The dynamics of phosphorus in turbid estuarine systems: Example of the Gironde estuary (France)

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Abstract

Suspended particles and surface waters were collected in the Gironde estuary (southwestern France) along the salinity gradient. Dissolved inorganic phosphorus (DIP) was analyzed in the filtered surface waters. The suspended particles were sequentially leached to determine five fractions of phosphorus: exchangeable or loosely sorbed P, reactive Fe-bound P, refractory Fe oxide–bound P, P associated with apatite and carbonates, and organic P. Experiments were conducted to determine the effects of temperature, salinity, and DIP concentration on phosphorus sorption/desorption processes. The concentration and distribution of particulate phosphorus was homogeneous along the salinity gradient of the estuary, whereas it was variable in time and space in the freshwater part. DIP showed a rapid desorption of loosely sorbed P at low salinities. Desorption depended on suspended particle concentration, but not on DIP concentration. At high suspended particle concentrations, some exchangeable P remained linked to particles, until suspended particle concentration decreased downstream of the estuary. This delayed desorption of bioavailable P occurs in waters in which the penetration of light is sufficient to support photosynthesis and probably plays a major role in primary production at high salinities. Mineralization of organic phosphorus also releases available phosphorus, but this process is slow relative to the water residence time in the estuary. The budget of DIP, the loss of particulate P from the organic fraction, and the water residence time suggest that the dynamics of P in the Gironde estuary is well explained by the two processes of P release from particles to waters without P uptake.

Eutrophication is a major problem in European river systems because of high release of nitrogen and phosphorus by farming, industrial, and domestic activities. The dynamics of these nutrients and the primary production in estuarine areas are strongly dependent on their availability—in other words, on their biogeochemical cycles (Benitez-Nelson 2000). Nutrients are intensely recycled between organic and inorganic forms within coastal systems (Smith et al. 1991). Estuaries transform phosphorus speciation through biogeochemical processes or purely geochemical processes, which control P evolution and distribution at the land–sea interface. P plays a limiting role for algal blooms in turbid plumes (Herbland et al. 1998). Therefore, it is important to know the processes that control phosphorus inputs and cycling in the coastal environment.

Smith et al. (1991) showed that estuaries are generally heterotrophic and represent therefore a source of dissolved inorganic phosphorus (DIP) to the ocean. Numerous studies have been devoted to P speciation in estuarine sediments and on the subsequent benthic exchanges (e.g., Sundby et al. 1992; Berner and Rao 1994; Huanxin et al. 1997). These studies have shown that the release of P to the water column was controlled by organic matter mineralization and iron oxide reduction (Anschutz et al. 1998; Coelho et al. 2004; Lillebo et al. 2004). The phosphorus cycle in turbid estuaries is, however, not really understood because dissolved P is not controlled only by benthic exchanges and metabolic processes. Suspended particles probably play a major role in P dynamics. Experimental studies showed that sorption/desorption processes of phosphorus occurred along salinity gradients (e.g., Chase and Sayles 1980; Maher and DeVries 1994; Gardolinski et al. 2004). However, these studies were performed with sediments and not suspended particles, which constitute a large pool of potentially desorbable P in estuaries with an extended and dense estuarine turbid maximum (ETM).

Particulate phosphorus is associated with different solid fractions such as detrital apatite or particulate organic matter. P is also adsorbed or coprecipitated with metallic oxides and carbonate minerals (Froelich et al. 1982). The understanding of P behavior in turbid estuaries requires the knowledge of which forms of phosphorus can be released from suspended particles, and under which conditions. Such was the objective of this study. In the case of the Gironde estuary (southwestern France), we had to identify and quantify the evolution of phosphorus speciation on suspended particles. Sequential extractions are reliable analytical methods that permit us to differentiate P fractions. We carried out a sequential extraction method
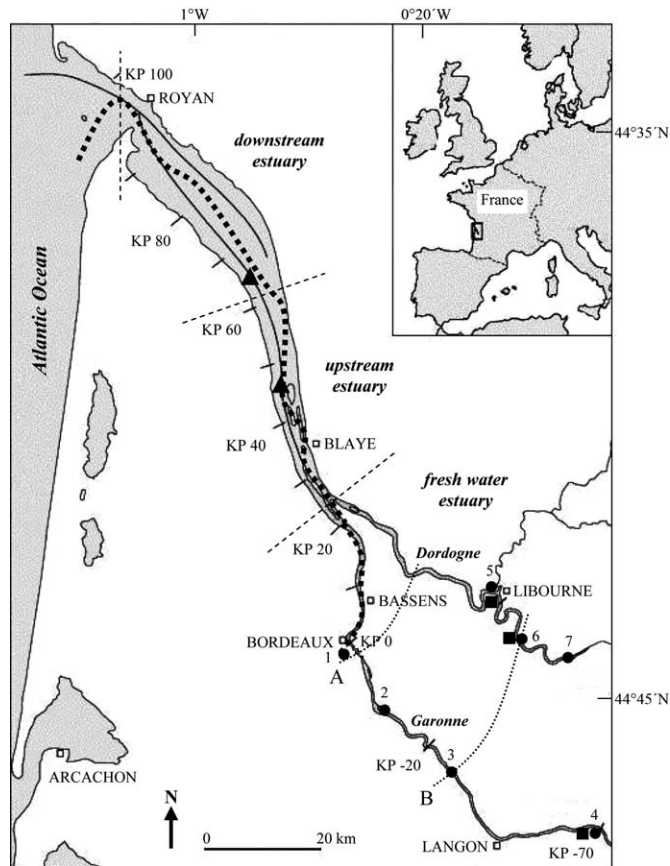
Fig. 1.   Geographic location of the Gironde estuarine system and location of sampling sites: GIROX cruises (dotted line), SOGIR cruise (triangle), fluvial stations of the 3-yr monitoring of 2001–2003 (square), and freshwater estuary stations (circles 1–7), which are located between the ETM and the upstream limit of dynamic tide. Upstream limit of saline intrusion is shown by line A. Upstream limit of tidal nodal point is shown by line B. KP, distance in kilometers from the city of Bordeaux; KP-70, upstream limit of dynamic tide.

for suspended particles that we applied to the Gironde estuary. The results have been presented with data of the dissolved fraction. Additionally, experiments in the laboratory, simulating particle transfer in a salinity gradient, have been performed to characterize dissolved particulate exchanges of phosphorus in turbid estuaries.

Study area, material, and methods

The Gironde estuarine system—The Gironde estuary is the largest estuary of Western Europe. It is formed by the junction of the Garonne and the Dordogne rivers (Fig. 1), which drain a 71,000 km^2 weakly industrialized basin. The mean discharge is 990 m^3 s^{-1} (Sottolichio and Castaing 1999). The Gironde estuary forms a macrotidal estuary, with a 1.5–5.5-m tidal range at the mouth (Castaing and Allen 1981). Water residence time in the estuary varies from 20 to 90 d depending on season and the intensity of residual currents (Castaing and Allen 1981). Annual mean solid discharge is estimated at 2.5 × 10^9 kg. About 80% of solid particle load is from the Garonne River (Parra et al. 1999).

Particles have a much longer residence time than waters in the estuary, ~2 yr on average.

The salinity gradient reaches upstream of Bordeaux (Fig. 1). The freshwater estuary, limited by the dynamic tide, extends 70 km upstream. The suspended particle concentrations reach 0.2–1 g L^{-1} at the surface of the ETM, and up to 10 g L^{-1} at the bottom. The position and extension of the ETM depends on hydrologic conditions and residual currents. During neap tides, a part of the maximum turbidity zone settles, forming anoxic fluid mud layers close to the bottom (Abril et al. 1999, 2000). Because of steep light attenuation in the ETM, primary production is limited in the Gironde estuary, and seasonal phytoplanktonic blooms occur only at high salinities downstream of the ETM (Irigoien and Castel 1997; Veyssy et al. 1998).

Material and methods—Surface water samples (−1 m) were collected with a 5-liter Niskin bottle along the salinity gradient from salinity 33 (mouth) to 0.3 (Bordeaux) during three cruises: GIROX 2, 3, 4, in September 2002, June 2003, and September 2003, respectively. Additionally, surface water samples were collected 1 month after a flood event in January 2004 at two sampling stations located in the middle and in the lower estuary (SOGIR cruise). Samples from the freshwater estuary were collected at seven sites, located upstream of the ETM (Fig. 1). The sampling was done during ebb tide in January, February, and March 2004. A previous monitoring of DIP concentrations in the Gironde estuary and tributaries was performed between 1995 and 1996. Suspended particles from the Garonne and Dordogne rivers were collected every month from 2001 to 2003. Particles were separated by centrifuging a large volume of water. Particulate P from these samples was extracted from a whole-rock digestion, which was performed according to Loring and Rantala (1992) with a triacid attack.

Water samples were filtered on 0.45-μm cellulose acetate membranes and stored at 4°C in polypropylene bottles before the measurement of DIP concentrations within 24 h by the molybdate blue method (Murphy and Riley 1962). Samples collected during the GIROX 4 cruise and in 2004 were filtered on board on two preweighed filters: one on GF/F filter to evaluate suspended particle concentrations and the other on 0.45-μm Millipore Teflon membrane, for sequential extractions of particulate P. Chlorophyll *a* (Chl *a*) concentrations were determined fluorometrically on 90% acetone extracts of particles from freshwater subsamples retained on GF/F filters.

Sequential extraction—Different methods have been used to extract P from marine sediments (e.g., Ruttenberg 1992; Anschutz et al. 1998; Tiyapongpattana et al. 2004). On the basis of these works, we tested an extensive sequential attack to optimize the particulate P analysis of estuarine suspended particles. One sample from the freshwater part of the Gironde estuary was filtered to give several aliquots. Suspended particles were leached separately with each solution as well as sequentially to examine the extraction potential of the solutions. The sequential extraction was done in duplicate for all samples. We noted

Table 1. The sequential extraction procedure for suspended particles. Hours represent the duration of each extraction.

Step	Extractant	Extracted fraction	Chemical reaction
I	H_2O + $HgCl_2$, 3×24 h = IDE	Exchangeable or loosely sorbed P	Natural desorption without bacterial activity in artificial water; pH in situ
II	Ascorbate, 24 h	Reactive Fe(III)- bound P	Ascorbic acid reduces reactive Fe oxides and dissolves associated P; pH 8
III	CDB, 4 h	Refractory Fe(III)-bound P	Dithionite reduces remaining Fe(III)-oxides and associated P; pH 7
IV	HCl (1 mol L^{-1}) 16 h	P associated with authigenic, detrital, and biogenic apatite and carbonates	Acid dissolution of all carbonates and apatites
V	H_2SO_4 (18 mol L^{-1}) 16 h	P bound with organic matter	Acid dissolution of organic matter (plankton, humic acids, …)

good reproducibility, with an error of <10%. We also obtained the same quantity of particulate P for fresh, frozen, and dried samples. We optimized the sequential extraction to five steps (Table 1) as follows.

Exchangeable or loosely sorbed phosphorus (IDE): The equilibrium between the suspended particles and the DIP concentrations is controlled by exchange of phosphorus between particles and water. Phosphorus involved in this reaction is qualified as exchangeable phosphorus and is mostly adsorbed phosphate. Aminot and Andrieux (1996) developed a thermodynamically satisfactory procedure called the infinite dilution extrapolation method (IDE), which reproduces the natural conditions of the phosphorus desorption with an increasing dilution of particles and with an inhibition of bacterial activity with $HgCl_2$.

Phosphorus associated with reactive and refractory Fe oxyhydroxides (ascorbate and CDB): The selective dissolution of amorphous iron oxides and associated P was performed with an ascorbate solution (Anschutz et al. 1998, 2005). Extraction of other Fe(III) phases was carried out with a solution of citrate-dithionite-bicarbonate (CDB; Lucotte and d'Anglejan 1985).

Phosphorus associated with carbonates and apatite (HCl): The detrital fraction of P associated with Ca, is commonly extracted by dissolution with 1 mol L^{-1} hydrochloric acid (Ruttenberg 1992; Berner et al. 1993; Conley et al. 1995). This extractant dissolves also biogenic apatite (fish debris) and authigenic apatite, commonly extracted by ammonium chloride and sodium acetate, respectively. We noted that the suspended particles of the Gironde estuary contained a very low quantity of phosphorus associated with these two extractants, and only 1 mol L^{-1} HCl extraction has been used.

Phosphorus bound with organic matter (organic P): The organic fraction is commonly extracted by an oxidation at 550°C with 1 mol L^{-1} HCl (Ruttenberg 1992; Berner et al. 1993), with H_2O_2, or by digestion with strong acids (HNO_3, H_2SO_4, or a mixture; Gleyzes et al. 2002). The digestion of the residue in sulfuric acid (97%) was the most reliable and reproducible for our samples.

After the extraction procedure, leaching solutions were clarified by centrifuge and diluted with water or 0.2 mol L^{-1} HCl. Extracted phosphorus was measured by colorimetric methods especially adapted for each matrix. The calibration solutions were prepared with blank solution. The analytical error was estimated at <10% from replicate samples. The final concentrations are given in micromoles per gram (μmol g^{-1}) of suspended sediment. The error on the results became high when the amount of particles on filters was <5 mg, which was not often the case. Iron was analyzed by Flame Atomic Absorption Spectroscopy on samples extracted with ascorbate and CDB.

Laboratory experiments—Temperature effect on the phosphorus release: A first experiment was conducted to determine the role of temperature on desorption of phosphorus, without change in any other parameters. A freshwater sample from the Garonne River at Bordeaux that contained 0.121 g L^{-1} suspended particles and with an in situ DIP concentration of 1.4 μmol L^{-1} was poisoned with $HgCl_2$ (40 mg L^{-1}) and maintained in the dark at various temperatures for 24 h (2.2, 4, 17.7, 19.5, 28, 35°C) before analysis of DIP.

Salinity effect on the phosphorus dynamics: We collected 45 liters of surface freshwater at Bordeaux that contained 0.031 g L^{-1} suspended particles. With a centrifuge, we prepared several vials (50 mL) with higher suspended particle concentrations: 3.0, 0.732, 0.5, and 0.083 g L^{-1}. An aliquot was poisoned with $HgCl_2$ for each vial. Samples underwent a continuous increase of salinity by slowly adding concentrated artificial seawater with a peristaltic pump. The salinity of the mixture was continuously controlled with a calibrated conductimeter. The suspensions were continuously stirred with a magnetic mixer and maintained in a ventilated environment to keep a constant partial pressure of CO_2 and O_2. Aliquots were collected with a bypass device. Each mixing experiment was carried out within 4 h, which is approximately the duration of the floodtide in the Gironde estuary. Vials were maintained at laboratory temperature in the dark. The distribution of particulate P was determined at the initial and final steps of the experiments with the sequential extraction on the suspended particles.

In a third experiment with a particle concentration of 0.732 g L^{-1}, we also tested the effect of an instantaneous jump of salinity from 0 to 5. First, saline water without DIP

Table 2.   Suspended particle matter (SPM), DIP, Chl *a*, phosphorus fractions, and total particulate P concentrations in freshwater estuary sites during winter.

Freshwater estuary sample station	Sampling date	SPM (g L^{-1})	DIP (μmol L^{-1})	Chl *a* (μg L^{-1})	Phosphorus fraction (μmol g^{-1})					Total P (μmol g^{-1})
					P_{IDE}	P_{ASC}	P_{CDB}	P_{HCl}	P_{H2SO4}	
1	January	0.121	1.39	1.06	5.0	4.7	5.7	6.4	8.3	30.2
	February	0.025	1.24	0.65	6.3	5.9	9.4	7.9	14.9	44.3
	March	0.006	0.74	4.21	11.7	5.4	10.7	9.5	14.3	51.5
2	January	0.109	1.39	0.89	6.0	5.9	4.3	5.7	8.9	30.9
	February	0.020	1.15	0.49	5.8	5.8	5.4	9.4	7.6	34.0
	March	0.004	0.64	4.02	11.7	4.5	6.0	19.2	19.7	61.1
3	January	0.068	1.35	0.87	6.8	5.2	6.5	4.9	18.1	41.4
	February	0.019	1.15	0.43	5.8	4.3	6.3	11.6	5.9	34.0
	March	0.007	0.64	3.90	6.2	4.1	1.9	14.6	15.6	42.4
4	January	0.078	1.30	1.01	6.4	4.1	4.0	5.7	15.6	35.8
	February	0.010	1.29	0.44	7.7	9.1	7.6	11.6	21.8	58.0
	March	0.004	0.59	3.79	8.7	10.8	7.5	18.5	18.3	63.9
5	January	0.062	0.77	0.62	7.4	8.4	7.4	9.9	30.7	63.9
	February	0.012	0.76	0.34	2.3	5.3	6.3	6.2	10.3	30.4
	March	0.013	0.30	2.37	8.6	6.3	3.2	22.5	20.2	60.9
6	January	0.060	0.72	1.03	5.2	3.9	5.3	8.5	29.4	52.3
	February	0.014	0.66	0.34	6.2	7.6	8.3	13.0	19.2	54.3
	March	0.006	0.30	2.10	4.9	10.7	5.4	14.6	18.7	54.3
7	January	0.019	0.63	0.44	6.1	5.4	5.7	5.1	7.0	29.3
	February	0.019	0.61	0.27	6.2	8.3	10.8	13.4	23.9	62.6
	March	0.004	0.30	2.10	12.8	12.6	8.3	12.1	10.5	56.3

was added, and subsequently, saline water that contained 10 μmol L^{-1} of DIP was added to the suspension.

Results

Suspended particles—The suspended particle concentrations of the freshwater estuary increased from the river to Bordeaux in January 2004 (Table 2). In March 2004, precipitation was low, and the river discharge decreased, inducing a decrease in particle concentration down to <0.01 g L^{-1}. In September 2003, the ETM was located in the upstream parts of the salinity gradient (Fig. 2) close to Bordeaux. The suspended particle concentrations showed a maximum of 9 g L^{-1} in surface waters at Bordeaux (salinity 0.3). The concentration decreased to <1 g L^{-1} 20 km downstream of Bordeaux (salinity 5) and fluctuated between 0.15 and 0.7 g L^{-1} from this point until salinity 23. They decreased to concentrations <0.065 g L^{-1} in the lower estuary.

Dissolved inorganic phosphorus—In the freshwater estuary, DIP concentrations remained approximately constant along the sections of the Garonne and the Dordogne rivers for a given period (Table 2). DIP concentrations were about twice as low in March as in January and February 2004. Chl *a* concentrations increased in March, from ~1 μg L^{-1} to 4 μg L^{-1} in the Garonne River and to 2 μg L^{-1} in the Dordogne River. The temporal variability of DIP concentrations in river waters showed no tendency and fluctuated between 5 and 0.8 μmol L^{-1}, with an annual average of 1.6 μmol L^{-1} for both rivers (Fig. 3). Downstream of Bordeaux, DIP concentration versus salinity keep always the same bell-shaped profiles for all

GIROX cruises, with only slight changes of concentrations (Fig. 2). We noted an increase in the low-salinity zone (0–7). For example, in September 2003, DIP concentration increased from 2.4 μmol L^{-1} at Bordeaux (salinity 0) to 3.2 μmol L^{-1} (salinity 7). Then, the concentrations decreased irregularly with increasing salinity by dilution and reached 0.6 μmol L^{-1} in seawater. These nonconservative profiles indicate an estuarine source of DIP.

Particulate phosphorus—Phosphorus speciation in a freshwater estuary: Concentrations of total particulate P from suspended particles of the Garonne and the Dordogne rivers collected between 2001 and 2003 were 33 ± 10 μmol g^{-1}, and 44 ± 13 μmol g^{-1}, respectively. These values corresponded also to the concentrations of total particulate P averaged for the 4 months before the sampling of particle P in the salinity gradient (May to September 2003). Organic P corresponded to an average of 11 ± 3 μmol g^{-1}. Ascorbate, CDB, and IDE each extracted ~15% of total P, which corresponded to an average of 5 ± 1 μmol g^{-1} for each fraction (Table 2). The Fe : P ratio from ascorbate extractions ranged between 9 and 30. Iron concentrations extracted by CDB were higher than ascorbate extractions, inducing a high CDB Fe : P ratio of between 10 and 70.

Phosphorus speciation in the saline estuary (ETM: The total particulate P concentrations of the estuarine suspended matter collected in September 2003 was almost constant over the salinity gradient, with values between 20 and 25 μmol g^{-1} (Fig. 4). We noted a slight decrease to 17 ± 1 μmol g^{-1} at salinities >28 . P concentrations of each fraction were fairly constant. The concentrations of P extracted with HCl, CDB,
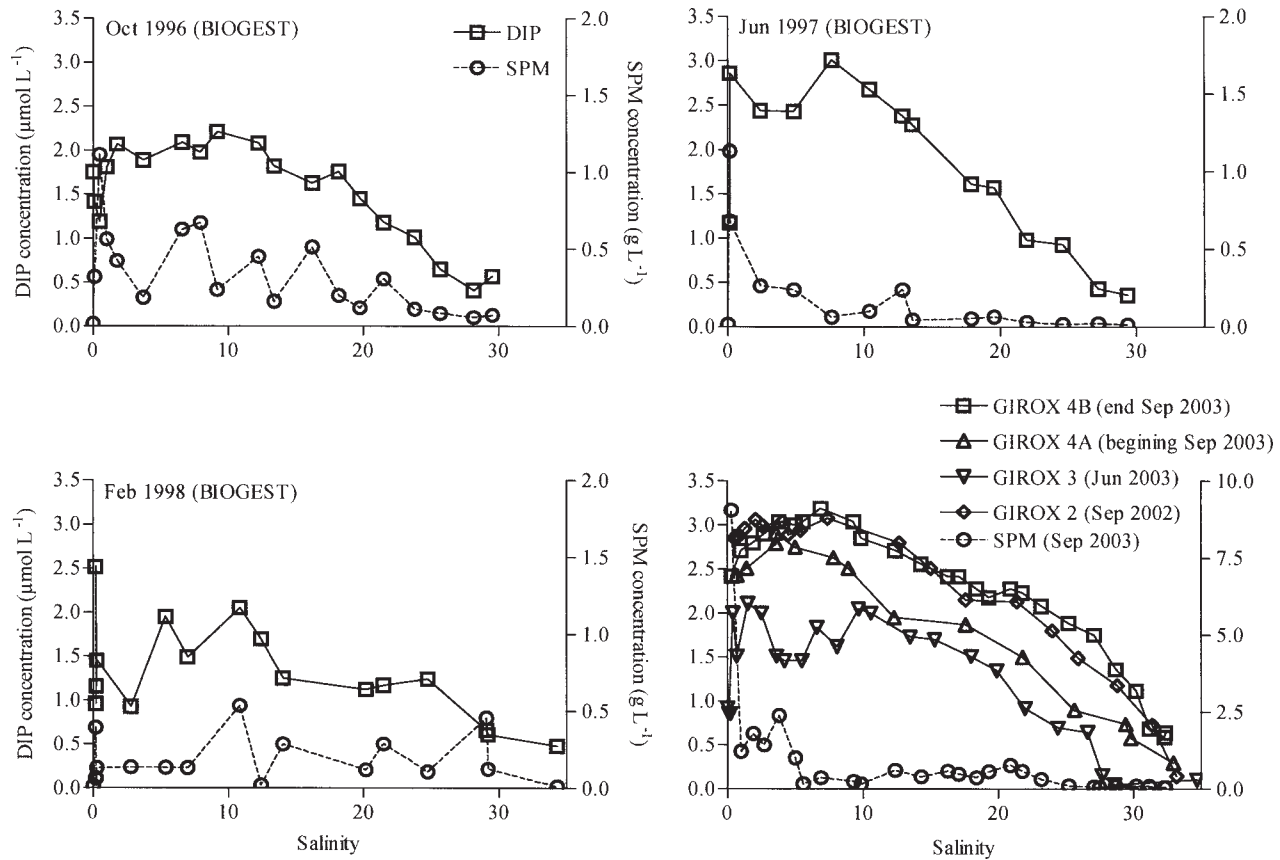
Fig. 2.   Dissolved inorganic phosphorus concentrations (μmol L^{-1}) and suspended particle matter (SPM, g L^{-1}) concentrations at the surface along the salinity gradient in the Gironde estuary at different times (data from BIOGEST program and GIROX cruises).

and ascorbate were within the range of values measured for freshwater particles. The IDE and organic P fractions were significantly lower. Exchangeable P extracted by the IDE procedure fluctuated between 2 and 4.3 μmol g^{-1}. The

organic fraction was around 4.7 μmol g^{-1} along the salinity gradient. The Fe:P ratio extracted by ascorbate was remarkably constant between salinities 0 and 28, with 10 $\pm$ 2. In more saline water, the value reached 13 $\pm$ 1. The Fe:P ratio
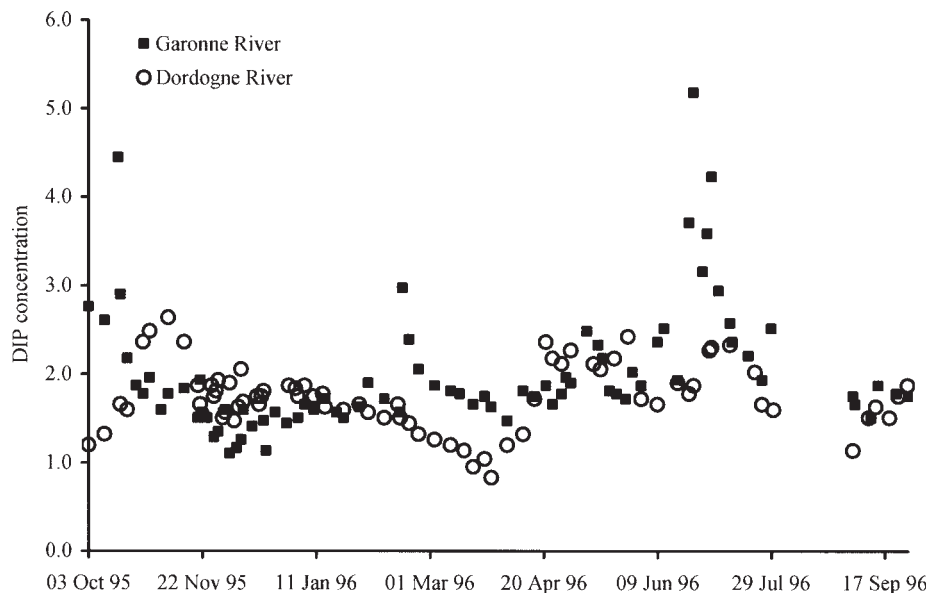
Fig. 3.   Dissolved inorganic phosphorus concentrations (μmol L^{-1}) in Garonne and Dordogne rivers between 1995 and 1996.
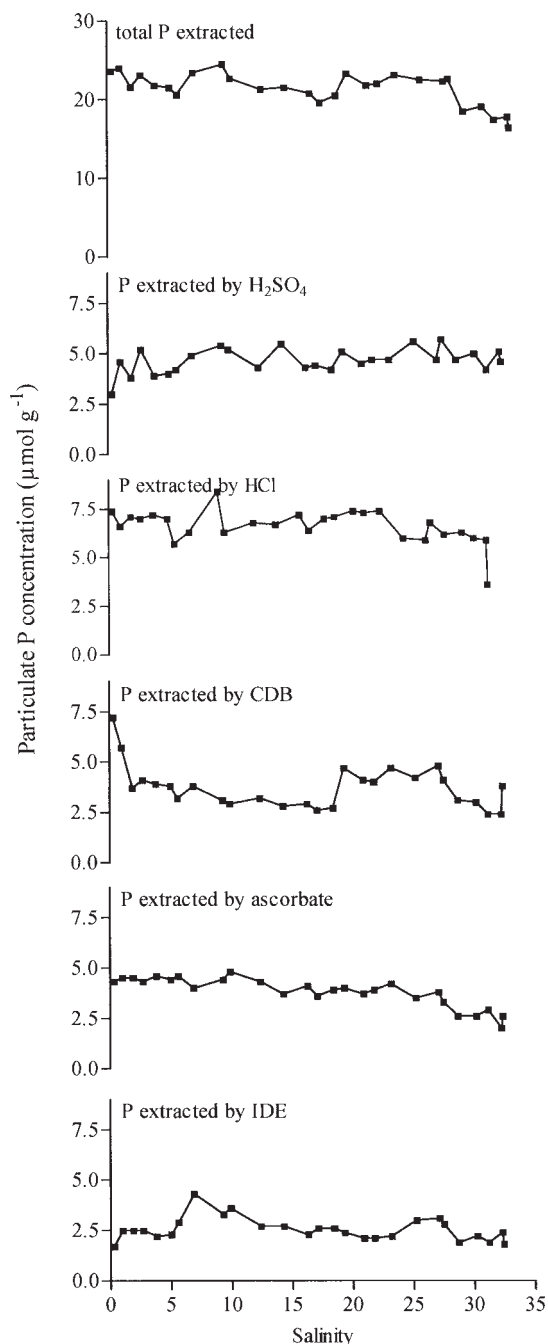
Fig. 4. Concentration of phosphorus (μmol g^{-1}) extracted from the suspended particles of the Gironde estuary along the salinity gradient (samples of GIROX 4B mission). See Table 1 for the relationship between chemical extraction and the speciation of P.

extracted by CDB was more variable (between 18 and 56) because of greater variability of P_{CDB} and to a relatively constant concentration of Fe_{CDB}.

The samples collected in January 2004 showed a higher total particulate P concentration ($\sim$30 μmol g^{-1}) than those collected in September 2003 (Fig. 5). The January 2004 sampling occurred after a huge flood event in December 2003, which brought fresh particles in the

estuary that contained >40 μmol g^{-1} of total P, explaining the higher particulate P concentrations (Table 3).

Influence of temperature and salinity on phosphorus desorption: During the experiment in which a suspension was maintained at different temperatures for 24 h from 2.2°C to 35°C, the DIP concentrations remained at the initial concentration 1.4 μmol L^{-1}. Therefore, the temperature, as a single variable, has no effect on phosphorus desorption.

The results of the second experiment are shown in Fig. 6. Most of the phosphate desorption occurred at low salinities, which is in agreement with the in situ bell-shaped DIP profile (Fig. 2). For the lowest suspended particle concentrations (0.083 g L^{-1}), the phosphate was released at salinity <5. For higher concentrations (0.500, 0.732, and 3.000 g L^{-1}), desorption occurred until salinity 15. The observed desorption occurred in <2 h, with and without $HgCl_2$, because each experiment lasted <4 h. The amount of desorbed P increased with particle concentrations (Fig. 7). The particles contained initially 30 μmol g^{-1} of total P and 7 μmol g^{-1} of exchangeable P extracted by the IDE method. Phosphate desorbed from the solid corresponded to an extraction of 35%, 14%, 11%, and 4% of exchangeable P for the experiment with 0.083, 0.5, 0.732, and 3 g L^{-1} of particles, respectively (Fig. 7).

Phosphorus desorption occurred after the sudden jump in salinity from 0 to 5 (experiment 3). The DIP concentration increased from 1.9 to a constant concentration of 2.4 μmol L^{-1} after 2 h (Fig. 8), corresponding to an addition of 0.5 μmol L^{-1}. We observed the same kinetics of desorption during mixing with seawater that contained initially 10 μmol L^{-1} of DIP. In that case, the addition of saline water with 10 μmol L^{-1} of DIP corresponded to a direct addition of 1.1 μmol L^{-1} of DIP, which induced the difference between both curves in Fig. 8. The DIP concentrations progressed from 1.9 to 3.0 μmol L^{-1} because of mixing and then to 3.5 μmol L^{-1} after 2 h because of phosphorus desorption. P extraction from the particles corresponded again to 0.5 μmol L^{-1}. Consequently, the quantity of P desorbed from estuarine particles by the salinity increase was independent on the initial DIP concentration of the water, within the range of DIP concentrations in the experiment.

Discussion

Spatial and temporal evolution of particulate phosphorus—Total P concentrations in particles collected in the freshwater estuary during winter 2004 and from 2000 to 2003 ranged between 20 and 70 μmol g^{-1}, with an average of 33 $\pm$ 3 μmol g^{-1}. Particulate P concentrations are probably linked to the particle size and organic matter content. Fine particles have a high sorption capacity for P (Berner et al. 1993; Maher and DeVries 1994; Bowes et al. 2003). The major form of particulate P was the organic fraction extracted with H_2SO_4. This fraction was higher in March, probably as a result of an intensification of primary production in the river water, which is in agreement with the increasing values of Chl *a* and the DIP decrease during this period (Table 2).
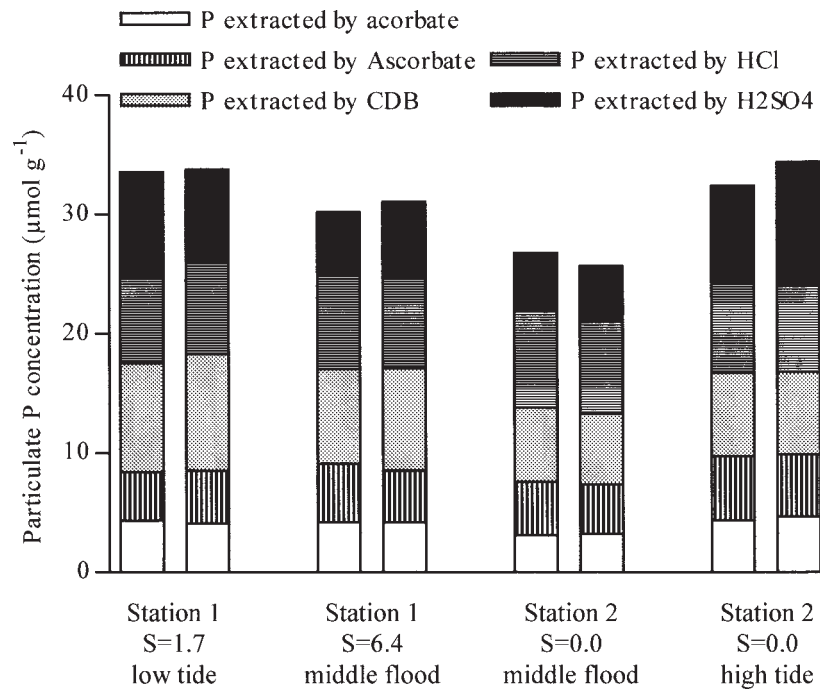
Fig. 5. Particulate phosphorus concentrations (μmol g^{-1}) of suspended particles of the Gironde estuary collected in January 2004 (SOGIR mission). The measures for Sta. 1 (downstream sampling site) and for Sta. 2 (upstream sampling site) were made in duplicate.

Total particulate P concentrations remained constant in the salinity gradient, as expected in a well-mixed turbid estuary. The concentration was 23 $\pm$ 2 μmol g^{-1} in September 2003 (Fig. 4) in the 0–28 salinity interval, which represented a net loss of ~10 μmol g^{-1} compared with the mean P concentrations of freshwater particles. This net loss corresponded basically to a decrease of organic P and of the most exchangeable P, whereas P associated with Ca (HCl) and Fe (ascorbate and CDB) remained constant. Organic P extracted with H_2SO_4 dropped from a mean value of 11 μmol g^{-1} in river particles to ~4.7 μmol g^{-1} in the saline estuarine particles. The concentration of P extracted with IDE dropped from values generally >5 μmol g^{-1} to 2.5 μmol g^{-1}. The higher values of total particulate P was measured on the lower and middle estuary during winter 2004 (30 $\pm$ 2 μmol g^{-1}; Fig. 5), probably derived from particle input from upstream by the previous flood (with ~40 μmol g^{-1}; Table 3). At salinities >28, suspended particle load and particulate P concentration were low. These samples were collected in the plume outside the estuary. These suspended particles originated

probably from an older particle pool that transited earlier through the estuary. The distribution of particulate P appears to be here a tool for segregating several consortia of mixed particles in the salinity gradient.

DIP release—The annual average DIP concentration of river waters was 1.6 $\pm$ 1.0 μmol L^{-1} (Fig. 3). DIP concentration reached 3.0 $\pm$ 1.0 μmol L^{-1} within the 0–10 salinity interval (Fig. 4), then it decreased by dilution with seawater toward the mouth of the estuary and dropped to 0.5 $\pm$ 0.2 μmol L^{-1} in the marine environment (Fig. 4). Such bell-shaped DIP profiles have already been noted in other estuaries (Kaul and Froelich 1984; Fox et al. 1985; Forsgren et al. 1996) and indicate a DIP release along the salinity gradient. This implies global processes of water particle interactions in the salinity gradient. Our experiments on Gironde particles (Figs. 5, 6) showed that the addition of saline water to freshwater induced a fast (minutes to hours) desorption of P, which started at the first contact of particles with saline water. We observed identical kinetics of desorption when the biological activity was inhibited with $HgCl_2$, which shows that the desorption process is purely abiotic. These results agree with the previous works of Chase and Sayles (1980) and Fox et al. (1986), which showed a fast (some hours) enrichment of DIP of 0.7–1 μmol L^{-1}, in seawater mixing experiments with Amazon River particles, to reach a final concentration of 2–2.5 μmol L^{-1} in the case of high particle concentrations (>0.5 g L^{-1}).

The proportion of desorbed P from suspended particles with concentrations >0.5 g L^{-1} corresponded to <3% of total particulate P and <15% of the most exchangeable fraction (IDE extraction). For the experiment at

Table 3. Mean total particulate P concentrations of suspended particles in freshwater estuary stations during the flood of the 05 and 06 December 2003.

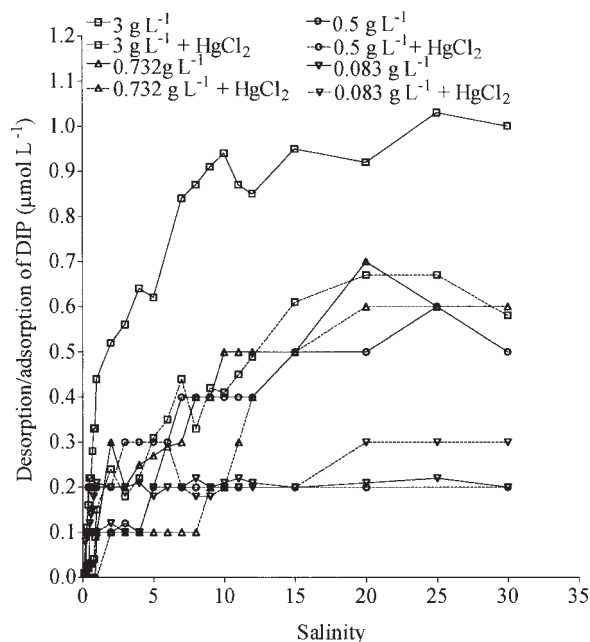| Sampling date	Time of day (h)	Total P (μmol g^{-1})
05 Dec	13:45	27.8
05 Dec	20:40	37.3
06 Dec	10:15	44.2
06 Dec	13:30	41.5
06 Dec	17:15	33.8

Fig. 6. Desorption/adsorption of phosphorus (μmol L^{-1}) from suspended particles of the Gironde estuary with a regular increase of salinity during in vitro experiments. Nonpoisoned units are represented with full lines, and poisoned units are represented with dotted lines.

0.083 g L^{-1}, particle P speciation at the end of the experiment was not performed because the mass of particles in the 50-mL experimental vial was too low. However, desorbed P was 2.5 μmol g^{-1}, which corresponded to ~35% of IDE extracted P. Our field data show that estuarine particles have lost >50% of their exchangeable P relative to river particles. This suggests that desorbed P came from the IDE-extracted fraction. Froelich (1988) and Suzumura et al. (2000) showed that phosphorus was a very reactive anion that was taken up by particles from freshwater through a complex series of sorption reactions, depending on particle mineralogy. In saline waters, other anions, such as OH$^-$, F$^-$, SO$_4^-$, and B(OH)$_4^-$, compete for adsorption sites. They replace P on the particle surface,
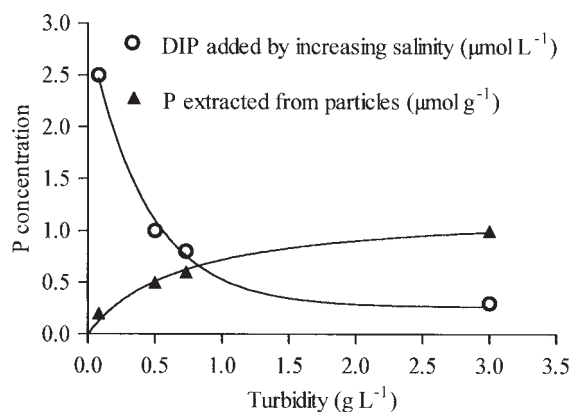

Fig. 7. Quantity of phosphorus desorbed from suspended particles of the Gironde estuary into saline solution (μmol L^{-1}) and extracted from the particulate exchangeable fraction (μmol g^{-1}) according to the suspended particle concentrations (g L^{-1}).
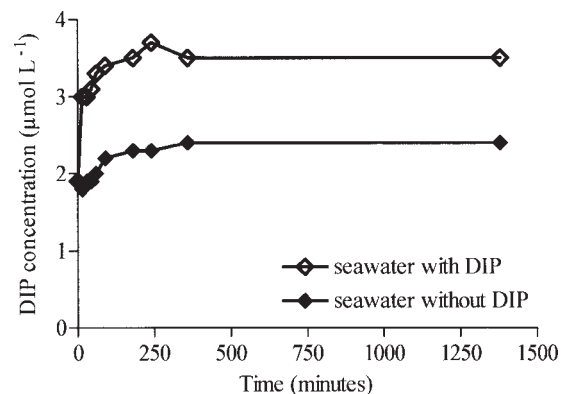

Fig. 8. Kinetics of phosphorus desorption (μmol L^{-1}) from suspended particles (0.732 g L^{-1}) during a sudden increase of salinity (jump from salinity 0 to 5) by addition of phosphorus-free saline water and a saline water that initially contained 10 μmol L^{-1} of dissolved inorganic phosphate.

inducing P desorption (Froelich 1988). Desorption of P was not dependent on the initial DIP concentration of saline water within the range of concentrations measured in the Gironde estuary (Fig. 8).

Desorption experiments (Fig. 6) show that particle P release was achieved within a narrow salinity interval (0–3) for low suspended particle concentration and, from salinity 0 to 15, for particle concentrations >0.5 g L^{-1}. The bell-shaped profiles of DIP versus salinity of the Gironde estuary are more regular than the profiles of suspended particles. This suggests that once P is released from particles because of the increasing salinity, it experiences limited resorption because the suspended matter concentration decreases also.

The quantity of DIP released by adding saline water increased with the suspended particle concentration. More P is desorbed from particles when the particle concentration is low (Fig. 7). In other words, some desorbable P remained linked to particles at high suspended matter concentrations. The consequence is that particles of hyperturbid estuaries release rapidly a part of adsorbed P at the boundary between fresh and saline waters. They also release another part downstream, at the boundary between the ETM and less turbid saline waters, often located at salinities >15. This delayed desorption of bioavailable P in waters where the penetration of light becomes sufficient to support photosynthesis probably plays a major role for primary production in estuarine parts downstream and plumes at sea (Herbland et al. 1998; Coelho et al. 2004).

Phosphorus associated with organic matter fraction represents theoretically a larger source for dissolved P originating from suspended particles than easily desorbable P. Experiments conducted with and without poisoned waters showed identical results of P desorption, which suggests that P was not released from organic matter mineralization within the course of the salt addition (3 h). Organic P follows organic C, which decreases from a mean value of 3.2 wt % in the Garonne River to a fairly constant concentration of 1.5 wt % in the Gironde ETM (Veyssy et al. 1998). Organic phosphorus loss must be related to the

Table 4.   Quantity of DIP in the Gironde estuarine system. All values are given for each 10-km section in the Gironde estuary. The wet section and water volume for each section are calculated from Jouanneau and Latouche (1981) for an average midtide situation. Salinity and the DIP concentration are deduced from the measures realized in September 2003 and averaged for each section. Total DIP is calculated from the concentration of DIP and from the water volume. Freshwater DIP is deduced from the proportion of freshwater in each section according to the mean salinity. Finally, added DIP is the difference between total DIP and freshwater DIP.

Position (PK)*	Wet section (1,000 m^2)	Average salinity	Water volume (10^8 m^3)	DIP (μmol L^{-1})	Total DIP (10^3 mol)	Freshwater DIP (10^3 mol)	Added DIP (10^3 mol)
0	0	1		1.6			
+10	3	1	0.15	2.71	32	23	9
+20	5	2	0.40	2.8	110	60	50
+30	11	3	0.80	3	232	117	115
+40	21	4	1.60	3	480	227	253
+50	28	6	2.45	3.1	747	325	422
+60	40	12	3.40	2.7	986	357	629
+70	54	17	4.70	2.4	1,199	387	812
+80	85	23	6.95	1.8	1,460	381	1,078
+90	105	29	9.50	1	1,330	261	1,069
+95	90	32	4.88	0.7	414	67	348
			—		—	—	—
			34.8		6,990	2,205	4,785

* KP, distance in kilometers from the city of Bordeaux.

mineralization of organic matter in the maximum turbidity zone (Berner and Rao 1994; Abril et al. 2002). The average molar C P ratio of river organic particles was 242. It increased to 266 in the estuary. We deduce that the mineralized part has a C P ratio of 225. This ratio is far above the Redfield ratio of 106, which indicates a continental origin for mineralized organic matter.

The shape of the DIP profile depends on the water residence times of waters and suspended matter. Table 4 presents the volume of water and the quantity of DIP for each 10-km section in the Gironde estuary. The volumes of water are given for an averaged midtide situation. The September 2003 conditions are used for salinities and DIP concentrations as a function of position. The total amount of DIP between Bordeaux and the mouth of the estuary is $\sim 7 \times 10^6$ mol. Column 7 of Table 4 represents the amount of DIP from direct input of freshwater. Values have been calculated from the proportion of freshwater in each section, with the use of salinity, with a mean concentration of the freshwater end member of 1.6 mol L^{-1}. Freshwater DIP represents 30% of total DIP. The difference between total DIP and freshwater DIP (i.e., DIP released from particles [column 8 of Table 4]) corresponds to 4.8×10^6 mol. The mean annual discharge of suspended matter of fluvial origin is 2.5×10^9 kg (Jouanneau and Latouche 1981). According to our data, it corresponds to an input of 83×10^6 mol yr^{-1} of particulate P (that contains 33 μmol g^{-1} of P). We observed that ~ 10 μmol g^{-1} of P was lost by the particles between the Garonne River and the saline estuary (i.e., 25×10^6 mol yr^{-1}). The ratio between added DIP (4.8×10^6 mol) and the annual loss of particulate P represents 0.19 yr, or 69 d. This time can be compared with the residence time of freshwater in the estuary. The volume of freshwater end member is 1.38×10^9 m^3. It is supplied during 69 d when the discharge is 230 m^3 s^{-1}. This value is low compared with the mean annual discharge, but it corresponds to the conditions in summer 2003, consistent with the above calculation. The

match between the budget of DIP, the loss of particulate P, and the water residence time suggests that the dynamics of P in the Gironde estuary is well explained by processes of P release from particles to water, without P uptake. Fluxes of P from the consolidated bottom sediment should be taken into account. However, organic carbon budgets have shown that <10% of organic matter input is mineralized into sediment, whereas 50% is mineralized in the ETM (Etcheber 1986), which suggests that benthic fluxes of DIP must be much lower than P released in the ETM.

P lost by the particles between the Garonne River and the saline estuary originates from the exchangeable fraction and the mineralization of the organic fraction. The experimental study shows that most of the P desorption occurred within the salinity range 0–12. Metabolic carbon release, and therefore metabolic P release, occurs mostly in the ETM (Abril et al. 2002), which is predominantly located within the same salinity range. Mass budget calculations show that this salinity range contains only 30% of added DIP (Table 4), even if it corresponds to the region in which DIP concentrations are maximal. Therefore, most of the added DIP is transferred toward the lower estuary.

One of the major processes of dissolved phosphorus release in pore water of sediment is iron oxide reduction below the oxic layer (Sundby et al. 1992; Fang 2000; Bowes et al. 2003). Anaerobic diagenetic processes, such as denitrification and manganese oxide reduction, occur periodically in the ETM of hyperturbid estuaries like the Gironde estuary (Abril et al. 1999). Ascorbate-extracted Fe shows no variations along the salinity gradient, which suggests that Fe oxide reduction and subsequent dissolved P release from suspended particles does not occur. The ascorbate Fe:P molar ratio of 10 all along the estuary is within the value noted for several oxic marine sediments (Anschutz et al. 1998) and is interpreted as a sorption equilibrium between phosphate and ascorbate-extractable Fe phases. The salinity gradient apparently does not alter this equilibrium.

Particulate P in the ETM is almost uniform, and the different fractions are homogeneous. Homogenization is due to the high residence time of particles, mixing, and low reactivity of most of particulate P. A part of particulate P is, however, reactive and is transferred to the dissolved fraction in the upper part of the salinity gradient in the maximum turbidity zone. Desorption of P and organic matter mineralization are responsible for the bell-shaped profile of DIP versus salinity. Abiotic desorption of most exchangeable P occurs once freshwater particles encounter saline waters. The proportion of P desorbed relative to exchangeable P depends on suspended matter concentration, and not on dissolved P concentration. At high suspended matter concentration, available P remains adsorbed on particles. Therefore, some exchangeable P is available for release downstream of the ETM and probably controls the P limitation of primary production in the Gironde plume (Herbland et al. 1998). The observation of a similar distribution of DIP in other turbid estuaries suggests that the same processes regulate the DIP concentrations. A great part of organic phosphorus is mineralized into the maximum turbidity zone. This process of DIP formation is slower than abiotic desorption but faster than particle residence time within the estuary. Therefore, water in contact with particles is renewed during organic P mineralization, and resulting DIP is diluted into a large volume of water and transferred toward the lower estuary and coastal ocean.

The phosphorus distribution in coastal areas has been used to define the autotrophy/heterotrophy balance, with the LOICZ method (Smith et al. 1991). This method presumes that phosphorus enters solely in reactions of biological uptake by primary production and of release during organic matter mineralization. The determination of carbon balance via phosphorus budget is made with the use of the Redfield ratio of the organic matter ($C:P = 106/1$). Our results suggest that the LOICZ method cannot be apply directly in turbid estuaries like the Gironde because a large part of phosphorus dynamics is controlled by purely abiotic particle–water exchanges. Actually, the LOICZ modeling procedure applied to DIP concentrations in systems receiving high loads of suspended particulate matter leads to a significant overestimation of net ecosystem production (Gazeau et al. 2005).

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