Biogeochemistry (2005) 72: 35–66
DOI 10.1007/s10533-004-0078-1

Review-article

Phosphorus budget in the Marne Watershed (France): urban vs. diffuse sources, dissolved vs. particulate forms

JULIEN NÉMERY*, JOSETTE GARNIER and CHRISTIAN MOREL
Laboratory Sisyphe, University Paris 6, 4 place Jussieu (case 123) 75005 Paris, France;
**Author for correspondence (e-mail: nmeery@ccr.jussieu.fr)*

Received 24 October 2003; accepted in revised form 10 February 2004

Key words: Diffuse and point sources, Dissolved and particulate phosphorus, Eutrophication, Exchangeability

Abstract. We evaluated the P sources (point, diffuse), through a nested watershed approach investigating the Blaise (607 km^2), dominated by livestock farming, the Grand Morin (1202 km^2), dominated by crop farming, and the Marne (12,762 km^2), influenced by both agriculture and urbanization. Fertilizers account for the main P inputs ($>60\%$) to the soils. An agricultural P surplus (0.5–8 kg P ha^{-1} $year^{-1}$) contributes to P enrichment of the soil. The downstream urbanized zone is dominated by point sources (60%, mainly in dissolved forms), whereas in the upstream basin diffuse sources dominate (60%, mostly particulate). Among the diffuse sources (losses by forests, drainage and runoff), losses by runoff clearly dominate ($>90\%$). P retention in the alluvial plain and the reservoir represents 15–30% of the total P inputs. Dissolved and particulate P fluxes at the outlet of the Marne are similar (340 and 319 tons of P $year^{-1}$, respectively). The Blaise sub-basin receives P from point and diffuse sources in equal proportions, and retention is negligible. The Grand-Morin sub-basin, influenced by the urbanized zone receives, as does to the whole Marne basin, 60% of P inputs as point sources. The total particulate phosphorus in suspended sediments averaged 1.28 g P kg^{-1}, of which about 60% are inorganic and 40% organic P. Particulate phosphorus exchangeable in 1 week and 1 year (^{32}P isotopic method) accounts for between almost 26% and 54% of the particulate inorganic phosphorus in the suspended sediment and might represent an important source of dissolved P, possibly directly assimilated by the vegetation.

Introduction

Phosphorus is a naturally occurring nutrient essential for plant growth. In natural conditions, i.e. without any human pressures, phosphorus is a limiting element for biomass growth (Ramade 1998). Since the 19th century greater use of fertilizers in agriculture and the increase of phosphorus in domestic effluents, due to population growth and, more recently, to polyphosphates contained in washing powders have completely modified the fluxes and stocks of phosphorus within the main biosphere reservoirs. These changes are often responsible for eutrophication of water bodies which reduces the patrimonial value of lakes, rivers and even coastal zones, and causes economical problems.

In the strongly human-impacted river systems of the Seine River basin, including the Marne sub-basin, phosphorus is the primary nutrient responsible for eutrophication. Phosphorus originates both from diffuse sources linked to agriculture, and point sources due to discharges from municipal wastewater treatment plants or of industrial sewage. Until recently, most studies have focused mainly on point sources considered to provide the major input of P into aquatic systems. Although it is technically possible to reduce phosphorus in wastewater treatment plants, the ecological model of the Seine basin has shown that the reduction of phosphorus must reach 90% to substantially reduce algal blooms (Garnier et al. 1998). The reduction is so high, that the results of the model led us to interest in the real part of diffuse sources at the basin scale and the necessity to reduce them.

Many studies have been carried out on the P inputs by diffuse sources into aquatic systems from agricultural soil runoff and leaching at the scale of small watersheds (Dorioz and Ferhi 1994; Haygarth and Jarvis 1999; Sharpley et al. 1999). It is generally admitted that phosphorus from diffuse sources arrives in aquatic systems essentially in particulate form. Thus the transport and fate of suspended sediment in catchments have increasingly become an important aspect of environmental research because of its role as a vehicle for sediment-associated phosphorus (Kronvang et al. 1997; Walling et al. 1997; Dorioz et al. 1998a; Verstaeten and Poesen 2000). Sediments also transport other contaminants such as metals (Idlafkih et al. 1997). Suspended sediments can constitute a reservoir of rapidly bioavailable phosphorus for algae. Boström et al. (1988) defined bioavailable P as the sum of immediately available P and P that can be transformed into an available form by natural biological, chemical and physical processes. As P has a strong affinity for reacting with sediments, the sorption and desorption of P from sediments are two of the main processes that regulate the behaviour and concentration of P in freshwaters. As the point sources are decreasing, while the use of fertilizers is still high, it is fundamental to understand and to quantify the diffuse sources because they may provide the water with dissolved phosphorus, which has to be taken into account in order to comply with the reduction of eutrophication recommended by the European directive.

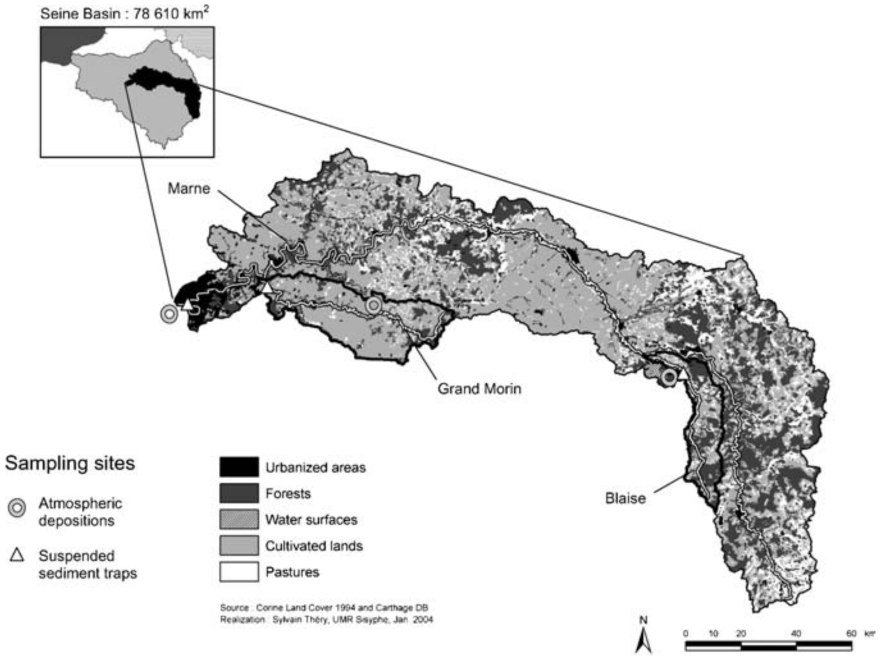
The aims of this study are twofold. In order to quantify the respective annual contributions of point sources and diffuse sources, we inventoried P sources to establish an agricultural phosphorus budget that will be linked to phosphorus losses from runoff and leaching. The P budget considers P-sources, pathways and fate in a nested approach of the Blaise sub-basin (607 km^2, dominated by livestock farming), the Grand Morin sub-basin (1202 km^2, dominated by industrial crops), and of the Marne basin (12,832 km^2, agricultural/urbanized), one of the major sub-basin of the Seine River, upstream from Paris.

As phosphorus originating from agricultural soils has long been considered as refractory to biological activity, we studied particulate phosphorus exchangeability using the ^{32}P isotopic exchange method developed in agronomy (Fardeau 1993; Morel et al. 1995). Finally, these two lines of studies converge to quantify the phosphorus really available for algal development in the Marne, the most eutrophic sub-basin of the Seine.

Materials and methods

Site description and sampling

The Marne river is a major tributary to the Seine river with a mean annual discharge of 190 $m^3 s^{-1}$. The surface area of the Marne watershed is 12,762 km^2 which represents 17% of the whole Seine basin. The Marne reservoir (Der Lake, 48 km^2), constructed on the upper reaches of the Marne river to regulate its flow, was impounded in 1974. Population density is high throughout the basin (160 inhab km^{-2}) but its downstream part is subjected to strongest urban pressure (976 inhab km^{-2}). According to the Corine Land Cover and Carthage datasets, the centre of the Marne watershed is dominated by agriculture (cereals and industrial crops) whereas its upstream part is dominated by livestock farming and forests (Figure 1). The Grand-Morin (1202 km^2) and Blaise sub-basins (607 km^2) are representative of these two different land uses. Annual discharges are 10–12 and 6–8 $m^3 s^{-1}$ respectively. The Agricultural Surface (AS: cultivated land + pastures) given by the



Source : Corine Land Cover 1994 and Carthage DB
Realization : Sylvain Théry, UMR Sisyphe, Jan. 2004

Figure 1. Land use and sampling sites in the Marne river basin and the Grand-Morin and Blaise sub-basins.

Table 1. Land use data in the Marne basin and in the Grand Morin and Blaise sub-basins (Data from Corine Land Cover and the Recencement Général de l'Agriculture 2000, RGA 2000).

	Area km^2 (% of the total area)	Pastures km^2 (% of the total area)	Cultivated lands km^2 (% of the total area)	Forests km^2 (% of the total area)
Marne basin	12,732	1400 (11)	6200 (49)	3500 (27)
Grand Morin sub-basin	1202	50 (4)	770 (64)	180 (15)
Blaise sub-basin	607	110 (18)	200 (33)	243 (40)

Recencement Général de l'Agriculture 2000 (RGA 2000) represents more than 50% in the three basins (Table 1). Silt is omnipresent across the basins and moderate altitudes (highest point: 521 m) explain the gentle slopes of the drainage network ranging from 0.1 to 0.3‰ (Meybeck et al. 1998a) characteristic of plain rivers.

Suspended sediments were sampled with sediment traps placed at the outlets of the three studied watersheds. The traps were equipped with a float and a counterweight that keep a 20-cm-diameter PVC cylinder filled with a tubular structure 70 cm from the surface. A plastic case with a same structure is put on the river bed when the river is too shallow (Blaise river). Annual surveys of the Marne basin and the Grand-Morin sub-basin from April 2001 to March 2002 and from April 2002 to April 2003 for the Blaise sub-basin were made by collecting samples at least once a month. Each sample includes suspended sediment transported during the whole collection period. Water samples were also taken and analysed in the laboratory for total suspended solids (TSS) and orthophosphate concentrations.

Sample preparation and P analyses

Particle-matter samples were wet-sieved < 200 μm, stored frozen and freeze dried before analysis. The particle size distribution (PSD) was determined with a Coulter Counter Technology based on the measurement of an electronic pulse triggered by the passing of a particle through a probe (Brun-Cottan 1986). With this method the PSD can be determined over a range of 0.1–2000 μm.

Total particulate phosphorus (TPP) was determined with a high temperature/HCl extraction technique (Aspila et al. 1976) where organic phosphorus is mineralized into inorganic forms at 550 °C, extracted into 1 N HCl for 15–20 h and analysed for phosphate. To estimate particulate inorganic phosphorus (PIP), the analysis was similar to that of TPP except that the high temperature organic P mineralization was omitted. The particulate organic phosphorus (POP) can be determined by difference of TPP and PIP (Svendsen et al. 1993). TPP, PIP and POP are expressed in g P kg^{-1} of suspended sediment. TSS were measured by filtration of 100–1000 mL water samples through pre-weighed GF/F Whatman filters (pore diameter of 0.7 μm, AFNOR T90-105, 1994). The filtrates were frozen and kept for dissolved P analysis. Dissolved P (DP) measurements in water were made by the Green-Malachite Colorimetric Method (Van Veldhoven and Mannaerts 1987), recommended for low orthophosphate concentration determination (Ohno and Zibilske 1991). The procedure is based on the complex formation of green malachite with phosphomolybdate in acidic conditions. The P concentration expressed in mg P-PO_4 L^{-1} can be determined by measuring the intensity of green colour using a colorimeter at 610 nm.

Determination of the amount of P ions exchanged between suspended sediment and solution

The transfer of P ions between solid and liquid phases has been extensively studied in soils (Morel et al. 2000), sediments (McGehan and Lewis 2002) and minerals such as oxides (Torrent 1997). This process is controlled by several physico-chemical mechanisms such as adsorption, precipitation/dissolution and diffusion caused by surface heterogeneity and porosity as well as by biological mechanisms such as mineralization of organic compound containing P. The transfer of P ions at the interface of solid and liquid phases varied both with time and the concentration of P ions in solution. When the concentration of P ions increases in the water body, a net amount of phosphate ions is transferred from the water to the solid phase (sorption). On the contrary phosphate ions are released from the solid phase to the liquid phase (desorption) when the phosphate concentration decreases in the water body due to algal uptake. To evaluate the exchangeability of P fixed on suspended sediments many methods have been proposed, e.g., bioassays (Williams et al. 1980), chemical extraction (Hieltjes and Lijklema 1980; Golterman 1982) sorption/desorption method (Froelich 1988; Aminot and Andrieux 1996). In agronomy, several experimental approaches have been developed to evaluate and model the dynamics of this transfer controlled by physico-chemical mechanisms (Morel et al., 2000). Two methods can be mentioned, both based on the preparation of suspensions. One involves sorption–desorption experiments that provide information on the net change in P ions transfer when the suspensions are put at disequilibrium. The other one consists in labelling P ions in solution with radioactive ^{32}P, (half-life: 14.3 days) and to analyse simultaneously the kinetics of isotopic dilution and P ion concentration in solution at steady state i.e. at a constant phosphate ion concentration (Fardeau 1993; Morel et al. 2002). The isotopic dilution principle, i.e. the isotopic composition ($^{32}P/^{31}P$) of P ions in solution is the same at equilibrium as that of the P ions sorbed on solid phase participating in the exchange, allows us to determine the gross transfer of P ions between solid and liquid phases. The gross transfer includes both the P initially existing in the solid phase and added P. Recently, Schneider and Morel (2000) have shown that in agricultural soils that resin-desorption and isotopic dilution experiments provide identical information.

Some authors have also used the exchange kinetics method to study P exchangeability in freshwater sediments (Capblancq et al. 1986; Vaas et al. 1987; Dorioz et al. 1998b).

The sediments collected here were analysed for the gross transfer of P ions as a function of the P concentration in solution and the time, using the isotopic dilution procedure. For each sample, five different amounts of phosphate (0, 20, 50, 100 and 200 μg P g^{-1}) were added as KH_2PO_4 to 1 g of dry suspended sediment and 9.89 mL of deionized water to create a range of phosphate ion concentrations in suspension (Morel et al. 2000). All suspensions received 10 μL of biocide (bacteria activity inhibitor: Micro-o-protect) and were shaken on a shaking table for 20 h to reach a steady state. This method does not account for the mineralization of POP by biological activities (bacterial). After 20 h of equilibration, 100 μL of carrier-free ^{32}P containing approximately 20 kg Bq (R) were introduced into the suspensions (solution/suspended sediment ratio of 10) at time zero. The suspensions were then gently shaken for 3, 30 and 300 min. For all periods of isotopic dilution, 2 mL of suspensions were removed with a polyethylene syringe and immediately filtered through a 0.22 μm pore size Millex filter consisting of composite cellulose acetate membranes. The radioactivity (r) remaining in the filtered solution and the initial radioactivity R were counted with a liquid scintillation cocktail (Lipoluma cocktail, Packard analyser) and the isotopic dilution ratio (r/R) was calculated. The Cp value (orthophosphate concentration) was determined by the green malachite colorimetric method (Ohno and Zibilske 1991). Although the molybdate reaction is widely used to analyse P ions concentration, it is now well known that the preparation of the solution that precedes the colour reading can readily transform colloidal, organic and polyphosphate P forms, resulting in over estimations (Haygarth and Sharpley 2000). Over estimations varied with the nature of solid phase (Sinaj et al. 1998) and the size distribution of colloidal molybdate reactive P (Haygarth et al. 1997). Therefore the determination of orthophosphate concentrations in both filtered water sampled in the Marne basin and re-suspended sediments in the experimental conditions of the isotopic method were investigated but did not show any significant difference between 0.7 and 0.22 μm filters (Némery 2003).

The gross amount of phosphate ions transferred between the solution and the suspended sediments is determined by measuring the isotopic composition ($^{32}P/^{31}P$) of phosphate ions in solution and applying the isotopic dilution principle. In suspensions at steady state, the transfers of phosphate ions, both from solution to soil and from soil to solution are equal, i.e. the net transfer is zero. The gross amount (Pr) of P ions transferred (released and sorbed) between solution and sediments are therefore calculated with the following equation:

$$r/\mathrm{Qs} = (R - r)/\,\mathrm{Pr} \tag{1}$$

where Qs is the amount of phosphate ions in solution (Qs, mg P kg^{-1}), r is the ^{32}P-radioactivity remaining in solution. The Qs value is determined by multiplying the soil solution P value by the ratio of solution to suspended sediment, i.e. Qs = 10Cp. The experimental Pr value is therefore obtained as follows:

$$\text{Pr} = \text{Qs}/(r/R)-, \text{with Pr lower than total isotopically exchangeable P} \quad (2)$$

For a given suspension, the 15 experimental observations (three periods of isotopic dilution and five Cp levels) were fitted by means of a kinetic Freundlich function (Barrow, 1978; Chardon, 1998; Morel, 2002; Morel, 2002):

$$\text{Pr} = v\text{Cp}^{w}t^{p}, \text{ with Pr lower than total isotopically exchangeable P} \quad (3)$$

Pr is in mg P kg^{-1}, Cp is in mg P L^{-1}, t is in minutes, and v, w and p are fitted parameters. With this method one can determine and describe mathematically the exchange of phosphate between the solid phase and the liquid phase. Depending on the conditions, i.e. microbial activities are inhibited, Pr can be calculated at any time but is limited by the total inorganic P (PIP) in the sediment as mentioned by Fardeau (1993) for agricultural soils. We explore different durations of P exchange compatible with phytoplanktonic bloom periods and/or suspended sediment transit time in the drainage network.

Statistical analyses

The standard deviation and estimate of the v, w and p parameters of Equation 3 and other associated statistics were determined with a procedure that minimizes the residual sum of squares (procedure NLIN of Statistical Analysis Software (SAS Institute 1995)).

Phosphorus mass balance calculations at the outlets of the sub-basins

The total phosphorus budget was calculated as the contribution of both dissolved P and particulate P forms. Daily DP fluxes result from the product of instantaneous orthophosphate concentration in the water column and the water flow rate. PP content of suspended sediments was multiplied by the average TSS concentration and the average water flow corresponding to the period of sediment collection in the traps and expressed as daily PP fluxes. Annual fluxes (AF) expressed in TP year^{-1} were calculated according to the load estimation procedure described by Verhoff et al. (1980), recommended by

Walling and Webb (1985) and commonly used by Aminot et al. (1998) and Meybeck et al. (1998b).

$$\mathrm{AF} = \frac{K\sum_{i=1}^{n} C_{\mathrm{i}}Q_{\mathrm{i}})}{\sum_{i=1}^{n} Q_i} Q_{\mathrm{m}} \tag{4}$$

K = conversion factor to take the recorded period into account (365 days),
C_{i} = instantaneous/mean concentration (mg P-PO$_4$ m^{-3}),
Q_{i} = instantaneous/mean discharge (m^3 s^{-1}),
Q_{m} = mean discharge for period of record (m^3 s^{-1}).

Point sources in the Marne watershed

Specific phosphorus load from sewage treatment plants (including industrial waste) is provided by the Agence de l'Eau Seine Normandie (AESN) database for the year 2000. Annual discharge was calculated from daily phosphorus fluxes (kg P day^{-1}) for seven sub-basins (including the Grand-Morin and Blaise sub-basins) and the main branch of the Marne river (Table 2). We make the assumption, discussed below, that P fluxes generated by the unconnected population are negligible.

Table 2. Annual phosphorus point source fluxes at different scales in the Marne basin (data for the year 2000).

	Population		Dissolved P T year^{-1}	Particulate org. P[b] T year^{-1}
	Inhab.	% connected to STW[a]		
Upstream rural area				
Grand-Morin sub-basin	88,975	72	26	2
Blaise sub-basin	14,267	64	7.5	2.7
Others	638,640	60–90	146.5	27
Total	741,882		172	32
Downstream urbanized area	1,309,873	> 90	220	41
Total Marne	2,051,755	90	392	73.2

[a] Sewage Treatment Plant, data AESN.
[b] Estimate from the ratio particulate organic carbon/particulate organic phosphorus = 40.

Retention of phosphorus in the flood-plain

Wetlands in valley bottoms can play an important role in retaining nutrients associated with suspended sediments transported by rivers (Fustec and Lefeuvre 2000). Recent studies of the role of flood plains as sediment sinks have

Table 3. Flood plain characteristics for several rivers in the Seine basin (AESN, 1974; Guerrini et al. 1998).

	Flood (km^2)	Led surface (% of basin)	Total length (km)	Mean flooded width[a] (m)	Frequency (% of flooded area)		
					< 1 year	1–3 year	3–10 year
Oise	478	2.75	756	632	36	4.5	59.5
Marne[b]	417	3.3	575	726	61	31	8
Gd-Morin	14.6	1.2	80	182	0	100	100
Blaise	0	0	0	0	0	0	0
Seine[b]	599	1.84	1047	572	68	21	0

[a] Surface-length ratio.

[b] Upstream of the confluence of the Marne and the Seine.

demonstrated that a significant proportion of the suspended sediment flux transported by a river system may be deposited on the flood plain during overbank floods (Behrendt and Opitz 2000; Thoms et al. 2000; Walling et al. 2000; Meybeck 2001). In the Seine basin, flood plains are characteristic of the fourth stream order rivers. The flooded width is in the same range throughout the basin because of its homogeneous hydrologic regime (Guerrini et al. 1998), (Table 3).

The study of sediment retention at local scales in the Seine basin by Fustec et al. (1998) (Table 4) was extrapolated here to estimate phosphorus sinks in the Marne basin and the Grand-Morin sub-basin. The Blaise sub-basin does not have a flood plain so that overbank floods are localized in small areas.

Annual phosphorus retention (APR) in the flood plains of the Marne Basin and Grand-Morin sub-basin is calculated as follows:

$$\mathrm{APR} = \sum_{5-700m} (\mathrm{PRR} * S) * \mathrm{FD} \tag{5}$$

PRR = phosphorus retention rate ($\mathrm{kg\ P\ km^{-2}\ day^{-1}}$) = daily sediment deposition rate ($\mathrm{kg\ km^{-2}\ day^{-1}}$) *PP content ($\mathrm{kg\ P\ kg\ TTS^{-1}}$) in suspended sediment during high flow periods at the basin outlets S = flood-plain surface (km^2) = distance from channel * total length of flooded area (the flood frequency for the studied year 2001–2002 is 5 years) FD = flood period

Table 4. Sedimentation rate at different sites in the upper part of the Seine basin (from Fustec et al. 1998) and P sink (see Equation 5).

Distance from channel (m)	Flood duration (days)	Sediment deposition rate (kg drysed m^{-2})	Daily phosphorus deposition rate (g P km^{-2} day^{-1})
5	119	17	128.6
35	149	10	60.4
70	149	2.6	15.7
700	149	2.2	13.3

(days) = 15 days (low hypothesis) to 30 days (high hypothesis) (Guerrini et al. 1998).

Retention of phosphorus in the Marne reservoir

The functioning of the Marne reservoir (48 km^2) has been extensively (Garnier et al. 1999, 2000). Here we consider the average retention for the three studied years (Table 5).

Table 5. Phosphorus balance in the Marne reservoir for 1993, 1994 and 1995 (from Garnier et al. 1999).

	Year	Flux in TP year^{-1}	%	Retention TP year^{-1}
P–PO$_4$	1993	9	78	7
	1994	26	85	22.1
	1995	17.2	73	12.5
	Mean			13.9
Total P	1993	27	52	14
	1994	63	78	49.1
	1995	32	63	20.16
	Mean			27.7

Diffuse sources calculations

P diffuse sources consist of the contribution by both runoff and leaching through drainage which are the two main processes of phosphorus transfer from cultivated land (Haygarth and Jarvis 1999; Kronvang et al. 2000).

The drained surfaces are 18% (140,000 ha), 74% (55,000 ha) and 11% (3500 ha) of the AS, respectively, for the Marne basin and the Grand Morin and Blaise sub-basins. The Grand Morin sub-basin was chosen as an experimental site in order to understand the behaviour of rural basins (Meybeck et al. 1998a). The specific phosphorus flux was calculated from a database collected during 8 years of monitoring at the outlet of 15 ha of cultivated land in the Grand Morin sub-basin. The calculations were based on a study of drained land by the Cemagref (Table 6; see also Riffard et al., 2002). Annual specific DP and TP fluxes are calculated according to the Equation 4 from P-PO$_4$ and TP concentrations, discharges of the drain (10–30 data for one hydrological year) and drained surface (15 ha). Specific DP (0.042 kg P ha^{-1} year^{-1}) and TP (0.118 kg P ha^{-1} year^{-1}) fluxes are averages of the eight considered years (a dry year: 89/90, a wet year, 93/94 and six intermediate years) and are used to estimate P losses from leaching by drainage at the basin scale.

Table 6. Values for eight hydrologic years from an agricultural heavily drained area (15 ha, 100% drained) in the Grand Morin sub-basin: mean annual discharges, mean P-PO$_4$ and total P concentrations; mean dissolved phosphorus (DP) and total phosphorus (TP) specific fluxes.

Year	Active drain (days)	Mean discharge (L s^{-1})	Mean P-PO$_4$ (mg P L^{-1})	Mean Ptot (mg P L^{-1})	DP fluxes (kg P ha^{-1})	TP fluxes (kg P ha^{-1})
89/90	65	0.05	0.225	0.264	0.004	0.004
90/91	101	1.34	0.019	0.074	0.034	0.170
91/92	111	0.16	0.022	0.027	0.002	0.002
92/93	156	0.71	0.017	0.054	0.011	0.033
93/94	233	1.58	0.031	0.134	0.077	0.400
94/95	151	1.29	0.033	0.059	0.057	0.101
98/99	127	1.10	0.074	–	0.059	–
99/00	151	0.79	0.111	–	0.095	–
Mean	137	0.88 (0.56)[a]	0.058 (0.072)	0.102 (0.087)	0.042 (0.035)	0.118 (0.152)

[a] Standard deviation.

Regarding P losses from runoff, they can be measured directly in the field by collecting surface or sub-surface runoff water (Catt et al. 1999; Smith et al. 2001). The results vary widely according to the slope, the soil type, the land use and the rainfall (Strauss 2002) and are difficult to extrapolate to other soils and regions. For this reason many authors (Reckhow et al. 1980; Johnes 1996; May et al. 2001) prefer to use export coefficient modelling with the aim of predicting the nutrient loading in the surface water drainage network of a basin as a function of the specific loss from each type of land use averaged from literature data.

Here P losses from runoff were calculated by difference between total phosphorus fluxes at the outlet of each of the three studied basins and all the known inputs and outputs (retention). To make such an estimate one must neglect other sources such as urban runoff, likely to be heavy downstream of the urbanized part of the Marne basin during rainy periods (see Discussion). We also consider that in the river bed, sedimentation compensates for resuspension at the scale of the hydrological cycle (Meybeck 2001). P losses from forests are determined from the specific P flux in the range of 0.02–0.05 kg P ha^{-1} year^{-1} (DP $<$ 50%) found in the literature (Johnes 1996; Dorioz and Trevisan 2001).

Agricultural phosphorus budget

Different phosphorus fluxes were estimated from agricultural statistics data of the year 2000 which provided the cultivated surface area of each type of crop and the number of animals of each type (cattle, poultry, etc.) at the scale of an administrative district (Agreste 2000). A Geographical Information System

Table 7. (a) Fertilizer inputs, phosphorus export ratio and phosphorus field restitution for main crops (CORPEN, 1998); (b) restitution for animal manures.

	(a) Crop			(b) Animals	
	Fertilizers inputs (kg P ha^{-1})	Export ratio (kg P 100 kg^{-1})	Field restitution (kg P 100 kg^{-1})	Animal types	Restitution (kg P head^{-1} year^{-1})
Cereals					
Wheat	17–22	0.53	0.132	Calf < 1 year	4.7
Barley	20–35	0.48	0.132	Cow	15.7
Maize	26–45	0.44	0.132	Bullock	11
Oleaginous				Horses	17.8
Rape	32–43	0.66	0	Goats	2.9
Sunflower	15–20	0.57	0	Sheep	2.9
Industrials cultures				*Pigs*	
Sugar beet	40–55	0.08	0.03	Sow	8
Permanent grass	–	0.26	0	Pork	2.9
Temporary grass	–	0.31	0	Poultry	0.5

was used to determine the proportion of the Blaise and Grand-Morin sub-basins and the Marne basin that belongs to each administrative district.

The fertilizer fluxes were obtained by multiplying the surface area of each type of crop (ha) by the fertilizer inputs given by the farmers association in each district and by the French Union of Fertilizer Industries (UNIFA).

The crop export fluxes are the product of the yield and the phosphorus export ratio for each crop (Table 7a). Crop residue fluxes are produced by the portion of the plant (stems and leaves) that remains in the field after harvest. The phosphorus flux of the food processing industry is calculated as the difference between the total crop export and the forage exported to feed animals.

Livestock effluent fluxes are the product of the numbers of each type of animal and P fluxes generated by livestock (kg P head^{-1} year^{-1}, Table 7b).

The import or export of phosphorus is obtained by difference between livestock effluent and consumed forage by assuming that animal products (milk, meat, etc.) export very low quantities of P.

Atmospheric depositions

Atmospheric depositions of phosphorus are known to contain mainly dissolved forms (90%) (Peters and Reese 1995; Dorioz and Trevisan 2001). Bulk atmospheric P depositions were thus estimated by colorimetry analysing orthophosphate concentrations in unfiltered rainfall samples from three different sites (urban, rural/urban and rural) in the Marne watershed (with a 2 week frequency throughout the year 2001), (Garban et al. 2002). Total P deposition expressed in kg P ha^{-1} year^{-1} is calculated by summing the product

Table 8. Annual rainfall, orthophosphate concentrations in rain and P fluxes at three different sites in the Marne river basin for the year 2000.

	Rainfall (mm $year^{-1}$)	P-PO_4 (mg P L^{-1})	P flux (kg P ha^{-1} $year^{-1}$)
Urban	771	0.002 (0.003)[a]	0.01
Rural-urban	861	0.060 (0.069)[a]	0.52
Rural	915	0.046 (0.073)[a]	0.42

[a]Standard deviation.

of the monthly mean orthophosphate concentration and the monthly cumulative rainfall (Table 8).

Total phosphorus stock in the soil

The total phosphorus stock in the soil is difficult to evaluate because of the lack of total phosphorus measurements in cultivated soils, as these data are not used in agronomy. The databank of soil analyses constructed in France from 1990 to 1994 (Schvartz et al. 1997; Walter et al. 1997) only provides data relative to labile P and are not interpretable in terms of total P. However, some authors (Aurousseau 2000) have attempted to establish a link between labile P extracted by the Dyer method (2% citric acid) and total P in soils from Brittany. The results show that estimates of the stocks can vary by a factor of 2 due to the different soil compositions. In addition, the mean soil P content found in the literature is in the range of 750 mg P kg^{-1} but may vary from 100 mg P kg^{-1} in the sandy soil of the Sahel to 3000 mg P kg^{-1} in volcanic soil or soil developed on chalk (Fardeau and Conesa 1994).

The Seine basin consists of several different geological units (Figure 2). The soil distribution in the basin is a result of the concentric ring structure of the Paris basin lithology, originating from Mesozoïc and Cenozoïc and discontinuous Quaternary loess deposits (Guerrini et al. 1998). The varied land use and agricultural practices in the Seine basin make it impossible to attribute a mean P content to a soil.

A survey of soil P content was therefore carried out across the Seine river basin (Figure 2). During the winter of 2002–2003, 70 samples were collected from the surface layer of pasture, forest and cultivated soils at depths of 0–0.25 m, which is the common tillage horizon. During this period cultivated soils are bare, often ploughed but not yet fertilized, and consequently homogeneous; conditions are therefore favourable for a realistic estimation of total P stocks.

The samples were dry-sieved (<2 mm) and analysed for TP (high temperature/HCl 1 N extraction). Considering the sampled soil depth (0.25 m) and a soil density of 1.4 g cm^{-3} (a mean density of loess, according to Duchaufour (2001)), we find a soil stock of 3500 tons ha^{-1}, and can calculate the P stock (kg P ha^{-1}) on the basis of the soil TP content (g P kg^{-1}).

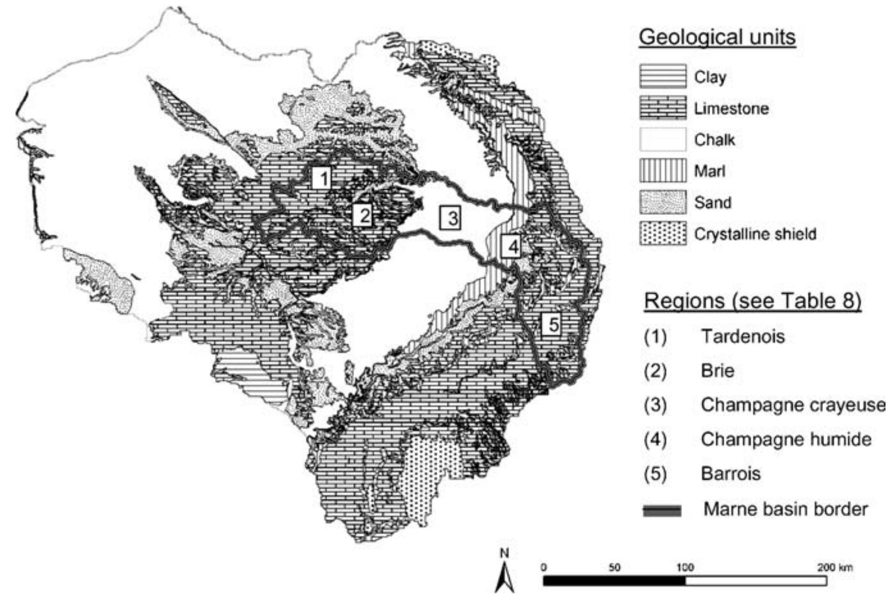


Figure 2. Geological map of the Seine basin including the Marne. Main regions of the Marne basin are numbered from 1 to 5.

Results

Agricultural phosphorus budget

Fluxes for (i) atmospheric depositions, (ii) fertilizer inputs, (iii) crop growth exports and (iv) crop and livestock restitutions are expressed in kg P ha^{-1} of AS per year, the proportion of each P input is also shown (Figure 3).

Results show that the greatest inputs are from fertilizers (22.3 kg P ha^{-1} year^{-1}) which represent 64% of the all inputs reaching the soil. Crop residues, livestock restitutions and atmospheric depositions contribute by respectively 21% (7.5 kg P ha^{-1} year^{-1}), 14% (5 kg P ha^{-1} year^{-1}) and 1% (0.39 kg P ha^{-1} year^{-1}). The calculated difference between these four estimated inputs and crop exports (33 kg P ha^{-1} year^{-1}) is positive. The surplus is 2.6 kg P ha^{-1} year^{-1} and represents a significant build-up of P content in the soils.

At the scale of the two sub-basins, the results show two different situations (Figure 4). The fertilizer inputs are twice as large in the Grand Morin sub-basin (27.8 kg P ha^{-1} year^{-1}), dominated by intensive agriculture, than in the Blaise sub-basin (13.3 kg P ha^{-1} year^{-1}) dominated by livestock farming. On the other hand, inputs from animals are four times smaller in the Grand Morin sub-basin (2 kg P ha^{-1} year^{-1}) than in the Blaise sub-basin

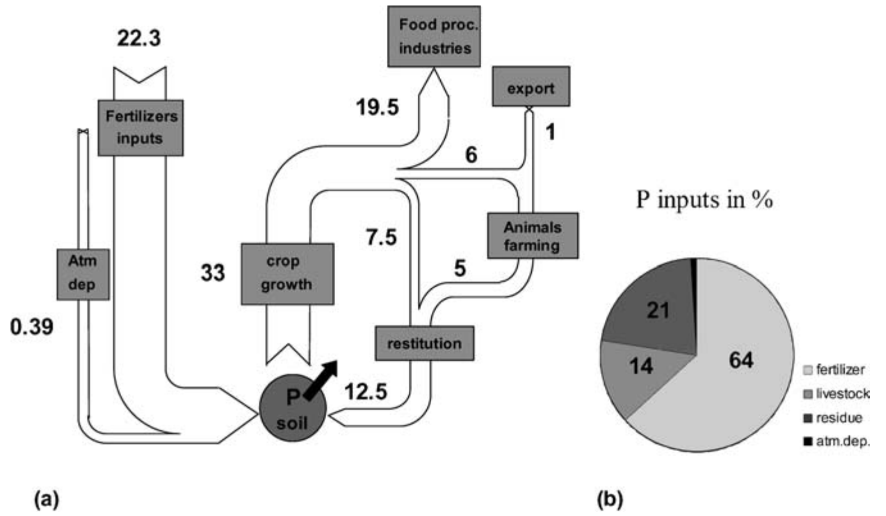


Figure 3. (a) Agricultural phosphorus budget in the Marne basin. Fluxes are expressed in kg P ha AS^{-1}. (b) proportion of P input from the considered sources in % of total inputs.

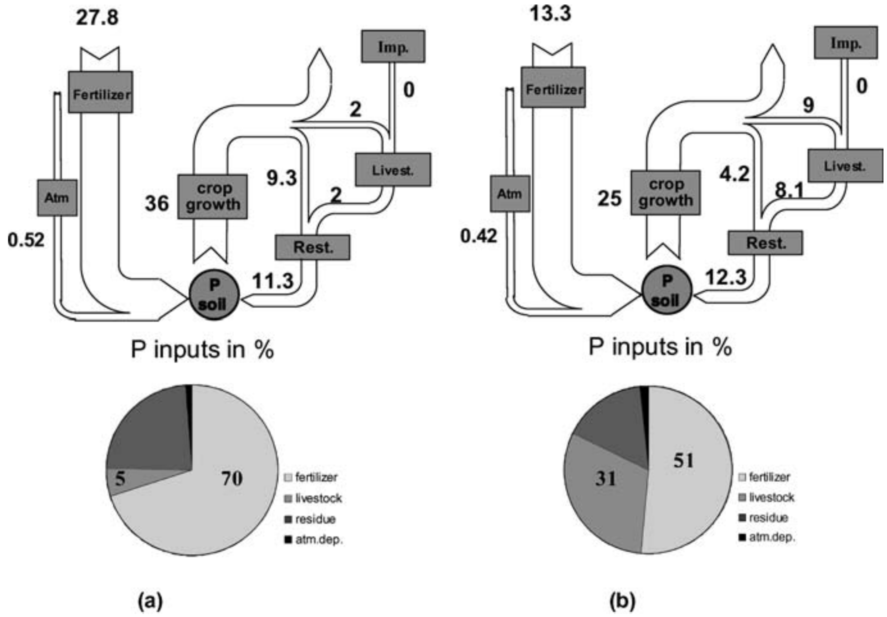


Figure 4. Agricultural phosphorus budget basins with different land uses: (a) in the Grand Morin sub-basin and (b) in the Blaise sub-basin. Fluxes are expressed in kg P ha AS^{-1}. Proportions of P input from the considered sources in % of total inputs are shown.

(8.1 kg P ha^{-1} $year^{-1}$). These results are in good agreement with the different types of agriculture in the two sub-basins. In both cases there is a surplus but it is much greater in the Grand Morin than in the Blaise sub-basin (3.6 kg P ha^{-1} $year^{-1}$ against 1 kg P ha^{-1} $year^{-1}$). The estimated surplus in the whole Marne basin represents an intermediate value.

These results are however estimates subject to statistical errors inherent in this type of data. Nevertheless the calculated surpluses are all in the range of 0.5–8 kg P ha AS^{-1}, considering a possible variation of 100% of the parameters, which is a pessimistic view. It is clear that fertilizers, estimated from inputs registered by farmer's associations of each administrative district, are the major contributors of P to the soil: respectively 64%, 70% and 51% of the total inputs in the Marne basin, Grand-Morin and Blaise sub-basins; these percentages are supported by the relationship ($r^2 = 0.85$, a slope ≈ 1) of the latter with the amount of fertilizer provided by the French Union of Fertilizer Industries (UNIFA) (Figure 5). The uncertainty range is ±15% between the two information sources. In addition, it is generally admitted that phosphate fertilizer inputs are at least equal to crop exportations in the agronomic context which is verified here. Note that fertilizer inputs can be underestimated through lack of data on biosolids originating from the spreading of waste from sewage treatment plants on the fields.

Data from the FAO (the United Union Food Agriculture Organization (FAO 2000)) allow to calculate a mean national fertilizer input of 15 kg P ha^{-1} $year^{-1}$ which is lower than the one found in the Marne basin (22.3 kg P ha^{-1} $year^{-1}$). This demonstrates the intensity of cereal growing in the Paris basin. Conversely, at the scale of the Marne, inputs from stock farming are lower than the fertilizer inputs which indicates that agriculture in the Marne basin is dominated by cereals and industrial crops.

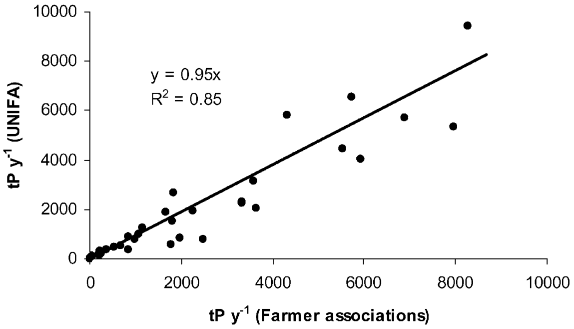


Figure 5. Relationship between fertilizer input estimates (tons P $year^{-1}$) from two different sources of information in all administrative districts of the Seine basin (UNIFA and Farmer association, see text). The linear equation ($y = ax$) and the variation coefficient (R^2) are indicated.

Total P stock in soils

In cultivated soils (Table 9), P contents are in the range of 0.52 g P kg^{-1} in the Brie region (especially in the Grand-Morin sub-basin) and 1.42 g P kg^{-1} in chalky layers of the Champagne region (where cereal and industrial crops dominate). Other soils show P contents within this range: grassland soils have P contents very close to the mean value of all cultivated soils (mean value of 0.69 g P kg^{-1}). Forest soils which can be considered as a reference without human impact have 3–10 times lower P content than cultivated soils. Vineyard soils present a mean P content of 0.89 g P kg^{-1}.

On this basis, the P stock in cultivated soils was estimated at 1800 kg P ha^{-1} in the Grand-Morin sub-basin, 2600–3100 kg P ha^{-1} for the Blaise sub-basin and 1800–5000 kg P ha^{-1} in the whole Marne basin.

Table 9. Mean content of total phosphorus in soils in different regions of the Marne basin.

Region	Basin and region overlap	Pedo-geological units	Arable land	Grassland	Forest	Vineyard
				Total P in g P kg^{-1}		
Tardenois (1)	Marne	Limestone, silt, sand, Marl	0.54[d]	–	0.10[e]	–
Brie (2)	Grand-Morin, Marne	Limestone, marl	0.52[b]	0.39[e]	0.16[e]	–
Champagne crayeuse (3)	Marne	Chalk	1.42[a]	–	–	0.90[e]
Champagne humide (4)	Blaise, Marne	Marl-clay	0.74[e]	0.68[e]	–	–
Barrois (5)	Blaise, Marne	Limestone	0.89[c]	0.80[e]	0.14[e]	–

[a] Mean ± standard deviation 0.24 (19 data).
[b] Mean ± 0.11(10 data).
[c] Mean ± 0.31 (5 data).
[d] Mean ± 0.24 (7 data).
[e] 1 to 3 data. (1–5) see Figure 3 for localisation.

P budget: quantification of the proportion of diffuse sources vs. point sources

The total flux of P at the outlet of the Marne river basin was estimated at 659 tons P $year^{-1}$ composed, in nearly equal proportions, of DP (52%) and PP (48%) (Figure 6). Point sources represent 60% (465 tons P $year^{-1}$, more than 80% in dissolved form) of the total inputs. As more than 50% of point sources (260 tons P $year^{-1}$) originate from the highly urbanized area downstream, the proportion of point sources is smaller (40%) upstream of this urbanized zone. This clearly indicates that diffuse sources dominate in the upper part of the Marne basin (60%).

Losses by leaching amount to 17 tons P $year^{-1}$ with 35% for DP and 65% for PP (140,000 ha drained; specific DP flux: 0.042 kg P ha $drained^{-1}$ $year^{-1}$;

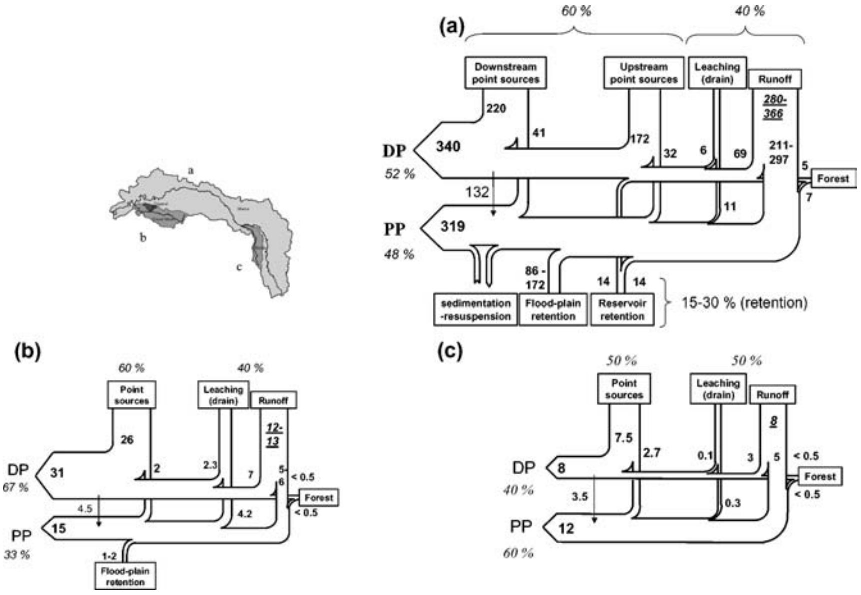


Figure 6. Phosphorus budget (a) in the Marne basin (b) in the Grand-Morin sub-basin and (c) in the Blaise sub-basin (fluxes in tons P year^{-1}). Percentages of P point sources vs. P diffuse sources, and of dissolved P vs. particulate P are indicated in the figure. The underlined results of runoff are calculated by difference (See Method section).

specific PP flux: 0.075 kg P ha drained^{-1} year^{-1}) whereas losses from forests are estimated between 7 and 17 tons P ha^{-1} (350,000 ha; 0.02–0.05 kg P ha^{-1} year^{-1}, see Method section); an intermediate value of 12 tons P ha^{-1} can be used here. Losses by runoff, estimated as the sum of the total P fluxes at the outlet of the Marne River and of the estimated P retention, deduced from all the quantified inputs, reach 280–366 tons P year^{-1} and represent a major proportion ($>90\%$) of all diffuse sources in comparison with losses from leaching (about 6%) and losses from forests (about 4%). As mentioned in the literature, we can show that phosphorus runoff is essentially under a particulate form (PP = 60–90%: (Dorioz and Trevisan 2001)). Data of dissolved nutrients gathered at the outlet of 100 small basins without any domestic contamination and drainage in the Seine basin (Thibert 1994) have made it possible to calculate a specific DP flux of 0.09 kg P ha^{-1} year^{-1} from agricultural land use (Billen et al. 1994). By considering the agricultural surface area in the Marne basin (760,000 ha), we can estimate a runoff flux of 69 tons of DP year^{-1} for the Marne basin, i.e. PP reaching 70–80% of the total P runoff estimate. However, a compilation surface runoff data, from European countries made available in the framework of the program Cost 832 (EC) shows great disparities in the estimates of PD and PP contribution (Strauss 2002).

Retention of P along the Marne river drainage network is not negligible. We estimate the Marne reservoir retention at 28 tons P year^{-1} in equal proportions of DP and PP and flood-plain retention in the range of 86–172 tons P year^{-1}. Both types of P retention, essentially as particulate P, account for 15–30% of all P inputs into the Marne basin.

It is worth mentioning that the DP:PP ratio at the outlet is lower than that determined on the basis of all inputs (diffuse and point sources) and outputs (retention); the quantity of DP entering the system (472 tons P year^{-1}) is higher than the exported one (340 tons P year^{-1}). This indicates that P exchanges occur between water and suspended sediments. To balance the budget, we can estimate that 132 tons P year^{-1} is transferred from the dissolved to the particulate form through adsorption on suspended sediment surfaces and/or phytoplankton consumption.

In the Grand-Morin and the Blaise sub-basins, retention is due to the upstream position of these two basins: the Blaise sub-basins does not present any significant flood-plain retention whereas the Grand-Morin sub-basin may retain 1–2 TP year^{-1} (less than 5% of the total P input). The total P flux at the outlet of the Grand-Morin river is estimated at 46 tons P year^{-1} (DP = 67%) and at 20 tons P year^{-1} for the Blaise river (DP = 40%), point sources contributing 60% in the former and 40% in the latter of the total P inputs. P losses from leaching account for 30% (6.5 tons P year^{-1}) of diffuse sources in the Grand-Morin sub-basin (74% of drained surface area) and less than 5% (0.4 tons P year^{-1}) in the Blaise sub-basin (11% of drained surface area). The remainder from diffuse sources is attributed to P losses from forests (less than 10%), from runoff, in the case of the Grand Morin sub-basin (12–13 tons P year^{-1}) dominated by agriculture, and probably from both runoff and losses from farmed animals in the Blaise sub-basin (8 tons P year^{-1}). Such farmed animal losses are not taken into account here, but preliminary investigations tend to show that they are on the order of 2–3 tons P year^{-1}.

Phosphorus content and exchangeability in re-suspended sediments

Thirteen samples from the outlet of the Marne river were selected to determine the P content and P ion transfer between the solid and the liquid phase of re-suspended sediments, in order to cover the whole range of both discharge values and types of particulate matter observed throughout the survey (April 2001–March 2002), (Table 10).

TPP values vary from 0.90 g P kg^{-1} during high flow periods to 1.97 g P kg^{-1} during the summer low flow ones. TPP averages 1.28 g P kg^{-1} and is distributed as 40% of POP and 60% of PIP. The particle size distribution shows low variability among the 13 samples: the 2–63 μm fraction, assimilated to silt, dominates (65% on average).

The Cp values vary within a very narrow range during the experiment (3–300 min), showing that the suspension (1 g:10 mL) is in steady state

Table 10. P content and particle size composition of suspended sediment collected at the outlet of the Marne river during the period April 2001 to March 2002.

Sampling period 2001–2002	Sample number	Mean discharge ($m^3 s^{-1}$)	TPP (g P kg^{-1})	POP (g P kg^{-1})	PIP (g P kg^{-1})	Particle size in %		
						< 2 μm	2–63 μm	63–200 μm
03/04–17/04	SM39	366	1.02	0.46	0.55	6	64.5	29.5
17/04–02/05	SM40	375	0.94	0.31	0.63	5.4	61.2	33.4
23/05–07/06	SM42	109	1.23	0.58	0.64	5.5	66.3	28.2
11/07–18/07	SM45	95	1.97	0.93	1.04	5.6	71	23.4
18/07–25/07	SM46	103	1.79	0.64	1.15	5.6	70	24.4
09/08–16/08	SM49	95	1.78	0.72	1.06	5.3	65.5	29.3
11/09–24/09	SM53	165	1.37	0.63	0.74	5.5	71.4	23.2
25/10–31/10	SM58	155	1.43	0.50	0.93	8.5	79	12.5
14/11–28/11	SM60	130	1.09	0.37	0.72	8.4	83.6	8.0
28/11–17/12	SM61	237	0.96	0.36	0.60	4.3	59	36.7
04/01–25/01	SM62	210	0.90	0.37	0.53	4.2	57.4	38.4
25/01–11/02	SM63	191	1.11	0.34	0.77	5	66.4	28.4
07/03–28/03	SM65	335	0.99	0.35	0.64	3.1	40.4	56.5
Mean			1.28 (0.36)[a]	0.50 (0.18)	0.77 (0.17)	6 (1.6)	65 (11.4)	29 (12.9)

[a] Standard deviation.

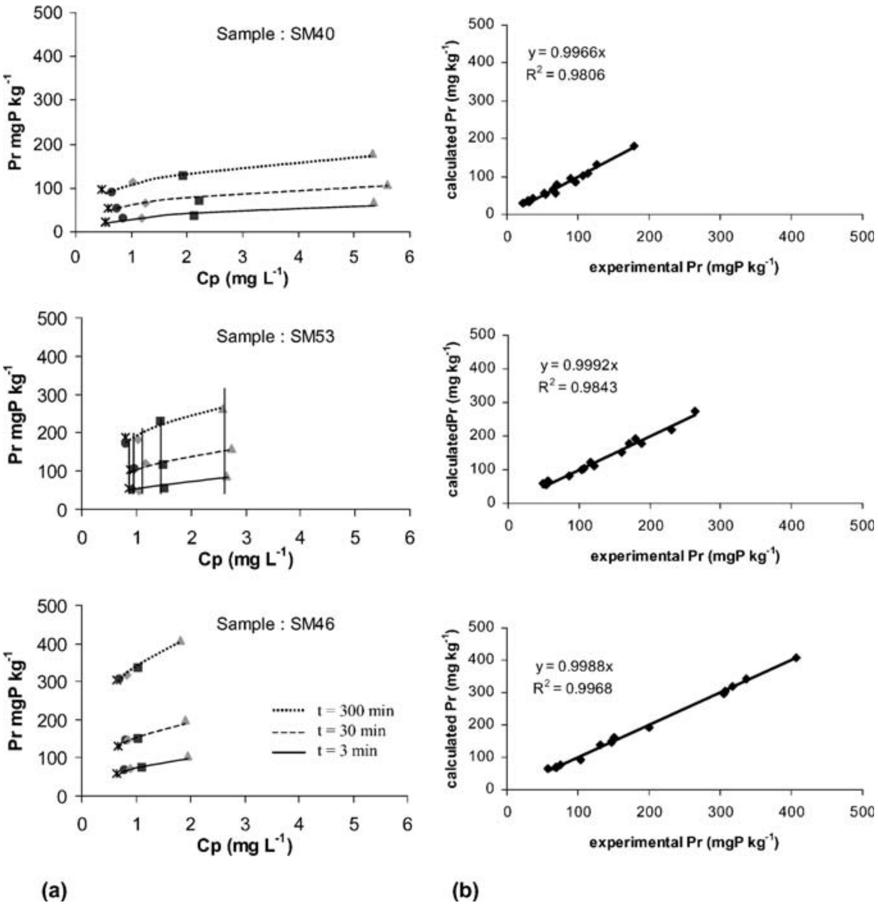


Figure 7. (a) Experimental values for three samples of the amount of phosphate ions transferred (Pr) as a function of both P concentration in suspended sediment solution (Cp) and time. The Cp range was obtained by adding 0, 20, 50, 100 and 200 mg P kg^{-1} and equilibrating suspended sediment. Vertical lines (cf SM 53) indicate the low Cp variations as functions of time. (b) Correlation between experimental values (Pr_e) and calculated values (Pr_c) with Equation 3. See parameter estimates and standard deviation in Table 11.

(Figure 7a). In the 13 samples, the P ion concentration in solution (Cp, mg P L^{-1}) ranged from 0.35 to 0.85 mg P L^{-1} (Table 11) while the exchangeability of the suspended sediments (Pr_e, calculated from experiment results with Equation 2) varies greatly with time at a given Cp level. For instance, in sample SM40, the amount (Pr, in mg P kg^{-1}) of P ions transferred between the suspended sediment and the solution was 54 mg P kg^{-1} after 3 min of isotopic dilution, 104 mg P kg^{-1} after 30 min and 185 mg P kg^{-1} after 300 min (Figure 7a). For a given suspended sediment, the Pr_e values increase both with Cp and time. To analyse the variability of Pr_e values as a

Table 11. Parameter estimates and their standard deviation (SD) of the kinetic Freundlich function ($\mathrm{Pr} = v\mathrm{Cp}^{w}\mathrm{t}^{p}$) calculating the amount of P ions transferred between solid and liquid phases of suspensions (1 g:10 mL).

Samples	Cp, mg P L^{-1} (SD)	Estimate (SD)			n	R^2
		v parameter	w parameter	p parameter		
SM39	0.554 (0.077)	32.75 (3.14)	0.271 (0.031)	0.255 (0.018)	15	0.966
SM40	0.536 (0.062)	24.22 (1.80)	0.303 (0.022)	0.250 (0.014)	15	0.980
SM42	0.584 (0.004)	27.44 (1.48)	0.371 (0.018)	0.291 (0.010)	15	0.993
SM45	0.745 (0.030)	39.74 (2.03)	0.358 (0.023)	0.303 (0.010)	15	0.993
SM46	0.648 (0.014)	46.34 (1.70)	0.310 (0.020)	0.332 (0.007)	15	0.997
SM49	0.593 (0.005)	43.20 (3.56)	0.339 (0.049)	0.289 (0.016)	15	0.978
SM53	0.846 (0.046)	43.34 (2.52)	0.372 (0.033)	0.261 (0.011)	15	0.986
SM58	0.682 (0.090)	44.77 (4.24)	0.320 (0.059)	0.297 (0.018)	15	0.973
SM60	0.537 (0.040)	40.79 (3.59)	0.316 (0.058)	0.250 (0.018)	15	0.960
SM61	0.485 (0.010)	48.96 (4.01)	0.328 (0.052)	0.212 (0.017)	15	0.945
SM62	0.582 (0.029)	38.68 (3.46)	0.272 (0.045)	0.246 (0.018)	15	0.958
SM63	0.355 (0.035)	52.35 (9.74)	0.312 (0.124)	0.269 (0.037)	15	0.861
SM65	0.479 (0.014)	40.51 (2.50)	0.320 (0.034)	0.248 (0.012)	15	0.981

n is the number of observations (five Cp values and three periods of isotopic dilution at steady-state). R^2 is the determination coefficient.

function of time (t, in min) and Cp (mg P L^{-1}), the results of the 13 samples were fitted on the Freundlich equation (Equation 3) for the 15 obtained values (three times, five P enrichments): v, w and p parameters and $\mathrm{Pr_c}$ were determined by a least-squared regression between $\mathrm{Pr_e}$ and $\mathrm{Pr_c}$ (Figure 7b, Table 11).

As in the results obtained for agricultural soils, the Freundlich equation as a function of time is well suited to calculating the Pr in suspended sediment for any chosen time (Morel 2002).

The extrapolation of the kinetics at different timescales up to one year as proposed by Fardeau (1993) allows us to calculate the amount of P ions on suspended sediment that can equilibrate with P ions in solution, i.e. $\mathrm{Pr}_{1\ \mathrm{week}}$, $\mathrm{Pr}_{1\ \mathrm{month}}$, $\mathrm{Pr}_{1\ \mathrm{year}}$ (Table 12).

In experimental conditions and for all samples (except SM 40), the total amount of inorganic P (PIP) is likely to be transferred to the liquid phase in less than one year which shows its ability to participate in the equilibration of P ions in solution. In some samples, i.e. SM46 and SM58, the total amount of PIP might be release in solution within less than one month. On average in the 13 samples, more than 80% of PIP can be released in solution within less than one month.

Forty values of orthophosphate concentrations available from the Marne river over the annual survey can be used to calculate $\mathrm{Pr}_{1\ \mathrm{week}}$, $\mathrm{Pr}_{1\ \mathrm{month}}$, $\mathrm{Pr}_{1\ \mathrm{year}}$, according to Equation 3. Orthophosphate concentrations, taken as Cp, vary between 0.009 and 0.188 mg P L^{-1} but when averaged for the corresponding period of sediment collection, the values range from 0.012 to 0.12 mg P L^{-1} (Table 12). $\mathrm{Pr}_{1\ \mathrm{week}}$, $\mathrm{Pr}_{1\ \mathrm{month}}$, $\mathrm{Pr}_{1\ \mathrm{year}}$ corresponding to the 13 dates averaged

Table 12. The amount of P ions that can equilibrated solution for different time scales, i.e. after 1 week ($Pr_{1\ week}$), 1 month ($Pr_{1\ month}$) and 1 year ($Pr_{1\ year}$) for (a) experimental concentrations of P-PO_4 (Cp) and (b) the measured concentration [P-PO_4] in natural water

Samples	PIP (mg P kg^{-1})	(a) Pr in experimental conditions			P-PO_4 In the Marne river (mg P L^{-1})	(b) Pr in natural conditions		
		$Pr_{1\ week}$ (mg P kg^{-1})	$Pr_{1\ month}$ (mg P kg^{-1})	$Pr_{1\ year}$ (mg P kg^{-1})		$Pr_{1\ week}$ (mg P kg^{-1})	$Pr_{1\ month}$ (mg P kg^{-1})	$Pr_{1\ year}$ (mg P kg^{-1})
SM39	552	293	424	552	0.022	122	177	335
SM40	630	201	289	540	0.030	84	121	225
SM42	645	329	502	645	0.067	147	225	465
SM45	1038	584	908	1038	0.084	267	416	886
SM46	1155	864	1155	1155	0.073	439	712	1155
SM49	1063	519	791	1063	0.113	296	451	928
SM53	741	452	660	741	0.104	207	303	581
SM58	930	612	930	930	0.123	354	545	930
SM60	726	336	483	726	0.031	136	196	366
SM61	596	273	371	596	0.036	116	158	269
SM62	533	322	461	533	0.036	151	216	400
SM63	771	452	669	771	0.036	222	328	642
SM65	640	315	452	640	0.012	97	139	258
Mean	770	427	623	764	0.065 (0.033)	203	*307*	572
%	100	55	81	99		26	*40*	74

26%, 40% and 74% of PIP respectively (Table 12). Considering the annual load of suspended sediment (317,000 tons year^{-1}), the exchangeable P can be estimated at 64 tons P year^{-1} ($Pr_{1\ week}$), 97 tons P year^{-1} ($Pr_{1\ month}$) and 181 tons P year^{-1} ($Pr_{1\ year}$), representing 10–30% of the total P fluxes in the Marne River (i.e. 20–57% of the particulate P fluxes).

Discussion

Agricultural phosphorus budget

We inventoried the agricultural P inputs and outputs for three nested sub-basins of the Seine and have shown that fertilizers dominate in agricultural budget (60%), as a result of intensively grown cereals and industrial crops.

It is interesting to notice that atmospheric P depositions are negligible compared to other inputs, but they still exist despite the scarcity of gaseous forms in the phosphorus biogeochemical cycle (Ramade 1998). A greater specific P flux in the rural zones may be explained by a loss of fine soil particles in the atmosphere (Pilleboue-Baptendier 1987). A similar range of values (0.04–1 g P ha^{-1} year^{-1}) is mentioned in recent literature (Dorioz et al. 1998a; Sutula et al. 2001; Pollman et al. 2002). The low specific flux calculated for urban sites is surprising. As industrial activities such as combustion are known to be sources of P, this value may be due to the location of the sampling site, East of Paris. As dominant winds blow from West to East, the pollution from industrial sites is carried eastwards (Garban et al. 2002).

Finally, the analysis of the agricultural P budget, shows a positive value for the year 2000, probably valid for the last two decades. The P surplus between the 1960s and the 1980s was undoubtedly higher than today due to fertilization adjustments launched to secure agriculture (Pellerin et al. 2000). Studies by agronomists have contributed to rationalize the use and application of phosphate fertilizers for both economic and environmental reasons (Morel et al. 1992; Pellerin et al. 2000). In France fertilizer inputs have decreased from 30 kg P ha^{-1} in the middle of the 70 s to 12 kg P ha^{-1} in 2001 (FAO 2000). This trend is noticeable throughout Western Europe. However, the widespread practice of over-fertilization has led to an increased P content in cultivated soils as demonstrated by an experimental field study of soils, subjected to different phosphate inputs during many years (Saragoni et al. 1988).

The very high P stocks found in soils within the three studied basins (1800–5000 kg P ha^{-1}) are illustrative. The main P export flux is from crops (33 kg P ha^{-1} year^{-1}) and accounts, in average, for 1% of the P stock in the soil. In addition, the surplus in the three basins (in the range of 0.5–8 kg P ha^{-1}) represents less than 0.1% of the stock already present in the soil, which is negligible from an agronomic point of view (Morel 2002). However, a few kilos could constitute a threat to the water quality given the critical threshold of dissolved phosphorus above which algal development is not P-limited in the

Seine basin (15–45 μg L^{-1}, Garnier et al., 1998). Therefore, any P losses to the rivers, such as P runoff or leaching, are of major environmental interest.

Specific phosphorus loss from runoff and leaching

We estimate specific phosphorus loss from runoff to be in the range of 0.37–0.47 kg P ha AS^{-1} with a 20–30% proportion of Dissolved P for the Marne basin, higher than the one for the Blaise (0.26 kg P ha AS^{-1}) and the Grand-Morin sub-basins (0.15–0.16 kg P ha AS^{-1}). The last result is surprising given that agricultural land cover 68% of the Grand-Morin surface area with a large proportion of bare soils during the autumn and winter when rainfall amounts are higher. A study of the runoff risk in the Grand Morin sub-basin indicated that the risk is moderate and discontinuous due mainly to the gentle slopes (0–3%) in the major part of the basin and to efficient collection of the water percolating through the soil by the sub surface drainage network which covers 74% of the agricultural surface area (Zimmer et al. 1991; Penven 1998). The low export to the river is further decreased by the existence of buffer zones, i.e. the valley bottom, situated between the edge of the plateau -that product solid particles- and the hydrosystem. Turtola and Paajanen (1995) have focused on the influence of subsurface drainage on phosphorus losses. They have clearly shown that P runoff losses are reduced by subsurface drainage; consequently, the proportion of P losses from drainage increases but to a lesser extent, resulting in an overall reduction of total P losses from the soils.

P losses from drainage are estimated at 0.112 kg P ha drained^{-1}. Similarly to the results in the Thames basin (Gardner et al. 2002), most of the P is transported in particulate form ($> 60\%$) and probably associated with organic or colloidal P forms as mentioned in the literature (Heathwaite and Dils 2000). In total, both runoff and leaching by drainage represent a very low percentage (0.01%) of the total P stock in the soil.

Phosphorus budget at hydrographic network scale

We have demonstrated that P from diffuse sources is mostly in particulate forms (50–80%), losses from runoff being the major contribution to the particulate P load in rivers. The proportions of annual particulate P fluxes amount to 48%, 30% and 60%, respectively, at the outlet of the Marne basin, and the Grand Morin and Blaise sub-basins. Similar proportions are often found in literature (Svendsen et al. 1995) and have led the scientists to focus on P export from agricultural land for a better understanding not only of diffuse P sources (Kronvang et al. 1997; Withers et al. 1999; McDowell et al. 2001) but also of the contribution of both point sources vs. diffuse sources to the P load in rivers (Drolc and Zagorc Koncan 2002; Pieterse et al. 2003). P losses from forests, representing only from 4 to 10% of diffuse sources, can be considered as being those of nearly "natural reference sites"; these natural low values show the strong human influence on the three studied basins.

As already mentioned by Behrendt and Opitz (2000), the annual P retention is not negligible in drainage networks. The estimates of P retention in the flood plain of the Marne river and the retention in the reservoir represent from 15 to 30% of the total inputs. Retention is relatively weak in the Grand Morin and the Blaise sub-basins, partly because they belong to a low stream-order (4).

Regarding the point sources, they are mainly composed of dissolved P (see also, Cooper et al. 2002) and amount to 60% of the total P inputs in the Marne basin of which more that half originates from the densely urbanized zone in the downstream part of the basin. Whereas P point sources dominate the P inputs in the downstream part of the basin, the contribution of diffuse sources is greater in the upstream zone. This means that the application of the EC directive must take these results into account for upgrading wastewater treatment.

Industrial effluents and all main connected domestic effluents (AESN data base, 2000) represent 90% of the population in the Marne basin, this proportion being lower in rural zones, e.g., in the Grand Morin sub-basin (72%) and the Blaise sub-basin (64%). The assumption that the unconnected domestic effluents were negligible at the basin scale is supported by literature that mentions efficiencies of septic tank in the range of 70–90% (Jacks et al. 2000; Steer et al. 2002) with a high but variable soil retention potential of infiltrated water (Jones and Lee 1976).

Note that effluents from livestock farming, localized similar to point sources but diffuse – issued from agriculture – might be underestimated in the Blaise sub-basin and need further studies.

Urban runoff losses were neglected. The sewage system of Paris and its suburbs receives both domestic and industrial effluents as well as water runoff from urbanized surfaces, street cleaning and rainfall. During the dry season, wastewater is transported to wastewater treatment plants and, in most cases treated by primary and secondary treatments. During storm events, combined-sewer overflows are discharged directly into the river and the largest discharges have been identified in Paris and its suburbs (BPR-Sogreha-Hydratec 1997). However, the study shows that most of the runoff from the urban zones in the downstream part of the Marne basin, is collected and transported downstream from Paris and discharged into the Seine, without reaching the Marne. Thus, we consider that the Marne river does not receive any significant amount of combined-sewer overflow (Chesterikoff et al. 1998).

Exchangeability of particulate P

^{32}P is a powerful tool to describe P transfer properties of suspended sediment. The exchangeability of particulate P, i.e. the ability of particulate P to equilibrate P ions in solution, was assessed by measuring the gross amount of P ions transferred between the liquid and the solid phase, when sediments were resuspended. For a given resuspended sediment, the variations in the exchangeability of particulate P as a function of the test duration and the concentration of P ions in solution is well described by a first order kinetic Freundlich isotherm (Table 11, Figure 7).

The w and p parameters are almost constant for all samples whereas the v parameter, i.e. the amount of P ions transferred after 1 min when Cp is 1 mg P L^{-1}, varied from 24.2 to 52.4 mg P kg^{-1}. These parameter estimates are higher than those found in agricultural soils which ranged from 0.6 in highly sandy soil to 24.2 in one calcareous clay soil (Morel 2002). This difference is explained by the fine particle size of suspended sediments (< 200 μm) compared to those of soil samples (< 2 mm sieve). A larger particle size in a soil strongly decreases its specific surface area and therefore the amount of P ions that can react with the solid phase. Similarly the variability during an annual hydrological cycle is partly explained by the variation in particle sizes of the suspended sediments. The Pr values are higher for suspended sediments with a high proportion of fine particles because of the increased in specific surface area which able to react with P ions.

Assuming that the description of the dynamics of Pr vs. Cp is valid for periods of up to 1 year, it was possible to extrapolate and calculate the amount of P ions exchanged in natural waters considering the concentration of orthophosphate measured in the Marne river (Table 12) and a range of equilibration periods from one week to one year.

It is worth mentioning that the hypothesis made to equilibrate the P budget (132 tons P $year^{-1}$) coincides well with the exchangeable P at the time scale from 1 month to 1 year (95–181 tons P $year^{-1}$). These results, calculated independently, tend to show the coherence of the P budget and demonstrate the strong reactivity of the suspended sediments.

Exchangeable P represents 10–30% of the total P fluxes in the Marne River but 20–57% of the particulate P fluxes. This means that despite a reduction of point sources – dissolved in majority – by improved wastewater treatment, the particulate phosphorus, essentially from runoff, may provide the water column with phosphate, still available for phytoplankton growth. Therefore, to reduce eutrophication in the Marne river both diffuse and point sources might have to be reduced (Garnier et al. 2004). Due to the high P content in the soils, the authorities will have to consider the fate of P in soils; new agricultural practices could be adopted to reduce the P losses by runoff (rationalization of the use of fertilizers, extension of intermediate or cover crops, increased acreage of fallow land, etc.).

Acknowledgements

This work was undertaken within the framework of the national program: PIREN-Seine (CNRS). We are indebted to Michel Roulier from the AESN

(Agence de l'Eau Seine Normandie), to François Dahy and Marie-Georges Mercelot from the DIREN Champagne-Ardenne (Direction Régionnale de l'Environnement) and to agronomists from each CDA (Chambre Départemental d'Agriculture) for providing data. Many thanks are also due to Dr. Jean-Marcel Dorioz (INRA, Thonon, France) and Gilles Billen (CNRS-Sisyphe) for fruitful discussions during the study. Precious help was provided by Sylvain Théry and Nicolas Bacq, geomaticians at the UMR Sisyphe, for GIS calculations and by Cyril Kao and Marine Riffard from Cemagref for drainage data.

References

Agreste 2000. http://www.agreste.agriculture.gouv.fr/

Aminot A. and Andrieux F. 1996. Concept and determination of exchangeable phosphate in aquatic sediments. Water Res. 30(11): 2805–2811.

Aminot A., Guillaud J.-F., Andrieux-Loyer F., Kérouel R. and Cann P. 1998. Apports de nutriments et développement phytoplanctonique en baie de Seine. Oceanol. Acta 21(6): 923–935.

Aspila K.I., Agemian H. and Chau A.S.Y. 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101: 187–197.

Aurousseau P. 2000. Le phosphore dans les sols de Bretagne. http://viviane.roazhon.inra.fr/spanum/diognostic/phosphore/phospho1.htm

Behrendt H. and Opitz D. 2000. Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. Hydrobiologia 410: 111–122.

Billen G., Garnier J. and Hanset P. 1994. Modelling phytoplankton development in whole drainage networks: the RIVERSTRAHLER Model applied to the Seine river system. Hydrobiologia 289: 119–137.

Boström B., Persson G. and Broberg B. 1988. Bioavailability of different phosphorus forms in freshwater systems. Hydrobiologia 170: 133–155.

BPR-Sogreha-Hydratec. 1997. Etude de l'assainissement en zone centrale d'Île de France. Rapport Agence de l'Eau Seine Normandie, ministère de l'Environnement, conseil régional d'Île de France, Syndicat interdépartemental pour l'assainissement de l'agglomération parisienne.

Brun-Cottan J.C. 1986. Vertical transport of particles within the ocean. The role of Air-Sea Exchange in Geochemical Cycling. Reidel Publishing Company, 83–111

Capblancq J., Labroue L. and Fardeau J.C. 1986. Echanges de phosphore entre les sédiments et l'eau. Influence de la dilution sur les cinétiques de traçage isotopique. Ann. Limnol. 22(3): 277–283.

Catt J.A. et al. 1999. Phosphorus losses from arable land in England. Soil Use Manage.. 14: 168–174.

Chesterikov A. et al. 1998. Le fleuve dans la ville, Chapitre 7. La Seine en son bassin: fonctionnement écologique d'un système fluvial anthropisé. Meybeck M., de Marsily G.and Fustec F.Elsevier, Paris. 301–344

Cooper D.M., House W.A., May L. and Gannon B. 2002. The phosphorus budget of the Thames catchment, Oxfordshire, UK: 1. Mass balance. Sci. Total Environ. 282/283: 233–251.

Dorioz J.M. and Ferhi A. 1994. Non-point pollution and management of agricultural areas: phosphorus and nitrogen transfert in an agricultural watershed. Water Res. 28(2): 395–410.

Dorioz J.M. and Trevisan D. 2001. Transfert de phosphore des bassins versants agricoles vers les eaux de surface: l'expérience du bassin Lémanique (France) et sa portée générale. Agrosol 12(2): 85–97.

Dorioz J.M., Cassell E.A., Orand A. and Eisenman K.G. 1998a. Phosphorus storage, transport and export dynamics in the Foron River watershed. Hydrol. Proc. 12: 285–309.

Dorioz J.M., Pelletier J.P. and Benoit P. 1998b. Physico-chemical properties and bioavailbility of particulate phosphorus of various origin in a watershed of Lake Geneva (France). Water Res. 32(2): 275–286.

Drolc A. and Zagorc Koncan J. 2002. Estimation of sources of total phosphorus in a river basin and assessment of alternatives for river pollution reduction. Environ. Int. 28: 393–400.

Duchaufour P. 2001. Introduction à la science du sol: sol, végétation, environnement, 6e édition, de l'Abrégé de pédologie. Dunod, Paris, 331pp.

FAO. 2000. Food and Agriculture Organization of United Nations http://www.fao.org

Fardeau J.C. 1993. Le phosphore biodisponible des sols: sa représentation par un modèle fonctionnel à plusieurs compartiments. Agronomie 3: 317–331.

Fardeau J.C. and Conesa A.P. 1994. Le phosphore. In: Bonneauet Souchier (eds), Pédologie, 2. Constituants et propriétés du sol. Masson, Paris, pp. 649–648.

Froelich P.N. 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnol. Oceanogr. 33(4, part 2): 649–648.

Fustec E. and Lefeuvre J.C. 2000. Fonction et valeurs des zones humides. Dunod, Paris,426.

Garban B., Blanchoud H., Moteley-Massei A., Chevreuil M. and Ollivon D. 2002. Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites. Atm. Environ. 36: 5395–5403.

Gardner C.M.K., Cooper D.M. and Hughes S. 2002. Phosphorus in soils and field drainage water in the Thames catchment, UK. Sci. Total Environ. 282/283: 253–262.

Garnier J., Billen G., Hanset P., Testard P. and Coste M. 1998. Développement algal et eutrophisationChapitre 14. In: Meybeck M., de Marsily G. and Fustec F. (eds), La Seine en son bassin Fonctionnement écologique d'un système fluvial anthropisé. Elsevier, Paris, pp. 593–626.

Garnier J., Billen G., Sanchez N. and Leporcq B. 2000. Ecological functioning of the Marne reservoir (upper Seine basin, France). Regul. Rivers: Res. Manage. 16: 51–71.

Garnier J., Leporcq B., Sanchez N. and Philippon X. 1999. Biogeochemical mass-balances (C, N, P, Si) in the three large reservoirs of the Seine basin (France). Biogeochemistry 47: 119–146.

Golterman H.L. 1982. Differential extraction of sediment phosphate with NTA solution. Hydrobiologia 92: 683–687.

Guerrini M.C. et al. 1998. Le bassin de la Seine : la confrontation du rural et de l'urbain. Chapitre 1. In: de Marsily G. and Fustec F. (eds), La Seine en son bassin: fonctionnement écologique d'un système fluvial anthropisé. Elsevier, Paris, pp.29–75.

Haygarth P.M. and Jarvis S.C. 1999. Transfer of Phosphorus from agricultural soils. Adv. Agron. 66: 195–269.

Haygarth P.M. and Sharpley A.N. 2000. Terminology for phosphorus transfer. J. Env. Qual. 29: 10–15.

Haygarth P.M., Warwick M.S. and House W.A. 1997. Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. Water Res. 31: 439–448.

Heathwaite A.L. and Dils R.M. 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. Sci. Total Environ. 251/252: 523–538.

Hieltjes A.S. and Lijklema L. 1980. Fractionation of inorganic phosphates in calcaerous sediment. J. Environ. Qual. 9: 405–407.

Idlafkih Z., Meybeck M., Chiffoleau J.F., CossaD. and Ficht A. 1997. Comportement des métaux particulaires (Al, Fe, Mn, Cd, Cu, Pb et Zn) dans la Seine à Poses en période de hautes eaux (1990–1995). Fresh Water Contamination, Vol. 243. IAHS Publ., 45–58.

Jacks G., Forsbreg J., Mahgoub F. and Palmqvist K. 2000. Sustainability of local water supply and sewage system-a case study in a vulnerable environment. Ecol. Eng. 15: 147–153.

Johnes P.J. 1996. Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modelling approach. J. Hydrol. 183: 323–349.

Jones R.A. and Lee G.F. 1976. Septic tank wastwater disposal system as phosphorus sources for surface water. J. Water Pollut. Control Fed. 51: 2764–2775.

Kronvang B., Laubel A. and Grant R. 1997. Suspended sediment and particulate phosphorus transport and delivery pathways in an arable catchment, Gelbaek stream, Denmark. Hydrol. Proc. 11: 627–642.

Kronvang B., Laubel A., Larsen S.E. and Iversen H.L. 2000. Soil erosion and sediment delivery through buffer zones in Danish slope units. The Role of Erosion and Sediment Transport in Nutrient Contaminant Transfert, Vol. 263. IAHS Publ., 67–73.

May L., House W.A., Bowes M. and McEvoy J. 2001. Seasonal export of phosphorus from lowland catchment: upper River Cherwell in Oxfordshire. Sci. Total Environ. 269: 117–130.

McDowell R., Sharpley A.N. and Folmar G. 2001. Phosphorus export from an agricultural watershed: linking source and transport mechanism. J. Environ. Qual. 30: 1587–1595.

McGehan M.B. and Lewis D.R. 2002. Sorption of phosphorus by soil, Part 1: principles and models. Biosyst. Eng. 2: 1–24.

Meybeck M. 2001. Transport et qualité des sédiments fluviaux: de la variabilité spatio-temporelle à la gestion. La Houille Blanche 6(1): 34–43.

Meybeck M., de Marsily G. and Fustec E. 1998a. La Seine en son bassin: Fonctionnement écologique d'un système fluvial anthropisé. Elsevier, Paris.749

Meybeck M., Mouchel J.M., Idlafkih Z., Andréassian V. and Thibert S. 1998b. Transfert d'eau, de matière dissoute et particulaire dans le réseau fluvialChapitre8. In: Meybeck M., de Marsily G. and Fustec F. (eds), La Seine en son bassin: fonctionnement écologique d'un système fluvial anthropisé. Elsevier, Paris, pp.345–387.

Morel C. 2002. Caractérisation de la phytodisponibilité du phosphore du sol par la modélisation du transfert des ions phosphates entre le sol et la solution. Habilitation à Diriger des Recherches Thesis. INRA-Bordeaux, Institut National Polytechnique de Lorraine, 80pp.

Morel C., Blaskiewitz J. and Fardeau J.C. 1995. Phosphorus supply to plants by soils with variable phosphorus exchange. Soil Sci. 160(6): 423–430.

Morel C., Plenchette C. and Fardeau J.C. 1992. La fertilisation phosphaté e raisonnée de la culture du blé. Agronomie 12: 565–579.

Morel C., Schneider A., Plénet D. and Fardeau J.C. 2002. International Symposium, Vienna, 16–20 October 2000, Joint FAO/IAEA Division Vienna. C & S Papers Series 11/C 486.

Morel C., Tunney H., Plénet D. and Pellerin S. 2000. Transfer of Phosphate ions between soil and solution: Perspectives in soil testing. J. Environ. Qual. 29(1): 50–59.

Némery J. 2003. Origine et devenir du phosphore dans le continuum aquatique de la Seine des petits bassins amont à l'estuaire: Rôle du phosphore échangeable sur l'eutrophisation. Thèse de doctorat d'Etat de l'Université Paris VI. INRA-Bordeaux, Institut National Polytechnique de Lorraine, 263pp.

Ohno T. and Zibilske L. 1991. Determination of low concentration of Phosphorus in soil extracts using Malachite Green. Soil Sci. Soc. Am. J. 55: 892–895.

Pellerin F., Pellerin S., Vilette C. and Boiffin J. 2000. Evolution du raisonnement de la fertilisation phosphaté e des grandes cultures. Etude par simulation des préconisations de fumure sur un échantillon test représentatif des sols et des successions de culture du nord du bassin Parisien.. Etude et gestion des sols. 7: 53–71.

Penven M.J. et al. 1998. Un bassin versant agricole et ses pratiques: le Grand Morin. Chapitre 3. In: de Marsily G. and Fustec F. (eds), La Seine en son bassin: Fonctionnement écologique d'un système fluvial anthropisé. Elsevier, Paris, pp.127–157.

Peters N.E. and Reese S.R. 1995. Variations of weekly atmospheric deposition for multiple collectors at site on the shore of lake Okeechobee, Florida. Atmos. Environ. 29(2): 179–187.

Pieterse N.M., Bleuten W., Jacks G. and JØrgensen S.E. 2003. Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. J. Hydrol. 271: 213–225.

Pilleboue-Baptendier E. 1987. Origines, bilans et mécanismes de transfert du phopshore et de l'azote d'un bassin versant vers un lac. Thèse de doctorat de l'Université Paris VI, 251p, 80pp.

Pollman C.D., Landing W.M., Perry J.J. and Fitzpatrick T. 2002. Wet deposition of phosphorus in Florida. Atmos. Environ. 36: 2309–2318.

Ramade F. 1998. Dictionnaire encyclopédique des sciences de l'eau. Ediscience International, Paris, pp.785.

Reckhow K.H.Beaulac M.N. Simpson J.T. 1980. Modelling phosphorus loading and lake response under uncertainty: a manual of compilation of export coefficients. Un. St. Env. Prot. Agency. 444/5-80-011

Riffard M.et al. 2002. Sources et puits d'eau et de polluants sur des bassins versants élémentaires. Rapport de synthè se Piren-Seine 3e phase: chap. Agriculture et qualité des eaux, 27pp.

Arpaa F. and Contat F. 1988. Des essais, des références. Association régionale pour la promotion des analyses en agriculture. Chambre Régionale d'Agriculture Bourgogne & Association productions végétales et Agronomie. Chambre d'Agriculture de la Haute-Marne, Barrois, pp.66.

SASInstitute1995. SAS/STAT Version 6.11 Ed. SAS Institute, Cary, NC.

Schneider A. and Morel C. 2000. Relationship between the isotopically exchangeable and resin-extractable phosphate of deficient to heavily fertlized soil. Eur. J. Soil Sci. 51: 709–715.

Schvartz C., Walter C., Claudot B., Bouedo T. and Aurousseau P. 1997. Synthèse nationale des analyses de terre réalisées entre 1990 et 1994. I. Constitution d'une banque de données cantonales. Etude et gestion des sols. 4(3): 191–204.

Sharpley A.N., Gburek W.J., Folmar G. and Pionke H.B. 1999. Sources of phosphorus exported from an agricultural watershed in Pennsylvania. Agri. Water Manage. 41: 77–89.

Sinaj S. et al. 1998. Interference of the colloidal particles in the determination of orthophosphate concentrations in soils waters extracts. Commun. Soil Sci. Plant Anal. 29(9–10): 1091–1105.

Smith K.A., Jackson D.R. and Withers P.J.A. 2001. Nutrient losses by surface run-off following the application of organic manures to arable land. 2. Phosphorus. Environ. Pollut. 112: 53–60.

Steer D., Fraser L., Boddy J. and Seibert B. 2002. Efficiency of small constructed wetlands for subsurface treatment of single-family domestic effluent. Ecol. Eng. 18: 429–440.

Strauss P. 2002. Phosphorus losses as a result of surface runoff: Field data. In: Chardon W.J. and Schoumans O.F. (eds), Phosphorus losses from agricultural soils/Processes at the field scale. COST Action 832. Alterra, Wageningen, The Netherlands, pp.93–101.

Sutula M., Day J.W., Cable J. and Rudnick D. 2001. Hydrological and nutrient budgets of freshwater and estuarine wetlands of Taylor Slaugh in Southern Everglades, Florida. Biogeochemistry 56: 287–310.

Svendsen L.M., Kronvang B., Kristensen P. and Græsbøl R. 1995. Dynamics of phosphorus compounds in a lowland river system: importance of retention and non-point sources Hydrol. Proc. 9: 119–142.

Svendsen L.M., Redsdorf A. and Nørnberg P. 1993. Comparison of methods for analysis of organic and inorganic phosphorus in river sediment. Water Res. 27(1): 77–83.

Thibert S. 1994. Exportations naturelles et anthropiques des ions majeurs et des éléments nutritifs dans le bassin de la Seine. Approche méthodologique. Université de Paris 6195pp.

Thoms M.C., Foster J.M. and Gawne B. 2000. Flood-plain sedimentation in a dryland river: the River Murray, Australia. The Role of Erosion and Sediment Transport in Nutrient Contaminant Transfert, Vol. 263.IAHS Publ., pp.227–236.

Torrent J. 1997. Interactions between phosphate and iron oxide. Adv. Geoecol. 30: 321–344.

Turtola E. and Paajanen A. 1995. Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from heavy clay soils. Agri. Water Manage. 28: 295–310.

Vaas L.H., R.N.J C., Das H.A., Reith J.M.M. and der Veijden C.H. 1987. Isotopically exchangeable phosphate in freshwater sediments: effects of U.V. - radiation, formaldehyde, solid/solution ratio and pH on its experimental determination. Water Res. 21(9): 1135–1142.

Van Veldhoven P.P. and Mannaerts G.P. 1987. Inorganic and organic measurements in the nanomolecular range. Anal. Biochem. 161: 45–48.

Verhoff F.H., Yaksich S.M. and Melfi D.A. 1980. River nutrient and chemical transport estimates. J. Environ. Eng. Div. ASCE 10: 591–608.

Verstaeten G. and Poesen J. 2000. Assessment of sediment-fixed nutrient export from small drainage basins in central Belgium using retention ponds. The Role of Erosion and Sediment Transport in Nutrient Contaminant Transfert, Vol. 263. IAHS Publ., 243–249.

Walling D.E., He Q. and Blake W.H. 2000. River flood plains as phosphorus sinks. The Role of Erosion and Sediment Transport in Nutrient Contaminant Transfert, 263. IAHS Publ., pp.211–218.

Walling D.E. and Webb W. 1985. Estimating the discharge of contaminants to coastal waters by rivers: some cautionnary comments. Mar. Poll. Bull. 16(12): 488–492.

Walling D.E., Webb W. and Russel M.A. 1997. Sediment-associated nutrient transport in UK rivers. Fresh Water Contamination, Vol. 243. IAHS Publ., pp. 69–81.

Walter C., Schvartz C., Claudot B., Bouedo T. and Aurousseau P. 1997. Synthèse nationale des analyses de terre réalisées entre 1990 et 1994. II. Description statistique et cartographie de la variabilité des horizons de surface des sols cultivés. Etude et gestion des sols 4(3): 205–220.

Williams J.D.H., Shear H. and Thomas R.L. 1980. Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materiels from Great Lakes. Limnol. Oceanogr. 25(1): 1–11.

Withers P.JA.Dils R.M. Hodgkinson R. 1999. Transfer of phosphorus from small agricultural basins with variable soil types and land use. Impact of land-use on nutrient loads from diffuse sources (Proceedings of IUGG 99 Symposium HS3, Birmingham, July 1999), Vol. 257, IAHS Publi.41–50.

Zimmer D., Bouzigues R., Chossat J.C., Favrot J.C. and Guiresse A.M. 1991. Importance et déterminisme des infiltrations profondes en luvisols-rédoxisols drainés. Incidence sur les modalités de drainage. Science du sol 29(4): 321–338.