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HYDROMORPHOLOGICAL CONTROL OF PHOSPHORUS IN A LARGE FREE-FLOWING GRAVEL BED RIVER: THE GARONNE RIVER (FRANCE)

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ABSTRACT

The objective of this paper is to relate phosphorus (P) transport dynamics and hydromorphological characteristics of a large human-influenced river, the River Garonne within a sector receiving the waste water of a sewage treatment plant for a population of 600 000. Two studies were conducted in 1997 and 1999 during two different hydrological conditions at low-flow periods. The 1997 study was carried out on an 18-km stretch with discharges varying between 33 and 53 m^3/s and with very small fluctuations. The 1999 study concerned a longer stretch of 47 km, divided into four smaller reaches, and with discharges fluctuating rapidly from 40 to 108 m^3/s.

Downstream of the sewage treatment plant, total phosphorus (TP) concentrations ranged from 0.19 to 0.27 mg/L and were mainly in the dissolved form: between 60 and 78% of TP was dissolved reactive phosphorus (DRP). P concentrations were significantly lower upstream of the sewage treatment plant.

By a mass-balance approach, we estimated that the sewage treatment plant represents more than half the input (between 59 and 67%) of the studied sector. TP dynamic is linked to suspended solids for discharges above 60 m^3/s.

During established low-flow period in the 1997 study (< 60 m^3/s), 22 and 27% of TP and DRP were retained by the river bed.

In the 1999 study, under different low-water period hydraulic conditions, we calculate that particulate P retention occurred in two reaches among the four under study and only for discharges below 60 m^3/s.

We show that for established discharges below 60 m^3/s, there is an active uptake of transported P by functional compartments (i.e. the hyporheic zone and the periphyton). During the low-water period with relatively high hydraulic fluctuations, and for discharges > 60 m^3/s, P retention is controlled as expected by suspended matter dynamics.

We conclude that management of the hydrological regime can influence P retention during sensitive low-water periods.

KEY WORDS: budget; discharges; fluxes; functional compartments; hydrological control; low-flow period; phosphorus; River Garonne

INTRODUCTION

River regulation entails changes within lotic ecosystems driven by the adjustment of channel form to suit the imposed flow and sediment transport regimes. The consequences of these structural modifications on river functioning are studied mainly through biological components (Greenwood *et al.*, 1999; Ward *et al.*, 1999) with the help of physical habitat assessment (Maddock, 1999). We know that numerous processes influence particulate and solute transport in streams, including mixing and dispersion, hydrodynamics, erosion/deposition, chemical sorption/desorption, biological cycling and biochemical transformation (Meyer *et al.*, 1988) and that the physical structure of streams including the porous media constituting the

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river bed influence the dynamics of the transported fluxes (Bencala, 1993; Butturini and Sabater, 1999). Studies that link the hydromorphological components and the biogeochemical functioning of running waters are rare and mostly focus on small streams (Valett *et al*., 1997) or on riparian processes for large rivers (Tockner *et al*., 1999; Pinay *et al*., 2000).

Before analysing the influence of channel changes on the biogeochemical functioning, it is important to establish the relationships between the hydromorphological characteristics and the transformation of reactive matter fluxes. Among these elements, phosphorus (P), which is transported in lotic ecosystems in soluble and particulate forms with no gaseous forms being involved, appears as a relevant model for this kind of study. P transport can be interrupted by a complex series of uptake and release pathways including biotic and abiotic processes (Elwood *et al*., 1983). P budgets have been studied extensively in lakes (Vollenweider, 1968; Campbell, 1994; Maurer *et al*., 1995; Ramm and Scheps, 1997; Bennett *et al*., 1999). This approach has been useful in a few studies on stream systems but only for small catchments (Svendsen *et al*., 1995; Brunet and Astin, 1998; Dorioz *et al*., 1998).

The objective of this paper is to relate P transport dynamics and hydromorphological characteristics of a large river, the Garonne. We focus on the low-water period when nutrient inputs can lead to important problems (Agnew *et al*., 2000). This river is strongly influenced by human activities, which has directly altered the fluvial dynamics controlling the ecological processes (Steiger *et al*., 1998). We hypothesize that retention of P can occur in a large gravel bed river and that processes occurring at the river bed can influence this retention depending on hydraulic and morphological conditions.

MATERIALS AND METHODS

Study sites

The River Garonne is the main river of southwestern France. Eighth order at its mouth, the Garonne is the third largest river in France. The catchment covers 60 000 km^2 and its length is 600 km. The sector under study, the sixth order part of the river, receives the waste water from a treatment plant for a population of 600 000 inhabitants downstream of Toulouse. The annual mean discharge calculated over the last 20 years at Verdun sur Garonne (Figure 1) (from the DIREN Midi-Pyrénées data) is 191 ± 23 m^3/s ($\pm$95% confidence interval).

The first study was carried out in 1997 from 30 September to 7 October on an 18-km long stretch delimited by an upstream transect (F1) and downstream transect (F2) (Figure 1). The stretch was situated downstream of the treatment plant for waste water (TWW). Two tributaries flow into the Garonne in the stretch: the Aussonnelle and the Hers tributaries. During the study period, the mean discharge measured at Verdun sur Garonne was 43 m^3/s.

The second study was conducted in 1999 from 26 to 29 July on an 47-km long stretch divided into four contiguous reaches delimited by the following transects: G1, located upstream of Toulouse, G2 located downstream of Toulouse and upstream of the TWW, G3, G4 and G5 located downstream of the TWW (Figure 1). The tributaries flowing into the Garonne between G1 and G5 are from upstream to downstream: the Touch, the Aussonnelle, the Hers and the Save. The TWW output flows into the G2–G3 reach. The mean discharge measured at Verdun sur Garonne during these 4 days was 68 m^3/s. So, this second study was also conducted in a low-water period but the flow discharges were significantly higher than in the first study.

Sampling strategy in the field

One of the methods used to estimate P retention is the mass balance based on input-output analysis. In fact, the use of the mass balance approach for P is attractive because unlike other nutrients (C, O, N), the P cycle has no major gaseous component. Thus, exchanges of P are limited to those between water and dissolved and particulate reservoirs.

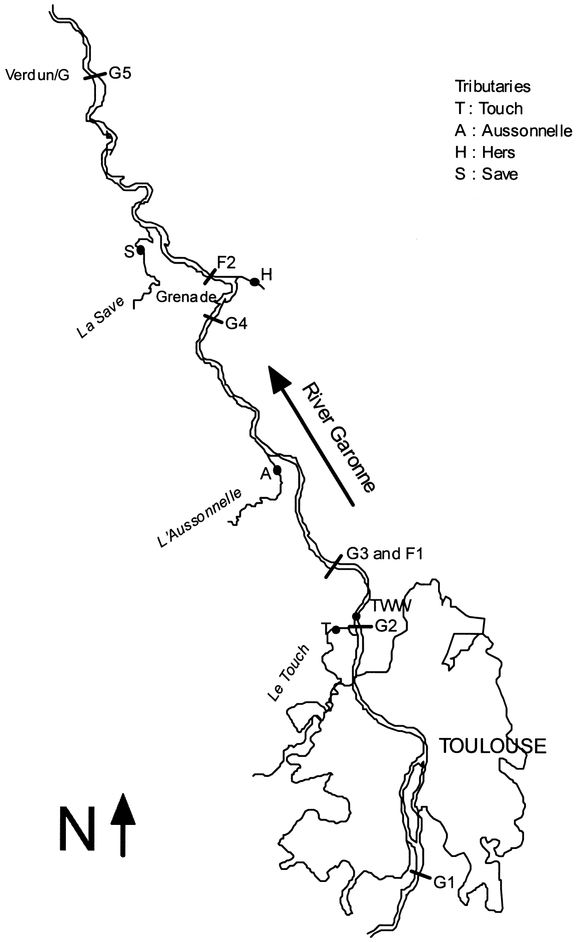

Figure 1. Studied site

For the 1997 study, the samples were collected at the two transects delimiting the sector studied with the assistance of automatic sample collectors (ISCO). Samples were also collected in the two tributaries, the Aussonnelle and the Hers rivers. Every hour, 100 mL was collected in order to constitute an 8-h mean sample, so per day three samples of 800 mL were collected.

In 1999, the study was a semi-experimental one. A tracer was added to outputs of the TWW and the marked plume was analysed within the river (Siméoni-Sauvage, 1999). The objective was to detect P changes within the same volume of water. For this second study, water samples were also collected in each transect and tributary, at another frequency. At each sampling station 2-h mean samples made of 10 subsamples (one every 12 min) of 100 mL of water were collected with an automatic sampler. So per day, 12 samples of 1000 mL were collected. For each tributary, 4-h mean samples made up of hourly 250 mL subsamples were collected over 24 h.

All the water samples were conserved at 4°C until laboratory analysis.

Analysis in the laboratory

Measures of total dissolved phosphorus (TDP) and dissolved reactive phosphorus (DRP) were made on samples filtered through Whatman GF/F filters (0.7 μm). Unfiltered samples were used for total phosphorus (TP) analysis. DRP was determined directly on the filtrate by molybdate-antimony analysis according to Murphy and Riley (1962). TP and TDP were also estimated by Murphy and Riley's method

(1962) after persulphate digestion of organic P and acid hydrolysis at 105°C. DRP and TDP are thought to be potentially completely bioavailable (Logan *et al.*, 1979; Bostrom *et al.*, 1988; Labroue *et al.*, 1995). Particulate P (PP) was determined by the difference between the TP and TDP.

In the 1999 study, suspended solids (SS) were also estimated by the measurement of the dry weight of particles from 600 mL of water retained on a Whatman GF/F filter after filtration.

Flow data

P retention was estimated for each reach by mass balance calculation. Input was obtained by the summation of the nutrient fluxes measured at the upstream station delimiting the reach and at the tributaries that discharge into the reach. Input was then compared to the output of nutrient at the station downstream of the reach.

The P fluxes in the tributaries were obtained by measuring concentrations and discharges. For the Garonne River, fluxes at each station were obtained from measured concentrations and estimated discharges measured at the closest gauging station (data were obtained by DIREN). The estimated discharges correspond to the outputs of the hydraulic model developed on the Garonne River by Siméoni-Sauvage (1999). With the residence time of the water calculated by the model, we were able to compare P fluxes of the same water body at all the stations of the same study.

RESULTS AND DISCUSSION

The Garonne River discharges during the two studies

Even if the mean discharges at Verdun sur Garonne of the two studies represent a low-flow period, the hydrological conditions were different (Figure 2). During the 8 days of the 1997 study, the Garonne River discharge was low and the fluctuations were low too, with a minimum of 33 m^3/s and a maximum of 53 m^3/s. In the 1999 study on the other hand, fluctuations were very strong with discharges ranging from 40 to 108 m^3/s.

Discharges from tributaries entering the river were negligible with regard to those of the river. In the 1997 study for example, the sum of the Aussonnelle and the Hers discharges represented less than 4% of the Garonne River discharge.

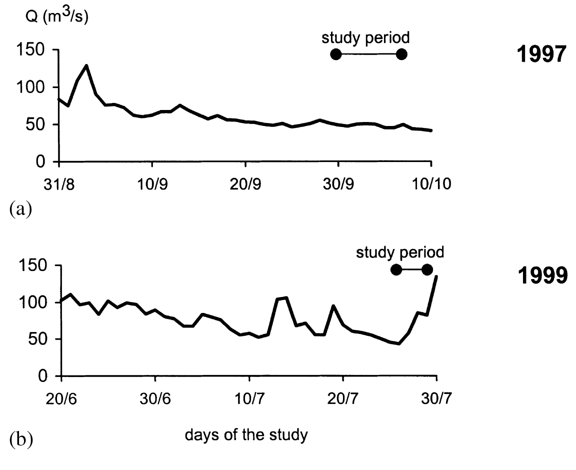

Figure 2. Measured River Garonne discharges at Verdun-sur-Garonne during the two studies: (a) from 30 September to 7 October 1997; (b) from 26 to 29 July 1999

Phosphorus composition in the Garonne downstream of the treatment plant for waste water (TWW)

Over the two studies, downstream of the TWW, the total mean P concentrations of the Garonne River ranged from 0.19 to 0.27 mg/L (Table I). These values are comparable with those found in other European river systems such as the Danube River which has a mean TP of 0.24 mg/L (Dokulil and Janauer, 1990; Cristofor *et al.*, 1993). But they are higher than those of Australian river systems where the mean TP values are below 0.1 mg/L (Nolan *et al.*, 1995; Hart *et al.*, 1999) or than Estonian ones (Loigu and Leisk, 1996).

Moreover, the Garonne River P is essentially represented by dissolved forms and specially DRP which varied between 0.13 and 0.17 mg/L. These values are lower than those of three major river catchments of central England, which all have median DRP concentrations greater than 0.75 mg/L (Muscutt and Withers, 1996; Young *et al.*, 1999). DRP in the Garonne surface water represented between 60 and 78% of TP (Figure 3).

The concentrations at station F1 in 1997 were significantly higher than those at stations downstream of the TWW in 1999. This is probably owing to the fact that in 1997, the water level was lower than in 1999.

Table I. TP min, max and mean (±95% CI) concentrations in the River Garonne, tributaries and waste water treatment plant during the studies of 1997 (A) and 1999 (B)

	Station	Min	Max	Mean ± IC
(A) 1997				
River Garonne	F1	0.20	0.40	0.27 ± 0.03
	F2	0.10	0.80	0.26 ± 0.08
Tributaries	A	1.70	2.60	2.13 ± 0.12
	H	0.25	5.80	1.10 ± 0.88
(B) 1999				
River Garonne	G1	0.03	0.06	0.05 ± 0.00
	G2	0.06	0.12	0.09 ± 0.01
	G3	0.13	0.26	0.19 ± 0.02
	G4	0.17	0.28	0.22 ± 0.01
	G5	0.18	0.22	0.20 ± 0.00
Tributaries	T	0.19	0.43	0.33 ± 0.05
	A	2.00	5.10	2.84 ± 0.61
	H	0.30	0.54	0.38 ± 0.05
	S	0.19	0.43	0.29 ± 0.05
TWW	TWW	5.10	11.00	7.81 ± 0.81

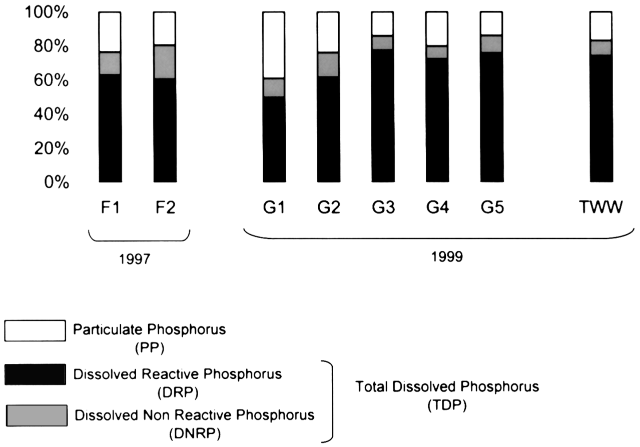

Figure 3. Type of River Garonne and waste water treatment plant TP

TP concentration in tributaries were significantly higher than in the Garonne River, especially in the Aussonnelle tributary where concentrations varied between 2.13 and 2.84 mg/L (Table I). These values are closer to the TWW output range than to that of natural surface water because of the presence of a small TWW which discharges into the tributary.

In 1997, TP concentrations varied considerably in the Hers tributary (from 0.25 to 5.8 mg/L) because of flooding, and it had an impact on Garonne River TP concentrations at station F2 situated downstream of the Hers input where TP varied from 0.1 to 0.8 mg/L (Table I).

TP dynamics, and particularly PP dynamics, is linked to SS for discharges above 60 m^3/s (Figure 4). In rivers where sediment transport is high a significant proportion of the TP load is associated with sediment phase (Logan *et al.*, 1979; Logan, 1987).

Quantification of treatment plant for waste water (TWW) phosphorus output from 1999 data

There was a significant difference between stations situated upstream and downstream of the TWW. At G1 and G2, mean TP concentrations were 0.05 and 0.09 mg/L, respectively, while at stations downstream of the TWW, concentrations varied from 0.19 to 0.22 mg/L (Table I). The P concentration in the TWW that treats the waste water of Toulouse was very high: it varied from 5 to 11 mg/L with a mean of 7.8 mg/L. It can explain to a great extent the differences in concentrations between stations located upstream and downstream of the TWW.

In 1999, we also noticed a longitudinal gradient in the types of P present: in the most upstream station (G1), 50% of the TP was DRP and in the stations located downstream of the TWW it represented 72 to 78% (Figure 3). These downstream values were similar to those in the TWW itself.

The 1999 study was used to estimate the proportion of TWW P in the inputs entering the river along the entire studied sector of 47 km. The only known inputs of P in the Garonne River along sector G1–G5

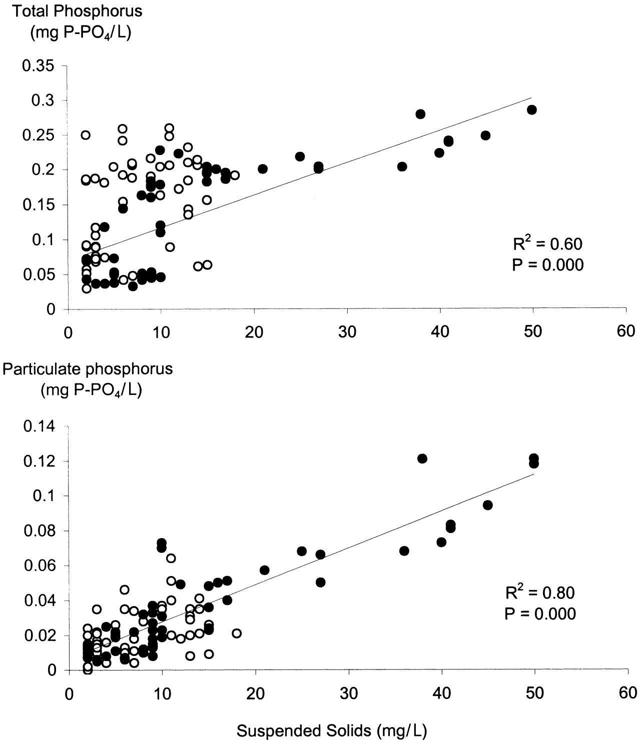

Figure 4. Relationships between P concentrations (TP and PP) and SS in the River Garonne. White circles correspond to discharges below 60 m^3/s. Black circles correspond to discharges above 60 m^3/s

are the fluxes at G1, tributary fluxes (at the Touch, the Aussonnelle, the Hers and the Save) and the TWW fluxes. In the studied sector and during low-water period, the industrial P sources and diffuse P sources owing to agricultural activities are negligible compared with P injected into the river by the TWW. The TWW contribution to P input was estimated for three situations. In the first case, we take into account the entire study of 1999. In the second case, and because we noticed that P does not behave in the same way in all river discharges, we only took into account data for discharges below 60 m^3/s. The third case only studied data for river discharges above 60 m^3/s. The results are given in Figure 5. The different cases were similar. The TWW contributed more than the half input (between 59 and 67%), G1 between 24 and 27% and the sum of the tributaries between 10 and 15%. So, the differences in P concentrations and type between stations located upstream and downstream the TWW can be largely explained for a great part by the presence of the TWW.

Phosphorus budgets

The P budgets show that average daily inputs and outputs were not in balance in the F1–F2 stretch of the 1997 study (Table II). In the 1999 study, the results varied according to the stretch and the discharge ranges (Table III).

In the 1997 study, the F1–F2 stretch showed a loss of DRP and TP. The mean daily loss was 307 and 173 kg P/day, respectively, for TP and DRP, which represents the removal of about 22 and 27%, respectively, of the P input during stream transport. Similar trends were observed by Hill (1982) during low summer flows: about 92 and 44%, respectively, of P input was retained by Duffin Creek and the Nottawasaga River in southern Ontario, Canada. In the same way, P uptake was observed in streams

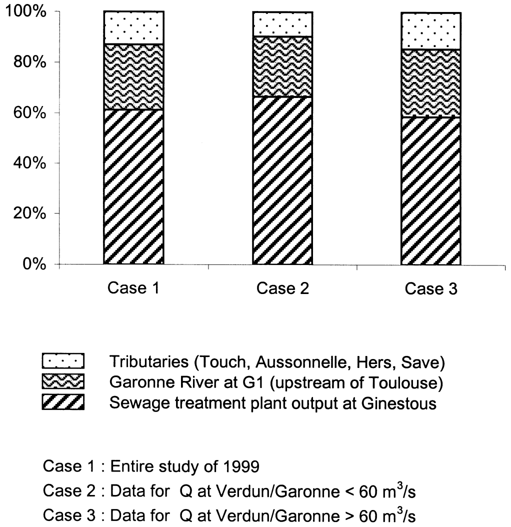

Figure 5. Proportions of various TP inputs onto the studied stretch of the Garonne River during the 1999 study

Table II. Mean (±95% CI) daily input and output of P in a stretch delimited by F1 and F2, during low river flows in October 1997

Form of P	Input (kg/day)	Output (kg/day)	Net retention (kg/day)	Loss (% of input)
DRP	650 ± 28	477 ± 24	−173 ± 36*	−27
TP	1389 ± 183	1082 ± 183	−307 ± 200*	−22

* Mean daily retention significantly different from zero at 5% level using a comparison *t*-test.

Table III. Mean (±95% IC) daily input and output of P from individual stretches in July 1999[a]

Forms of P	Q (m^3/s)	Reach	Input (kg/day)	Output (kg/day)	Net gain (+) or loss (−) (kg/day)	Loss or gain (% of input)
TP	$Q<60$	G1–G2	262 ± 17	310 ± 77	+49 ± 70	+19
		G2–G3	1046 ± 232	851 ± 106	−195 ± 165**	−19
		G3–G4	876 ± 112	897 ± 99	+21 ± 123	+2
		G4–G5	977 ± 104	892 ± 27	−85 ± 112**	−9
	$Q>60$	G1–G2	304 ± 15	395 ± 37	+91 ± 35*	+30
		G2–G3	1019 ± 61	983 ± 56	−36 ± 68	−3.5
		G3–G4	1056 ± 60	1252 ± 149	+197 ± 182*	+19
		G4–G5	1337 ± 149	1378 ± 35	+41 ± 130	+3
DRP	$Q<60$	G1–G2	115 ± 14	156 ± 20	+41 ± 29*	+36
		G2–G3	650 ± 81	669 ± 91	+19 ± 57	+3
		G3–G4	687 ± 94	692 ± 82	+5 ± 100	+1
		G4–G5	742 ± 82	717 ± 22	−25 ± 95	−3
	$Q>60$	G1–G2	162 ± 11	235 ± 32	+72 ± 30*	+44
		G2–G3	715 ± 26	748 ± 41	+32 ± 26	+4
		G3–G4	784 ± 41	846 ± 47	+62 ± 73*	+8
		G4–G5	902 ± 44	963 ± 22	+61 ± 42*	+7

[a] Mean daily loss significantly different from zero at 5% level (*) or 10% level (**) using a comparison *t*-test.

draining pine and hardwood catchments in the southern Appalachian mountains (D'Angelo and Webster, 1991). P retention was constituted about 30% of gross P transport in the Galbaek catchment during summer and 20% in the Gjern A watershed (Svendsen *et al.*, 1995). In our study there was also loss of PP, because the loss of DRP represented a little more than the half of the TP loss. Moreover, in the 1997 study it can be noticed that the quantity of P retained by the stretch is positively correlated with the quantity of P that entering the stretch (Figure 6): the greater the amount of P entering the stretch, the more retained by the stretch. The assimilative capacity of the river adapts to the P inputs.

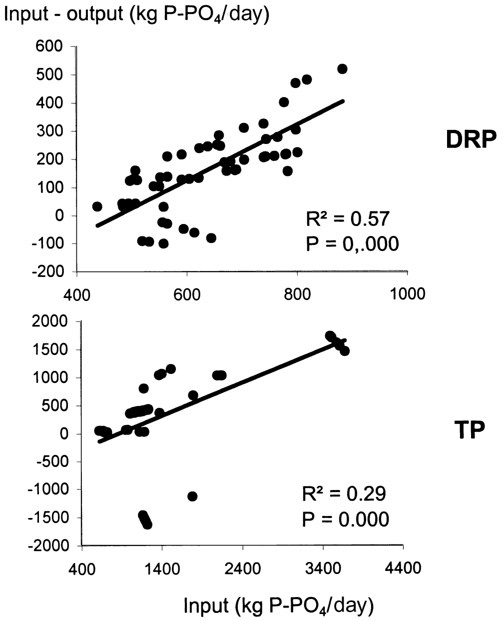

Figure 6. Relationships between P inputs and P retention in the stretch delimited by F1 and F2 of the River Garonne in 1997

In the 1999 study, there were only two stretches that retained TP and only for discharges below 60 m^3/s: G2–G3 and G4–G5. The mean daily loss for TP was, respectively, 195 and 85 kg P/day representing the removal of about 19 and 9%, respectively, of the P input during stream transport. Moreover, in these two stretches, inputs and outputs of dissolved forms of P were in balance, meaning that P is retained in particulate form. This suggested that in these two cases, biotic processes do not participate in P retention. P was retained by SS sedimentation. In the same way, for $Q < 60$ m^3/s only the G1–G2 stretch showed DRP output greater than to DRP input, the gain being 41 kg/day, which represented a contribution of about 36% of the DRP input. This suggests that an unmeasured source of nutrient input was present in this stretch.

In the other cases, when differences between inputs and outputs were significant, there was a gain of TP in the stretches for Q above 60 m^3/s. Gains of TP varied from 91 kg/day (30% of inputs) to 197 kg/day (19% of inputs). Gains of DRP varied from 61 kg/day (7% of input) to 72 kg/day (44% of input). These gains corresponded to resuspension of sediment during the increased discharge.

Phosphorus behaviour and hydrological characteristics of the Garonne River

A variety of processes may be responsible for P removal during stream transport. Biotic and abiotic processes must be considered. The two-way exchange of water between the stream and a subsurface groundwater reservoir can cause nutrient loss from the stream (Rigler, 1979; Hynes, 1983; Gibert *et al.*, 1990; Vervier *et al.*, 1992; Findlay, 1995; Brunke and Gonser, 1997; Boulton *et al.*, 1998). Exchanges of this type have been pointed out in the Garonne River (study in progress) which has an extensive hyporheic zone, with frequent interactions occurring between surface water and river bed sediment. Research on lakes and streams has repeatedly attributed the major loss of P from the water column to settling of particles as sediment (Caraco *et al.*, 1991). The role of sediments in regulating the P concentrations of the overlying water column is well known (Johnson *et al.*, 1976; McCallister and Logan, 1978; Hill, 1982). In the Garonne River, bed sediments constitute a long-term P sink. We have estimated that P subsurface sediment concentrations vary between 280 and 375 μg P/g.dw and that this P is formed essentially by non-labile forms. Moreover, in the Garonne River the layer of subsurface sediments can reach more than 2 m and can thus store large quantities of P: between 60 and 117 g/m^3 of subsurface zone. Studies of P assimilation by macrophytes indicate that they account for only a small percentage of P removal in stream systems (Meyer and Likens, 1979; Reddy *et al.*, 1987). Studies on assimilation of P by the periphyton show that this functional compartment can play a major role in regulating P concentrations of the water column (Bentzen *et al.*, 1992). In the Garonne River, the periphyton can be an important temporary P sink.

The potential of retention by the hyporheic zone and the periphyton, which represent two functional compartments of this river seems to be high: when TP input increased by about 10 times, its retention increased by about 50 times (Figure 6).

So, in the 1997 study under very low discharge, the stretch retained P and specially DRP. On the contrary, in the 1999 study, under discharges a little higher than the first one and overall under discharges that increased rapidly during the study, we noted only two cases of P retention for $Q < 60$ m^3/s and in particulate form. The other cases showed no differences between inputs and outputs or a gain of P. These observations can be explained by the fact that even if the two studies took place during a low-flow period, in the first case, this period had been well established for a relatively long time whereas, in the second study, the low-flow period had not yet stabilized. So, in the first case all the biotic processes (assimilation by vegetation, plankton, periphyton and microorganisms) and abiotic processes (sedimentation, adsorption by sediments, precipitation and exchange processes between sediment and the overlying water column) allowing P uptake were in place and playing an important role whereas, in the second case, the stream velocity was higher, biotic processes were not entirely established and were very weak. Some studies even showed that P uptake was negatively correlated with stream velocity (Meyer, 1979; Newbold *et al.*, 1983). Much of the P retained in the river during low-flow is probably transported downstream during the increase of discharge either as part of the sediment load or in solution following desorption from sediment (Johnson *et al.*, 1976; Meyer and Likens, 1979).

CONCLUSIONS

Our objective was to highlight those characteristics of the Garonne River that control P fluxes. The mechanisms that control instream P retention or release are not the same under different hydrological conditions during low-water period. The expected process, i.e. control of P dynamics by sedimentation, took place only during hydrological changes. In established low-flow conditions the amount of P, especially in the dissolved form, stored in a river may be very large. It is an active process of trapping by the functional compartments represented by the hyporheic zone and the periphytic biofilm. These two compartments' activity can remove 22% of TP from the water column.

Our study shows that the hydrological regime controls the influence of the biophysical characteristics (i.e. the periphyton and the hyporheic zone) on nutrient retention. Therefore, management of the hydrological regime can help to reduce the P fluxes circulating within the water column of the river during sensitive periods such as summer low-flow.

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