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Origin and fate of phosphorus in the Seine watershed (France): Agricultural and hydrographic P budgets

Julien Némery[1] and Josette Garnier[2]

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[1] Phosphorus (P) sources (point and diffuse) in the human-impacted Seine basin (64,840 km^2) were evaluated for the year 2000. An agricultural P budget showed that fertilizers represented 59% (20–25 kgP ha^{-1}) of P inputs to the soils. A P surplus (2.5 kg P ha^{-1} y^{-1}) contributed to P enrichment of the agricultural soils whose stocks amounted to 1800–5000 kgP ha^{-1}. A hydrographic P budget showed that runoff (0.39–0.51 kgP ha^{-1}) dominated the diffuse sources. These losses represented a very low percentage (0.01%) of the P stocks in soils and contributed to 19–25% of the total P inputs to the drainage network. Point sources remained the main source of P (75–81%), particularly in the downstream urbanized zone. Phosphorus retention in the river drainage network accounted for 9–15% of the total P inputs, indicating that it must not be ignored in large river P budget calculations. The Seine basin exported 8000 tP y^{-1} (44% as particulate P) to its estuary. The annual mean particulate P in suspended sediment at the outlet (2.9 gP kg^{-1}) was fourfold greater than in headwaters and in rural zones. The similar increase of the particulate inorganic P/particulate organic P ratio in suspended sediment along the river continuum clearly indicated the increasing pressure of point sources. The close relation between P content of suspended sediment during the high-flow period and the P content of agricultural soils resulted in proposing a novel method to calculate the PP losses from runoff.

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1. Introduction

[2] Phosphorus (P) is most likely to limit the growth of algae in freshwater aquatic ecosystems [*Vollenweider*, 1968]. The P loading of river systems in human-impacted areas is controlled by a multitude of factors, including the hydrology, the point (effluents) and diffuse sources (agriculture), and the in-stream processes, all leading to transformation or retention of P during its travel downstream through the river continuum [*Jarvie et al.*, 2006a]. Since the 19th century, greater use of fertilizers in agriculture and increasing P in domestic effluents due to the use of polyphosphates in washing powders in the 1950s have extensively modified the fluxes and stocks of P within the main biosphere reservoirs. These changes are often responsible for eutrophication of water bodies. Point sources are being progressively reduced by the improvement of P treatments in sewage treatment works (STWs) and by the reduction of polyphosphates. As the point sources are decreasing while the use of fertilizers remains high, it has become essential to quantify the diffuse sources, whose relative contribution is on the rise. For the last 15 years, many studies have focused on the P inputs stemming from diffuse sources such as agricultural soil runoff and leaching on the scale of small watersheds [*Dorioz and Ferhi*, 1994; *Haygarth and Jarvis*, 1999; *Sharpley et al.*, 1999]. For instance, a synthesis of European data was compiled in the framework of the EU Cost Action 832 project entitled "Quantifying the Agriculture Contribution to Eutrophication" [*Chardon and Schoumans*, 2002; *Kronvang*, 2002]. More recently, a special issue of a scientific journal was devoted to the study of the relation between landscape sources of P, water and sediment, and consequent ecological impacts on surface waters [*Haygarth*, 2005].

[3] The issue of the management of P is of prime importance in the context of the European Water Framework Directive (2000/60/EC). Here, the Seine basin provides a very well-documented example of a strongly human-impacted river system subjected to a highly populated area (Paris and its suburbs), heavy industrial demands, and intensive agriculture [*UNESCO*, 2003; *Billen et al.*, 2007a, 2007b]. The ecological model (Riverstrahler) developed over the last 10 years [*Billen et al.*, 1994; *Garnier et al.*, 1995] on the Seine basin has shown that the reduction of P in STWs must reach 90% to substantially reduce algal blooms [*Garnier et al.*, 1998]. The need for such a sizable reduction motivated us to investigate the P inputs through diffuse sources on the basin scale in order to explore their possible reduction.

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Table 1. Land Use, Mean Flows, and P Point Sources (STWs, Industries, and CSOs) in the Seine Basin and in the Main Subbasins (for Land Use: Data From Corine Land Cover and the Recensement Général de l'Agriculture, RGA 2000, i.e., General Agricultural Statistics; for Point Sources, Data From the Agence de l'Eau Seine Normandie (AESN) and the Syndicat Interdépartemental d'Assainissement à l'Agglomération Parisienne (SIAAP))

				Land Use Cover, %			Point Sources, TP y^{-1}	
Basin	Area, km^2	Mean Flow (1999–2001), $m^3\ s^{-1}$	Inhab., Eq. 10^6	Urbanized Zones	Forests	Agriculture	STWs	CSOs[a]
Upper Seine	30,718	300	2.5	3.8	28.8	56.6	1606	/
Marne	12,732	170	1.1	4.8	27	60	465	/
Oise	16,973	150	1.7	4.4	21.7	64	851	/
Paris–Poses Axis	4,417		9.7	21	17	47	3930	206
Seine at Poses[b]	64,840	750	15	5.3	26	58.5	6852	206

[a] Based on mean urban specific P losses (0.5–2.5 kgP ha^{-1}, >60% as PP [*Dorioz and Trevisan*, 2001]).

[b] Total Seine basin: 73,793 km^2 with the intra-estuarine basin.

[4] To quantify the respective annual contributions of point and diffuse sources, we inventoried P sources to establish an agricultural P budget and estimated P stocks in soils, which we linked to P losses from runoff and leaching. We also established a P budget in the drainage network considering P sources, pathways, and fate. P dynamics along the drainage network can therefore be analyzed using a nested watershed approach.

2. Materials and Methods

2.1. Site Description

[5] The Seine River drains a large (73,793 km^2), densely populated basin (200 inhab. km^{-2}, concentrated mostly in the Paris conurbation of 10 million inhabitants). Agricultural land accounts for approximately 60% of the area and is largely dominated by industrial crops grown in the center of the basin (Table 1). The Poses dam (km 202 from Paris) marks the downstream limit of the fluvial part of the Seine basin (64,840 km^2, 8th hydrological order); the hydrodynamic marine influence is observable up to Poses (Figure 1). The estuarine sector of the Seine was specifically studied for P dynamics in a previous paper [*Némery and Garnier*, 2007]. For the present study, P budget calculations within the Seine basin were based on three main subbasins and one main axis downstream of Paris (Figure 1a and Table 1). Three large reservoirs have been built over the last 40 years upstream of the Seine basin in order to regulate the flow of the main tributaries (the Aube, Marne, and Seine, Figure 1b). The mean annual precipitation is 800 mm and the mean annual runoff is 200 mm. The years studied (1999–2002) were characterized by high discharges at Poses (600 $m^3\ s^{-1}$ in 1999, 750 $m^3\ s^{-1}$ in 2000, 900 $m^3\ s^{-1}$ in 2001 and 590 $m^3\ s^{-1}$ in 2002) as compared with the average flow of the Seine during the last decade (500 $m^3\ s^{-1}$).

[6] Silt is omnipresent across the basin and the gentle slopes of the drainage network (0.1–0.3‰) are characteristic of plain rivers with a moderate elevation. As a consequence, the erosion and suspended sediment fluxes are among the lowest in the world (10t $km^2\ y^{-1}$ [*Meybeck et al.*, 2003]).

2.2. Sampling and Laboratory Analyses

[7] The purpose of the sampling strategy was to estimate P fluxes and study the spatial and temporal variability of P content in suspended matter using a nested watershed approach integrating hydrological order and land use vari-

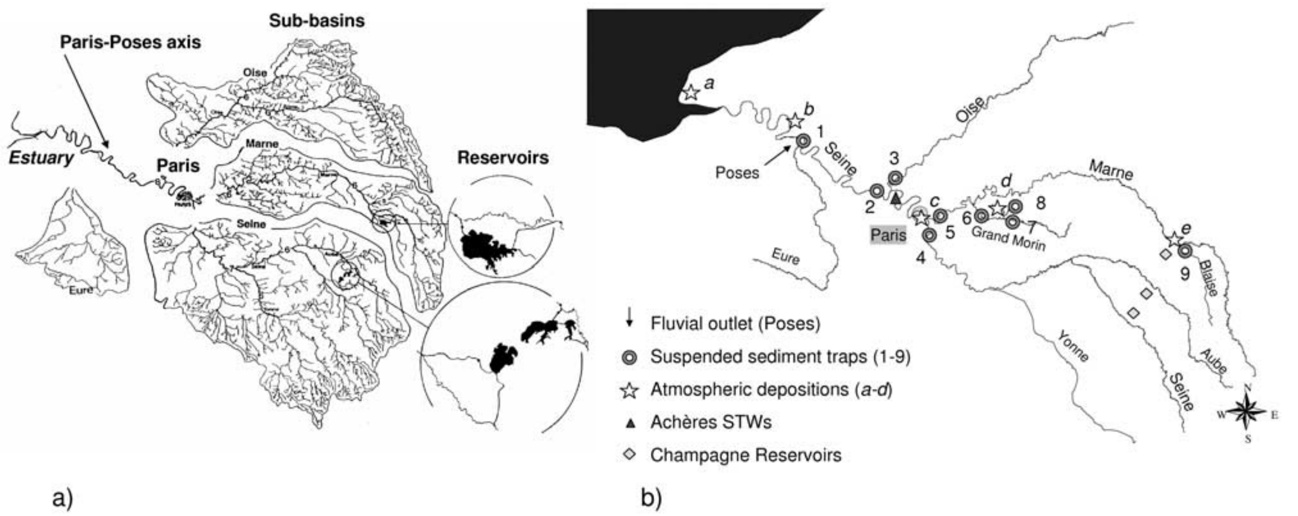


Figure 1. (a) General map of the Seine basin with main subbasins, the Paris–Poses axis, and reservoirs and (b) the hydrographic network and sampling sites in the Seine basin (see Table 2 for site characteristics).

Table 2. Sampling Sites: Characteristics and Period of Collection (see Figure 1 for Location of the Sites)

Site No.	Site	Surface of Drainage, km^2	Hydrologic Order	Period of Collection	n[a]	Characteristics
	Paris-Poses Axis					
1	*Poses (Seine)*	64,840	8	Jul 1999–Jul 2000	15	Influenced by Achères STW effluents
2	*Andrésy (Seine)*	61,755	8	Jul 1999–Aug 2000	16	
2	*Denouval (Seine)*	61,755	8	Jul 1999–Oct 1999	6[a]	
	Oise Basin					
3	*Eragny*	16,973	7	Jul–Aug 2000	3[a]	Influenced by STW effluents and agriculture
	Upper Seine basin					
4	Vitry	30,718	7	Aug 2000–Dec 2001	9[a]	Influenced by STW effluents and agriculture
	Marne basin					
5	St Maurice	12,732	6	Apr 2001–Mar 2002	25	Influenced by STW effluents and agriculture
	Grand Morin basin					
6	Saint-Germain	1202	5	Apr 2001–Mar 2002	16	Dominated by agriculture and heavily drained
7	Martroy	617	5	Apr 2001–Mar 2002	15	
8	Mélarchez	7	1	Apr 2001–Mar 2002	20	
	Blaise basin					
9	Pont Varin (Blaise)	607	4	Apr 2002–Mar 2003	13	Dominated by livestock farming

[a]The disparity in the number of samples is due to the loss of sediment traps.

ability (see Table 2 for the watershed description). The center of the Seine basin is dominated by agriculture (cereals and industrial crops), whereas its upper part is taken up by livestock farming and forests. The Grand-Morin (1202 km^2) and Blaise subbasins (607 km^2) are representative of these two different land uses. The Marne subbasin (12,732 km^2), which includes these two small basins, is both agricultural and highly urbanized in its downstream section. The two other main subbasins (Oise, 16,973 km^2, and Upper Seine, 30,718 km^2) present similar characteristics in terms of anthropogenic pressures and were investigated at their outlets. Then the impact of Paris and especially of its main STWs at Achères (km 60) was investigated along the Paris–Poses axis (202 km) between the Andrésy-Denouval (km 73) and Poses dams, the latter of which is a reference station for budget calculations as it integrates all the perturbations of the entire Seine basin (64,840 km^2). Note that the outlets of large rivers are sampled monthly to fortnightly by the French National Water Quality Survey (Réseau National de Bassin) and analyzed for routine water quality variables and flow rates.

[8] Suspended sediments were sampled with sediment traps placed at the outlets of the watersheds studied (Figure 1b). For deep rivers, traps were built with a float and a counterweight that kept a 20-cm-diameter PVC cylinder filled with a tubular structure 70 cm from the surface. For shallow rivers, a plastic case with an identical tubular structure was put on the river bed. These traps collected suspended sediment transported during the sampling period (monthly on average); an annual survey was done (see Table 2 for the collection period). Water samples were also taken using a bucket and analyzed in the laboratory for total suspended solids (TSSs) and orthophosphate concentrations.

[9] The suspended sediments sampled were passed through 200-μm sieves, centrifuged, stored frozen, and then freeze-dried before analysis. Total particulate P (TPP) content of suspended sediment was determined using a high temperature/HCl extraction technique [*Aspila et al.*, 1976]; organic P was mineralized into inorganic forms at 550C. Both inorganic and mineralized organic forms were extracted into 1N HCl for 15–20 h and analyzed for phosphate using the colorimetric method [*Murphy and Riley*, 1962]. To estimate particulate inorganic P (PIP), the analysis was similar to that for TPP, except that the high-temperature organic P mineralization was omitted. Particulate organic P (POP) was determined by calculating the difference between TPP and PIP [*Svendsen et al.*, 1993]. TPP, PIP, and POP are expressed in gP kg^{-1} of suspended sediment. Note, however, that higher TPP contents were found by using HF-HClO$_4$ extraction [*Némery*, 2003], indicating that the HCl 1N method, used here, underestimates TPP content by 10–15% compared with HF-HCl0$_4$ extraction. TSSs were measured by filtration of 100- to 1000-ml water samples through preweighed GF/F Whatman filters (pore size diameter, 0.7 μm; AFNOR T90-105, 1994).

[10] The filtrates were frozen and kept for dissolved P (DP) analysis. DP in the water was analyzed using the blue-molybdate colorimetric method [*Murphy and Riley*, 1962].

2.3. Hydrographic Budget Calculation

2.3.1. Flux Calculation

[11] The total P budget was calculated as the contribution by both DP and particulate P (PP) forms. Daily DP fluxes were derived as the product of instantaneous orthophosphate concentration in the water column and the water flow rate measured the same day. The PP content of suspended sediment was multiplied by the average TSS concentration and the average water flow corresponding to the period of suspended sediment collection in the traps and expressed as daily PP fluxes. Annual fluxes (AF) expressed in TP y^{-1} were calculated according to the load estimating procedure described by *Verhoff et al.* [1980], recommended by *Walling*

and Webb [1985] and commonly used [*Aminot et al.*, 1998; *Meybeck et al.*, 1998].

$$AF = \frac{K \sum_{i=1}^{n} (C_i Q_i)}{\sum_{i=1}^{n} Q_i} Q_m \qquad (1)$$

where K is conversion factor to take the recorded period into account (365 days), C_i is instantaneous/mean concentration (mg P-PO_4 m^{-3}), Q_i is instantaneous/mean discharge (m^3 s^{-1}), and Q_m is mean discharge for period of record (m^3 s^{-1}). Discharge data were extracted from the French Water Databank.

2.3.2. Point Sources (STWs and Combined Sewage Overflows [CSOs])

[12] The specific P load from STWs (including industrial waste) was provided by the Agence de l'Eau Seine Normandie (AESN) and the Syndicat Interdépartemental d'Assainissement de l'Agglomération Parisienne (SIAAP) database for the year 2000 (Table 1). Overall, 90% of the population of the Seine basin are connected to STWs. Phosphorus fluxes generated by the unconnected population are assumed to be negligible (see Discussion below).

[13] The sewage system of Paris and its suburbs receives both effluents and runoff from urbanized surfaces. During the dry season, all collected wastewater is treated in STWs. During storm events, some of the CSOs discharge directly into the river and the largest ones have been identified within Paris and its suburbs [*BPR-Sogreah-Hydratec*, 1997]; during these wet episodes, it has been estimated that 60% of CSOs generated by the Paris conurbation are collected in retention basins and subsequently treated in STWs [*AESN*, 2003]; 40% reach the rivers directly (Table 1).

2.3.3. Diffuse Sources

[14] Diffuse sources of P consist of contributions by both runoff and leaching through drainage, which are the two main processes of P transfer from cultivated land [*Haygarth and Jarvis*, 1999; *Kronvang et al.*, 2000]. Phosphorus losses from runoff can be measured directly in the field by collecting surface or subsurface runoff water [*Catt et al.*, 1999; *Smith et al.*, 2001]. The results vary widely depending on slope, soil type, land use, and rainfall [*Strauss*, 2002] and are difficult to extrapolate to other soils and regions. For this reason, many authors [*Bowes et al.*, 2005; *Johnes*, 1996; *May et al.*, 2001; *Reckhow et al.*, 1980] prefer to use export coefficients, especially when the aim is to model, on the basin scale, the nutrient load to the surface water drainage network as a function of the specific loss from each type of land use gathered from the literature and averaged. In addition, more and more studies are conducted on increasing geographical scales in a nested headwaters-to-river channel approach [*Haygarth et al.*, 2005].

[15] The leached P flux was calculated from a data set collected over 8 years of monitoring (1990–2000 period) at the outlet of a 15-ha basin in the Marne subbasin, a cultivated and drained area (data from Cemagref [*Riffard et al.*, 2002]). Specific DP (0.042 kgP ha^{-1} y^{-1}), TP (0.118 kgP ha^{-1} y^{-1}) and PP (PP = PT−DP = 0.076 kgP ha^{-1} y^{-1}) fluxes were averages of the 8 years considered and were used to estimate P losses from leaching by drainage on the whole basin scale [*Némery*, 2003; *Némery et al.*, 2005].

[16] Here P losses from runoff were calculated by the difference between TP fluxes at the outlet of the Seine basin and all the known inputs and outputs (e.g., retention). Here, sedimentation at the scale of the hydrological cycle is considered to compensate for resuspension within the river bed [*Meybeck*, 2001] so that fluxes are in equilibrium in the P budget.

[17] Phosphorus losses from forests were determined from a specific P flux in the range of 0.02–0.05 kgP ha^{-1} y^{-1} (DP < 50%), as found in the literature [*Dorioz and Trevisan*, 2001; *Johnes*, 1996].

2.3.4. Retention (Reservoirs and Flood Plains)

[18] The functioning of the three main reservoirs has been extensively studied [*Garnier et al.*, 2005, 1999]. According to the in-out P budget determined in these studies, the retention averages 37.7 tP y^{-1}.

[19] Wetlands on valley bottoms can also play an important role in retaining nutrients associated with suspended sediments transported by rivers [*Fustec and Lefeuvre*, 2000]. Recent studies on the role of flood plains as sediment sinks have 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; *Meybeck*, 2001; *Thoms et al.*, 2000; *Walling et al.*, 2000]. In the Seine basin, flood plains are characteristic of the 4th stream order rivers and the flooded width of the valley is within the same range within the basin, since the hydrologic regime of the Seine is quite homogenous [*Guerrini et al.*, 1998]. The percentage of flooded area is then given by the flood frequency [*AESN*, 1974].

[20] A study of sediment retention conducted in the large flood plains of the upper Seine basin [*Fustec et al.*, 1998] was extrapolated here to estimate P sinks for the two other subbasins (Oise and Marne) and the Paris–Poses axis. In the aforementioned study, the mean annual sedimentation rate was estimated using isotopic tracers (^{137}Cs) measured in deposited sediment cores. The sediment and associated P retention were estimated at different distances from the river channel during exceptional floods in the winter of 1994–1995 (Table 3). The transversal deposition rate presents an increasing gradient from the river bank to the end of the flood plains. Annual P retention (APR) in the flood plains is calculated as follows:

$$APR = \sum_{5m-700m} (PRR * S) * FD \qquad (2)$$

where PRR is P retention rate (kgP km^{-2} d^{-1}) equal to daily sediment deposition rate (kg km^{-2} d^{-1}) * PP content (kgP $kgTTS^{-1}$) in suspended sediment during high-flow periods at the basin outlets; S is flood-plain surface (km^2) equal to distance from channel * total length of flooded area; FD is flood period (days) equal to 15 days (low hypothesis) to 30 days (high hypothesis) [*Guerrini et al.*, 1998].

2.4. Agricultural P Budget

2.4.1. Agricultural Fluxes

[21] Phosphorus fluxes were estimated from agricultural statistical data for the year 2000; these statistics provide the cultivated surface area of each type of crop and the number of animals of each type (cattle, poultry, etc.) on the scale of

Table 3. Sedimentation Rate in Flood Plains in the Seine Basin and Corresponding P Sink at Various Distances From the Channel

Distance From Channel, M	Flood Duration, days	Sediment Deposition Rate,[a] kg drysed m^{-2}	Daily P Deposition Rate, kgP km^{-2} d^{-1}			
			Upper Seine	Marne	Oise	Paris–Poses Axis
5	119	17	311[a]	128.6[b]	128.6[b]	280[b]
35	149	10	182	60.4	60.4	131.5
70	149	2.6	55	15.7	15.7	34.2
700	149	2.2	35	13.3	13.3	29

[a] Estimated using sediment traps placed in large flood plains of upper Seine basin at different distances from the main channel (Engerran (1998) in *Fustec et al.* [1998]); P content included between 2.1 and 3.1 gP kg^{-1}.

[b] Calculated values (see equation (2)).

an administrative district (Agreste, http://www.agreste.agriculture.gouv.fr/, 2000). The fertilizer fluxes were obtained by multiplying the surface area of each type of crop (ha) by the fertilizer inputs as provided both by the farmers' association in each district and the French Union of Fertilizer Industries (UNIFA). The crop export fluxes are the product of the yield (q = 100 kg) and the P export ratio for each crop (Table 4). Crop residue fluxes were drawn from the portion of the crop (stems and leaves) that remains in the field after harvest. The P flux of the food-processing industry was calculated as the difference between the total crop export and the forage exported to feed animals.

[22] Livestock effluent fluxes were determined as the product of the numbers of each type of animal and the P fluxes generated by livestock (kgP head^{-1} y^{-1}, Table 4). The P import was obtained by the difference between the livestock effluent and the forage consumed, assuming that animal products (milk, meat, eggs, etc.) export very low quantities of P.

2.4.2. STW Biosolid Inputs

[23] The P inputs from STW biosolids were estimated with a data set of P content in biosolids from the Achères STWs (SIAAP data) and by studying the area of biosolids spread within the Seine basin [*Roy de Lachaise et al.*, 2003]. Such inputs are locally high at the spread surface scale (4.5–7 kgP ha^{-1}) but quite low (0.3–1.9 kgP ha^{-1}) when the entire agricultural area is considered. However, these results are a minimum estimate on the Seine basin scale because they concern only biosolids coming from the Achères STWs, despite the large quantities of effluents treated by the Achères STWs (one-third of those in France; see Discussion below).

2.4.3. Atmospheric Deposition

[24] Atmospheric depositions of P are known to contain mainly dissolved forms (90%) [*Dorioz and Trevisan*, 2001; *Peters and Reese*, 1995]. Bulk atmospheric P depositions were thus estimated by colorimetric analysis of orthophosphate in unfiltered rainfall samples from five different sites (urban, rural/urban, rural and estuary) in the Seine basin [*Garban et al.*, 2002]. Total P deposition expressed in kgP ha^{-1} y^{-1} was calculated by summing the product of the monthly mean orthophosphate concentration and the monthly cumulative rainfall [*Némery et al.*, 2005].

2.4.4. Phosphorus Stock in Soils

[25] The total P stock in soils is difficult to estimate because of the lack of TP measurements from cultivated soils, because these TP 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 related to labile P, which are not interpretable in terms of TP. 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 various land uses and agricultural practices in the Seine basin make it impossible to attribute a mean P content to one soil type. Moreover, the Seine basin consists of several different geological units [*Guerrini et al.*, 1998]. Such soil characteristics are integrated into the description of hydro-ecoregions by which the

Table 4. Fertilizer Inputs, P Export Ratio and P Field Restitution for Main Crops [*CORPEN*, 1998]; and Restitution for Animal Manures

	Crop			Animals	
	Fertilizers Inputs, kgP ha^{-1}	Export Ratio, kgP 100kg^{-1}	Field Restitution, kgP 100kg^{-1}	Animal Types	Restitution, kgP head^{-1} y^{-1}
Cereals					
Wheat	17–22	0.53	0.132	*Calf* < 1 *year*	4.7
Barley	*20–35*	0.48	0.132	*Cow*	15.7
Corn	*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
Industrial crops				**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

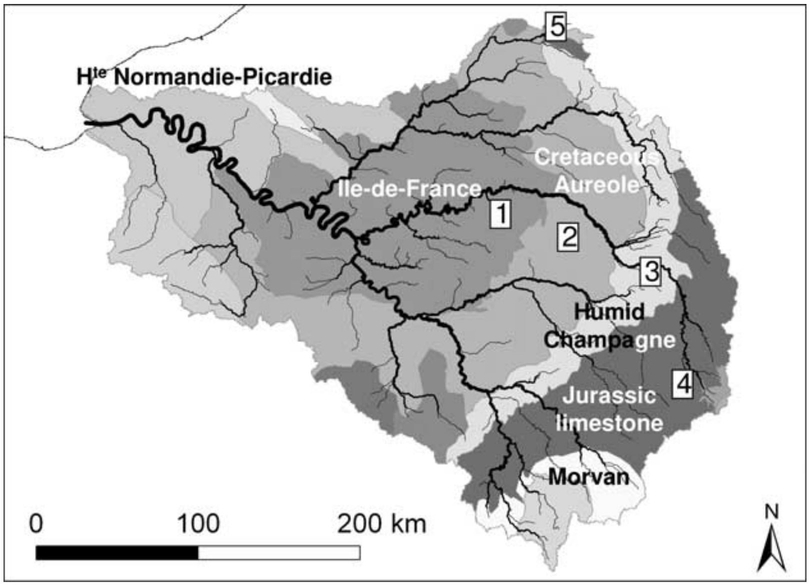


Figure 2. Soil sampling sites (1–5; see Table 6 for characteristics) in the Seine basin according to the main hydro-ecoregion units [*Wasson et al.*, 2002] (figure adapted from *Garnier and Billen* [2006]).

Seine basin can be mapped according to the main geological and hydrological units (Figure 2 [*Wasson et al.*, 2002]). A survey of soil P content was carried out within the Seine basin. 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. At this time, cultivated soils are bare, often plowed but not yet fertilized, and consequently homogeneous; conditions are therefore favorable for a realistic estimate of total P stocks.

[26] The samples were dry-sieved (<2 mm) and analyzed for TP (high-temperature/HCl 1N 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 can estimate a soil stock of 3500 tons ha^{-1} and calculate the soil P stock (kgP ha^{-1}) considering its TP content (gP kg^{-1}).

3. Results

3.1. Agricultural P Budget

[27] The Agricultural P budget (Figure 3) shows that the greatest inputs are from fertilizers, which account for 59% of all inputs reaching the soil. Crop residues, livestock restitution, STW biosolids, and atmospheric deposition contribute 23%, 16%, 2%, and 1%, respectively. The calculated difference between these four estimated inputs and crop exports is positive: the surplus amounts to 2.5 kgP ha^{-1} y^{-1} and necessarily leads to a significant increase in the P content in soils. This result obtained for the entire basin agrees well with what is observed in the four main subbasins considered separately (Table 5).

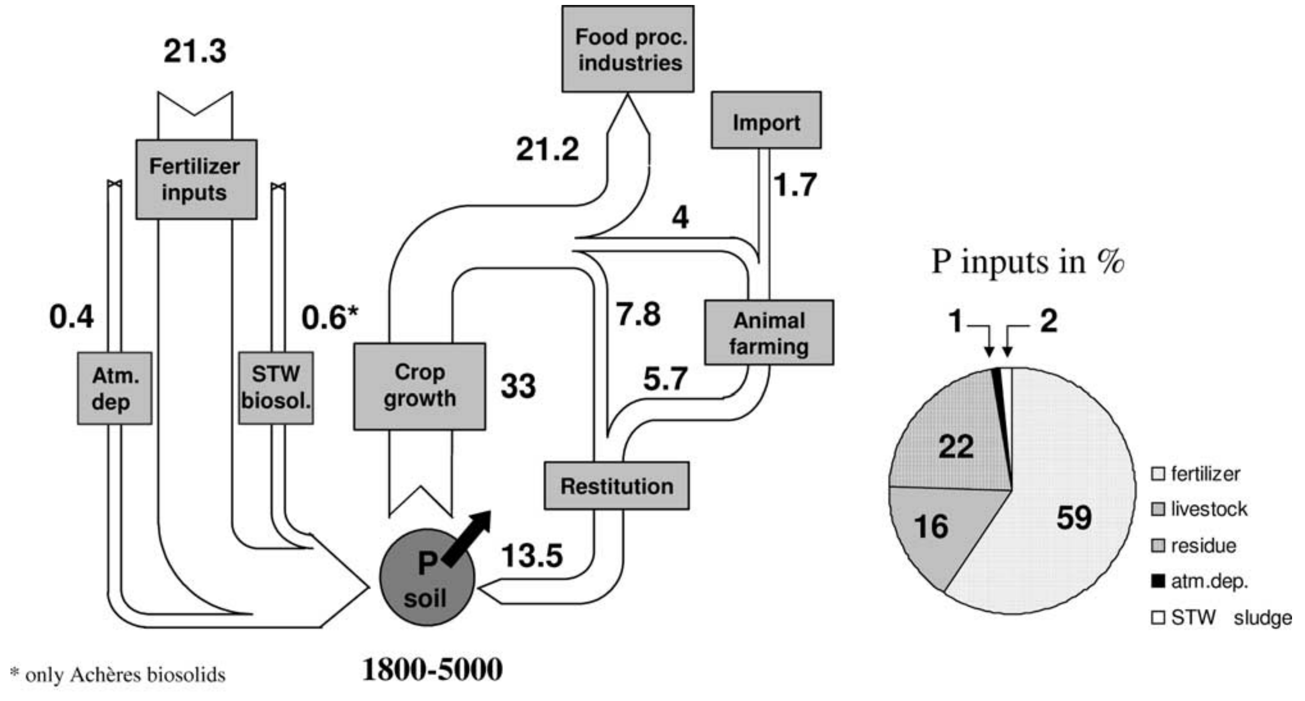
[28] The results are, however, subject to uncertainties inherent in this type of data. A possible variation of 100% would be a pessimistic view. Therefore, the calculated surplus varying between 1.8 and 4 kgP ha^{-1} can be said to range roughly within one order of magnitude, from 1 to 10 kgP ha^{-1}. Fertilizers are the major P contributors to soils. These calculations are supported by the significant relationship with the amount of fertilizers provided by the French Union of Fertilizer Industries (UNIFA) [*Némery et al.*, 2005]; the uncertainty range reaches ±15% between the two information sources. In addition, agronomists generally admit that P fertilizer inputs are at least equal to crop exportations, which is verified here.

3.2. Phosphorus Stock in Soils

[29] In cultivated soils (Table 6), P contents are within the range of 0.52 gP kg^{-1} in the Ile-de-France region (center of the basin) and 1.42 gP kg^{-1} in chalky layers of the Champagne region (cereal and industrial crops). Grassland soils have P contents very close to the mean value of all cultivated soils (0.69 gP kg^{-1}). Vineyard soils present a mean P content of 0.90 gP kg^{-1}. The P content in forest soils, considered as a reference without human impact, is three to ten times lower than in cultivated soils. On this basis, the P stock in cultivated soils is estimated to be from 1800 kgP ha^{-1} at the lowest and up to 5000 kgP ha^{-1} in the chalky layers.

3.3. Phosphorus Content in Suspended Sediment Along the River Network: PIP/POP Ratio

[30] The results presented here correspond to different sampling periods but can be analyzed together since these years (from 1999 to 2002) belong to the same wet period. The annual mean P content of suspended sediment can be analyzed for three different zones: (i) small rural basins (sites 6–9), (ii) outlets of main subbasins (sites 3–5), and (iii) the main branch downstream from Paris (sites 1 and 2) (Figure 4a). In the Blaise subbasin (site 9), the annual mean TPP content is 1.5 gP kg^{-1}, with a large proportion of POP (50%). In the Grand Morin subbasin, annual mean TPP contents are similar (0.8–0.9 gP kg^{-1}) for the three sites studied (6, 7, and 8). The POP fraction averages 40% at the outlet of the Grand Morin subbasin (site 6) and is within the same range for the other sites (7 and 8), where fewer data



a) b)

Figure 3. (a) Agricultural P budget in the Seine basin. Fluxes are expressed in kgP ha^{-1}; (b) proportion of input from the considered sources in % of total inputs (Atm. Dep, atmospheric deposition; STW biosol, STW biosolid inputs; Food proc. Industries, food-processing industries; P soil, P content of soils; the arrow indicates an increase).

are available (Table 7). At the outlets of the three main subbasins, Oise, upper Seine, and Marne, the annual mean TPP contents are, respectively, 1.7, 2.2, and 1.4 gP kg^{-1} (see sites 3, 4, and 5, respectively), with POP fractions decreasing (Figure 4a). As only three samples were analyzed for site 3, these data must be considered tentative. In the main branch, the annual mean TPP content found at site 2 (4.1 gP kg^{-1}) is two to three times greater than that measured at the outlets of the main subbasins and three to four times greater than that in small rural watersheds, with a POP proportion decreasing to 25%. Further downstream at Poses (site 1), the TPP content is a mean 2.9 gP kg^{-1}, with a 19% proportion of POP (Figure 4a).

[31] Following *Owens and Walling* [2002], the mean and standard deviations of the PIP/POP ratio were calculated for each sample (sites 3, 7, and 8 were omitted because of insufficient data). Calculated values increased from 1.0 (SD = 0.3) upstream, at site 9, to 4.1 (SD = 3.7) at Poses (Figure 4b). Plotted as a function of hydrologic order, the upper rural zones can be distinguished from the urbanized zones located farther downstream, and the PIP/POP ratio increased fourfold together with the TPP. The decrease in the Seine estuary, indicatively presented in Figure 4b, was attributed mainly to a P desorption in the salinity gradient [*Némery and Garnier*, 2007].

3.4. Phosphorus Budget in the Seine Drainage Network

[32] The total P flux at the outlet of the Seine basin was estimated at 8000 tP y^{-1} composed of DP (56%) and PP (44%) (Figure 5). Point sources account for 75–81% of the total inputs to the hydrographic network; more than 80% of point sources are in dissolved inorganic form. Estimated CSOs account for a very low percentage of point sources (<3%), while 57% of point sources originate from the highly urbanized area of the Paris conurbation. Achères STWs alone contribute 38% of total P inputs, i.e., more than

Table 5. Specific P Fluxes in the Different Subbasins on the Seine Basin for the Year 2000

	Atmospheric Depositions	Fertilizers	STW Biosolids	Crop Growth	Restitution	Animal Farming	Surplus
				kgP ha^{-1} y^{-1}			
Upper Seine	0.42	20.6	0.6	33 (6)[a]	7.5	5.7	1.8
Marne	0.39	22.3	0.4	33 (4)	7.5	5	2.6
Oise	0.42	21.9	0.3	34 (5)	8.6	6.3	3.5
Paris–Poses axis	0.28	20.8	1.9	32 (4)	7.9	5.1	4
Total Seine at Poses	*0.40*	*21.3*	*0.6*	*33 (4)*	*7.8*	*5.7*	*2.5*

[a] In parentheses: animal forage.

Table 6. Mean P Contents in Soils in Different Hydro-Ecoregions of the Seine Basin[a]

		Arable Land	Grassland	Forest	Vineyard
Hydro-Ecoregion	Pedogeological Units	gP kg^{-1}			
Ile-de-France (1)	Limestone, silt, sand, marl	**0.52** (*n* = 17; 0.17)	**0.39** (*n* = 1)	**0.15** (*n* = 3; 0.05)	/
Champ. Crayeuse (2)	Chalk	**1.42** (*n* = 19; 0.24)	/	/	**0.90** (*n* = 1)
Champ. Humide (3)	Marl-clay	**0.74** (*n* = 3; 0.09)	**0.68** (*n* = 1)	/	/
Barrois + Argonne (4)	Limestone, Gaize, marl-limestone	**1.0** (*n* = 8; 0.32)	**0.82** (*n* = 4; 0.26)	**0.12** (*n* = 4; 0.08)	/
Thiérache (5)	Marl, limestone, shield	**0.64** (*n* = 2)	**0.58** (*n* = 2)	**0.34** (*n* = 1)	/

[a]See Figure 2 for site location (sites 1–5).

all combined diffuse sources (leaching, runoff, and forest, i.e., 19–25%).

[33] Losses by runoff comprise a major proportion (>90%) of all diffuse sources in comparison with the losses from leaching (0.5–3%) and from forests (0.6–3.5%). Dissolved nutrient concentrations gathered at the outlet of 100 small basins with no domestic contamination and drainage in the Seine basin [*Thibert*, 1994] made it possible to calculate a specific DP flux of 0.09 kgP ha^{-1} y^{-1} from the agricultural area [*Billen et al.*, 1994]. By considering the agricultural surface area in the Seine basin (3,793,100 ha), the runoff flux can be estimated at 341 tons of DP y^{-1}, i.e., PP reaching 78–85%. These proportions, although commonly mentioned in the literature (PP = 60–90% [*Dorioz and Trevisan*, 2001]), can show great disparities (see compilation of surface runoff data from European countries available in the framework of the Cost Action 832 (EC) program [*Strauss*, 2002]. Specific total P flux from runoff can thus be estimated at 0.41–0.59 kgP ha^{-1} for the Seine basin.

[34] P retention along the Seine River drainage network is relatively high compared to all P inputs. Overall, approximately 8–15% of all P inputs to the Seine basin are retained, 80% in the upper flood plains.

[35] It is worth mentioning that the DP:PP ratio at the outlet of the Seine drainage network 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 (6800 tP y^{-1}) is higher than the exported quantity (4600 tP y^{-1}). On the contrary, more PP is exported by the system than the quantity entering. This indicates that P exchanges occur between water and suspended sediments, which is in good agreement with the increase in TPP and PIP content of suspended sediment observed along the hydrographic network. To balance the budget, one can estimate that 2700 tP y^{-1} are transferred from the dissolved to the particulate phase through adsorption onto suspended sediment and/or through phytoplankton consumption (see discussion section).

3.5. Is P Content of Suspended Sediment an Indicator of PP Losses From Runoff?

[36] To evaluate the relevance of our runoff calculation, which is subject to many uncertainties, the relationship between discharge and TPP content in suspended sediment is presented at three nested sites (Figure 6). The TPP content in suspended sediment shows a similar trend at the three sites, i.e., an increase in TPP content with a decrease in discharge. The underlying hypothesis is that the minimum

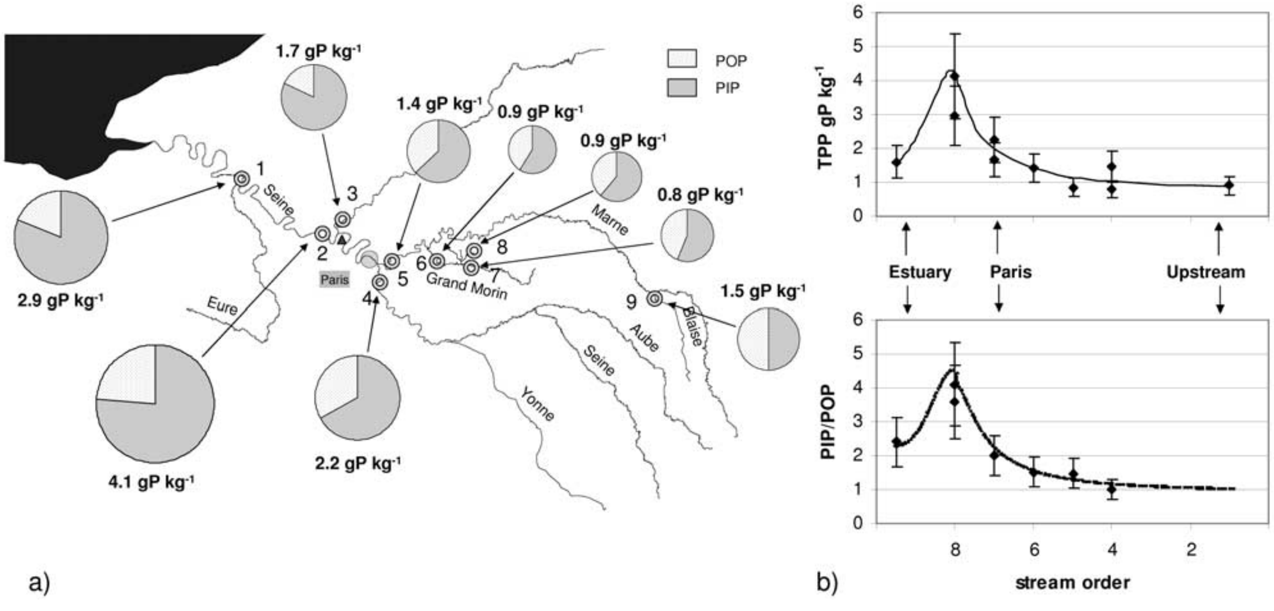


Figure 4. (a) Annual mean TPP content and PIP, POP proportions of suspended sediment collected along the Seine river continuum and (b) TPP content and PIP/POP ratio of suspended sediment sampled at different stream orders.

Table 7. Average TPP, PIP, and POP of Suspended Sediments Collected at Different Sites of the Seine Basin (in Parentheses: Standard Deviation)

		TPP		PIP		POP		
Site No.	Sites	*n*	gP kg^{-1}	*n*	gP kg^{-1}	*n*	gP kg^{-1}	% of TPP (Min-Max)
	Paris–Poses axis							
1	*Poses (Seine)*	15	2.92 (0.49)	15	2.33 (0.33)	15	0.59 (0.34)	19 (4–29)
2	*Andrésy + Denouval (Seine)*	22	4.13 (1.02)	16	3.06 (0.84)	16	1.00 (0.41)	24 (12–32)
	Oise							
3	*Eragny (Oise)*	3	1.67 (0.21)	3	1.35 (0.02)	3	0.32 (0.23)	18 (7–29)
	Upper Seine							
4	*Vitry (Seine)*	9	2.24 (0.36)	9	1.49 (0.22)	9	0.75 (0.16)	33 (28–39)
	Marne							
5	*St Maurice (Marne)*	25	1.40 (0.44)	13	0.77 (0.21)	13	0.53 (0.18)	37 (31–51)
	Grand Morin							
6	*Saint-Germain (Gd Morin)*	16	0.85 (0.32)	12	0.50 (0.17)	12	0.38 (0.19)	41 (31–52)
7	*Martroy (Gd Morin)*	15	0.78 (0.26)	1	0.43	1	0.33	44
8	*Mélarchez (Mélarchez)*	19	0.88 (0.43)	3	0.70 (0.37)	3	0.45 (0.26)	39 (31–45)
	Blaise							
9	*Pont Varin (Blaise)*	13	1.47 (0.66)	13	0.71 (0.28)	13	0.77 (0.41)	50 (37–51)

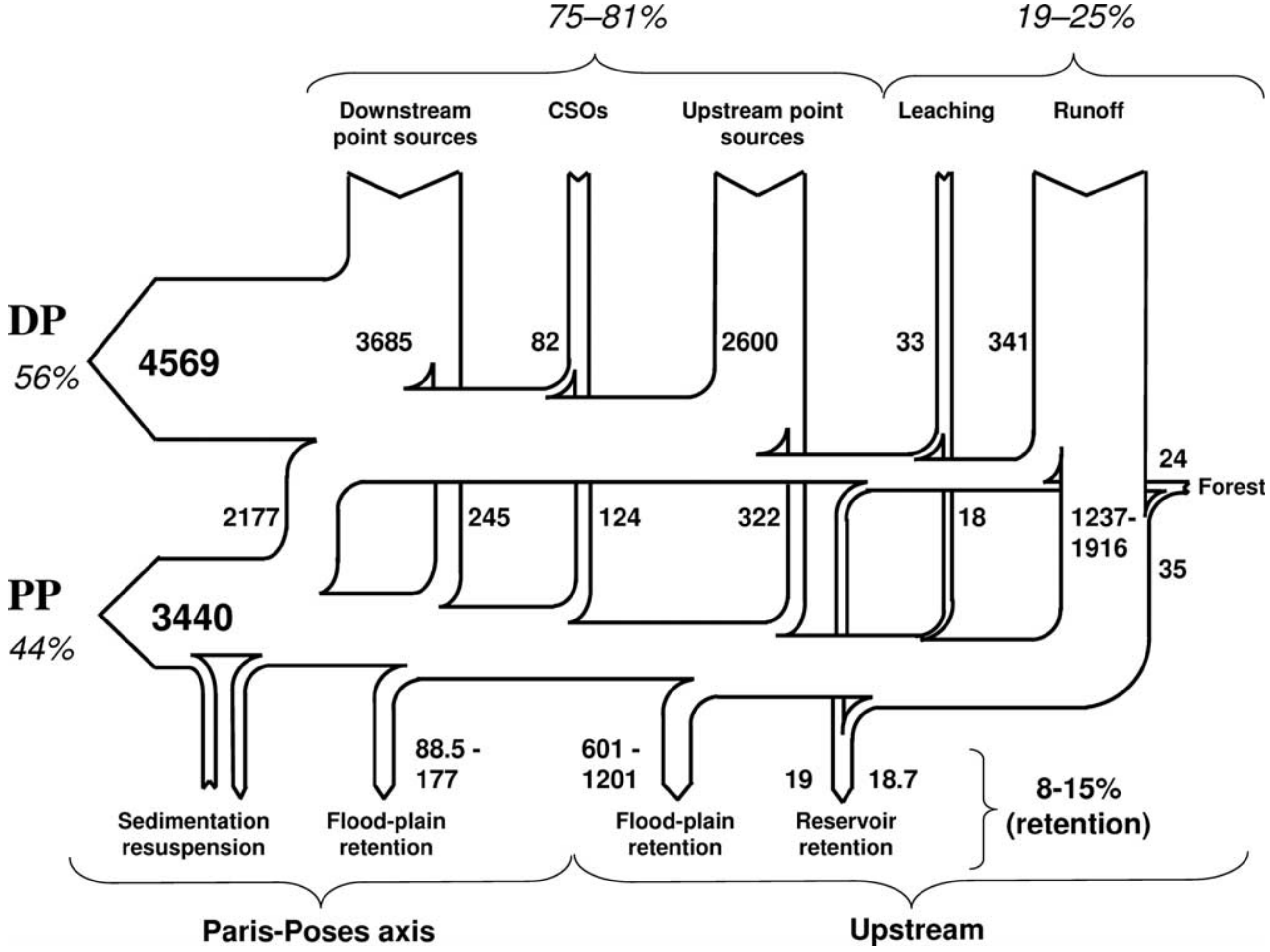
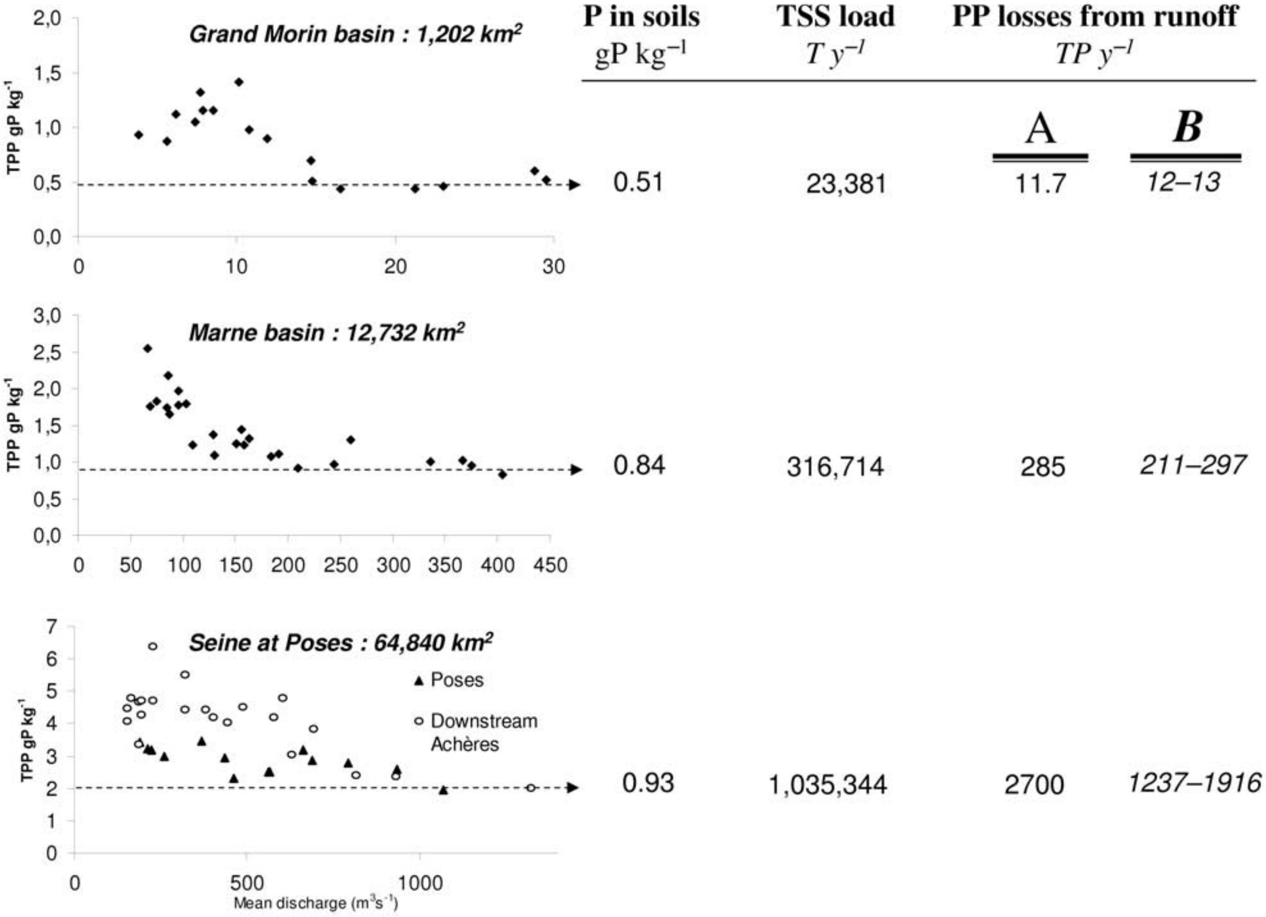


Figure 5. P Budget in the Seine basin (corresponding values rounded in the text).



P in soils gP kg⁻¹	TSS load *T y⁻¹*	PP losses from runoff *TP y⁻¹* A	PP losses from runoff *TP y⁻¹* ***B***
0.51	23,381	11.7	*12–13*
0.84	316,714	285	*211–297*
0.93	1,035,344	2700	*1237–1916*

Figure 6. Relationship between P content of suspended sediment and mean discharge of sampling period at the outlet of the Grand-Morin, Marne, and Seine at Poses basins. Minimum TPPs in suspended sediment are compared with mean TPPs in cultivated soils (calculated proportionally to the surface of corresponding hydro-ecoregions; see Table 6). TSS load is calculated according to equation (1). A: PP from runoff calculated by multiplying TSS load at the outlet by minimum TPP content observed during the high-flow period. B: PP from runoff from Figure 5 and as reported by *Némery et al.* [2005].

value of P content observed during the high-flow period corresponds mainly to P content in particles mobilized by runoff from agricultural soils, i.e., other sources such as bank erosion are not significant. Thus runoff contribution can be calculated by multiplying annual suspended sediment flux at the outlet by minimum TPP content observed during the high-flow period (Figure 6).

[37] The results agree with the PP losses from runoff estimates at the Seine basin scale (1237–1916 tP y^{-1}; see Figure 5), as well as with the Grand Morin and Marne subbasin runoff values (12–13 tP y^{-1} and 211–297 tP y^{-1}, respectively, as reported in *Némery et al.* [2005]).

[38] A comparison of the P content in the soils sampled across the Seine basin (Table 7) with the minimum TPP content measured during a high-flow period at the outlets of the basins (Figure 6) shows that the values found for the Grand Morin and the Marne are in good agreement. The factor of two found at Poses between P content in soils and the minimum TPP content measured during a high-flow period (Figure 6) may stem from the small number of soils sampled in this area, but it also highlights the strong urban pressure of point sources, even during wet periods. Note that the soil P content was initially measured on the less than 2-mm size fraction, in accordance with agronomic analyses. To validate the comparison presented above, the P content was analyzed on the same size fraction as suspended sediments, i.e. less than 200 μm, and no significant difference was observed [*Némery*, 2003].

[39] Phosphorus runoff losses calculated using the annual TSS load and its lowest P content during high-flow periods could therefore offer an alternative way of quantifying PP runoff losses from agricultural soils.

4. Discussion

4.1. Agricultural P Budget and P Diffuse Losses to the River

[40] An inventory of agricultural P inputs for the Seine basin has shown that fertilizers dominate in the agricultural budget (59%) as compared to other sources (atmospheric deposition, biosolids, crop residue, and livestock restitution). The specific fertilizer flux (21.3 kgP ha^{-1}) in the Seine basin is significantly higher than the French national average for 2000 (15 kgP ha^{-1} (Food and Agriculture

Organization (FAO) of United Nations, http://www.fao.org, 2000)) as a result of intensive cultivation of cereals and industrial crops in the basin.

[41] Atmospheric P deposition (1%) is very low compared to other inputs, but must not be neglected, considering the scarcity of gaseous forms in the P biogeochemical cycle. Such inputs are very variable in space and time [*Némery et al.*, 2005; *Neal et al.*, 2004].

[42] Phosphorus inputs by biosolids (2%) are within a range similar to that of atmospheric deposition. This value includes only biosolids from Achères STWs, which are spread over 12% of the agricultural land of the Seine basin (530,000 ha [*Roy de Lachaise et al.*, 2003]), i.e., 59% of the total area where spreading occurs (900,000 ha [*IFEN*, 2002]). For recent years, the quantity of P spread in France can be estimated at 10,000 tP y^{-1}; the annual production of dry matter is 850,000 tons. Among the biosolids produced, with a mean P content of 2.5% of dry matter [*Sommelier et al.*, 1996], 50–60% would be suitable for spreading [*IFEN*, 2002]. According to this rough estimate, the Achères STWs contribute to 20–30% of this biosolid recycling on the national scale. The use of spread biosolids could therefore be increased, since recent studies have shown that they are as efficient as chemical fertilizers regarding crop yields [*Guivarch*, 2001].

[43] The analysis of the agricultural P budget (surplus) shows a positive value for the year 2000 within a wide range of 1–10 kgP ha^{-1}. The P surplus between the 1960s and the 1980s was undoubtedly higher when fertilizer inputs were double the current value (30 kgP ha^{-1} in the middle of the 1970s (Food and Agriculture Organization (FAO) of United Nations, http://www.fao.org, 2000)). The rationalization of the use and application of fertilizers for both economic and environmental reasons has resulted in a progressive decrease in P inputs [*Morel et al.*, 1992; *Pellerin et al.*, 2000]. However, the widespread practice of over-fertilization in the past has led to the increased P contents in cultivated soils observed throughout Western Europe [*Sibbesen and Runge-Metzger*, 1995] as well as in the United States [*Sharpley and Rekolaimen*, 1997]. The very high P values in the soils of the Seine basin (1800 kgP ha^{-1} for calcareous limestone soils to 5000 kgP ha^{-1} for chalky soils) are illustrative of this practice. Phosphorus stocks are three to eight times higher than those found in forests, considered as natural background. An annual mean surplus of 25–90 kgP ha^{-1} on cultivated soils over 50 years (versus 1–10 kgP ha^{-1} in 2000) would explain these high P values, since the main P export flux is from crops (33 kgP ha^{-1} y^{-1}) and accounts, on average, for only 1% of the P stocks in soils. Although the present annual surplus in the Seine basin represents less than 0.1% of the stock already present in the soil, which is insignificant from an agronomic point of view [*Morel*, 2002], a few kilograms could nevertheless constitute a threat to water quality. The critical threshold of DP (i.e., the half-saturation constant) above which algal development is not P-limited in the Seine basin is as low as 15–45 μgP L^{-1} [*Garnier et al.*, 1995; *Garnier et al.*, 1998], so that any P losses to the rivers, such as P runoff or leaching, are of major environmental interest, threatening aquatic ecosystems for an extended period.

[44] Values of specific P losses from runoff in the Seine basin (0.41–0.59 kgP ha^{-1}) are within the range of those in the Marne subbasin [*Némery et al.*, 2005] and in other specific small rural basins less than 100 km^2 in size [*Dorioz and Ferhi*, 1994; *Jordan-Meille et al.*, 1998; *Svendsen et al.*, 1995]. This supports our method of quantifying runoff on a large basin scale. As reported by *Strauss* [2002] for many European cases, the PP fraction of surface runoff losses in the Seine basin appears to be the largest one (>90%).

[45] Phosphorus losses from drainage are estimated to be 0.12 kgP ha^{-1}. Like the results for 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 [*Heathwaite and Dils*, 2000]. In total, runoff and leaching by drainage account for a very low percentage (0.01%) of the total P stock in soils, despite the increase for several decades. This shows the high capacity of soils to retain agricultural P, and thus to act as a buffer in such environments strongly controlled by human activities.

4.2. Phosphorus Content of Suspended Sediment and Increasing Urban Pressure

[46] The PP runoff calculation method illustrated in Figure 6 shows its limitation on the scale of the entire Seine basin since the minimum P content in suspended sediment at the Seine outlet is twice as high as the average P content in agricultural soils. Undoubtedly, on the scale of a basin such as the Seine basin, additional soil samples are needed. However, the P content in suspended sediment appears to be strongly influenced by hydrology for any size of basin considered. The P content decreases with increasing water flow down to a minimum value (Figure 6). This minimum is very close to the P content in the agricultural soils of the basin concerned, which shows that P content in the soils, runoff, and PP transfer in the drainage network are closely related. On this basis, PP losses from runoff were estimated as the product of the minimum P content in suspended sediment at high flow and the annual TSS load, which gave satisfactory results for the three basins tested. However, we did not take into account bank erosion which might contribute significantly to the PP load in rivers [*Dorioz et al.*, 1998; *Laubel et al.*, 1999]. This source still remains unknown in the Seine basin but could be investigated in the future with a combined use of P content and ^{137}Cs, a common technique used to measure erosion/sedimentation rates over several decades [*Steegen et al.*, 2000; *Walling et al.*, 2000].

[47] The fact that the P content of suspended sediments increases from rural zones to highly urbanized zones indicates the magnitude of the influence of human pressure through point sources, mainly of dissolved mineral forms [*Russell et al.*, 1998; *Smith*, 1977], possibly rapidly adsorbed onto suspended sediments. Note that this increase in P content is attributable more to a PIP content increase than to a POP content increase. Similarly, studies of the P content of fluvial sediment in rural and industrialized river basins in England have demonstrated a clear increase in P content in suspended sediment with urban and industrial growth. This supports the notion that the PIP/POP ratio is a good complementary indicator to characterize the intensity of point source pressure [*Owens and Walling*, 2002]. Furthermore, the fingerprint procedure, which has been successfully used in many studies in the UK [*Walling*,

2005], implies a selection of a chemical or physical property that clearly differentiates potential source material in order to locate its spatial origin within a catchment. In the Seine River basin, significant changes in the PIP/POP ratio would allow the use of the PIP/POP ratio as a fingerprint (i.e., suspended sediment source tracing) by comparing the PIP/POP ratios of suspended sediment and soil.

4.3. Point Sources Versus Diffuse Sources: An Upgrade Contribution From Upstream to Downstream

[48] To establish a P budget for the Seine hydrographic network down to its estuary, all possible point and diffuse sources in the drainage network were exhaustively quantified. A diffuse source contribution ranging from 19 to 25% of total P inputs (mostly in particulate form: 78–85%) is often found in the literature [*Svendsen et al.*, 1995]. A major contribution by runoff losses to the diffuse P load in rivers (>90%), where forests account for a very low percentage (<4%), again highlights the substantial human influence on the Seine basin. These findings have led the scientist to quantify P export from agricultural land to gain a better understanding of P behavior in hydrosystems, focusing not only on diffuse P sources [*Kronvang et al.*, 1997; *McDowell et al.*, 2001; *Withers et al.*, 1999], but also on the contribution by diffuse sources versus point sources to the P load in rivers [*Drolc and Zagorc Koncan*, 2002; *Pieterse et al.*, 2003].

[49] Point sources, mainly composed of DP greater than 80% [*Cooper et al.*, 2002; *Jarvie et al.*, 2002], make up the major input in the Seine basin, i.e., 75–81% of the total P inputs, principally from the most urbanized zone and its largest STWs (Achères with currently a P abatement of 60%). CSOs are negligible (<3%) compared to other point sources, but discharge mainly downstream from Paris and its suburbs [*BPR-Sogreah-Hydratec*, 1997]. Although P point sources dominate the P inputs in the downstream part of the basin, the contribution of diffuse sources is greater in the upper zone where urban pressure is weaker. In the Marne and Grand Morin subbasins, P diffuse sources can reach 40–50% of the total P inputs [*Némery et al.*, 2005], which is often reported for agricultural basins [*Cooper et al.*, 2002; *Vervier et al.*, 1999; *Pieterse et al.*, 2003]. This means that the application of the EU directive for eutrophication reduction must take these results into account to upgrade wastewater treatments and reduce the cost of management [*Garnier et al.*, 2005].

[50] Industrial effluents and all sewage-connected domestic effluents account for waste from 90% of the population in the Seine basin, with a lower proportion in rural zones [*Némery et al.*, 2005]. The assumption made here, considering that unconnected domestic effluents were negligible on the basin scale, is supported by the efficiency (70–90%) of individual septic tanks [*Jacks et al.*, 2000; *Steer et al.*, 2002], together with a high but variable soil retention potential for infiltrated water [*Jones and Lee*, 1976].

[51] The estimates of P retention in the hydrographic network, principally in the upper flood plain of the Seine River but also in the three reservoirs, i.e., 8–15% of the total inputs, can be locally higher (15–30% in the Marne basin [*Némery et al.*, 2005]). Recent studies of the flood plain role in P retention have indicated a similar range, 10–50% [*Behrendt and Opitz*, 2000; *Meybeck*, 2001; *Thoms et al.*, 2000; *Walling et al.*, 2001], which means that retention must not be ignored in large river P budget calculations [*Billen et al.*, 2007b].

[52] Flux calculations at the Seine outlet show a high proportion of PP (44%), in accordance with that found in the literature [*Walling et al.*, 2001]. In addition to diffuse sources generally assumed to be essentially in particulate forms, adsorption of DP from point sources onto suspended sediment also significantly enriches the P content, especially in the downstream sectors. As a result of this exchange between dissolved and particulate forms, more DP (all sources combined) enters the system than is exported at the outlet. The increase in the P content and the PIP/POP ratio in suspended sediment from upstream to downstream made it possible to add such an adsorption flux between DP and PP to balance the P budget of the Seine.

[53] Annual P delivery found here for the fluvial part of the Seine (8000 tP, 44% as PP) has declined since the late 1980s, undoubtedly because of the reduction in P point sources and the improvement in wastewater treatments in the entire Seine basin [*Aminot et al.*, 1998; *Billen et al.*, 2001]. However, the Seine estuary receives highly P-rich suspended sediment and its fate in the turbidity maximum of the estuary, which has been specifically studied [*Némery and Garnier*, 2007], is of major importance for understanding coastal eutrophication [*Billen et al.*, 2001; *Cloern*, 2001; *Cugier et al.*, 2005]. The total specific P flux of the Seine river (125 kgP km^{-2} y^{-1}) is much lower than that in a subtropical river in North Vietnam (Red River, 325 kgP km^{-2} y^{-1}) where both erosion and P rock content are high [*Le et al.*, 2005].

5. Conclusions and Implications

[54] Most large rivers of developed countries are eutrophicated by nutrient inputs from both point and diffuse sources with increasing anthropic influence along their course and agriculture intensification. Phosphorus concentration plays an important role in the control of the algal growth in the freshwater ecosystem. The framework of this study is in line with the global scheme of nutrient reduction, an important issue within the European Water Framework Directive. The P budget approach is appropriate and essential for exhaustive identification of the sources on the large river scale. Results showed that even if work has been accomplished to reduce P point sources, these sources remain considerable and likely to sustain eutrophication [*Jarvie et al.*, 2006b]. Nevertheless, in rural zones there is a worrying concern over the diffuse sources, especially the high P stocks found in agricultural soils, which are more difficult to prevent. Agricultural P management therefore appears to be a key issue in the struggle against eutrophication.

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