, because mean TP concentrations within sediments deposited during two floods in 1992, which give a picture of the suspended matter, were $960 \; \mu g \; g^{-1}$ (Steiger and Gurnell, 2002).

Whereas the quantity of P in Garonne River sediments may be similar to that found in other systems, the quality of P associated with the sediments differed. In our study, bioavailable P (extracted by water and by 0·1 N NaOH) represented a very small proportion of the total P extracted (less than 5%), whereas in most studies in superficial sediments, this pool of P is larger. For example, more than 27% was found to be bioavailable in a non-polluted river (Redon watershed in France) (Dorioz *et al.*, 1989), between 20 and 71% in stream sediments in the Lake Okeechobee Basin, USA (Reddy *et al.*, 1995), between 13 and 53% in agricultural runoff (Sharpley *et al.*, 1991) and 60% in the Klein A stream sediments (Pacini and Gachter, 1999) and in a German river (Kleeberg, 1996).

Relationship between phosphorus concentration and grain size composition

The grain size composition of the gravel beds, which is heterogeneous within the river, controls P retention processes in the riverbed sediments, because sediment TP content was found to increase as grain size decreased. A similar pattern was observed for P_{H_2O} and $P_{H_2SO_4}$. This increase in P content with decreasing grain size is in agreement with results generally found in the literature (Viner, 1982; Murdoch and Duncan, 1986; Stone and English, 1993). The second most bioavailable phosphorus form, P_{NaOH}, did not conform to this trend but, according to Dorich *et al.* (1984), bioavailable P is not necessarily concentrated in the small size fractions.

Relationship between hydrological parameters and phosphorus

Phosphorus retention is due to both biotic and abiotic processes. When downwelling water exchanges are weak and stable over time, the residence time of water in the hyporheic zone is higher and favours physical and chemical P retention processes between interstitial water and sediments. Moreover, it allows biotic uptake by a well-developed biofilm on hyporheic sediments (Jarvie *et al.*, 2002). In contrast, strong negative VHG values with great fluctuations indicate strong downwelling of SW in the hyporheic zone. In this situation, the higher water velocity in the hyporheic zone does not allow a long contact time between interstitial water and subsurface sediment and can disturb the sediment biofilm activity.

CONCLUSIONS

Running water systems are sensitive to nutrient inputs, but while a significant proportion of added nitrogen can leave the aquatic system via gaseous forms, mainly through denitrification processes, P inputs usually accumulate. In gravel-bed rivers, such as the Garonne River, the hyporheic zone can act as a zone of active retention. The hyporheic zone and surface water are highly connected, allowing surface water P to enter into the river sediment. Within the hyporheic zone, exchanges between interstitial water and sediments entail long-term P storage. The non-labile pools of P are much larger than the labile P pool within the sediments.

This retention process is controlled both by hydrological connectivity between surface water and river sediments and by their grain size composition. Retention of the most bioavailable form of P (P_{H_2O}) and the non-labile form of P ($P_{H_2SO_4}$) by subsurface sediments seems to be controlled by the grain size distribution of the sediment and by the dynamics of hydrological exchanges between surface water and the hyporheic zone (Figure 7).

This study provides more information about the importance of grain size composition of the sediment, showing that the P retention capacity of the finest grain size fractions (<50 μm) increases with the percentage of these fractions in the sediment. Likewise, the P retention capacity of the coarse grain size fraction (>200 μm) decreases with an increasing percentage of this fraction in the sediment.

Subsurface sediments retain water column P during stable and moderate hydrological exchanges between the surface water body and the hyporheic zone, which allow long residence times for the water in the sediment and thus physical, chemical and biological exchanges of P between these two compartments.

We have previously shown that P retention is more efficient during low water and stable hydrological periods and within reach of rivers that contain the highest occurrence of riffles (Bonvallet-Garay *et al.*, 2001; Bonvallet-Garay, 2003). The present work highlights the role of the hyporheic zone in this P retention process. This means that P retention within gravel-bed rivers does not derive from passive sedimentation of adsorbed P particles in pool zones, but from active exchange between surface water and the hyporheic zone and from biogeochemical processes that occur within riverbed sediments.

For gravel-bed rivers such as the Garonne, it can be assumed that the hyporheic zone constitutes an active trap zone for P and an active zone of transformation of bioavailable P into refractory forms. The hyporheic zone seems to act as a P sink, at least during the hydrological cycle between two flood events that can move the sediments and release the adsorbed phosphorus.

This study provides essential information for implementation of the European Water Framework Directive, because hydromorphology has to be linked with 'good status' of surface water. Our work highlights the relationships between hydrodynamic processes that control grain size distribution within the riverbed sediments and hydrological exchanges between surface water and porous sediments, morphology (gravel bar location) and water quality of the river. Further research is needed on the relationships between hydromorphology and water quality.

% of fine sediments → / Inensity of hydrological interactions ↓	Low	High
Low	++	+++
High	+	+++

Figure 7. Conceptual model of P retention by proportion of fine sediment and intensity of hydrological exchange between water and hyporheic zone

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