Bilan et modélisation du phosphore mobile dans le bassin de la Marne. Exploration, par le modèle, de scénarios de réduction du phosphore ponctuel et diffus.

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Introduction

Le phosphore est un élément rare dans la lithosphère mais essentiel pour le vivant. Introduit massivement dans l'environnement depuis la fin de la seconde guerre mondiale sous forme d'engrais phosphatés et d'agents détersifs dans les lessives, il est, depuis les années 70 (Vollenweider, 1968), désigné comme le principal responsable de l'eutrophisation des lacs mais aussi des rivières. Ce dysfonctionnement concerne également les zones côtières dont la seule source appréciable de phosphore provient du lessivage des bassins versants et de son transport par les rivières (Billen and Garnier, 1997; Cugier et al., 2003 soumis; Filippelli, 2002; Garnier et al., 2001).

Présent sous de multiples formes, la géochimie du phosphore est complexe avec l'alternance sans cesse renouvelée de phase minérale et organique, dissoute ou particulaire. Les apports par les bassins versants, sous forme ponctuelle ou diffuse, sont nombreux et quantitativement importants. Depuis une trentaine d'années, les efforts se sont concentrés sur la réduction des apports ponctuels qui aujourd'hui sont en nette régression. L'exemple de l'eutrophisation du Lac Léman est à ce titre remarquable (CIPEL, 2001). Une nouvelle problématique, liée aux mécanismes de transfert du phosphore d'origine diffuse qui augmente en proportion avec l'amélioration des traitements en station d'épuration, mobilise alors les scientifiques. Par exemple, cette thématique a regroupé de nombreux chercheurs de toutes l'Europe pendant 6 années autour du programme de l'UE Cost 832, intitulé « Quantifying the Agricultural Contribution to Eutrophication), qui a fait l'objet d'une synthèse importante de données de toute l'Europe (Chardon and Schoumans, 2002; Kronvang, 2002). En France, le CORPEN (Comité d'Orientation pour des Pratiques agricoles respectueuses de l'Environnement), mis en place depuis 1984, s'intéresse également de près à cette problématique. Alors que les apports ponctuels en P sont essentiellement sous forme dissoute, les pertes diffuses de phosphore apparaissent majoritairement sous forme particulaire et l'étude du devenir de ce phosphore dans les milieux aquatiques est primordiale.

En effet, le phosphore a une forte affinité pour les sédiments, la sorption et la désorption sont donc deux des principaux mécanismes qui régulent les concentrations en P dans les milieux aquatiques. Les sédiments en suspension dans la colonne d'eau peuvent constituer un réservoir de P rapidement disponible pour les végétaux aquatiques. Le devenir des sédiments dans les bassins versants est un aspect de plus en plus important dans les recherches environnementales pour son rôle dans le transport du phosphore (Dorioz et al., 1998; Kronvang et al., 1997; Verstaeten and Poesen, 2000; Walling et al., 1997) mais aussi d'autres contaminants comme les métaux (Idlafkih et al., 1997; Thévenot et al., 2002).

Le récent rapport du programme mondial de l'eau des Nations Unies (Unesco, 2003), cite le bassin de la Seine, aux côtés de six autres cas à travers le monde, pour illustrer les défis qui doivent être relevés pour éviter un conflit lié à l'usage de l'eau, ressource de plus en plus sollicitée avec l'anthropisation croissante (besoin en eau potable, irrigation etc.). Le bassin de la Seine fait en effet figure d'exemple de bassin versant européen devant concilier un approvisionnement en eau potable d'une très grande agglomération (Paris, 10 10^6 habitants) en s'accommodant d'une très forte activité industrielle et agricole. Cette forte pression anthropique place les gestionnaires du bassin face à de nombreux problèmes de qualité d'eau telles la contamination par différents polluants (pesticides et les métaux) ou encore l'eutrophisation, caractérisée par le développement intense d'algues perturbant les traitements pour la fabrication de l'eau potable et par la charge organique qu'elles constituent, entraînant des désoxygénations importantes (De Diamous et al., 1995).

Le phosphore est le facteur limitant de la croissance algale dans le bassin de la Seine (Garnier et al., 1995). Le modèle écologique développé sur la Seine (RIVERSTRAHLER, (Billen et al., 1994; Garnier et al., 1995), en accord avec le River Continum Concept (Vannote et al., 1980) prend en compte de manière détaillée la physiologie des algues, mais la représentation de la dynamique du phosphore reste encore très simplifiée des têtes de bassins aux grandes rivières. Les échanges entre les phases dissoute et particulaire dans les matières en suspension et dans les sédiments ne sont pas pris en compte, bien qu'ils puissent représenter un stockage important en phosphore. Dans un contexte de réduction des apports ponctuels du phosphore (d'un facteur 2 depuis 1991, Garnier et al., 2002b), il est désormais important de quantifier le rôle eutrophisant de ce phosphore stocké, potentiellement mobilisable.

En outre, les simulations de réduction du phosphore (Garnier et al., 1998) n'ont jusqu'à présent porté que sur la diminution dans les apports ponctuels qui n'ont, au total, qu'un effet assez limité dans le réseau hydrographique, même une réduction drastique, peu réaliste. Ces résultats nous ont conduits à réfléchir sur la part réelle du phosphore diffus et la nécessité d'agir aussi sur ces sources.

L'enjeu de gestion actuel est important. On constate en effet une diminution des phosphates d'origine ponctuelle (traitement en stations d'épuration, réduction dans les produits lessiviels), mais des phosphates vont être par ailleurs introduits dans les eaux de distribution pour éviter le relargage de l'effet du plomb des canalisations des habitations anciennes. Dans un cadre général d'une augmentation constante des zones de grandes cultures, les apports diffus augmentent en proportion des apports ponctuels, et pourraient même devenir quantitativement dominants, et plus difficiles à maîtriser.

Les objectifs de ce travail sont :

1) Estimer de la manière la plus exhaustive possible la contribution respective des apports diffus par rapport aux apports ponctuels et étudier les transferts de phosphore ente les phases dissoute et particulaire.

Dans cette perspective, nous avons quantifié les différentes sources (diffuses et ponctuelles) et formes du phosphore (particulaire, dissous, incluant la mobilité) à l'échelle du bassin de la Marne (12 732 km^2) situé en amont de l'agglomération parisienne. L'étude a également été menée sur le sous-bassin de la Blaise (607 km^2), dominé par des activités d'élevages et sur le sous-bassin du Grand Morin (1202 km^2), caractéristique d'une intense activité agricole tournée vers les cultures céréalières.

Cette étude a fait l'objet d'un article soumis à *Biogeochemistry*, accepté le 14 janvier 2004 et présenté en chapitre 2 de ce rapport. Le bilan du phosphore agricole montre pour les années récentes (2000) que les engrais minéraux phosphatés représentent 60 % des apports aux sols (soit 20-25 kgP ha^{-1}) et que ces pratiques de fertilisations génèrent un surplus de l'ordre 1-10 kgP ha^{-1}. Au regard de ces chiffres, les stocks de P dans les 25 premiers centimètres des sols cultivés du bassin de la Seine apparaissent énormes (1800-5000 kgP ha^{-1}). De même les pertes par érosion (0.2-0.6 kgP haSAU^{-1} an^{-1}) et par lessivage (0.12 kgP haSAUdrainée^{-1} an^{-1}) vers les rivières représentent un faible pourcentage de ce stock (<0.01%) et suggèrent que des pertes puissent se produire sur le très long terme, sans apports supplémentaires.

Ces pertes diffuses (majoritairement sous forme particulaire) représentent 40 à 50 % des apports totaux de phosphore dans les bassins versants étudiés. La fraction particulaire du phosphore contribue pour 60 % du flux total de P à l'exutoire de la Blaise, i.e. 20 tP an^{-1}, 30 % à l'exutoire du Grand Morin, i.e. 46 tP an^{-1}, et 48 % à l'exutoire de la Marne, i.e 679 tP an^{-1}. La mobilité du PP a été étudiée par la méthode des cinétiques d'échanges isotopiques au ^{32}P (Fardeau et al., 1991; Morel et al., 1995). Les résultats montrent une proportion importante de P échangeable en 1 mois, de l'ordre de 40 % du PP total (1.3 g P kg^{-1}), ce qui peut représenter une source non négligeable de P dissous directement disponible pour la croissance algale.

2) Proposer une nouvelle représentation mathématique de la dynamique du phosphore pour être intégrée au modèle RIVERSTRAHLER et tester des scénarios de réduction des apports ponctuels et diffus de phosphore et leurs impacts sur le développement algal.

Ce travail est présenté dans un second article soumis à *Journal of Hydrology* le 30 novembre 2003 (chapitre 3). La mobilité du phosphore a été incluse dans le modèle RIVERSTRAHLER, à l'échelle du bassin de la Marne (12 732 km^2), le plus eutrophisé du bassin de la Seine. Les simulations par le modèle permettent de reproduire les teneurs en phosphore ainsi que les biomasses phytoplanctoniques dans les conditions hydrologiques contrastées de la dernière décennie. Le modèle a permis d'explorer le rôle relatif des apports ponctuels et diffus sur l'état d'eutrophisation de la Marne. Cette étude révèle au total que dans un contexte de diminution des apports ponctuels du phosphore en application de la Directive Cadre Européenne, la réduction du phosphore en stations d'épuration n'est probablement pas le seul levier d'une politique de maîtrise de l'eutrophisation. Les résultats de simulation par le modèle montrent que seuls une réduction combinée des apports ponctuels et diffus aurait un impact important sur le développement algal dans le bassin de la Marne en période d'étiage d'année sèche.

Références

Billen, G. and Garnier, J. (1997). The Phison River plume: coastal eutrophication in response to changes in land use and water management in the watershed. *Aquat. microb. ecol.*, **13**: 3-17.

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.

Chardon, W.J. and Schoumans, O.F. (2002). Phosphorus losses from agricultural soils: processes at the field scale. *COST Action 832. Alterra, Wageningen, The Netherlands (Chardon, W.J. & Schoumans, O.F., eds)137 pp*.

CIPEL (2001). Rapport sur les études et recherches entreprises dans le bassin lémaniques. *Commission Internationnale pour la Protection des Eaux du Léman, Lausanne*.

Cugier, P., Billen, G., Guillaud, J.-F., Garnier, J. and Ménesguen, A. (2003 soumis). Modelling the eutrophication of the Seine Bight (France) under historical, present and future nutrient loading, submitted to Journal of Hydrology. *submitted to Journal of Hydrology, nov 2003*.

De Diamous, F., Billen, G., Garnier, J., Hanset, P., Jovy, V., Grimaud, A. and Vandevelde (1995). De Dianous F., Billen G., Garnier J., Hanset Ph., Jovy V., Grimaud A. et Vandevelde (1995). Un Modèle opérationnel pour la prédiction des variations de qualité des eaux lors d'efflorescences algales. *CR. Congrès A.G.H.T.M., Nîmes, juin 1994: 55-59.*

Dorioz, J.M., Cassell, E.A., Orand, A. and Eisenman, K.G. (1998). Phosphorus storage, transport and export dynamics in the Foron River watershed. *Hydrological Processes*, **12**: 285-309.

Fardeau, J.C., Morel, C. and Boniface, R. (1991). Cinétique de transfert des ions phosphate du sol vers la solution du sol: paramètres caractéristiques. *Agronomie*, **11**: 787-797.

Filippelli, G.M. (2002). The Global Phosphorus Cycle. Chapitre 10. in: Reviews in mineralogy and geochemistry: Phosphates; geochemical, geobiological and materials importance (Kohn, M.J., Rakovan, J. & Hughes J. eds). *Mineralogical Society of America, Ribbe, P.H Series Editor, Geochemical Society, Rosso, J.J Series Editor,* **48**: 392-425.

Garnier, J., Billen, G. and Coste, M. (1995). Seasonnal succesion of diatoms and Chlorophyceae in the drainage network of the Seine river: Observations and modelling. *Limnol. Oceanogr.*, **40**(4): 750-765.

Garnier, J., Billen, G., Hanset, P., Testard, P. and Coste, M. (1998). Développement algal et eutrophisation. Chapitre 14. In: La Seine en son bassin Fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., de Marsily G & Fustec F. eds). *Elsevier, Paris*: p593-626.

Garnier, J., Billen, G., Némery, J., Akopian, M., Pinault, S., Desruelle, M., Dufayt, O., Flipo, N., Even, S. and Poulin, M. (2002). Développement des végétaux et dynamique des nutriments: contrôle par les organismes filtreurs. *Rapport synthèse Piren-Seine. 1998-2001, 43p.*: p43.

Garnier, J., Dufayt, O., Billen, G. and Roulier, M. (2001). Eutrophisation et gestion des apports de phosphore dans le bassin de la Seine. *Acte du Colloque, Lyon 2001. Scientifiques & Décideurs: agir ensemble pour une gestion durable des systèmes fluviaux. CD-rom. 8p.*

Idlafkih, Z., Meybeck, M., Chiffoleau, J.F., Cossa, D. 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, IAHS Publ.*, **243**: 45-58.

Kronvang, B. (2002). Diffuse phosphorus losses at catchment scale. *COST Action 832. Alterra, Wageningen, The Netherlands (Kronvang, B., ed), 48 pp.*

Kronvang, B., Laubel, A. and Grant, R. (1997). Suspended sediment and particulate phosphorus transport and delivery pathways in an arable catchment, Gelbaek stream, Denmark. *Hydrological Processes*, **11**: 627-642.

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

Thévenot, D., Meybeck, M. and Lestel, L. (2002). Métaux lourds : des bilans en mutation. *Rapport de synthèse Piren-Seine 3e phase : chap. Rejet et contamination urbaine*: 41p.

Unesco, 2003. Water for People, Water for life, World Water Assessment Programme. Unesco and Berghahn Books, 575p pp.

Vannote, R.L., Minshall, G.W., Cummins, K.W., Sedell, J.R. and Cushing, C.E. (1980). Vannote R.L., Minshall G.W., Cummins K.W., Sedell J.R. & Cushing C.E., (1980). The river continuum concept. Can. J. Aquat. Sci. 37:130-137. *Can. J. Aquat. Sci.*, **37**: 130-137.

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. IAHS Publ.*, **263**: 243-249.

Vollenweider, R.A. (1968). Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors of eutrophication. *O.C.D.E. Paris, Technical Report, DA 5/SCI/68.27, 250 p.*: 182p.

Walling, D.E., Webb, W. and Russel, M.A. (1997). Sediment-associated nutrient transport in UK rivers. *Fresh water contamination, IAHS Publ.*, **243**: 69-81.

1 Bilan du phosphore dans le bassin de la Marne : sources ponctuelles vs sources diffuses, formes dissoutes vs formes particulaires (*article accepté au journal Biogeochemistry le 14 janvier 2003*)

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

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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 to 8 kg P ha^{-1} y^{-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 y^{-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.

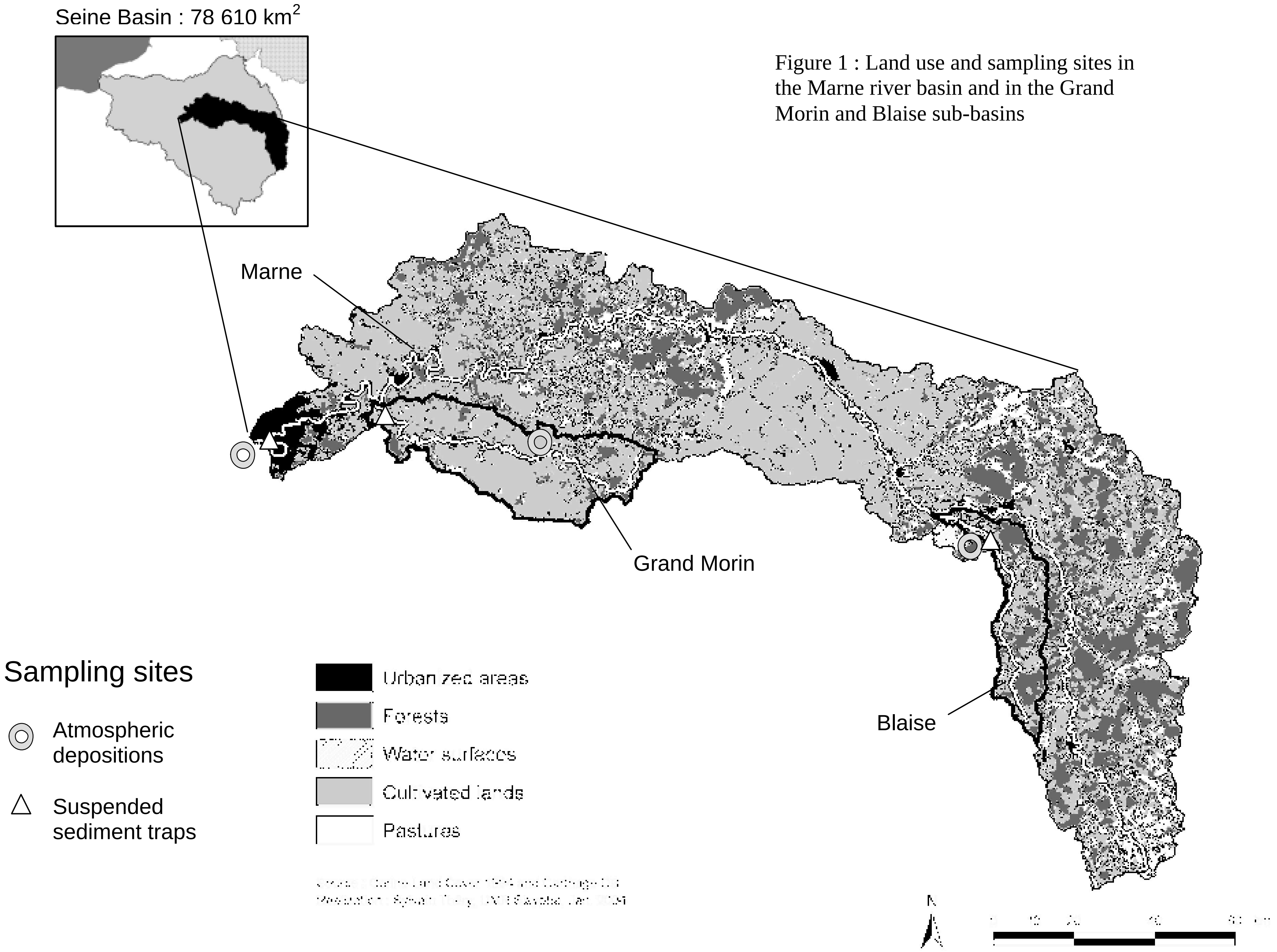
Introduction

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. 1998b). 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 & Ferhi 1994; Haygarth & 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 (Dorioz et al. 1998a; Kronvang et al. 1997; Verstaeten & Poesen 2000; Walling et al. 1997). 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.

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



Source : Corine Land Cover 1994 and Carthage 3.0
Réalisation : Sylvain Théry, UMR Sisyphe, Jan 2004

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 $m^3 s^{-1}$ and 6-8 $m^3 s^{-1}$. The Agricultural Surface (AS: cultivated land + pastures) given by the Recencement Général de l'Agriculture 2000 (RGA 2000) represents more than 50 % in the 3 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.

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	**Pastures**	**Cultivated lands**	**Forests**
	km^2 (% of the total area)			
Marne basin	12732	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 %)

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 centimetres 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 from of the Marne basin and the Grand-Morin sub-basin 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 µm to 2000 µm.
Total Particulate Phosphorus (TPP) was determined with a high temperature/HCl extraction technique (Aspila et al. 1976) where organic phosphorus is mineralised into inorganic forms at 550 °C, extracted into 1N HCl for 15-20 hours 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 gP 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 & Mannaerts 1987), recommended for low orthophosphate concentration determination (Ohno & 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 & 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 (Golterman 1982; Hieltjes & Lijklema 1980), sorption/desorption method (Aminot & Andrieux 1996; Froelich 1988). 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 d) and to analyze 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 & 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; Dorioz et al. 1998b; Vaas et al. 1987).

The sediments collected here were analyzed 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 µgP g^{-1}) were added as KH_2PO_4 to 1g of dry suspended sediment and 9.89 ml of deionised 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 hours to reach a steady state. This method does not account for the mineralization of POP by biological activities (bacterial). After 20h of equilibration, 100 µL of carrier-free ^{32}P containing approximately 20 kgBq (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 & Zibilske 1991).

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:

$$\mathbf{r/Qs = (R-r)/Pr} \qquad \mathbf{[1]}$$

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:

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

For a given suspension, the 15 experimental observations (3 periods of isotopic dilution and 5 Cp levels) were fitted by means of a kinetic Freundlich function (Barrow 1978; Chardon & Blauuw 1998; Morel 2002; Morel et al. 2002):

$$\mathbf{Pr = vCp^{w}\,t^{p},} \quad \text{with Pr lower than total isotopically exchangeable P} \qquad \mathbf{[3]}$$

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 Eq. [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 y^{-1} were calculated according to the load estimation procedure described by Verhoff et al. (1980), recommended by Walling & Webb (1985) and commonly used by Aminot et al. (1998) and Meybeck et al. (1998b).

$$AF = \frac{K\sum_{i=1}^{n}(C_i Q_i)}{\sum_{i=1}^{n} Q_i} Q_m \quad \textbf{[5]}$$

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^3s^{-1})
Q_m = Mean discharge for period of record (m^3s^{-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 (kgP d^{-1}) for 7 sub-basins (including the Grand-Morin and Blaise sub-basins) and the main branch of the Marne river (Table 2).

Table 2 :Annual Phosphorus point source fluxes at different scales in the Marne basin (Data for the year 2000)

	Population		**Dissolved P**	**Particulate Org. P**[2]
	Inhab.	**% connected to STW**[1]	**T y^{-1}**	**T y^{-1}**
Upstream rural area				
Grand-Morin sub-basin	88975	72	26	2
Blaise sub-basin	14267	64	7.5	2.7
Others	638640	60-90	146.5	27
Total	741882		172	32
Downstream urbanised area	1309873	> 90	220	41
Total Marne	2051755	90	392	73.2

[1] Sewage Treatment Plant, data AESN
[2] estimate from the ratio Particulate Organic Carbon/Particulate Organic Phosphorus = 40

We make the assumption, discussed below, that P fluxes generated by the unconnected population are negligible.

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 & Lefeuvre 2000). Recent studies of 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 & 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. The flooded width is in the same range throughout the basin because of its homogeneous hydrologic regime (Guerrini et al. 1998), (Table 3).

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

	Flooded surface		**Total length**	**Mean flooded width***	**Frequency (% of flooded area)**		
	km^2	% of basin	km	m	< 1 year	1-3 y.	3-10 y.
Oise	478	2.75	756	632	36	4.5	59.5
Marne[1]	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[1]	599	1.84	1047	572	68	21	0

* surface-length ratio:

[1] upstream of the confluence of the Marne and the Seine

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 localised in small areas.

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 [6])

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

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

$$APR = \sum_{5m-700m} (PRR * S) * FD \qquad [6]$$

PRR = phosphorus retention rate (kgP km^{-2} d^{-1}) = 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 = 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 (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. 2000; Garnier et al. 1999). Here we consider the average retention for the 3 studied years (Table 5).

Table 5 : In-out phosphorus balance in the Marne reservoir for 1993, 1994 and 1995 (from Garnier et al. 1999)

	Year	**Flux in**	**Retention**	
		TP y^{-1}	%	TP y-1
P-PO4	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 source 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 & Jarvis 1999; Kronvang et al. 2000).

The drained surfaces are 18 % (140 000 ha), 74 % (550 00 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 [5] from P-PO$_4$ and TP concentrations, discharges from values the drain (10 to 30 data for one hydrological year) and drained surface (15 ha). Specific DP (0.042 kgP ha^{-1} y^{-1}) and TP (0.118 kgP ha^{-1} y^{-1}) fluxes are averages of the 8 considered years (a dry year: 89/90, a wet year, 93/94 and 6 intermediate years) and are used to estimate P losses from leaching by drainage at the basin scale.

Table 6 : Values for 8 hydrologic years from an agricultural heavily drained area (15 ha, 100 % drained) in the Grand Morin sub-basin: mean annual discharges, meanP-PO$_4$ and total P concentrations; mean Dissolved Phosphorus (DP) and Total phosphorus (TP) specific fluxes

year	**Active drain**	**Mean discharge**	**Mean P-PO$_4$**	**Mean Ptot**	**DP fluxes**	**TP fluxes**
	days	**L s^{-1}**	**mg P L^{-1}**		**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 (Johnes 1996; May et al. 2001; Reckhow et al. 1980) 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 3 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 kgP ha^{-1} y^{-1} (DP < 50 %) found in the literature (Dorioz & Trevisan 2001; Johnes 1996).

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 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 (q) 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 (kgP head^{-1} y^{-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.

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	**Export ratio**	**Field restitution**	**Animal types**	**Restitution**
	kgP ha^{-1}	**kgP 100kg^{-1}**	**kgP 100kg^{-1}**		**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
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

Atmospheric depositions.

Atmospheric depositions of phosphorus are known to contain mainly dissolved forms (90%) (Dorioz & Trevisan 2001; Peters & Reese 1995). Bulk atmospheric P depositions were thus estimated by colorimetry analysing orthophosphate concentrations in unfiltered rainfall samples from 3 different sites (urban, rural/urban and rural) in the Marne watershed (with a two week-frequency throughout the year 2001), (Garban et al. 2002). Total P deposition expressed in kgP ha^{-1} y^{-1} is calculated by summing the product of the monthly mean orthophosphate concentration and the monthly cumulative rainfall (Table 8).

Table 8: Annual rainfall, orthophosphate concentrations in rain and P fluxes at 3 different sites in the Marne river basin for the year 2000.

	rainfall	**P-PO$_4$**	**P flux**
	mm y^{-1}	**mgP L^{-1}**	**kgP ha^{-1} y^{-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

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 1990-1994 (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 & 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).

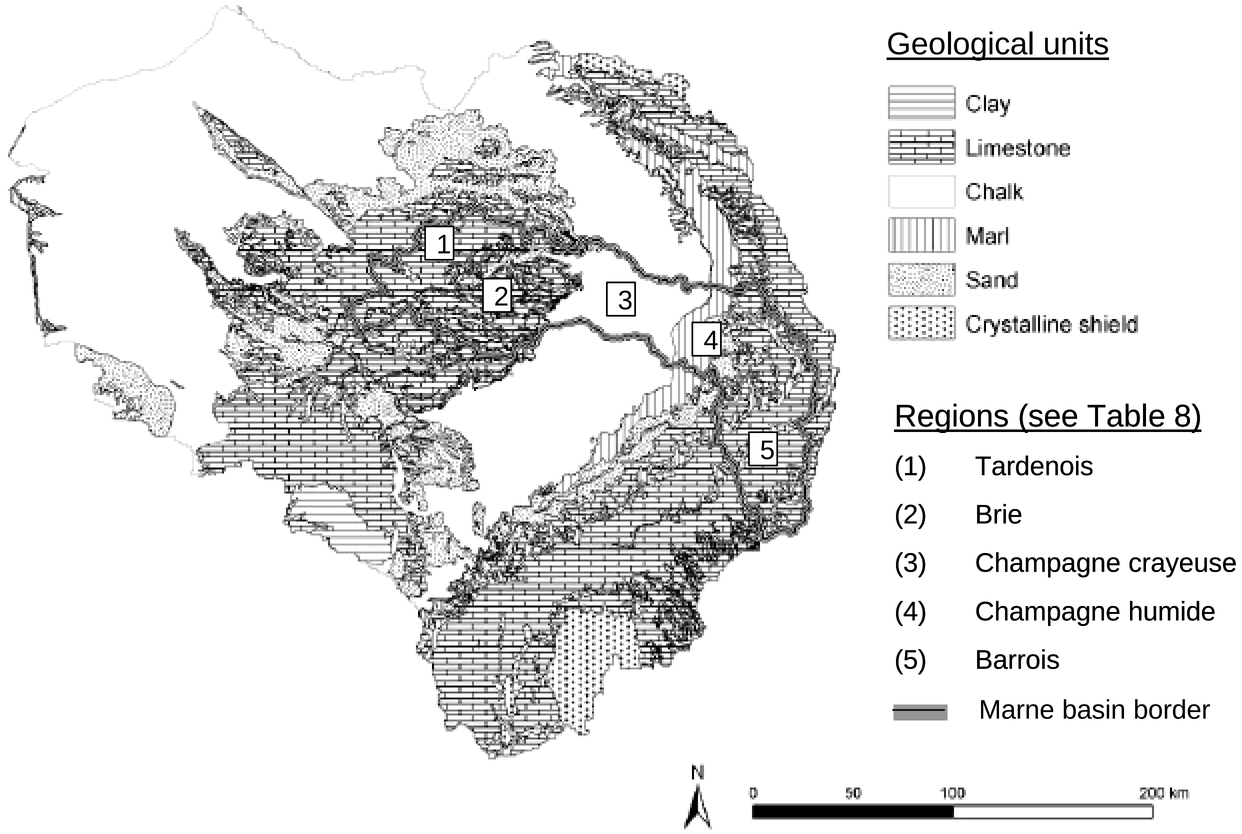


Figure 2 : Geological map of the Seine basin including the Marne. Main regions in the Marne basin are numbered from 1 to 5.

The varied land use and agricultural practices in the Seine basin make it impossible to attribute a mean P content to a soil.

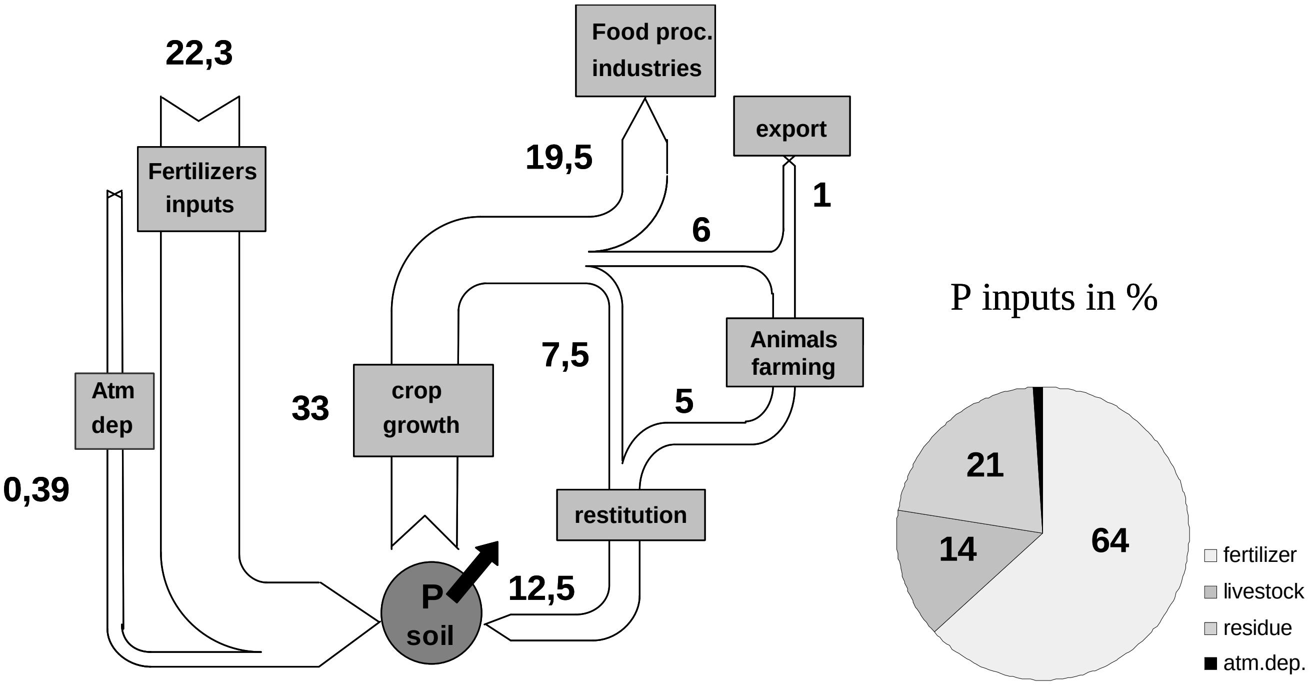
A survey of soil P content was therefore carried out across the Seine river basin. During the winter of 2002-2003, 70 samples were collected from the surface layer of pasture, forest and cultivated soils at depths of 0 to 0.25 m, which is the common tillage horizon. During this period cultivated soils 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 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 find a soil stock of 3500 tons ha^{-1}, and can calculate the P stock (kgP ha^{-1}) on the basis of the soil TP content (gP kg^{-1}).

Results

Agricultural phosphorus budget

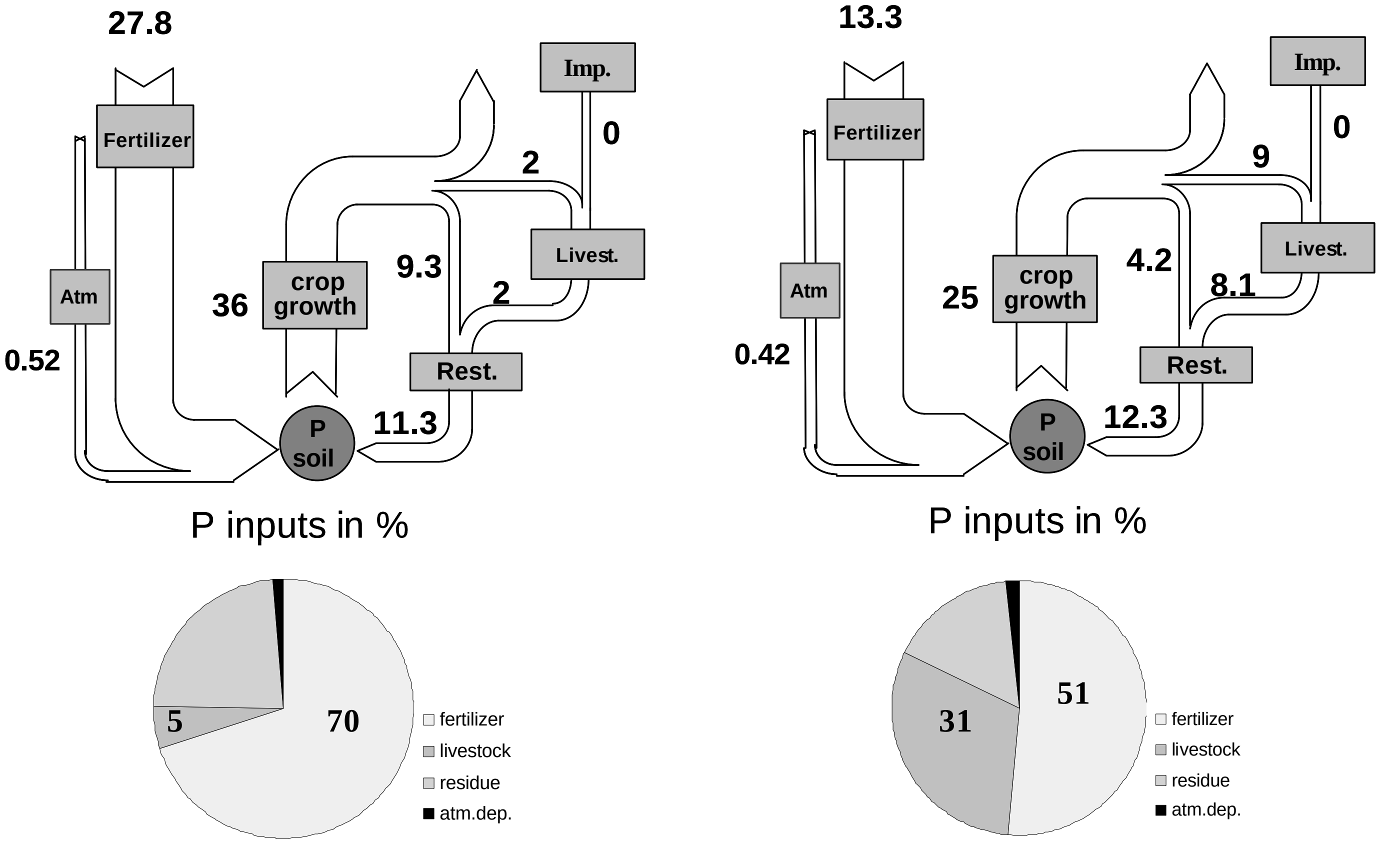
Fluxes for i) atmospheric depositions, ii) fertilizer inputs, iii) crop growth exports and iv) crop and livestock restitutions are expressed in kgP per ha of AS per year, the proportion of each P input is also shown (Figure 3).



a) b)

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

Results show that the greatest inputs are from fertilizers (22.3 kgP ha^{-1} y^{-1}) which represent 64% of the all inputs reaching the soil. Crop residues, livestock restitutions and atmospheric depositions contribute by respectively 21 % (7.5 kgP ha^{-1} y^{-1}), 14 % (5 kgP ha^{-1} y^{-1}) and 1 % (0.39 kgP ha^{-1} y^{-1}). The calculated difference between these 4 estimated inputs and crop exports (33 kgP ha^{-1} y^{-1}) is positive. The surplus is 2.6 kgP ha^{-1} y^{-1} and represents a significant build-up of P content in the soils.



a) b)

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

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 kgP ha^{-1} y^{-1}), dominated by intensive agriculture, than in the Blaise sub-basin (13.3 kgP ha^{-1} y^{-1}) dominated by livestock farming. On the other hand, inputs from animals are four times smaller in the Grand Morin sub-basin (2 kgP ha^{-1} y^{-1}) than in the Blaise sub-basin (8.1 kgP ha^{-1} y^{-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 kgP ha^{-1} y^{-1} against 1 kgP ha^{-1} y^{-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 kgP haAS^{-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 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.

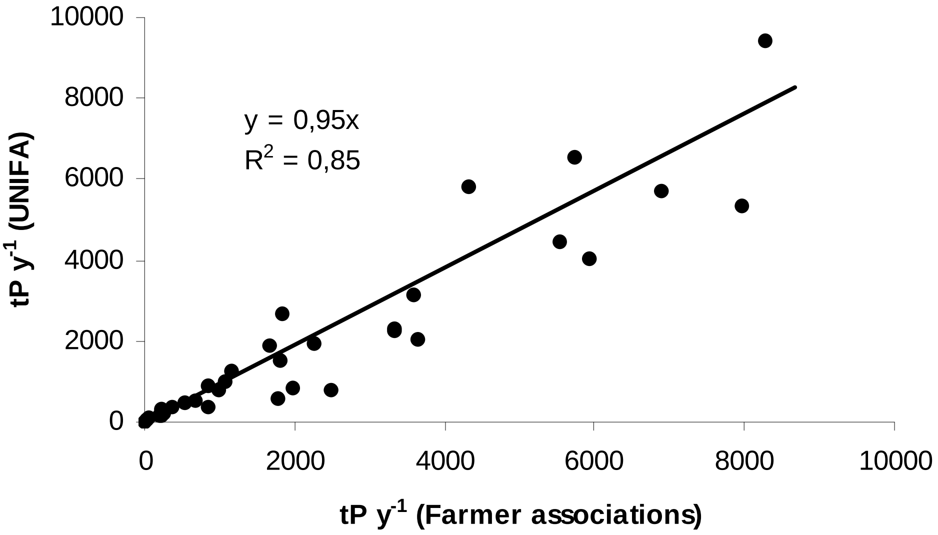


Figure 5 : Relationship between fertilizer input estimates (tP y^{-1}) from 2 different sources of information in all administrative districts of the Seine basin (UNIFA and Farmer association, see text). The linear equation (y=ax) and the variation coefficient (R^2) are indicated

Data from the FAO (the United Union Food Agriculture Organization (FAO 2000)) allow to calculate a mean national fertilizer input of 15 kgP ha^{-1} y^{-1} which is lower than the one found in the Marne basin (22.3 kgP ha^{-1} y^{-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.

Total P stock in soils

In cultivated soils (Table 9), P contents are in the range of 0.52 gP kg^{-1} in the Brie region (especially in the Grand-Morin sub-basin) and 1.42 gP 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 gP kg^{-1}). Forest soils which can be considered as a reference without human impact have 3 to 10 times lower P content than cultivated soils. Vineyard soils present a mean P content of 0.89 gP kg^{-1}.
On this basis, the P stock in cultivated soils was estimated at 1800 kgP ha^{-1} in the Grand-Morin sub-basin, 2600-3100 kgP ha^{-1} for the Blaise sub-basin and 1800-5000 kgP ha^{-1} in the whole Marne basin.

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 tP y^{-1} composed, in nearly equal proportions, of DP (52 %) and PP (48 %), (Figure 6). Point sources represent 60 % (465 tP y^{-1}, more than 80 % in dissolved form) of the total inputs. As more than 50 % of point sources (260 tP y^{-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 %).

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]	/

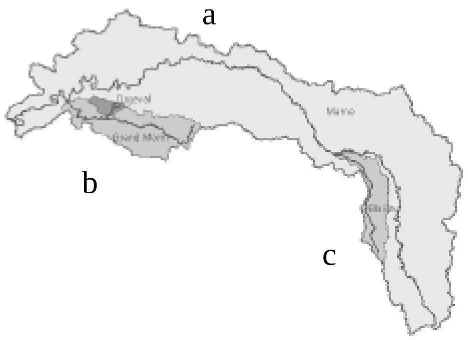
[a] mean +/- std dev. 0.24 (19 data)
[b] mean +/- 0.11 (10 data)
[c] mean +/- 0.31 (5 data)
[d] mean +/- 0.24 (7 data)
[e] 1 to 3 data
(1-5) see figure 3 for localisation

Losses by leaching amount to 17 tP y^{-1} with 35 % for DP and 65 % for PP (140 000 ha drained; specific DP flux : 0.042 kgP ha drained^{-1} y^{-1}; specific PP flux : 0.075 kgP ha drained $^{-1}$ y^{-1}) whereas losses from forests are estimated at between 7 and 17 tP ha^{-1} (350 000 ha; 0.02-0.05 kgP ha^{-1} y^{-1}, see method section); an intermediate value of 12 tP 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 tP y^{-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 to 90 %: (Dorioz & 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 kgP ha^{-1} y^{-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 y^{-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).

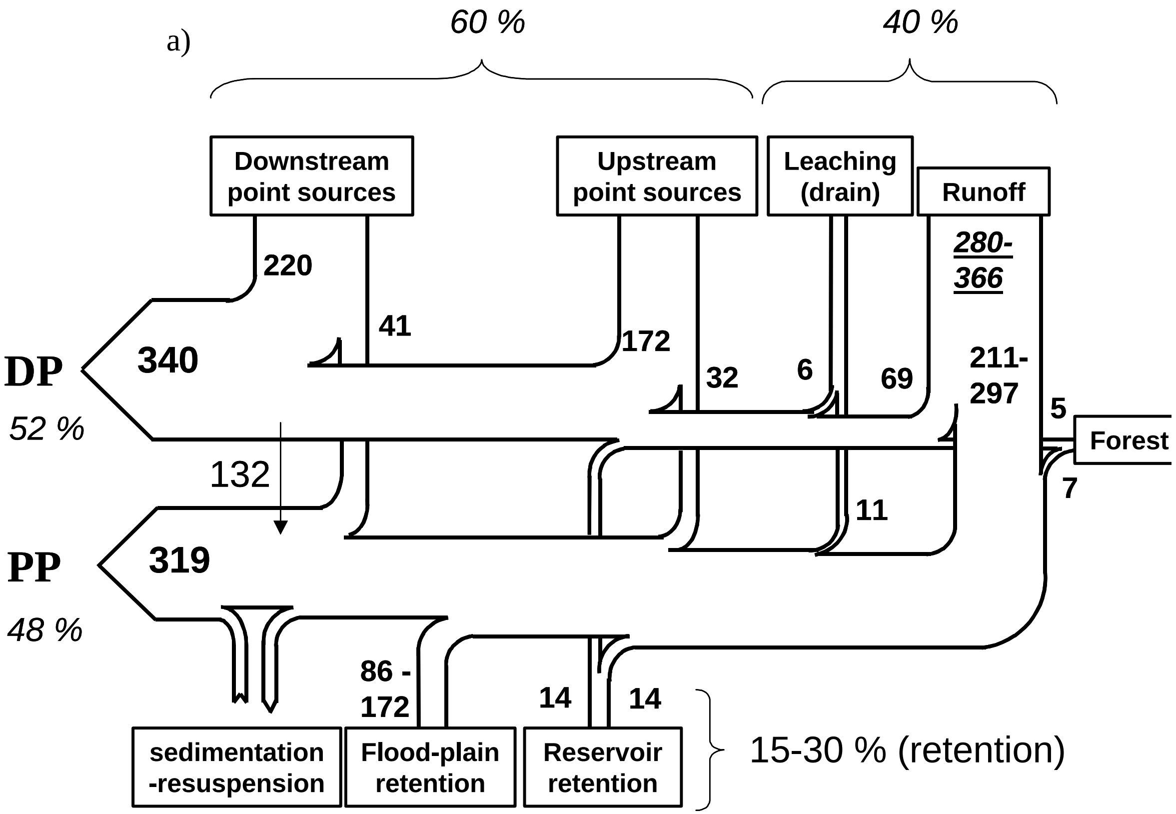
Retention of P along the Marne river drainage network is not negligible. We estimate the Marne reservoir retention at 28 tP y^{-1} in equal proportions of DP and PP and flood-plain retention in the range of 86-172 tP y^{-1}. Both types of P retention, essentially as particulate P, account for 15-30 % 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 tP y^{-1}) is higher than the exported one (340 tP y^{-1}). This indicates that P exchanges occur between water and suspended sediments. To balance the budget, we can estimate that 132 tP y^{-1} is transferred from the dissolved to the particulate form through adsorption on suspended sediment surfaces and/or phytoplankton consumption.

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 tP y^{-1}). Percentages of P point sources vs P diffuse sources, and of dissolved P vs particulate P are indicated in the figure. NB: the underlined results of runoff are calculated by difference, (See method section).



a)



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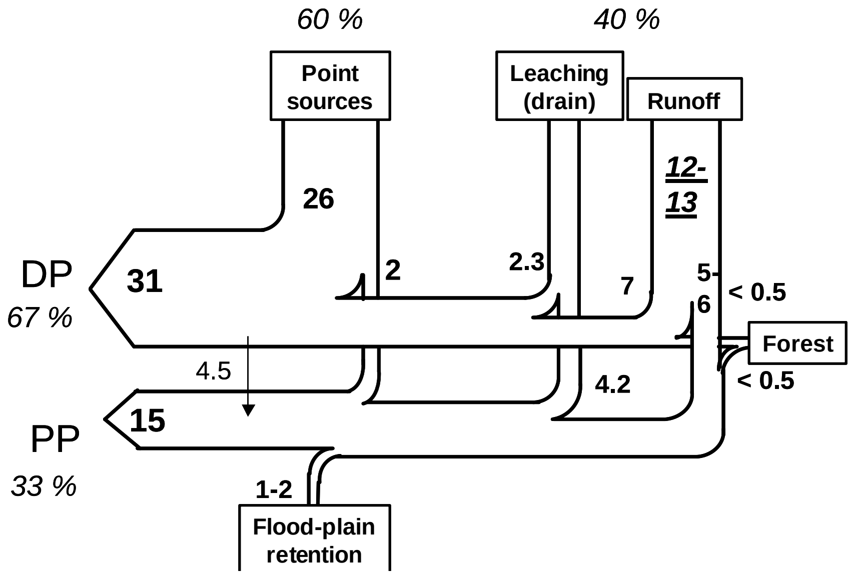

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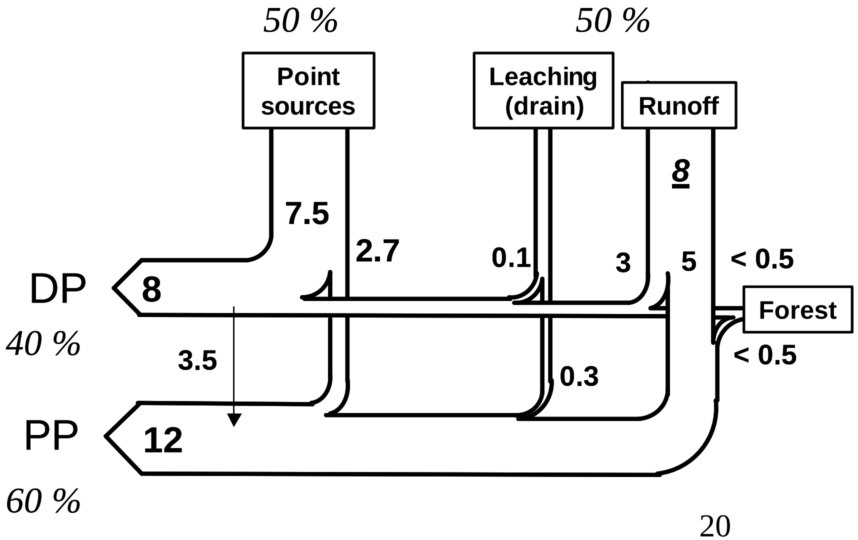


In the Grand-Morin and the Blaise sub-basins, retention is due to the upstream position of these two basins: the Blaise sub-basins does not present any significant flood-plain retention whereas the Grand-Morin sub-basin may retain 1 to 2 TP y^{-1} (less than 5 % of the total P input). The total P flux at the outlet of the Grand-Morin river is estimated at 46 tP y^{-1} (DP = 67 %) and at 20 tP y^{-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 tP y^{-1}) of diffuse sources in the Grand-Morin sub-basin (74 % of drained surface area) and less than 5 % (0.4 tP y^{-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 tP y^{-1}) dominated by agriculture, and probably from both runoff and losses from farmed animals in the Blaise sub-basin (8 tP y^{-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 tP y^{-1}.

Phosphorus content and exchangeability in re-suspended sediments

13 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).

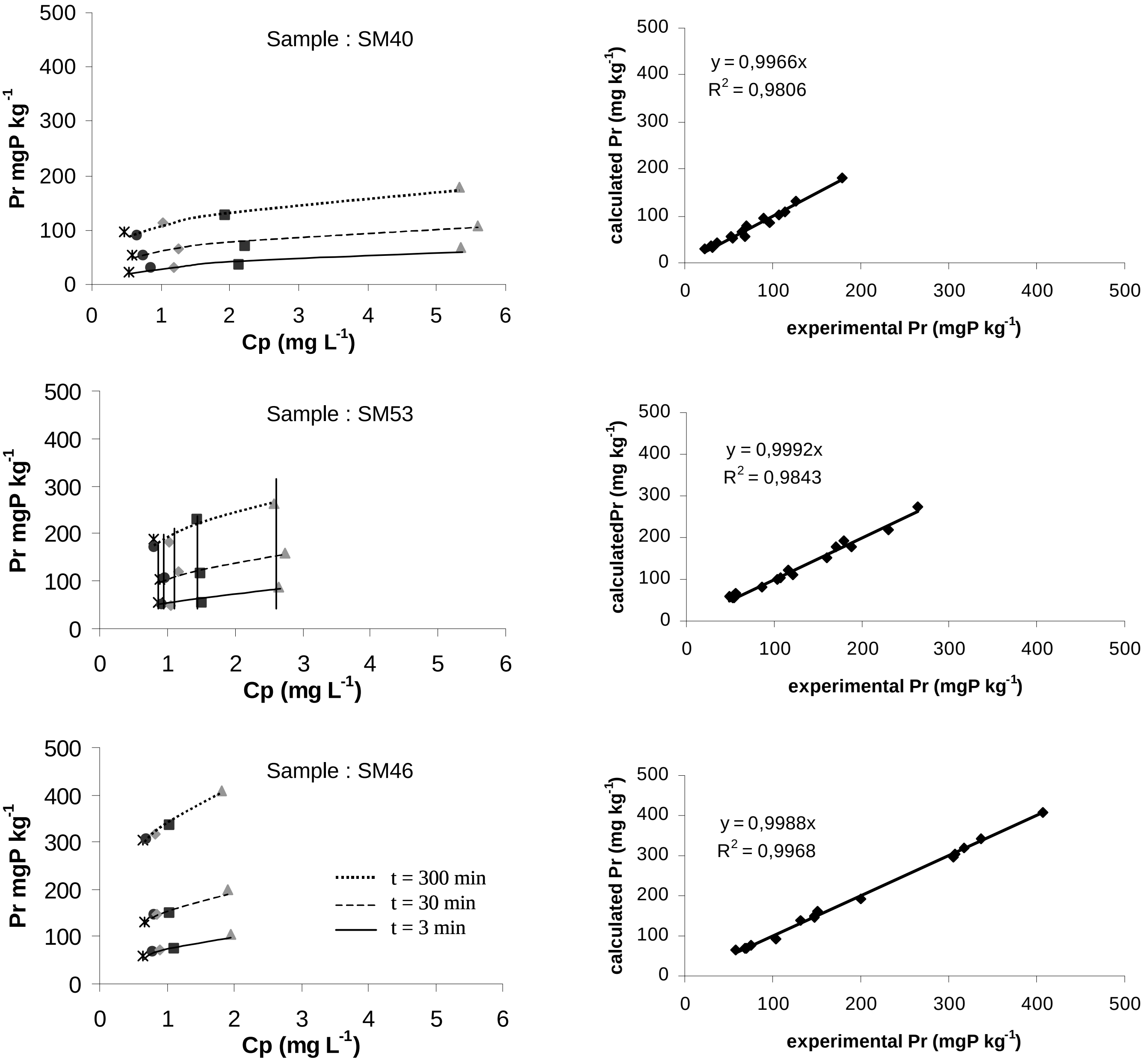
TPP values vary from 0.90 gP kg^{-1} during high flow periods to 1.97 gP kg^{-1} during the summer low flow ones. TPP averages 1.28 gP kg^{-1} and is distributed as 40 % of POP and 60 % of PIP. The particle size distribution shows low variability among the 13 samples: the 2-63 µm fraction, assimilated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

The Cp values vary within a very narrow range during the experiment [3-300 minutes], showing that the suspension (1g:10 ml) is in steady state (Figure 7). 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 [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 minutes of isotopic dilution, 104 mg P kg^{-1} after 30 minutes and 185 mg P kg^{-1} after 300 minutes (Figure 7a). For a given suspended sediment, the Pr_e values increase both with Cp and t. To analyze the variability of Pr_e values as a function of time (t, in min) and Cp (mg P L^{-1}), the results of the 13 samples were fitted on the Freundlich equation (Eq. [3]) for the 15 obtained values (3 times, 5 P enrichments): v, w and p parameters and Pr_c were determined by a least-squared regression between Pr_e and Pr_c (Figure 7, Table 11).

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	**Sample Number**	**Mean Discharge**	**TPP**	**POP**	**PIP**	**Particle size in %**		
2001 - 2002		**$m^3 s^{-1}$**	**gP kg^{-1}**	**gP kg^{-1}**	**gP kg^{-1}**	**<2µm**	**2-63µm**	**63-200µm**
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



a) b)

Figure 7: a) Experimental values for 3 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.

Table 11. Parameter estimates and their standard deviation r (SD) of the kinetic Freundlich function ($Pr=vCp^w t^p$) calculating the amount of P ions transferred between solid and liquid phases of suspensions (1g:10ml). n. is

the number of observations (five Cp values and three periods of isotopic dilution at steady-state). R² is the determination coefficient.

Samples	**Cp**	**v parameter**	**w parameter**	**p parameter**	**n.**	**R²**
	mgP L^{-1}(SD)	**Estimate (SD)**	**Estimate (SD)**	**Estimate (SD)**		
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

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. Pr_{1week}, Pr_{1month}, $Pr_{1\ year}$. (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.

Table 12. The amount of P ions that can equilibrated solution for different time scales , i.e. after one week (Pr $_{\text{1 week}}$*), one month (Pr* $_{\text{1 month}}$*) and one year (Pr* $_{\text{1 year}}$*) for a) experimental concentrations of P-PO4 (Cp) and b) the measured concentration [P-PO4] in natural water.*

Samples	**PIP**	**a) Pr in experimental conditions**			**P-PO4 In the Marne river**	**b) Pr in natural conditions**		
		Pr $_{\text{1 week}}$	**Pr** $_{\text{1 month}}$	**Pr** $_{\text{1 year}}$		**Pr** $_{\text{1 week}}$	**Pr** $_{\text{1 month}}$	**Pr** $_{\text{1 year}}$
	mgP kg^{-1}	mgP kg^{-1}	mgP kg^{-1}	mgP kg^{-1}	mgP L^{-1}	mgP kg^{-1}	mgP kg^{-1}	mgP 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

40 values of orthophosphate concentrations available from the Marne river over the annual survey can be used to calculate Pr_{1week}, Pr_{1month}, $Pr_{1year,}$ according to equation [3]. Orthophosphate concentrations, taken as Cp, vary between 0.009 and 0.188 mgP L^{-1} but when averaged for the corresponding period of sediment collection, the values range from 0.012 to 0.12 mgP L^{-1} (Table 12). Pr_{1week}, Pr_{1month}, Pr_{1year} corresponding to the 13 dates averaged 26, 39 and 54 % of PIP respectively (Table 12). Considering the annual load of suspended sediment (317 000 tons y^{-1}), the exchangeable P can be estimated at 64 tP y^{-1} (Pr $_{\text{1 week}}$), 97 tP y^{-1} (Pr $_{\text{1 month}}$) and 181 tP y^{-1} (Pr $_{\text{1 year}}$), representing 10 to 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 3 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 kgP ha^{-1} y^{-1}) is mentioned in recent literature (Dorioz et al. 1998a; Pollman et al. 2002; Sutula et al. 2001). 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 kgP ha^{-1} in the middle of the 70s to 12 kgP 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 3 studied basins (1800–5000 kgP ha^{-1}) are illustrative. The main P export flux is from crops (33 kgP ha^{-1} y^{-1}) and accounts, in average, for 1 % of the P stock in the soil. In addition, the surplus in the 3 basins (in the range of 0.5-8 kgP 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., 1998b). 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 to 0.47 kgP haAS^{-1} with a 20-30 % proportion of Dissolved P for the Marne basin, higher than the one for the Blaise (0.26 kgP haAS^{-1}) and the Grand-Morin sub-basins (0.15-0.16 kgP haAS^{-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 (Penven et al. 1998; Zimmer et al. 1991). 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 & 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 kgP 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 & 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; McDowell et al. 2001; Withers et al. 1999) but also of the contribution of both point sources *vs* diffuse sources to the P load in rivers (Drolc & 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 3 studied basins.

As already mentioned by Behrendt & 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 to 90 % (Jacks et al. 2000; Steer et al. 2002) with a high but variable soil retention potential of infiltrated water (Jones & Lee 1976).

Note that effluents from livestock farming, localised 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 one 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 of from one week to one year.

It is worth mentioning that the hypothesis made to equilibrate the P budget (132 tP y^{-1}) coincides well with the exchangeable P at the time scale from 1 month to 1 year (97-181 tP y^{-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. 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.).

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References

AESN (1974) Les bassins de la Seine et les cours d'eau normands. Agence de l'eau Seine-Normandie, Nanterre, 1973-1978, 12 volumes + atlas, tome 1, fasc. 4.

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

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

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

Aspila KI, Agemian H & Chau ASY (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

Barrow NJ (1978) The description of phosphate adsorption curves. J. Soil Sci. 29: 447-462

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

Billen G, Garnier J & 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 & 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 JC, 1986. Vertical transport of particles within the ocean. The role of Air-Sea Exchange in Geochemical Cycling. Reidel Publishing Company, 83-111 pp.

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

Catt JA et al. (1999) Phosphorus losses from arable land in England. Soil Use and Management. 14: 168-174

Chardon WJ & Blauuw D (1998) Kinetic Freundlich equation applied to soils with a high residual phosphorus content. J. Soil Sci. 169: 30-35

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. & Fustec F. eds). Elsevier, Paris, 301-344 pp.

Cooper DM, House WA, May L & Gannon B (2002) The phosphorus budget of the Thames catchment, Oxfordshire, UK: 1. Mass balance. The Science of the Total Environment. 282/283: 233-251

CORPEN (1998) Programme d'action pour la maîtrise des rejets de phosphore provenant des activités agricoles. Ministère de l'aménagement du territoire et de l'environnement: 85p

Dorioz JM, Cassell EA, Orand A & Eisenman KG (1998a) Phosphorus storage, transport and export dynamics in the Foron River watershed. Hydrological Processes. 12: 285-309

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

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

Dorioz JM & 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

Drolc A & Zagorc Koncan J (2002) Estimation of sources of total phosphorus in a river basin and assessment of alternatives for river pollution reduction. Environment International. 28: 393-400

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

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

Fardeau JC (1993) Le phosphore biodisponible des sols: sa représentation par un modèle fonctionnel à plusieurs compartiments. Agronomie. 3: 317-331

Fardeau JC & Conesa AP, 1994. Le phosphore. in: Bonneau et Souchier, Pédologie, 2.Constituants et propriétés du sol. Masson, 557-568 pp.

Froelich PN (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, Greiner I, Schanen O, Gaillard S & Dzana JG (1998) Les zones humides riveraines: des milieux divers aux multiples fonctions. Chapitre 5. La Seine en son bassin : fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., de Marsily G. & Fustec F. eds). Elsevier, Paris, 211-262 pp.

Fustec E & Lefeuvre JC, 2000. Fonction et valeurs des zones humides. Dunod, Paris, 426p pp.

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

Gardner CMK, Cooper DM & Hughes S (2002) Phosphorus in soils and field drainage water in the Thames catchment, UK. The Science of the Total Environment. 282/283: 253-262

Garnier J, Billen G, Hanset P, Testard P & Coste M (1998b) Développement algal et eutrophisation. Chapitre 14. In: La Seine en son bassin Fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., de Marsily G & Fustec F. eds). Elsevier, Paris: p593-626

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

Garnier J, Leporcq B, Sanchez N & 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 HL (1982) Differential extraction of sediment phosphate with NTA solution. Hydrobiologia. 92: 683-687

Guerrini MC et al. (1998) Le bassin de la Seine : la confrontation du rural et de l'urbain. Chapitre 1.La Seine en son bassin : fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., de Marsily G. & Fustec F. eds). 29-75

Haygarth PM & Jarvis SC (1999) Transfer of Phosphorus from agricultural soils. Advances in Agronomy. 66: 195-269

Heathwaite AL & Dils RM (2000) Characterising phosphorus loss in surface and subsurface hydrological pathways. The Science of the Total Environment. 251/252: 523-538

Hieltjes AS & Lijklema L (1980) Fractionation of inorganic phosphates in calcaerous sediment. J. Environ. Qual. 9: 405-407

Idlafkih Z, Meybeck M, Chiffoleau JF, Cossa D & 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, IAHS Publ. 243: 45-58

Jacks G, Forsbreg J, Mahgoub F & Palmqvist K (2000) Sustainability of local water supply and sewage system-a case study in a vulnerable environment. Ecological Engineering. 15: 147-153

Johnes PJ (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. Journal of Hydrology. 183: 323-349

Jones RA & Lee GF (1976) Septic tank wastwater disposal system as phosphorus sources for surface water. Jour. Water Pollut. Control Fed. 51: 2764-2775

Kronvang B, Laubel A & Grant R (1997) Suspended sediment and particulate phosphorus transport and delivery pathways in an arable catchment, Gelbaek stream, Denmark. Hydrological Processes. 11: 627-642

Kronvang B, Laubel A, Larsen SE & Iversen HL (2000) Soil erosion and sediment delivery through buffer zones in Danish slope units. The Role of Erosion and Sediment Transport in Nutrient Contaminant Transfert. IAHS Publ. 263: 67-73

May L, House WA, Bowes M & McEvoy J (2001) Seasonal export of phosphorus from lowland catchment: upper River Cherwell in Oxfordshire. The Science of the Total Environment. 269: 117-130

McDowell R, Sharpley AN & Folmar G (2001) Phosphorus export from an agricultural watershed: linking source and transport mechanism. J. Environ. Qual. 30: 1587-1595

McGehan MB & Lewis DR (2002) Sorption of phosphorus by soil, Part 1: principles and models. Biosystems Engineering. 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 & Fustec E (1998a) La Seine en son bassin: Fonctionnement écologique d'un système fluvial anthropisé. Paris: Elsevier: 749p

Meybeck M, Mouchel JM, Idlafkih Z, Andréassian V & Thibert S (1998b) Transfert d'eau, de matière dissoute et particulaire dans le réseau fluvial. Chapitre 8. La Seine en son bassin : fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., de Marsily G. & Fustec F. eds). Elsevier, Paris, 345-387 pp.

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, 80 pp.

Morel C, Blaskiewitz J & Fardeau JC (1995) Phosphorus supply to plants by soils with variable phosphorus exchange. Soil Science. 160(6): 423-430

Morel C, Plenchette C & Fardeau JC (1992) La fertilisation phosphatée raisonnée de la culture du blé. Agronomie. 12: 565-579

Morel C, Schneider A, Plénet D & Fardeau JC (2002) Transfer of phosphorus in soil-plant and soil-solution systems using isotopic labeling and dilution methods. In: Nuclear Techniques in integrated plant nutrient, water and soil management (pp 49-56). International Symposium, Vienna, 16-20 October 2000, Joint FAO/IAEA Division Vienna. C&S Papers Series 11/C.: p486

Morel C, Tunney H, Plénet D & Pellerin S (2000) Transfer of Phosphate ions between soil and solution: Perspectives in soil testing. Journal of environmental quality. 29(1): 50-59

Ohno T & 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 & Boiffin J (2000) Evolution du raisonnement de la fertilisation phosphatée 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 MJ et al. (1998) Un bassin versant agricole et ses pratiques : le Grand Morin. Chapitre 3. La Seine en son bassin: Fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., de Marsily G & Fustec F. eds). Elsevier, Paris. p. 127-157.

Peters NE & Reese SR (1995) Variations of weekly atmospheric deposition for multiple collectors at site on the shore of lake Okeechobee, Florida. Atmospheric Environment. 29(2): 179-187

Pieterse NM, Bleuten W, Jacks G & JØrgensen SE (2003) Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. Journal of Hydrology. 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 6, 251p.

Pollman CD, Landing WM, Perry JJ & Fitzpatrick T (2002) Wet deposition of phosphorus in Florida. Atmospheric Environment. 36: 2309-2318

Ramade F (1998) Dictionnaire encyclopédique des sciences de l'eau. Paris, Ediscience international: 785p

Reckhow KH, Beaulac MN & Simpson JT (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 synthèse Piren-Seine 3e phase : chap. Agriculture et qualité des eaux: 27p

Saragoni F, Arpaa F & 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.

SASInstitute (1995) SAS/STAT Version 6.11 Ed. SAS Institute, Cary, NC.

Schneider A & Morel C (2000) Relationship between the isotopically exchangeable and resin-extractable phosphate of deficient to heavily fertlized soil. European Journal of Soil Science. 51: 709-715

Schvartz C, Walter C, Claudot B, Bouedo T & 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 AN, Gburek WJ, Folmar G & Pionke HB (1999) Sources of phosphorus exported from an agricultural watershed in Pennsylvania. Agricultural water management. 41: 77-89

Smith KA, Jackson DR & Withers PJA (2001) Nutrient losses by surface run-off following the application of organic manures to arable land. 2. Phosphorus. Environmental Pollution. 112: 53-60

Steer D, Fraser L, Boddy J & Seibert B (2002) Efficiency of small constructed wetlands for subsurface treatment of single-family domestic effluent. Ecological Engineering. 18: 429-440

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

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

Svendsen LM, Kronvang B, Kristensen P & Græsbøl R (1995) Dynamics of phosphorus compounds in a lowland river system: importance of retention and non-point sources. Hydrological Processes. 9: 119-142

Svendsen LM, Redsdorf A & Nørnberg P (1993) Comparison of methods for analysis of organic and inorganic phosphorus in river sediment. Water research. 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. p195, Université de Paris 6.

Thoms MC, Foster JM & 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. IAHS Publ. 263: 227-236

Torrent J (1997) Interactions between phosphate and iron oxide. Advances in GeoEcology. 30: 321-344

Turtola E & Paajanen A (1995) Influence of improved subsurface drainage on phosphorus losses and nitrogen leaching from heavy clay soils. Agricultural water management. 28: 295-310

Vaas LH, R.N.J C, Das HA, Reith JMM & van der Veijden CH (1987) Isotopically exchangeable phosphate in freshwater sediments: effects of U.V. - radiation, formaldehyde, solid/solution ratio and pH on its experimental determination. Water research. 21(9): 1135-1142

Van Veldhoven PP & Mannaerts GP (1987) Inorganic and organic measurements in the nanomolecular range. Anal. Biochemistry. 161: 45-48

Verhoff FH, Yaksich SM & Melfi DA (1980) River nutrient and chemical transport estimates. J. Environ. Engng. Div. ASCE. 10: 591-608

Verstaeten G & 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. IAHS Publ. 263: 243-249

Walling DE, He Q & Blake WH (2000) River flood plains as phosphorus sinks. The Role of Erosion and Sediment Transport in Nutrient Contaminant Transfert. IAHS Publ. 263: 211-218

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

Walling DE, Webb W & Russel MA (1997) Sediment-associated nutrient transport in UK rivers. Fresh water contamination, IAHS Publ. 243: 69-81

Walter C, Schvartz C, Claudot B, Bouedo T & 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 JDH, Shear H & Thomas RL (1980) Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materiels from Great Lakes. Limnol. Oceanogr. 25(1): 1-11

Withers PJA, Dils RM & 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), IAHS Publi. 257: 41-50

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

2 Dynamique des nutriments et contrôle de l'eutrophisation dans le bassin de la Marne : modélisation du rôle du phosphore echangeable (*article soumis le 30 novembre 2003 à Journal of Hydrology, special issue*)

Nutrient dynamics and control of eutrophication in the Marne River system: modelling the role of exchangeable phosphorus.

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Abstract

The Marne River (12 762 km²) is one of the main tributaries of the Seine river, upstream from the City of Paris, with its 2 million inhabitants of which 70 % are concentrated to the downstream part of the basin, its high industrial activity and intensive agriculture. The Marne River water supplies drinking water production to a large number of Parisians. A diversion reservoir (350 10^6 m^3) is used mainly to sustain summer low flows.

On the basis of field observations and experimental studies, a hydrological and ecological model of this river system was built using the RIVERSTRAHLER approach (Billen et al., 1994; Garnier et al. 1995). In order to take into account the role of the reservoir, the modelling strategy was to consider separately 9 sub-basins and the main branch, to which was coupled a model of the reservoir. The point and diffuse sources of nutrients were analysed over more than 10 years (1991-2001) taking into account the role of exchangeable phosphorus (Némery, 2003; Némery et al. submitted). The model was validated through its ability to reproduce available water quality observations. Different realistic scenarios of future reduction of phosphorus load were tested, in various hydrological conditions (dry and wet years). Phytoplankton development can be slightly reduced by a further 85 % abatement of phosphorus in all the wastewater treatment plants of the basin, but a reduction both of diffuse and point phosphorus sources of would be necessary to further decrease eutrophication.

Key-words: eutrophication, rivers, exchangeable phosphorus, ecological modelling

1. Introduction

Eutrophication of large river systems, i.e. enhanced phytoplankton development caused by excessive inputs of nutrients, particularly phosphorus, from point and non-point sources in the watershed, is one of the major water quality problems facing Water Authorities in European countries. Instream algal production represents an internal source of organic load, often greater than the treated wastewater inputs and capable of inducing heterotrophic conditions and oxygen depletion in downstream sectors of the river network (Garnier et al., 1999). Moreover, intense algal development creates problems for drinking water production by clogging filters, raising the pH, which prevents the use of aluminate flocculating reactants in the treatment process, and by releasing dissolved organic carbon which leads to bacterial re-growth in drinking water supply pipes (de Dianous et al., 1995).

The river Marne (Figure 1), one of the 3 major tributaries of the Seine River, which is an important source of drinking water for Paris and its suburbs, is a typical example of a eutrophicated river. Strong spring blooms of diatoms (up to 150 µg Chl*a*L^{-1}) regularly occur in its downstream sectors, adding to the production costs of the water plants.

In the last 15 years, wastewater treatments have progressed in most European countries, leading to obvious improvements in the state of organic pollution of river systems (Billen et al. 2001, in press) The reduction in eutrophication is less obvious, however, although the phosphorus loading from domestic and industrial sources tends to decrease. The link between nutrient loading and eutrophication is very difficult to assess from data collected in water quality surveys, especially because of the complex mechanisms by which hydrological and meteorological conditions interfere with nutrient and top-down controls in determining algal development (Garnier et al., 1998; Garnier et al., 1999).

In the case of the Marne river, for instance, the effect on eutrophication, of the efforts devoted in the last 10 years to reducing the phosphorus loading is difficult to determine, because in the last 5 years (1997 to 2001) conditions have been particularly wet, while dry conditions prevailed at the beginning of this period (1989-1993). Recent return of dry conditions (2002-2003) have again focused attention on eutrophication.

The complexity of the eutrophication process argues in favour of a modelling approach aimed at understanding available field observations and identifying the most beneficial environmental measures. A model of the ecological functioning of river systems, linking the kinetics of microbiological and chemical processes to their macroscopic manifestations at the scale of the whole drainage network, has been developed during the last 15 years, with the main objective of treating eutrophication problems and nutrient delivery to the costal zone (RIVERSTRAHLER : Billen *et al.*, 1994; Garnier et al., 1995). The model, mainly developed on the Seine river system (Billen & Garnier, 1999; Billen et al., 2001), has been applied to several other European rivers, e.g. the Mosel (Garnier et al., 1999), the Schelde (Billen et al., submitted) and the Danube (Garnier et al., 2001; Trifu, 2002) and more recently, to the tropical Red River (Viet Nam) (Garnier et al., 2002; Le Thi Phong et al., 2003).

In this study, we used the Riverstrahler model to explore the link between eutrophication, nutrient loading and hydrological conditions in the Marne river system. This objective required a better representation in the model of the processes involved in the dynamics of phosphorus, particularly regarding its interaction with its inorganic form in suspended solids. In the previous versions of the model, these latter processes were represented in a somewhat oversimplified way, because point sources of dissolved phosphate dominated. In the context of phosphorus point source reduction, the relative role of diffuse phosphorus inputs from soil erosion is expected to be a major source, due to high phosphorus content of the soil (Némery et al., submitted) as result of continued of fertilization procedures, although reduced since the 1970s. Newly gained knowledge of the kinetics of phosphorus exchange between particulate and dissolved compartments (Némery, 2003) has been incorporated into the Riverstrahler model. This new version is able to explore the role of diffuse *vs* point sources of phosphorus and to establish nutrient budgets at the scale of the whole river system.

2. Description of the site, field studies and construction of the data base

The Marne River basin

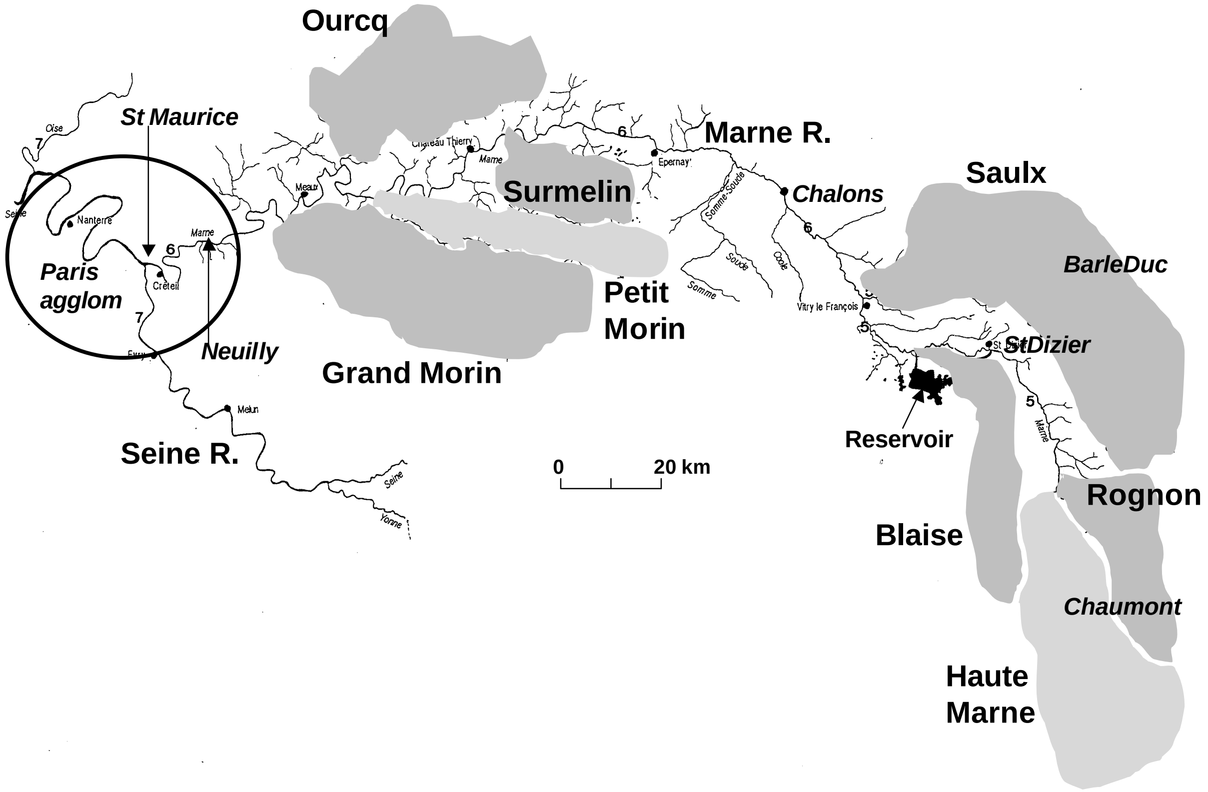

Figure 1. Map of the Marne basin and its 8 main sub-basins.

The Marne is a major tributary to the Seine river situated in the upstream basin of the Seine river (France), in the temperate region of Champagne, east of the Paris Basin (Figure 1). Its watershed area is 12 762 km^2 which represents 17 % of the whole Seine basin. The Marne river system includes a diversion reservoir (Der Lake, 48 km^2), impounded in 1974, and constructed on the upper reaches of the Marne river to regulate its flow (Garnier et al., 1999, Garnier et al., 2000). The main branch, 410 km long, is of the 6th order. The reservoir is connected to the Marne, through a diversion canal, at km 50, and the release canal joins the river at km 70.

At the outlet, the mean annual discharge of the Marne River ranges from 60 to 200 m^3 s^{-1} (Figure 2).

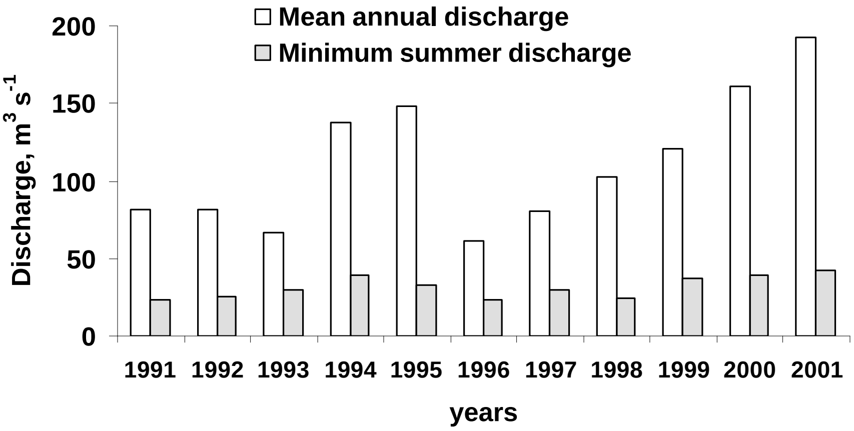

Figure 2. Mean annual discharge at the outlet of the Marne River from 1991 to 2001. Minimum values are also indicated.

The population density is high throughout the basin (160 inhab km^{-2}) but the downstream part is subjected to the strongest urban pressure (976 inhab km^{-2}). The centre of the Marne watershed is dominated by agriculture (cereals and industrial crops) whereas in its upstream part livestock farming and forests dominate. The Marne river comprises 8 main sub-basins: the Haute-Marne (993 km^2), the Rognon (667 km^2), the Blaise (607 km^2), the Saulx (1953 km²), the Surmelin (430 km²), the Petit Morin (548 km²), the Ourcq (1248 km²) and the Grand-Morin (1202 km^2), representative of the different land uses.

Nutrients, phytoplankton biomass and suspended solids

Phosphate, total phosphorus (P), nitrate and ammonium (N) as well as reactive silica (Si) concentrations were measured spectrophotometrically according to Eberlein and Kattner (1987), Jones (1984) and Rodier (1984) respectively. Chlorophyll *a* (Chl *a*) was analysed according to Lorenzen (1967). Suspended Solids (SS) were weighed on GF/F filters dried at 450°C.

Suspended sediments were sampled with sediment traps at the outlets of the Marne River and of two of the sub-basins (the Blaise and the Grand Morin, representative of the two major types of land use, see Némery, 2003; Némery et al., submitted). Their phosphorus content was determined with a high temperature/HCl extraction technique (Aspila et al. 1976), as well as by mineralisation into inorganic forms at 550 °C, extraction into 1N HCl for 15-20 hours and phosphate analysis, in order to distinguish between Particulate Inorganic Phosphorus (PIP) and Total Particulate Phosphorus (TPP). The Particulate Organic Phosphorus (POP) was calculated by difference between TPP and PIP (Svendsen et al. 1993).

The data base

The data used by the model, both to define the constraints to the system, and to validate the calculations, are taken from various National Institutions and from our own measurements made in the framework of the PIREN-Seine programme. All data are organized as a GIS-Seine data base under ARC-Info software. The rainfall data are issued from the National Meteorological Institute (Météo France), while the discharge data are gathered from the Hydro-Bank managed by the French Ministry for the Environment. The data on urban and industrial wastewater release (P, N, organic matter, and SS) were provided by the Seine-Normandy Water Agency (AESN). The GIS allows the data to be distributed according to the 8 sub-basins and the main branch. The determination of diffuse P, N sources is based on the distribution of the land use types into percentages of forests, meadows and arable land (from the Corine Land Cover data base). The validation data are mainly results of our own surveys at the Marne outlet, the Grand Morin and the Blaise, and taken from the RNB (Réseau National de Bassin) for the other rivers.

3. The RIVERSTRAHLER model applied to the Marne river

The RIVERSTRAHLER model (Billen et al. 1994; Garnier et al. 1995; Billen et al., 1999; Garnier et al. 2002) is a generic model of the biogeochemical functioning of whole river systems. It results from the coupling of a hydrological module (HYDROSTRAHLER) calculating the water flows through the drainage network, with a module describing the kinetics of the biological and physical-chemical in-stream processes (RIVE).

Hydrological model

The complex network of tributaries of the whole Marne basin is described as 8 sub-basins, each represented by a regular pattern of the confluence of rivers of increasing stream orders (according to Strahler, 1957) with mean morphological characteristics, connected to the main branch of the Marne river. The Marne reservoir, for which a specific model has been developed (Garnier et al., 1999) is also taken into account (see Figure 1).

In each sub-basin, the HYDROSTRAHLER calculates the discharge in order n, as the sum of the discharges of their two n-1 order tributaries, the discharges of lateral tributaries of order 1 to n-1, and the flow from its direct watershed, i.e. the part of the watershed that does not belong to the catchment of the affluents (see Billen et al. 1994). The latter is calculated from rainfall and potential evapotranspiration data with a classical rain-discharge conceptual model, taking into account the role of a soil reservoir and an aquifer (see *e.g.* Bultot *&* Dupriez, 1976). This model, which involves 4 parameters (soil saturation, infiltration rate, internal flow rate, aquifer flow rate), distinguishes between two components of the discharge from the watershed: the base flow supplied by the water table, and the surface (or hypodermic) flow supplied by the upper soil reservoir and the surface runoff. In the main branch of the river, the calculation is similar, taking into account the contribution to the flow of both the direct watershed and the considered sub-basins. Depth is calculated at each time and at each point of the network from local values of the discharge, width and slope, using a rearrangement of Manning's formula (Billen et al, 1994). In sectors regulated by navigation locks, the depth is forced to a constant, prescribed value.

Modelling in-stream processes

The RIVE Model consists of 28 variables, including inorganic suspended solids, nutrients (nitrate and ammonium, phosphate, dissolved silica), dissolved and particulate organic matter (as two classes of biodegradability), 3 taxonomic groups of phytoplankton (diatoms and green algae and cyanobacteria), two groups of zooplankton (rotifers and microcrustaceans) and bacteria (heterotrophs and nitrifiers . The kinetic representation of the ecological processes involved, as well as the value of the corresponding parameters are described in detail in Garnier et al. (1999) and Garnier et al. (2002).

The present version of the model is improved by a new description of the exchange of inorganic phosphorus between the dissolved and particulate phases, based on recent work by Némery (2003). From kinetic equilibration experiments using $^{32}PO_4^{3-}$ (Fardeau & Jappe, 1982; Fardeau et al., 1991; Fardeau, 1993; Morel et al., 1994; Morel et al., 1996; Némery, 2003; Némery et al., submitted), it was shown that:
(1) a large proportion (20-90%) of inorganic particulate phosphorus present in the Marne river system is exchangeable with dissolved inorganic phosphate in less than one month.
(2) the equilibrium between mobile (in less than one month) inorganic particulate phosphorus and dissolved ortho-phosphate can be described by the following relationship, based on Freundlich kinetics (Barrow, 1978; Chardon, 1998; Morel et al., 2002)

$$Pr = a\, Cp^{b}$$

where Pr, in mg P $kgSS^{-1}$, is the content of suspended solids in inorganic phosphorus exchangeable in less than 1 month,

Cp, in mg P L^{-1}, is the dissolved ortho-phosphate concentration in steady state, a and b are fitted kinetic parameters, estimated, for the Marne River system, to 800 and 0.2 according to the results of Némery (2003).

At each time step the model calculates the total exchangeable inorganic phosphorus (TIP) and inorganic suspended solids (SS) concentrations in the water mass resulting from all inputs and in-stream processes. The partition between dissolved (DIP) and particulate (PIP) inorganic phosphorus is then calculated by numerically solving the system of equations formed by equation (1) and (2):

$$PIP/SM = a' \, DIP^{b} \qquad (1)$$
$$TIP = DIP + PIP \qquad (2)$$

Diffuse sources of nutrients

Diffuse sources of nutrients are taken into account by assigning a constant concentration of each variable to the two components of the water flow from the watershed (surface runoff and groundwater respectively) as calculated by the Hydrostrahler model.

Regarding nitrate and ammonium-nitrogen in surface runoff, these concentrations are calculated from land use in the watershed, using an empirical formula derived by Billen & Garnier (1999) from a compilation of lysimetric and porous-candle experimental data. The composition of groundwater base flow was obtained from the most recent inventory of available analyses of groundwater intakes (RNDE, French Mnistry for the Environement) (Table 1). For nitrates, the model takes into account a calibrated riparian transfer coefficient which accounts for high denitrification rate which, in some areas, eliminates up to 50% of the nitrate input from the watershed before it reaches the surface water (Billen and Garnier, 1999; Sebilo et al., 2003).

Table 1. Concentrations in Nitrate, Silica, Suspended Solids (SS) and phosphates (PO_4) assigned to surface runoff and groundwater flow of the Marne sub-basins, for calculation of the diffuse inputs.

Sub-basins		Nitrate, mgNL^{-1}		Silica, mgSi L^{-1}		SS, mg L^{-1}		PO_4, mgP L^{-1}
	Area, km²	surf.	groundw.	surf.	groundw.	surf.	groundw.	surf & groundw
Hte Marne	993	7,0	4,2	2,8	4,2	53	6	0.04
Rognon	667	5,6	3,5	2,8	4,2	47	6	0.04
Blaise	607	7,7	5,6	2,8	4,2	54	6	0.04
Saulx	1953	7,7	3,1	2,8	4,2	56	6	0.04
Surmelin	430	7,0	6,0	2,8	4,9	58	6	0.04
Petit Morin	548	9,1	5,9	2,8	4,2	90	6	0.1
Ourcq	1248	11,9	5,9	2,8	4,2	80	6	0.1
Grand Morin	1202	10,5	6,0	4,2	5,6	96	6	0.1
Main Branch*	5114	12,8	6,3	3,8	4,6	76	6	0.07

* direct watershed of the main branch, i.e. part of the basin not included in the sub-basin watersheds

Rock weathering determines the silica concentration in surface- and groundwater. On the basis of the compilation by Meybeck (1986), a silica concentration was assigned to each lithological class represented in the Marne watershed (Table 1).

The suspended solid concentration observed in headwater streams varies considerably both with the season and the land use. At high specific discharge (24 L km^{-2} sec^{-1} on average), the suspended solid concentration is correlated to the proportion of arable land as compared to forest or grassland (Figure 3), indicating the former is more vulnerable to erosion than the latter. At low discharge (1.8 L km^{-2} sec^{-1} on average), the level of suspended solids is much lower. On this basis, suspended solid concentration in surface runoff was calculated for each sub-basin according to land use in the watershed, while a constant value of 6 mg L^{-1} has been assigned to the base runoff (Table 1).

As far as dissolved ortho-phosphate is concerned, the observed concentration does not vary greatly around a value of 0.10 mgP L^{-1} and 0.04 mgP L^{-1}, whatever the discharge, for arable land and forest + meadow respectively. With equation (1) above one can thus derive a value of 470 mgP kg^{-1} for the mobile phosphorus content of suspended solids originating from soil erosion. This value is coherent with the mean value of phosphorus content measured on samples of arable soils collected in the Marne basin (560 mgP kg^{-1}, n=37), implying that a large proportion of the total inorganic phosphorus in arable soils is mobile.

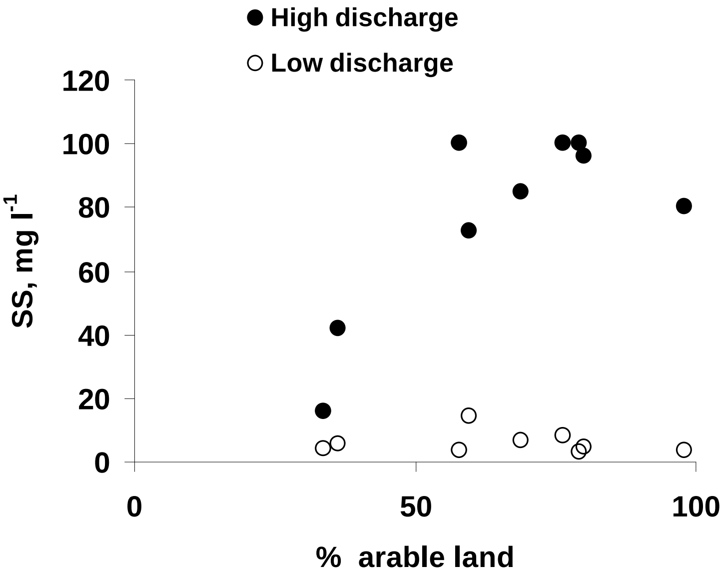

Figure 3. Relationship between suspended solids at high and low discharge and the percentage of arable land.

Point sources

The point sources for each sub-basin and the main branch are calculated on the basis of data on the loading from municipal wastewater treatment plants and from industrial establishments, communicated by the Seine-Normandy Water Agency. In the 8 sub-basins, these inputs are attributed by stream-order; on the main branch, they are represented by kilometric points at the sites of their discharge into the river. The data were provided by the AESN for the years 1991, 1996 and 2000, as total N, total P, suspended solids and biological oxygen demand (BOD) (Figure 4). The data show a distinct trend toward reduction of point sources during the considered period, related to a general improvement in the treatment of wastewater. In the case of phosphorus, this trend is reinforced by a reduction in the general domestic P loading due to a decreased of polyphosphate in washing powders.

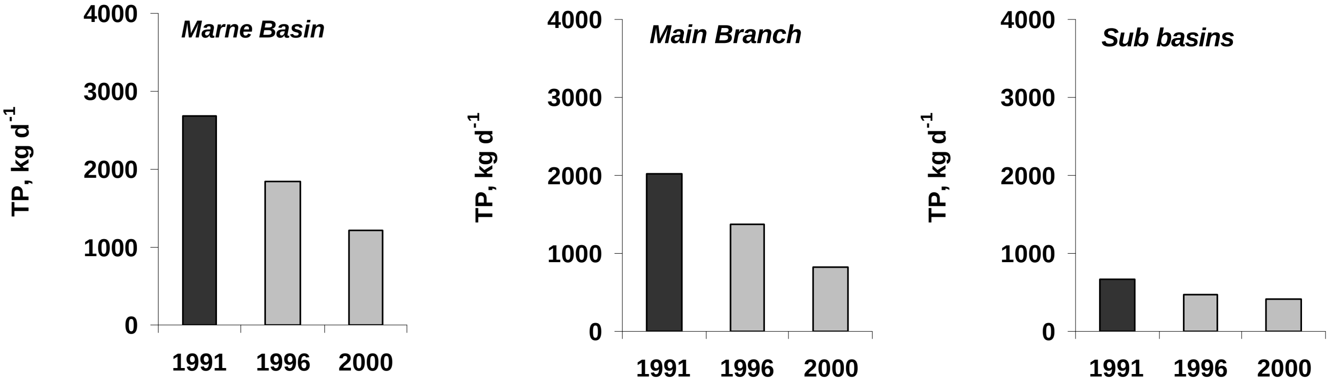

Figure 4. Decrease in total phosphorus point source loading from 1991 to 2000 for the entire Marne basin, the main branch and the 8 sub-basins.

Studies carried out on the treated and untreated wastewater in the Paris urban area (Servais *et al.*, 1999; Garnier et al., submitted) made it possible to convert these variables into state variables in the RIVE model (for example, relationships are established between BOD and the different fractions of organic carbon).

4. Model results

Year-to-year variations in phytoplankton development

As the kinetic formulation of the ecological processes and the value of the parameters have been determined separately, the comparison between the model simulations and the observations represents a true validation of the model. Discrepancies between simulations and observations therefore provide information on the limits of our understanding of the complex interactions involved. However, they can also be due to inaccurate estimates of the constraints, particularly concerning point and diffuse sources.
Results are shown for two 3 year series: the period from 1991 to 1993 (Figure 5) is representative of dry hydrological conditions with low summer flow, while the period from 1999 to 2001 (Figure 6) is characterized by very wet conditions with much higher summer discharge (see Figure 2).

For the phytoplankton biomass a good agreement is found between the simulations and the observations for the two of the 3-year series. Phytoplankton blooms can be predicted to occur as soon as the discharge has decreased to the level when the phytoplankton growth rate is higher than the dilution rate (Billen et al., 1994, Garnier et al., 1999). In dry hydrological years, the maximum phytoplankton biomass is observed in April at the outlet of the Marne river, but it is delayed until May or June during wet hydrological years (e.g. 2001). The amplitude of the bloom also differs; it is less pronounced at higher spring discharges.
Regarding nutrient simulations, the model adequately simulates the level and the main trends of the annual variations of nitrate, silica and phosphates during contrasting hydrologically different years such as 1991, 1995 and 1999 (Figures 5 & 6).

The year 2000 was selected for an analysis of the phosphate simulations at the outlet of the sub-basins and of the main branch in a new representation by the model (Figure 7). Again the model reproduces quite well the level of phosphates within each of the sub-basins and their variations throughout the year. Phosphate concentrations are generally higher in summer than in winter showing the importance of point sources that are diluted in winter by higher water flow, except in the Rognon sub-basin which has the lowest population density and the least arable land. On the other hand, phosphate concentrations are highest in the rivers of the downstream sub-basins, the ones closest to the densely populated Paris urban area, or where land use is dominated by industrial and cereals crops (Grand Morin and Petit Morin, notably).

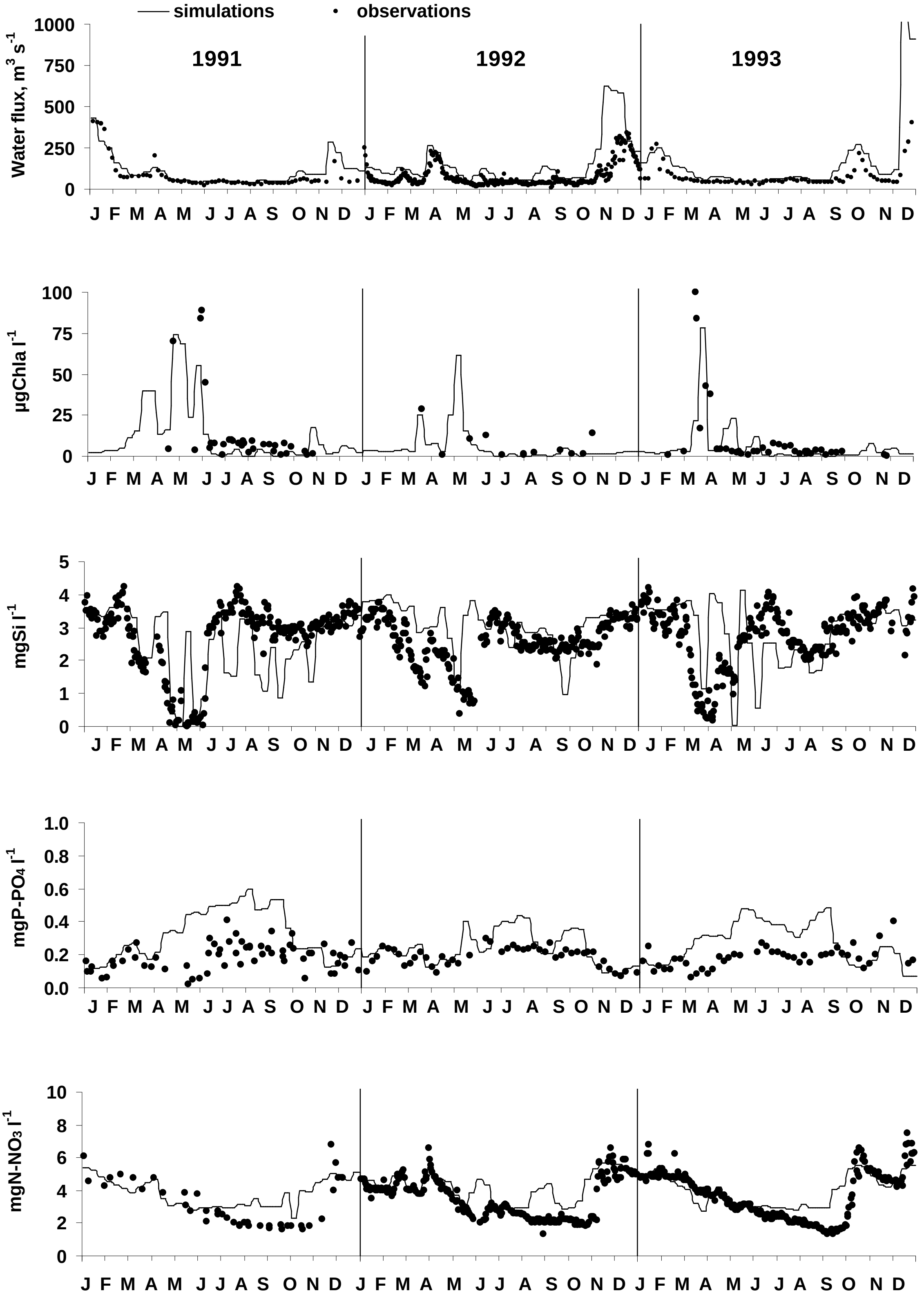

Figure 5. Seasonal variations of water fluxes, phytoplankton biomass (Chla) and nutrients (nitrate, phosphates and silica) during the dry years 1991 to 1993. The simulations are compared with the observations.

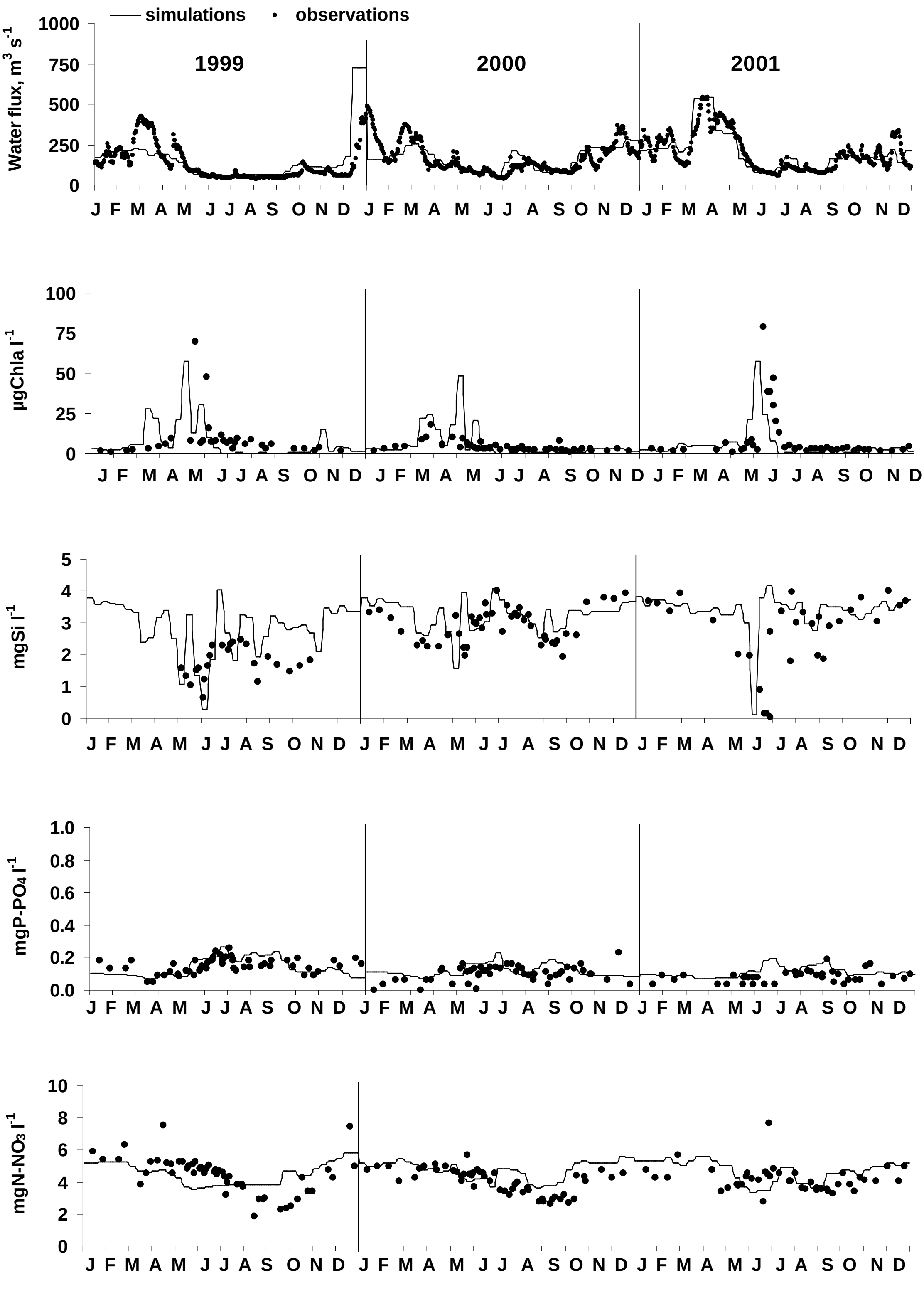

Figure 6. Seasonal variations of water fluxes, phytoplankton biomass (Chla) and nutrients (nitrate, phosphates and silica) during the wet years 1999 to 2001. The simulations are compared with the observations.

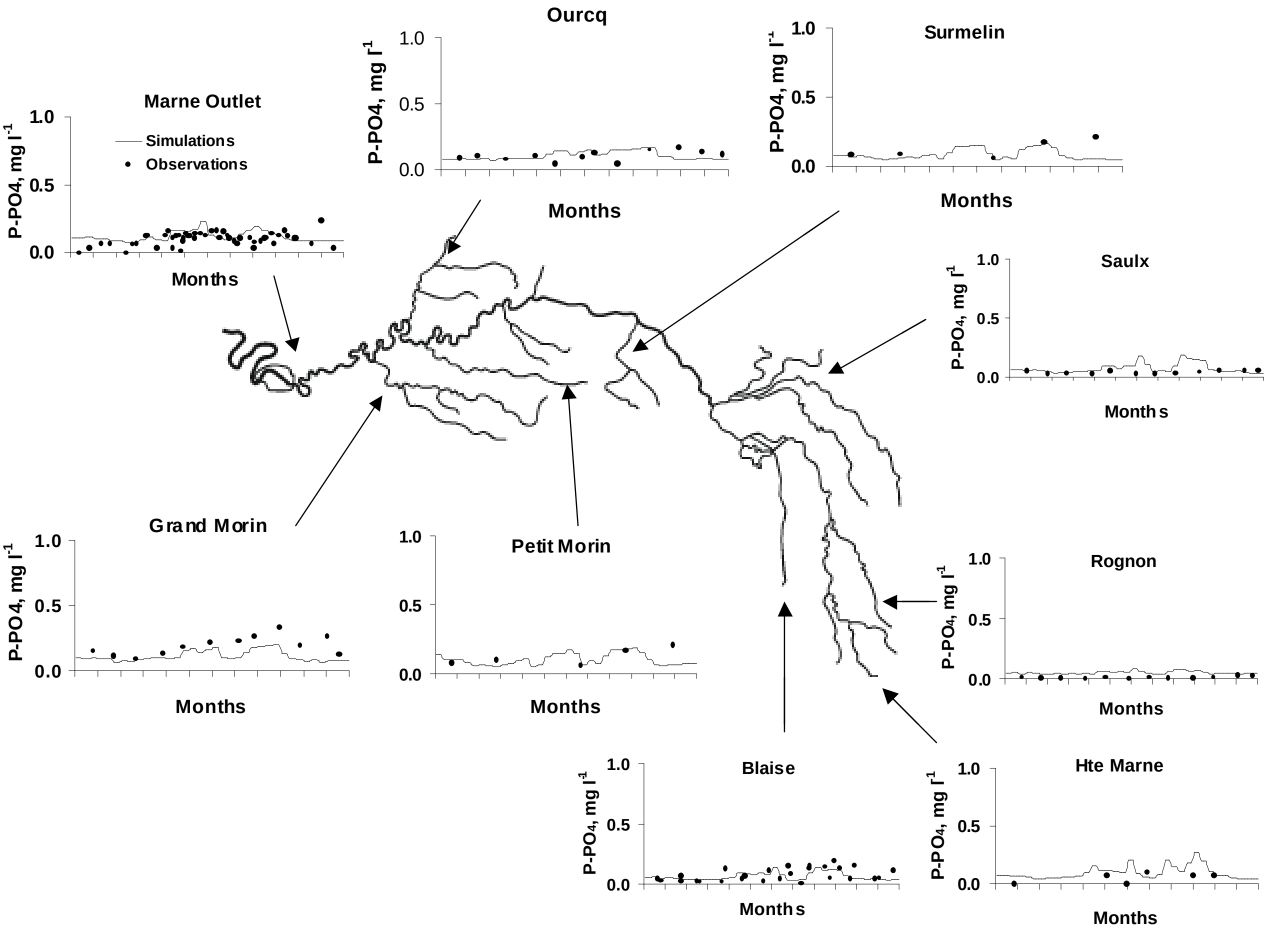

Figure 7. Seasonal variations of phosphates at the outlet of the sub-basins as taken into account in the model of the Marne, for the year 2000.

Nutrient budgets

The model can calculate nutrient budgets at the scale of the Marne basin, taking into account (i) the diffuse and point source fluxes used by the model as constraints (see above), and (ii) the calculated fluxes at the outlet of the Marne basin (Table 2).

The difference gives an insight into the retention within the drainage network and includes the retention within the Marne reservoir (Garnier et al., 1999; Garnier et al., 2000).

***Table 2**. Mean annual fluxes of suspended solid (SS.) and nutrient fluxes (Total phosphorus: Total P; phosphate: P-PO4; Dissolved silica DSi:; Total nitrogen: Total N: Nitrates: N- NO3) in the Marne basin for dry (1991,*

1992, 1993) and wet (1999, 2000, 2001) years. The balance is calculated as the difference between the fluxes at the outlet of the Marne river and the sum of the fluxes of diffuse and point sources. The ratio of the balance to the in-fluxes, given as a percentage, represents the retention in the drainage network (% retention).

Fluxes	**SS** *10 ^{3}Tons y^{-1}*		**Total P** *10 ^{3}Tons P y^{-1}*		**P-PO4** *10 ^{3}TonsP y^{-1}*		**DSi** *10 ^{3}TonsSi y^{-1}*		**Total N** *10 ^{3}TonsN y^{-1}*		**N-NO3** *10 ^{3}TonsN y^{-1}*	
	Dry	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*	*Dry*	*Wet*
Diffuse	204	250	0.35	0.44	0.24	0.31	15.3	19.3	20.9	26.2	20.5	25.7
Point	9	6	0.97	0.45	0.79	0.37	0	0	2.6	3.4	0.35	1.8
Marne R. outlet	83	147	0.97	0.66	0.88	0.54	11.4	17.9	18.0	28.4	16.1	27.0
balance	*- 130*	*-109*	*-0.35*	*-0.23*	*-0.16*	*-0.14*	*-3.9*	*-1.4*	*-5.5*	*-1.2*	*-4.7*	*-0.5*
% retention	**61**	***43***	**26**	***25***	**15**	***21***	**26**	***8***	**23**	***4***	**23**	***2***

For any variable considered, the retention percentages, as calculated by the model, are logically lower in wet years, when the residence time is short and does not favour the processes of sedimentation, nutrient uptake by the algae or microbial activity such as denitrification. Nitrogen fluxes are dominated by nitrates of diffuse origin (90 % of total nitrogen) and phosphorus fluxes by phosphates (80 % of total phosphorus for both diffuse and point sources). Whereas the differences in retention percentages between wet and dry years are large for suspended solids, silica and nitrogen, the differences in phosphorus retention are comparatively small between the years, in the range of 15-25 %. It is interesting to note that, during dry years, P point sources were almost three times greater than P diffuse sources, due to the improvements in wastewater treatment. During wet years, diffuse sources of P are only 20 % greater than during dry years. Diffuse and point source P fluxes are presently quantitatively similar in accordance with the figures presented by Némery et al. (submitted) who used a budgeting approach based only on observations. However, as opposed to this approach, which leads to an even partition of particulate and dissolved phosphorus fluxes at the outlet of the Marne basin, the model calculates a dominance of the dissolved form.

The model does not take into account any silica point sources, which were considered few as compared to the diffuse ones (Garnier et al., in press).

5. Reducing eutrophication in the Marne

Nutrient limitation

The values chosen for the model for the half-saturation constant of nutrient uptake by the dominant algae are 14 µgN l^{-1} for both the diatoms and the Chlorophyceae, 46.1 µg P l^{-1} and 7.1µg P l^{-1} for the diatoms and the Chlorophyceae respectively, and 0.12 mg Si l^{-1} for the diatoms that incorporate silica to build up their frustule (Garnier et al., 1995; Garnier et al., 1999). Given the concentrations observed in headwaters, phosphate seems to be the factor limiting algal development. When the specific maximum photosynthesis rate (PBm: µgC µg Chl*a*$^{-1}$ h^{-1} : ^{14}C, Steeman-Nielsen, 1952) was measured in surface water of the Marne River in natural and P-enriched conditions, there is a clear P-limitation in the sub-basins and in the reservoir, while the effect of P enrichment has already disappeared in middle of the main branch of the Marne (Figure 8). Others nutritional factors (N, Si) and energetic environment (light, temperature) were unlimited (Garnier et al., 2000).

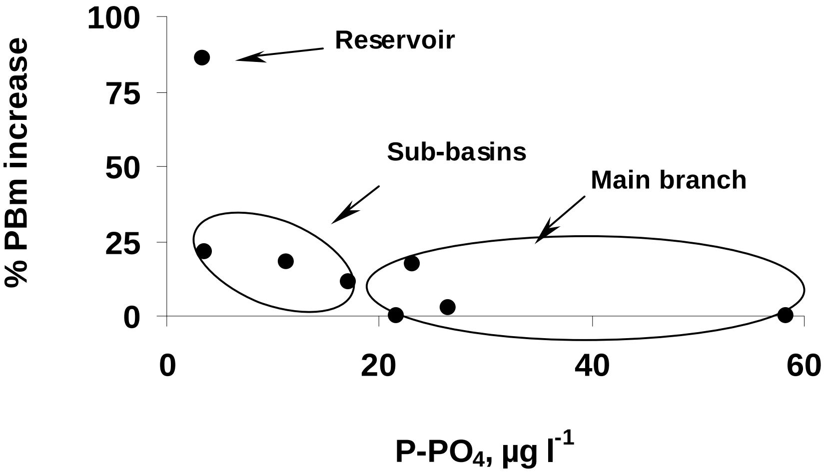

Figure 8. Increase of the specific maximal photosynthesis rate (PBm: µgC µg Chla^{-1} h^{-1}) measured on enriched water at various sites of the Marne river (PBm enriched – PBm in situ/ PBm in situ, given in percentage (%). P-PO$_4$ is the natural concentrations at the experimental sites, N and Si being were set at non limiting concentrations, generally found in the rivers (N = 6 mgN l^{-1}, Si = 6 mg Si l^{-1}). With enrichment, P equal 100 µg l^{-1}.

When the P concentration is far above the half saturation constant as it is the case at the outlet of the Marne river, silica may become the limiting factor for diatoms. According to Redfield (1958), Redfield et al. (1963), and Conley & Kilham (1989), the ratio between these nutrients is relatively constant and illustrates the true requirement of the algae. Thus, the N:P:Si ratios in the water are compared with those of the organisms to define nutrient limitations (C/N = 5.68 g.g^{-1}, N/P = 7.2 g.g^{-1}, C/P = 41 g.g^{-1}; Si/C = 0.98 in g.g^{-1}). The seasonal evolution of these ratios determines the ecological succession of the species (Tilman et al., 1982). In the model, these ratios are used to take into account the limitation of the phytoplankton by nutrients but also to calculate the seasonal and spatial dynamics of these elements.

Effect of the hydrology

Once the model is validated, it can be used to explore various controlling factors of phytoplankton development. The effect of hydrological variations as well as the phosphorus loading from both point and diffuse sources can be explored.

When the present conditions of diffuse and point sources were applied to the hydrological conditions of 1991, the driest in our data base, phytoplankton development reached values similar to those really observed for the year 1991, before the reduction in point sources (Figure 9). This result shows that, in hydrological conditions that are not extreme, the hydrosystem remains eutrophic, despite the reduction of the point sources by a factor of 3. Phytoplankton biomass can reach 80 µg Chl*a* L^{-1}, as the phosphorus concentration is higher due to the weaker dilution of the point inputs by low water flow.
These results tend to show that further or additional P treatment efforts are needed to prevent phytoplankton development.

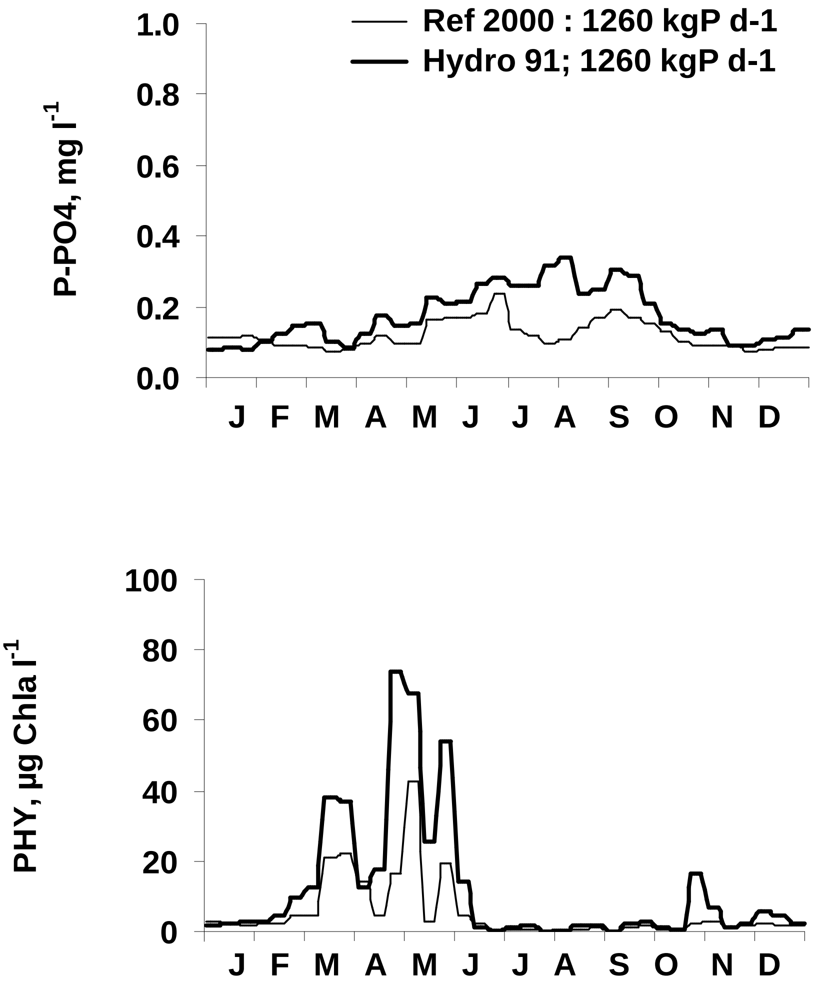

Figure 9. Seasonal variations in phosphate concentrations and phytoplankton biomass (given in chlorophyll a concentrations) for the actual year 2000 and the year 2000 with the dry hydrological conditions of 1991 (point and diffuse sources from 2000).

Effect of phosphorus reduction

Recently constructed wastewater treatment plants in the Seine basin (e.g. the Colombes treatment plant downstream from Paris), using advanced tertiary treatment technology are able to reduce the specific phosphorus load to less than 0.2 gP.inhab^{-1}.d^{-1} (Garnier et al., submitted). A value of 0.15 gP.inhab^{-1}.d^{-1} in the discharge of all WWTPs in the Marne would decrease the point load from the present one of 1260 kgP d^{-1} in 2000 to 200 kgP d^{-1}. The lower P value has a significant effect on phytoplankton biomass, which remains however as high as 60 µg Chl*a* l^{-1} during the spring bloom (Figure 10a).

It appears clearly from these results that action aimed solely at the point sources is not sufficient to completely prevent eutrophication. A further test by the model consisted in reducing diffuse sources of phosphorus. For that purpose, we reduced by a factor of 2 the phosphate concentrations in surface and groundwater runoff and considered an additional 50 % riparian retention of suspended solids. In these conditions, the spring bloom falls below 40 µg Chl*a* l^{-1} (Figure 10b).

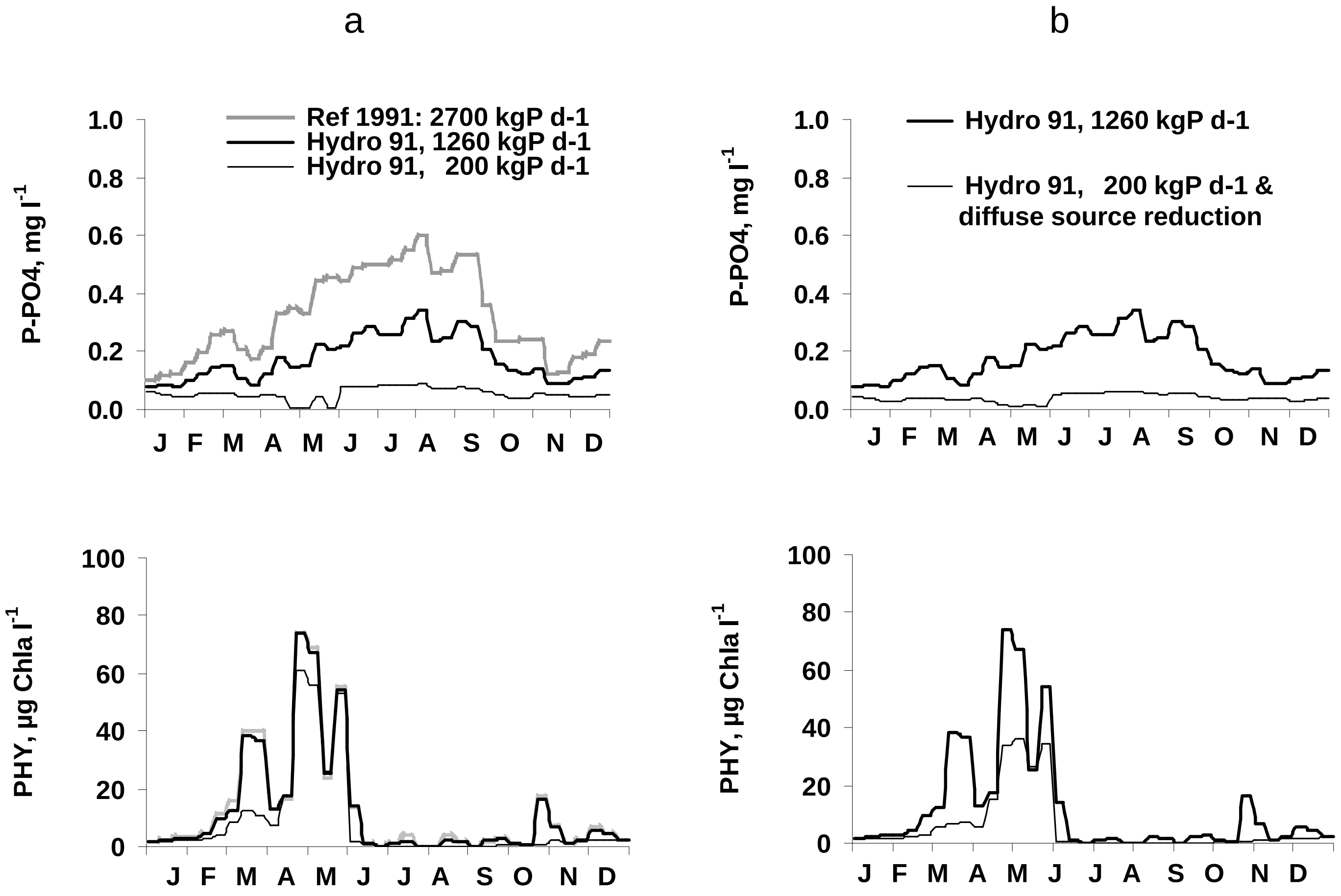

Figure 10. a) Response of the model to a reduction of point source phosphorus in the hydrological conditions of 1991 (2700 kg P d^{-1}: phosphorus load in 1991, 1260 kg P d^{-1}: phosphorus load in 2000; 2000 kg P d^{-1}: further reduction tested). b) response of the model to a further reduction of diffuse sources of phosphorus. Upper panel: variations in the phosphorus concentrations; lower panel: variations in the phytoplankton biomass levels given in chlorophyll a concentrations.

6. Discussion

Most large European rivers are eutrophicated due to nutrient enrichment by both point and diffuse sources with increasing population density along their course and agriculture intensification. A voluntary scheme of point sources has not always succeeded in decreasing eutrophication (Raïke et al., 2003).

In the Marne basin, as well as in the main branch of the upstream Seine and Oise rivers, algal development during low water causes problems for drinking water production (de Dianous et al., 1995). Note that in small streams of the some sub-basins (the Grand Morin for example), periphyton can form large biomasses able to deplete oxygen during storm events, when the biomass swept away by storm consumes more oxygen than what is produced (Flipo, 2001). Macrophytes development occurring in about 10 % of the length of the rivers in the upstream basins have not been shown to influence the ecological functioning (Garnier et al., 2001; Garnier et al., 2002).

Eutrophication by phytoplankton remains a major problem in dry hydrological conditions. As shown by our model, dry years e.g. those at the beginning of the 1990s (as well as 2002 and 2003) were characterised by algal spring blooms that threatened drinking water production, even after the implementation of drastic programmes of point source reduction down to 85% of the present loading, which had already been reduced to 65% of the 1990 level. Diffuse phosphorus sources from agriculture are not negligible, especially because a high proportion of particulate phosphorus originating from soil erosion is exchangeable with the dissolved phase (Némery et al., subm) and available for phytoplankton growth (Figure 11). Phosphorus reduction in WWTPs, has a significant effect in reducing river eutrophication, and preventing harmful algal blooms in coastal marine zones (Cugier et al., subm, this volume), but it is not sufficient to completely control freshwater eutrophication; it must be accompanied with measures to reduce diffuse sources linked to agricultural leaching and erosion.

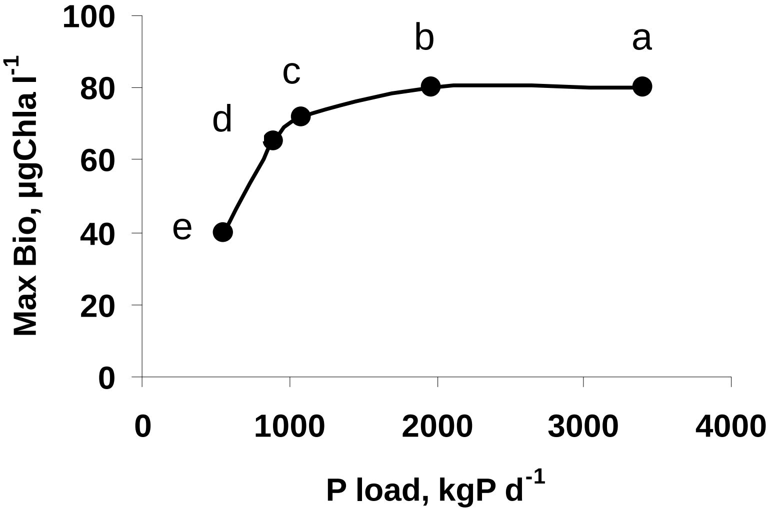

Figure 11. Relationship between maximum phytoplankton biomass and phosphorus load (point sources + diffuse sources) as calculated by the Riverstrahler model. Hydrological conditions are those of the dry year 1991. P load is the sum of diffuse sources (700 kg P d^{-1}, for the whole period considered) and point sources. ***a*** *: Point sources of 1991 + present diffuse sources;* ***b*** *: Point sources of 2000 + present diffuse sources;* ***c*** *: Reduced point sources of 2000 to 0.2 gP treated inhab equ^{-1} d^{-1} + present diffuse sources;* ***d*** *: Reduced point sources of 2000 to 0.15 gP treated inhab equ^{-1} d^{-1} + present diffuse sources;* ***e*** *: Reduced point sources of 2000 to 0.15 gP treated inhab equ^{-1} d^{-1} + 50 % reduction of diffuse sources. Maximum effect on phytoplankton biomass is obtained by reducing both point and diffuse sources.*

In this respect, the high (and increasing) content of phosphorus in agricultural soil constitutes a long term threat for water quality. Particulate phosphorus from the soil can be directly transferred to surface water through erosion and exchanged with the water column. This can be mitigated by suitable landscape-based measures such as buffer strips (Withers and Jarvies, 1998; Jordan-Meille et al, 1998; McDowell et al., 2003; Pieterse et al., 2003). Even so, a relatively high dissolved phosphate content is acquired by drainage water due to the high exchangeable phosphorus content in soil particles. This dissolved contamination is more difficult to prevent, as anaerobic riparian zones, able to reduce agricultural nitrate contamination (Hill, 1996; Hanson et al., 1994), are inefficient in retaining phosphorus (Richardson, 1985).

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7. References

Admiraal W., Breugem P., Jacobs D.M.L.H.A. & de Ruyter Van Steveninck E.D. (1990). Fixation of dissolved silicate in the lower river Rhine during diatom blooms. Biogeochemistry, 9: 175-195.

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

Barrow N.J. (1978). The description of phosphate adsorption curves. J. Soil Sci., 29: 447-462.

Billen G., Garnier J. & Meybeck M. (1998). Les sels nutritifs: l'ouverture des cycles. Chapitre 12. In: La Seine en son bassin Fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., De Marsily G & Fustec F. eds). Elsevier, Paris. p. 531-565.

Billen G., Garnier J. & Hanset Ph. (1994). Modelling phytoplankton development in whole drainage networks: the RIVERSTRAHLER model applied to the Seine river system. *Hydrobiologia*, 289:119-137.

Billen G. & Garnier J. (1999). Nitrogen transfers through the Seine drainage network: a budget based on the application of the Riverstrahler model. *Hydrobiologia, 410: 139-150.*

Billen G., Garnier J., Ficht A. & Cun C. (2001). Modelling the response of water quality in the Seine Estuary to human activity in its watershed over the last 50 years. Estuaries, 24 (6): 977-993.

Billen G., Garnier J. & Rousseau V. (submitted). Nutrient fluxes and water quality in the drainage network of the Scheldt basin over the last 50 years. Hydrobiologia.

Bultot F. & Dupriez G. (1976). Conceptual hydrological model for an average-sized catchment area. J. hydrol., 39:251-292.

Chardon W.J. and Blaauw D. (1998). Kinetic Freundlich equation applied to soils with a high residual phosphorus content. Soil Science, 163: 30-35.

Conley D.J. & Kilham S.S. (1989). Differences in silica content between marine and freshwater diatoms. Limnol. Oceanogr. 34(1): 205-213.

Conley D., Schleske C. & Stoemer E. (1993). Modification of the biogeochemical cycle of silica with eutrophication. Mar. Ecol. Prog. Ser., 101:179-192.

Cugier Ph., Billen G. , Guillaud, J.F., Garnier, J. & Ménesguen A. (This volume, submitted). Modelling the eutrophication of the Seine Bight (France) under historical, present and future riverine nutrient loading. J. Hydrol.

De Dianous F., Billen G. Garnier J, Hanset Ph., Jovy V., Grimaud A. & Vandevelde T. (1995). Algarde-Oise : un modèle opérationnel pour la prédiction des variations de qualité des eaux lors d'efflorescences algales. Techniques Sciences Méthodes, 1995 : 55-59.

Eberlein K. & Katter G. (1984). Automatic method for the determination of orthophosphate and dissolved

Flipo N. (2001). Site Atelier du Grand Morin : modélisation biogéochimique et étude d'un compartiment benthique. Mémoire du DEA Hydrologie, Hydrogéologie, Géostatistique et Géochimie, Ecole des Mines de Paris.

Garnier J., Billen G. & Coste M. (1995). Seasonnal succession of diatoms and Chlorophyceae in the drainage network of the river Seine: Observations and modelling. *Limnol. Oceanogr.* 40: 750-765.

Garnier J., Billen G., Hanset Ph., Testard P. & Coste M. (1998). Développement algal et eutrophisation. Chapitre 14. In: La Seine en son bassin Fonctionnement écologique d'un système fluvial anthropisé (Meybeck M., De Marsily G & Fustec F. eds). Elsevier, Paris. p. 593-626.

Garnier J., Billen G. & Palfner L. (1999). Understanding the oxygen budget od the Mosel drainage network with the concept of heterotrophic/autotrophic sequences: the Riverstrahler approach. *Hydrobiologia, 410: 151-166.*

Garnier J., Leporcq B., Sanchez N. & Philippon X. (1999). Biogeochemical budgets in three large reservoirs of the Seine basin (Marne, Seine & Aube reservoirs). Biogeochemistry, 47: 119-146.

Garnier J., Billen G., Sanchez N. & Leporcq B. (2000). Ecological functioning of the Marne Reservoir (Upper Seine Basin, France). Regulated Rivers: Research & Management, 16: 51-71.

Garnier J., Dufayt O., Billen G. & Roulier M. (2001). Eutrophisation et gestion des apports de phosphore dans le bassin de la Seine. Colloque "Scientifiques & Décideurs : agir ensemble pour une gestion durable des systèmes fluviaux". Lyon (France), 2001. CD-ROM. 8 p.

Garnier J., Billen G., Hannon E., Fonbonne S., Videnina Y. & Soulie M. (2002). Modeling transfer and retention of nutrients in the drainage network of the Danube River. Estuar. Coast. Shelf Sciences, 54: 285-308.

Garnier J. & Billen G. (2002). The Riverstrahler modelling approach applied to a tropical case study (The Red -Hong- River, Vietnam): nutrient transfer and impact on the Coastal Zone. SCOPE, Coll. Mar. Res. W., 12: 51-65.

Garnier J., d'Ayguesvives A., Billen G., Conley D. & Sferratore A. (2003). Silica dynamics in the hydrographic network of the Seine River. Océanis: in press.

Garnier J., Laroche L. & Pinault S. (submitted). Characterization of the effluents of two large waste water plants of the city of Paris (France): how to comply with the European directive. Water Research.

Hanson G.C., Groffman P.M. & Gold A.J. (1994). Denitrification in riparian wetlands receiving high and low groundwater nitrate inputs. J. Environ. Qual. 23: 917-922

Jordan-Meille L., Dorioz J.M. & Wang D. (1998). Analysis of the export of dissfuse phosphorus from small rural watershed. *Agronomie* 18:5-56

Le Thi Phong Q., Garnier J., Billen G. & Théry S (2003). Application of the Riverstrahler model to the Red River. Euro-Asia conference. 10/2003. Proceedings: in press.

Meybeck M. (1986). Composition chimique des ruisseaux non pollués de France. Sci. Géol. Bull. 39: 3-77.

McDowell R.W., Sharpley A.N. & Folmar G. (2003). Modification of phosphorus export from an eastern USA catchment by fluvial sediment and phosphorus inputs. Agr. Ecosyst. & Environ. 99:187-199.

Morel C., Schneider,A., Plénet D. & Fardeau J.C. (2002). Transfer of phosphorus in soil-plant and soil-solution systems using isotopic labelling and dilution methods. In: Nuclear Techniques in integrated plant nutrient, water and soil management (pp 49-56). International Symposium, Vienna, 16-20 October 2000, Joint FAO/IAEA Division Vienna. C&S Papers Series 11/C.: p486.

Nalewajko C. & Lean D.R.S. (1980). Phosphorus: 235-258. In: the Physiological Ecology of Phytoplankton. I. Morris (ed). Blackwell Scientific Publication, Oxford.

Némery J., Garnier J. & Morel C. (submitted). Phosphorus budget in the Marne watershed (France): urban *vs*. diffuse sources, dissolved *vs.* particulate forms. Biogeochemistry.

Némery (2003). Origine et devenir du phosphore dans le continuum aquatique de la Seine, des petits basins à l'estuaire. Rôle du phosphore échangeable sur l'eutrophisation. Thèse Univ. Paris 6, XXXp

Piterse N.M., Bleuten W. & Jorgensen S.E. (2003). Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. J. Hydrol. 271: 213-225.

Räike A., Piettiläinen O.-P., Rekolainen S., Kauppila P., Pikänen H., Niemi J., Raateland A. & Vuorenmaa J. (2003). Trends of phosphorus, nitrogen and chlorophyll a concentrations in Finnish rivers and lakes in 1975-2000. The Sci. Tot. Environm., 310: 47-59.

Redfield A.C. (1958). The biological control of chemical fators in the environment. Am. Sci. 46: 205-222.

Redfield A. C., Ketchum B. H. & Richards F. A. (1963). The influence of organisms on the composition of sea-water. In M. N. Hill (ed.), The Sea, John Wiley & Sons, New York, p. 12-37.

Richardson C.J (1985). Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228:1424-1427.

Rodier J. (1984). L'analyse de l'eau. 7ème édition. Dunot (ed). 1365 p.

Sebilo M., Billen G., Grably M. & Mariotti A. (2003). Isotopic composition of nitrate-nitrogen as a marker of riparian and benthic denitrification at the scale of the whole Seine River system. Biogeochemistry, 63: 35-51.

Sommer U., Gliwitcz M., Lampert W. & Duncan A. (1986). The PEG-model of succession of planktonic events in fresh waters. Arch. Hydrobiol. 106: 433- 471.

Steeman-Nielsen E. (1952). The use of radioactive carbon (14C) for measuring organic production in the sea. J. Cons. Perm. Expl. Mer., 18: 117-140.

Strahler A.H., 1957. Quantitative analysis of watershed geomorphology. Geophys. Union Trans. 38: 913-920.

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

Tilman D., Kilham S.S. & Kilham P. (1982). Phytoplankton community ecology : The role of limiting nutrients. Ann. Rev. Ecol. Syst. 13: 349-372.

Trifu M.C. (2002). Transfert des nutriments dans le Bassin du Danube et les apports à la Mer Noire. These Université Paris 6, Paris (France). 145 p.

Withers P.J.A & Jarvies S.C. (1998). Mitigation options for diffuse phosphorus loss to water. *Soil Use and Management* 14: 186-192