

River basin nutrient delivery to the coastal sea: Assessing its potential to sustain new production of non-siliceous algae

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Abstract

The amount of nutrients (N, P, Si) carried to the coastal zone by large river systems, as well as the balance between these elements, are the major determinants of coastal marine eutrophication problems. Many of these problems are the consequence of the *new* production of non-siliceous algae, sustained by nitrogen and phosphorus delivered by rivers in excess over dissolved silica, in regard to the requirements for diatom growth.

Besides their N:P:Si ratios, an indicator of coastal eutrophication potential (ICEP) of riverine nutrient inputs is proposed. It represents the carbon biomass potentially produced in the receiving coastal water body through *new* production sustained by the flux of nitrogen or phosphorus (according to which one is limiting with respect to the other) delivered in excess over silica. For the purpose of a river to river comparison, it is expressed by unit of watershed area, in $\text{kg C km}^{-2} \text{ day}^{-1}$.

This indicator reaches high, positive values in many temperate European and North American river systems known to cause severe eutrophication problems in their receiving coastal zones, while it remains at negative values for pristine Nordic rivers as well as for most (sub-)tropical river systems.

The analysis of reconstructed past scenarios of the biogeochemical functioning of the Seine and Scheldt river systems, as well as a number of retrospective studies carried out for other river systems under temperate conditions and strong human influence, shows that both nitrogen and phosphorus were delivered to the coastal zone in excess over silica as soon as the beginning of the 19th century. The period 1950–1990 was the worst in terms of unbalanced nutrient delivery to the coastal zone. Since the 1990's, phosphorus fluxes have decreased very rapidly, largely as a result of improved urban wastewater treatment and concomitant banishment of polyphosphates in the washing powders, while nitrogen delivery still remains at high levels as a consequence of intensive agricultural practices, creating an unprecedented biogeochemical situation in the coastal zone, with low phosphorus but high nitrogen contamination.

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1. Introduction

Increased nutrient delivery to the coastal ocean, a consequence of the opening of the nitrogen and phos-

phorus cycles at the global scale (Green et al., 2004; Seitzinger et al., 2002), is now recognized as a major threat for the structure and function of nearshore coastal ecosystems (Nixon, 1995; Smayda, 1990; Cloern, 2001). In the plume area of large rivers draining heavily populated or intensively cultivated watersheds, the increased nutrient loading has resulted in severe eutrophication problems. The manifestation of these

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problems may be quite diverse according to the local physiographical and hydrological conditions of the coastal area: blooms of toxic algae, as in the Seine Bight (Cugier et al., 2005), massive development of mucilaginous, unpalatable, algal species as in the North Sea (Lancelot et al., 1987, 2005, 2007), the Black Sea (Cociasu et al., 1996) or the Adriatic sea (Marchetti, 1991), deposition of increased amount of organic material resulting in anoxic bottom waters as in the Gulf of Mexico (Turner and Rabalais, 1994; Rabalais et al., 1996), the Chesapeake Bay (Officer et al., 1984) and the Northern Adriatic (Justic, 1991). Deep changes in the structure of the food webs are also often observed in eutrophicated coastal marine areas, with a decline of planktonic grazing and commercial fish production (Turner et al., 1998; Rousseau et al., 2000; Dortch et al., 2001).

In spite of the diversity of the manifestations of coastal eutrophication, it is now well recognized that the basic cause of the phenomenon is related, not only to the general nutrient enrichment of the marine system, but rather to the unbalance in the delivery of nitrogen and phosphorus with respect to silica. Thus, Officer and Ryther (1980) and many other authors thereafter (Conley et al., 1993; Conley, 1999; Turner and Rabalais, 1994; Justic et al., 1995; Billen and Garnier, 1997; Turner et al., 1998; Cugier et al., 2005), have shown that many coastal eutrophication problems are the consequence of excess nitrogen and phosphorus delivery with respect to silica, compared to the requirements of diatom growth. Indeed, coastal enrichment with nutrients brought in proportion of the Redfield ratios (Redfield et al., 1963) characterizing the requirement of diatoms growth seldom results in any problem, but, on the contrary stimulates a healthy food web, as is the case in upwelling areas. In such areas, new planktonic primary production is mostly ensured by diatoms, while non-siliceous algae are restricted to regenerated production. According to this view, coastal eutrophication problems are the manifestation of *new* production of non-siliceous algae sustained by external inputs of nitrogen and phosphorus brought in excess over silica, thus in conditions where diatom growth is limited.

Irrespective of the local peculiarities of the coastal zone, its particular morphology and hydrology or its prevailing meteorological conditions, it could therefore be possible to assess the potential for coastal eutrophication of a given river from its nutrient (N, P, Si) loading. The origin of these three elements in river water, as well as their fate during their travel from land based sources to the sea, differ largely according to climate, hydrological regime, and human management

of the watershed and its drainage network, so that both the absolute amount and the relative proportions of N, P and Si delivered vary highly among rivers, and reflect the regional differences in natural forcing as well as anthropogenic influence (Billen et al., 1991). Silica in river mainly originates from rock weathering, a process which is enhanced by high temperature, moisture and active vegetation (Cochran and Berner, 1996; Conley, 2002; Humborg et al., 2006). Direct inputs through urban or industrial wastewater inputs are minor (Sferratore et al., 2006; Garnier et al., 2006). Diatom growth in rivers and reservoirs, and subsequent settling of their frustules can retain substantial amount of silica before it reaches the coastal zone; the construction of large dams has therefore resulted globally in a decreased input of silica into the coastal zone (Conley et al., 1993; Humborg et al., 2006). Phosphorus, by contrast, is massively brought into river water through urban wastewater discharge, so that point sources of P are dominant over diffuse sources linked to soil erosion and leaching in most populated river basins. Effective wastewater treatment processes are now available, on the other hand, and can considerably reduce the phosphorus riverine loading (Garnier et al., 2005). Nitrogen comes from both diffuse and urban sources, the former being often dominant in agricultural basins. Nitrogen retention by riparian and in-stream denitrification processes can be quite significant (Billen and Garnier, 1999; Sebilo et al., 2003).

Nutrient loading is now well documented for a number of large regional river systems (Meybeck, 1982, 1987; Turner et al., 2003a), making possible a comparative analysis of their potential for coastal eutrophication. On the other hand, several modelling approaches have been developed allowing relating the nutrient loading of large river systems to climate, land use and urban activities in the watershed (Billen and Garnier, 1997; Alexander et al., 2001). We recently used such an approach for reconstructing the past trends of nutrient delivery by the Seine (Billen et al., 2001, *in press*) and Scheldt (Billen et al., 2005) river systems.

In this paper we first discuss a new synthetic indicator for characterizing the potential of river systems for coastal eutrophication. We then calculate these indicators for a number of well documented river systems of various climate, land use and population densities in their watershed. Finally, based on the results of modelling approaches applied to the Seine and Scheldt river systems, as well as on similar approaches conducted by other authors, we discuss the long-term and recent changes in nutrient deliveries by large river systems under changing human pressures.

2. Characterizing riverine nutrient delivery

We will consider, after several authors (Officer and Ryther, 1980; Conley et al., 1993; Billen and Garnier, 1997), that coastal eutrophication is the consequence of unbalanced riverine nutrient inputs, with excess nitrogen and phosphorus with respect to silica, compared to the requirements of the diatom growth.

The latter may be characterized by the molar C:N:P:Si ratios 106:16:1:20. The C:N:P value is that proposed by Redfield et al. (1963). The silica content of marine diatoms is more variable according to environmental conditions. Conley et al. (1989) has shown that marine diatoms have a lower Si:C ratio than freshwater ones. Rousseau et al. (2002) described how weakly silicified diatoms species succeed to highly silicified ones during the course of a spring diatom bloom depleting dissolved silica. Overall, the ratio 106:20 for the C:Si of marine diatoms is an acceptable average value.

In order to assess the unbalance of riverine nutrient delivery we will here compare the river loading in total N, total P and dissolved silica with the Redfield ratios. Both organic (dissolved or particulate) and inorganic forms of nitrogen are rapidly available for sustaining marine primary production (Seitzinger and Sanders, 1999; Wiegner and Seitzinger, 2001) and should therefore be taken into account all together. Total phosphorus often includes, besides dissolved ortho-phosphates and organic phosphorus, a significant fraction of particulate inorganic phosphorus, a large proportion of which being desorbed and remobilized in the estuarine and marine environment (Conley et al., 1995; Nilsson and Jansson, 2002; Némery and Garnier, in press). We therefore use total P figures for our analysis. When only dissolved inorganic phosphorus data are available, we have considered that this represents 46% of total P loading, as observed by Turner et al. (2003a) for large rivers in North America. For tropical rivers with a very high suspended load, when the particulate phosphorus was not provided in the original data set, it has been calculated by considering a P content of suspended matter in equilibrium with the dissolved inorganic phosphorus concentration, according to a relationship established for the Red River (Le Thi Phuong, 2005; Le Thi Phuong et al., 2005, see Table 1). Besides dissolved silica, rivers are also carrying significant load of silica as biogenic particulate silica originating either from diatom growth in the drainage network or phytoliths eroded from the watershed soils (Conley, 1997; Conley and Schelske, 2001; Garnier et al., 2002b; Sferatore et al., 2006). This can amount up to 20% of the dissolved silica loading, but is not often routinely measured in monitoring programs (Garnier

et al., 2002b). On the other hand, the rate of redissolution of this material once discharged in the sea is rather long. In the following analysis, we will therefore neglect the particulate biogenic silica load of rivers. We admit that this might underestimate, probably by about 10%, our silica flux figures.

In addition to their N:P:Si ratio, we here define an indicator of coastal eutrophication potential (ICEP) of riverine nutrient inputs as the carbon biomass potentially produced in the receiving coastal water body based on the flux of nitrogen or phosphorus (according to which one is limiting with respect to the other) delivered in excess over silica. This indicator thus express the potential for *new* production of non-siliceous algae sustained by the riverine nutrient delivery. We express it in carbon per day, the units generally used for reporting marine primary production. For the purpose of river to river comparison, it is expressed by unit of watershed area, thus in kg C km⁻² day⁻¹. It can be calculated by the following relationships (based on the Redfield molar C:N:P:Si ratios 106:16:1:20):

$$\text{ICEP} = [\text{NFlx}/(14*16) - \text{SiFlx}/(28*20)] * 106 * 12$$

if N/P < 16 (N limiting)

(1)

$$\text{ICEP} = [\text{PFlx}/31 - \text{SiFlx}/(28*20)] * 106 * 12$$

if N/P > 16 (P limiting)

where PFlx, NFlx and SiFlx are respectively the mean specific fluxes of total nitrogen, total phosphorus and dissolved silica delivered at the outlet of the river basin, expressed in kg P km⁻² day⁻¹, in kg N km⁻² day⁻¹ and in kg Si km⁻² day⁻¹.

A negative value of the ICEP indicates that silica is present in excess over the limiting nutrient (among nitrogen and phosphorus) and thus, on the basis of our hypothesis, characterizes the absence of eutrophication problems. Positive values indicate an excess of nitrogen or phosphorus over the potential for diatom growth, thus a condition for harmful non-siliceous algal development. As defined, the ICEP does not take into account the particular conditions determining the response of the coastal zone into which the river is discharging, but simply represents the potential impact of the riverine fluxes.

The time period over which the indicator should be calculated is however a matter of discussion. According to the residence time of the freshwater masses within the coastal marine zone and the surface area of the impacted zone, the ICEP should be calculated on a daily, monthly or yearly basis. For instance, in the well documented case of the Seine Bight (Cugier et al., 2005), late summer blooms of dinoflagellates are restricted to the extreme

Table 1

Specific nutrient fluxes delivered by a number of rivers from different climatic regions of the world; calculated values of the molar N:P:Si ratios and of the indicator of coastal eutrophication potential (ICEP)

River basins	Annual nutrient delivery							Annual average		Reference	
	Watershed	Population	kg N/km ² /yr	kg P/km ² /yr	kg Si/km ² /yr	Si/N	Si/P	N/P	Lim nut		ICEP
	km ²	hab/km ²				mol:mol	mol:mol	mol:mol	kg C/km ² /day		
<i>Temperate European rivers</i>											
Rhone	101,000	101	697	142	1612	1.16	12.6	10.9	N	1	El Boukhary (2005)
Seine (1998)	73,000	195	1995	186	1080	0.27	6.4	23.8	P	14	Billen and Garnier (1999)
Somme (1996)	5566	100	911	49	438	0.24	9.9	41.2	P	3	Thieu, unpubl.
Scheldt (1978)	16,150	510	2978	389	1505	0.25	4.3	17.0	P	34	Billen et al. (2005)
Rhine (1986)	159,800	291	2791	242	1158	0.21	5.3	25.5	P	20	Lancelot et al. (1991)
Elbe (1988)	125,480	185	1785	76	940	0.26	13.8	52.2	P	3	Lancelot et al. (1991)
Daugava	84,100	33	456	14.9	411	0.45	30.5	67.8	P	-1	Humborg et al. (2006)
Vistula	194,400	121	639	31.8	768	0.60	26.7	44.5	P	-1	Humborg et al. (2006)
Oder	118,900	138	628	53.8	525	0.42	10.8	25.8	P	3	Humborg et al. (2006)
Loire (1982–1985)	115,000	63	909	50	1739	0.96	38.5	40.3	P	-5	Meybeck et al. (1988)
Morlaix River (1979–1980)	132	20	3337	64	1573	0.24	27.3	115.8	P	-3	Wafar et al. (1989)
Danube (1988–91)	817,000	95	1146	62	360	0.16	6.4	40.6	P	5	Garnier et al. (2002a)
Po (1881–1984)	70,100	228	1427	154	2267	0.79	16.3	20.5	P	3	Marchetti et al. (1989) Justic' et al. (1995)
<i>North American rivers</i>											
Potomac (1983–1988)	29,785	50	833	80	1000	0.60	13.8	23.0	P	3	Jaworski et al. (1992)
Mississippi (1981–1987)	3,221,000	20	566	33	260	0.23	8.7	37.9	P	2	Turner and Rabalais (1994) Turner et al. (2003a,b)
<i>Nordic rivers</i>											
Kemijoki	50,900	<1	129	8	1134	4.39	165.4	37.7	P	-6	Humborg et al. (2003)
Torne	34,063	1	133	8	1197	4.50	160.0	35.6	P	-7	Humborg et al. (2003)
Rane	3788	1	107	6	1118	5.23	210.0	40.2	P	-6	Humborg et al. (2003)
Pite	11,204	1	142	6	1045	3.69	190.0	51.5	P	-6	Humborg et al. (2003)
Skellefte	11,236	1	118	4	544	2.31	140.0	60.7	P	-3	Humborg et al. (2003)
Ume	26,499	1	130	7	730	2.80	118.3	42.3	P	-4	Humborg et al. (2003)
Angerman	30,640	1	143	5	719	2.52	157.0	62.3	P	-4	Humborg et al. (2003)
Indals	25,760	1	177	5	513	1.45	106.3	73.3	P	-3	Humborg et al. (2003)
Ljusnan	19,811	1	157	7	946	3.02	146.8	48.7	P	-5	Humborg et al. (2003)
Dalalven	26,908	1	198	8	835	2.10	110.5	52.5	P	-4	Humborg et al. (2003)
Lule	25,100	1.2	136	7.1	793	2.92	123.7	42.4	P	-4	Humborg et al. (2006)
Kalix	23,600	2	202	13.3	1261	3.12	105.0	33.6	P	-6	Humborg et al. (2006)
Yukon	860,000	0.07	160.5	5.6	786.8	2.45	156.6	63.9	P	-4	Telang et al. (1991)
<i>Tropical rivers</i>											
Red River (Vietnam)	156,440	192	855	325	2920	1.71	9.9	5.8	N	-5	Le et al. (2005)
Jiazhou (China)	6388	500	2802	809	2884	0.51	3.9	7.7	N	26	Liu et al. (2005)
Changjiang (China)	1,808,500	194	346	145	1365	1.97	10.4	5.3	N	-3	Zhang (1996)
Minjiang (China)	60,992		763	116	5167	3.39	49.3	14.6	N	-20	Zhang (1996)
Jiulongjiang (China)	14,741		838	75	7874	4.70	116.5	24.8	P	-41	Zhang (1996)
Zhujiang (China)	442,585	249	836	177	3004	1.80	18.8	10.5	N	-6	Zhang (1996)
Amazon (Brasil)	6,144,000	4.3	224	50	5236	11.69	116.9	10.0	N	-29	Edmond et al. (1981)
<i>Mediterranean rivers</i>											
Axios	25,000	78	952	665.2	1972	1.04	3.3	3.2	N	3	El Boukhary (2005)
Aliakmon	8700	49	782	106.2	2638	1.69	27.5	16.3	P	-4	El Boukhary (2005)
Gallikos	5000		850	37.0	2550	1.50	76.4	50.9	P	-12	El Boukhary (2005)
Pinios	9500	74	1163	175	3489	1.50	22.1	14.7	N	-4	El Boukhary (2005)
Ria de Vigo	350	5	791	42	1733	1.10	45.9	41.9	P	-6	Gago et al. (2005)

area of the Seine river plume where the suspended matter has settled out of the water column, ensuring favorable light conditions. The residence time of the water masses in the concerned sector varies from days to weeks. By contrast, in the case of the continental coastal zone of the Southern Bight of the North Sea, characterized by heavy blooms of *Phaeocystis* during late spring, the residence time of the concerned water masses is in the order of several months, and the winter pool of nutrient accumulated during the non-vegetative season is as important for determining the eutrophication conditions than the spring or summer riverine fluxes (Lancelot et al., 2005). The ICEP might therefore be defined for variable integration periods over the seasonal cycle: its mean value over both summer months and the whole year cycle are often useful to consider.

3. Assessing the coastal eutrophication potential of present river systems

We have assembled a data set of regional river systems for which the fluxes of N, P and Si delivered to the sea have been monitored from literature together with our own results (Table 1). The number of river systems for which reliable values of all three elements are documented is rather limited. The data includes 15 temperate European and North American rivers, with variable levels of anthropogenic pressure, five Mediterranean rivers, 7 sub-tropical Asian river systems and 13 nearly pristine arctic rivers. The specific values of nutrient delivery range from 450 to 3300 kg N km⁻² yr⁻¹ for nitrogen, from 50 to 390 kg P km⁻² yr⁻¹ for P and from 360 to 2200 kg Si km⁻² yr⁻¹ for silica in the temperate European and North American rivers, while the range for the pristine Nordic rivers is 100–200 kg N km⁻² yr⁻¹, 4–13 kg P km⁻² yr⁻¹ and 500–1200 kg Si km⁻² yr⁻¹. The specific fluxes of silica are significantly higher in mediterranean and sub-tropical river systems (1300–7800 kg Si km⁻² yr⁻¹). Sub-tropical rivers also show elevated values of phosphorus specific delivery.

The mean annual values of nutrient delivered have been used here to calculate the N:P:Si ratios as well as the indicator of coastal eutrophication potential according to relation (1) above. The rivers from the different parts of the world (see Table 1) distribute among distinct clusters, when plotted according the N:P and Si:N ratios of their nutrient delivery as proposed by Turner et al. (2003b), or alternatively, according to the Si:N and Si:P ratios (Fig. 1). The group of nearly pristine Nordic rivers is characterized by N:P ratios well above the Redfield values and by a substantial excess of Si over both P and N. By contrast, most

rivers from temperate Europe and North America, with high human pressure, are characterized by N:P ratios above the Redfield values, indicating an excess of nitrogen over phosphorus with respect to algal growth requirements, hence a potential P limitation of new

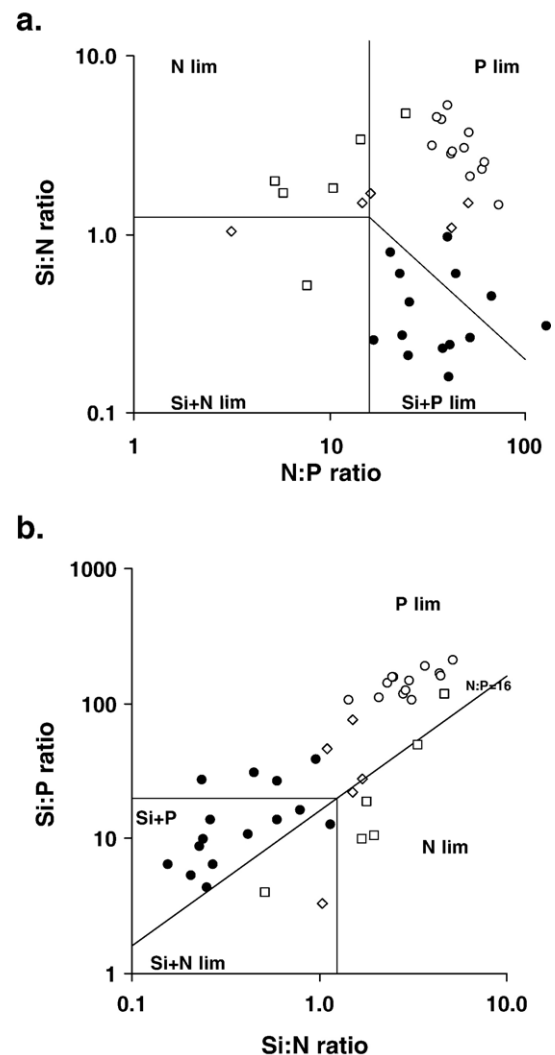


Fig. 1. Molar ratios of nutrient delivery by rivers from different climatic regions of the world: black dots: temperate European and North American rivers; white circles: pristine Nordic rivers; white square: sub-tropical rivers (see Table 1). a. Si:N vs N:P log plot. The theoretical lines separates 4 areas representing respectively, from the upper left quadrant clockwise, an area with N in limiting amounts and Si in excess, an area with P in limiting amount and Si in excess, an area with P in limiting amounts and Si deficiency, an area with N in limiting amounts and Si deficiency. b. Si:P vs Si:N log plot. The theoretical lines separate 4 areas representing respectively, from the lower right quadrant counter-clockwise, an area with N in limiting amounts and Si in excess, an area with P in limiting amount and Si in excess, an area with P in limiting amounts and Si deficiency, and an area with N in limiting amounts and Si deficiency.

primary production (Fig. 1). All of the latter also show Si:N ratios below the Redfield value of 1.25, indicating an excess of nitrogen with respect to silica. The majority of them also show a Si:P ratio below 20, indicating a shortage of silica with respect to the new production potentially to be sustained by the phosphorus inputs. Most sub-tropical rivers are characterized by N:P ratio below the Redfield value (thus indicating potential N limitation of new primary production), (Fig. 1). Within our data set, an excess of N over Si is only observed for the rivers discharging into the eutrophicated Chinese Jiazhou Bight (Liu et al., 2005). Mediterranean rivers distribute themselves between the temperate European and the sub-tropical rivers.

The calculated ICEP values summarize in an easy way these observations. ICEP is negative for all Nordic pristine rivers, while it is positive for most of the temperate European and North American rivers, many of which are known to discharge into severely eutrophicated coastal areas (Gulf of Mexico (Rabalais et al., 1996); Seine Bight (Cugier et al., 2005); Southern Bight of the North Sea (Lancelot et al., 1987, 1991); North Adriatic Sea (Justic, 1991)). The value of the indicator tends to increase with increasing population density (Fig. 2). At similar population densities, (sub)-tropical and Mediterranean rivers, which deliver higher specific flux of silica, show lower ICEP than the temperate rivers.

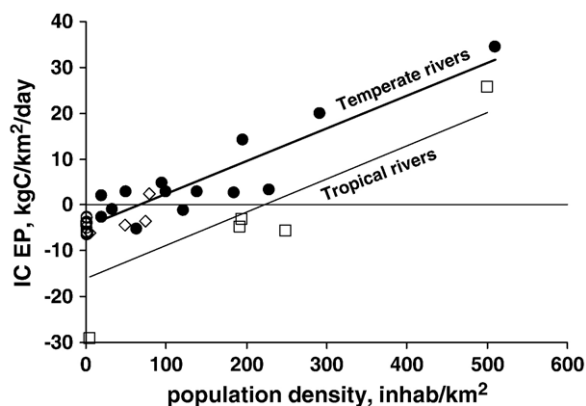


Fig. 2. Indicator of coastal eutrophication potential (ICEP) calculated for rivers from various climatic regions of the world, with different population densities. The ICEP represents the new primary production of non-siliceous algae potentially sustained by the nutrient fluxes delivered by the river. It takes negative values when silica is in excess over the N and/or P fluxes. Black dots: temperate European and North American rivers; white diamonds: Mediterranean rivers; white circles: pristine Nordic rivers; white squares: sub-tropical rivers (see Table 1). The dark line is the regression line calculated for temperate rivers only ($n=14$; $r^2=0.82$). The thin line is a parallel line fitted to the data of tropical and sub-tropical rivers ($n=5$; $r^2=0.8$).

4. Reconstructing long-term trends of nutrient delivery by man-impacted river systems

Previous work on the Seine (Billen et al., 2001) and on the Scheldt (Billen et al., 2005) river systems have permitted to reconstruct the changing anthropogenic constraints in their watershed over the last 50 years. For the former system, this analysis has been recently extended back to the 10th century (Billen et al., in press). This reconstruction made it possible to model the long-term changes of nutrient delivery to the coastal zone for these two contrasting river systems. For both cases, a pristine situation was considered as well, assuming complete forest cover of the basins and no hydraulic regulation. A prospective scenario, corresponding to the application of the European Water Framework Directive (WFD, 2000) was also established. This scenario involves a 90% abatement of phosphorus, and a 70% abatement of nitrogen, from all urban wastewater inputs by 2015.

In order to separate the variations caused by hydrology from those resulting from direct anthropogenic constraints, the reconstructed human pressure scenarios have been run with three different hydrological regimes, corresponding to wet, average and dry situations respectively. For the recent years, the results are compared with the measured fluxes (Fig. 3). From these data the N:P:Si ratios (Fig. 4) and the ICEP (Fig. 5) were also calculated on the basis of total annual flux values.

For both river systems, the pristine reconstruction shows low N and P fluxes, with an N:P molar ratio higher than the Redfield ratio. Silica delivery is logically slightly higher than the present level, owing to the lack of Si retention (no algal blooms, no reservoirs) within the drainage network. As soon as traditional agriculture becomes the dominant land use (i.e. as early as the 10th century in Western Europe), the nutrient fluxes delivered by the Seine basin are considerably altered, with a large increase in nitrogen leaching and in phosphorus losses from soil leaching and erosion, although phosphorus increases to a lesser extent. Enhanced diatom production within the river system (including in small ponds established everywhere in the rural landscape) provokes a significant silica retention. All this leads to notably decrease the Si:N and Si:P ratios (Billen et al., in press), but the ICEP remains at negative values.

The first phase of urbanization and industrialization characterizing the period from the beginning of the 19th to the mid of the 20th century shows an increase of the phosphorus fluxes and a decrease of the N:P ratios. The ICEP value increases and reaches positive values.

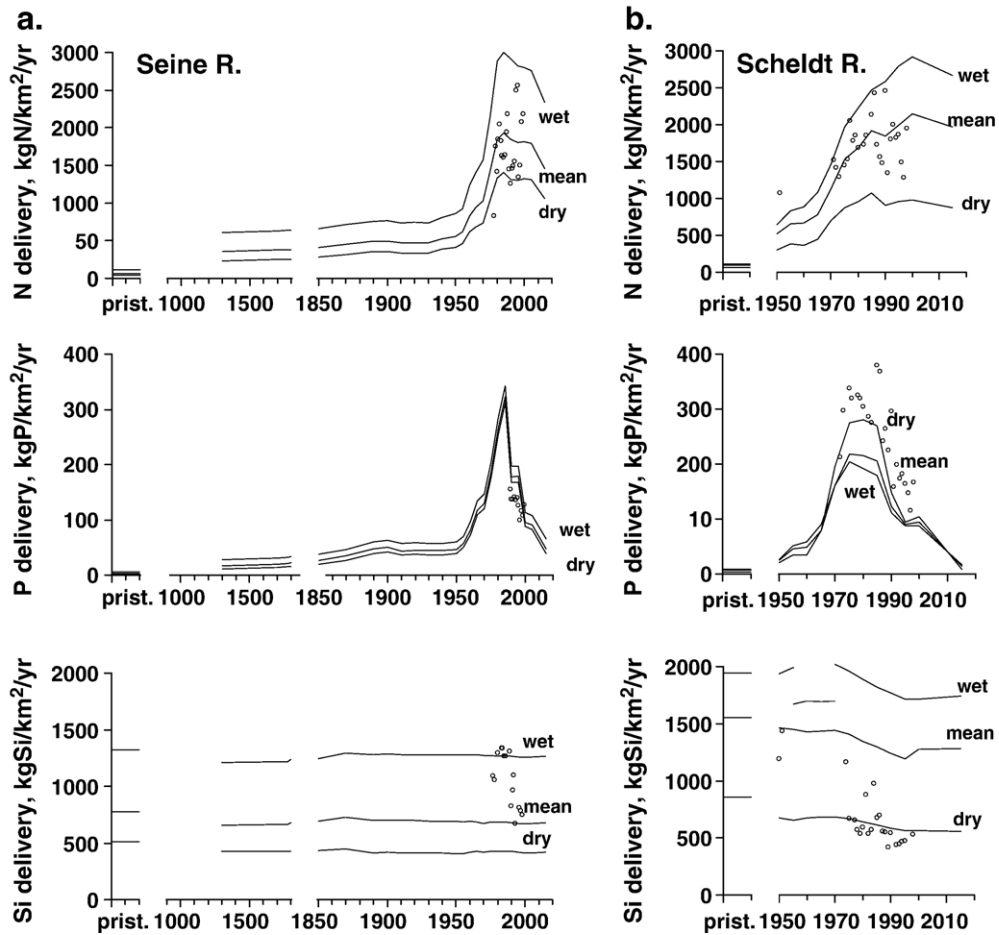


Fig. 3. Reconstitution by the Riverstrahler model of the annual fluxes of N, P and Si delivery by the Seine (a) and Scheldt (b) river systems for historical scenarios of anthropogenic constraints from the pristine state to 2015, considering dry, mean and wet hydrology respectively (Billen et al., 2005, in press). For recent periods, the calculated annual fluxes are compared with fluxes derived from the observations of discharge and concentrations of the elements.

From the 1950's to the 1990's, both the Seine and the Scheldt basins shows an accelerated increase of nitrogen and phosphorus fluxes, linked to the combined effect of three causes (Billen et al., 2001, 2005, in press): (i) the generalization of modern intensive agriculture, involving the massive use of synthetic fertilizers, resulting in increased rate of nitrate contamination of both surface and ground water; (ii) the introduction of polyphosphates containing washing powders which resulted in a 3–4 fold increase of domestic P-release; (iii) the generalization of urban wastewater collection and the lack of efficient nutrient treatment, which resulted in increased point discharge of nutrients. This period is characterized by a general decrease of the N:P ratio of nutrient delivery to the coastal environment, with nitrogen becoming limiting with respect to phosphorus,

and a further decrease of the Si:N ratio, leading to a considerable increase of the ICEP. This period is the one when the perception of coastal eutrophication problems reached a maximum in Western European coastal zones, even if historical records of their previous occurrence have been traced back to the end of the 19th century (Cadée and Hegemann, 1991; Marchetti, 1991; Billen et al., 1999), in accordance to the trends calculated here.

Since the late 1980's, it seems that the Seine and Scheldt basins enter a new period. Improved wastewater treatment considerably reduces phosphorus and, to a lesser extent, nitrogen point sources. However, diffuse sources of nitrogen from agricultural soil leaching and contaminated aquifers remain prevalent, owing to a lack of appropriate agro-environmental measures. This results in a considerable change in nutrient delivery to

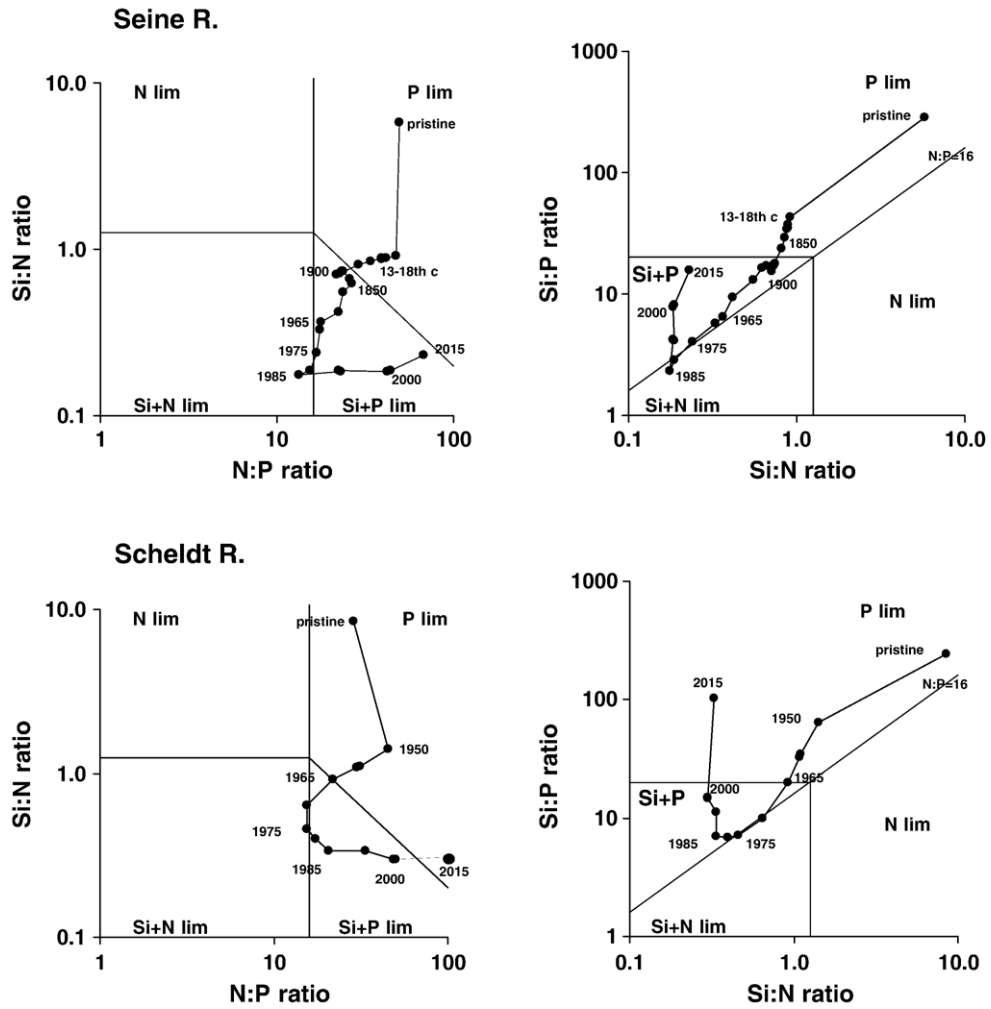


Fig. 4. ‘Trajectories’ of the Seine and Scheldt river systems within the Si:N vs. N:P and Si:P vs. Si:N diagrams along the different scenarios of the reconstituted long-term variations of anthropogenic constraints, under median hydrological conditions.

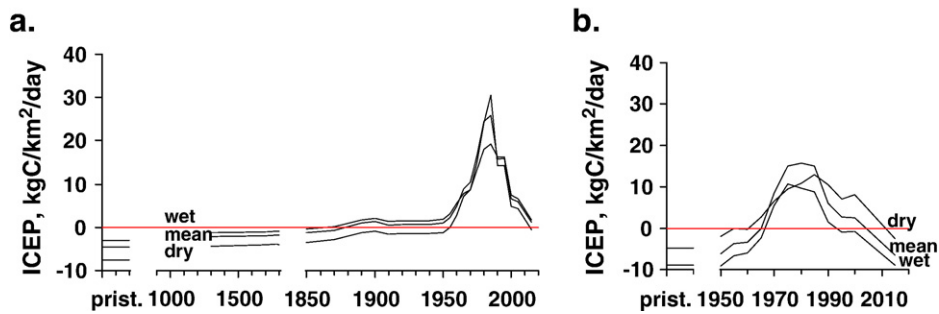


Fig. 5. Long-term variations of the Indicator of Coastal Eutrophication Potential (ICEP) calculated from the results of the Riverstrahler model for historical scenarios of anthropogenic constraints for the Seine (a) and the Scheldt (b) river systems, for three (dry, mean and wet) hydrological conditions (cf. Fig. 3). Note that for the Scheldt in the years 1970 to 1990, the calculated ICEP is lower under mean hydrological conditions than under the extreme ones (dry and wet). The reason is that N is limiting over P under dry conditions, while the reverse is true for mean and wet conditions. Should P be limiting under dry conditions, the ICEP values under dry conditions would have been higher.

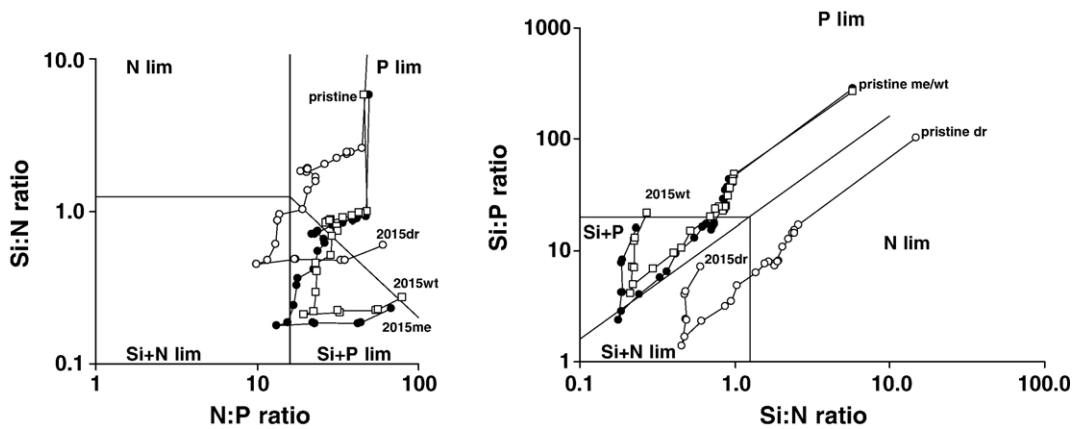


Fig. 6. ‘Trajectories’ of the Seine river systems in the Si:N vs. N:P and Si:P vs. Si:N diagrams along the different scenarios of the reconstituted long-term variations of anthropogenic constraints, under dry (white circles), median (black dots) and wet (white squares) hydrological conditions.

the coastal zone with a shift back to phosphorus limitation of coastal new primary production. Although the amount of nitrogen delivered remains far in excess over the amount of silica available for diatom blooms, the trend is toward an increasing Si:P ratio of these inputs which, combined with P limiting conditions, might prevent the development of undesirable non-siliceous algae. The large amounts of nitrogen still delivered into the coastal zone, on the other hand, create an unprecedented situation, the consequences of which are still difficult to assess.

The trends described above are the same for all three hydrological regimes tested (mean, dry or wet), (Figs. 5 and 6). By wet conditions, fluxes of Si and N from diffuse sources increase with respect to dry conditions, while point sources of N and P remain the same. This explains the fact that N:P and Si:P ratios do

not reach as low values as under dry conditions, and that the ICEP is higher than under dry conditions when N is the limiting element, while it is lower when P is limiting. The above trends are also quite similar when the N:P:Si ratios and the ICEP are calculated based on summer values of the fluxes delivered instead of on the annual mean fluxes (Fig. 7), with, however, more frequent occurrences of nitrogen limitation.

Trends similar to those revealed by our retrospective reconstitution of the biogeochemical functioning of the Seine and Scheldt watersheds were also observed by other authors in a number of historical studies of other river basins. Thus, the general increase of N and P river loading accompanying agricultural settlement of previously nearly pristine areas has been inferred from indirect observations in the Gulf of Mexico (Turner and Rabalais, 2003), the Great Laurentian Lakes (Conley

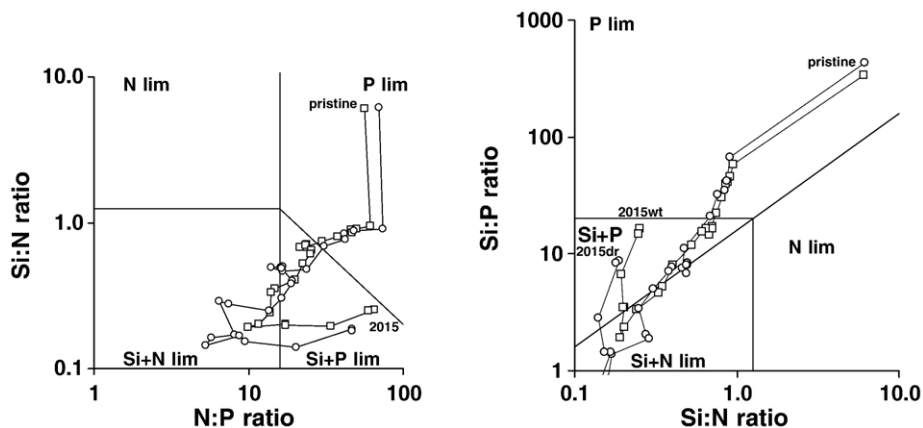


Fig. 7. ‘Trajectories’ of the Seine river systems in the Si:N vs. N:P and Si:P vs. Si:N diagrams along the different scenarios of the reconstituted long-term variations of anthropogenic constraints, under dry (white circles), and wet (white squares) hydrological conditions, during summer conditions. Only the summer low flow months (July, August, September) are taken into account for the calculations.

and Schelske, 2001). Time series analysis of direct measurements of nitrogen, phosphorus and silica in a number of river systems over the period 1960–1990 all reveal the general increase of their nitrogen and phosphorus loading and the decrease of their N:P and Si:N ratios (e.g. the Mississippi, Turner and Rabalais, 2003); the Po, Marchetti et al., 1989; Justic' et al., 1995). This trend has also been evidenced from measurements of the nutrient loading of a number of coastal systems themselves (e.g. the German Bight: Hickel et al., 1993; the Irish Sea: Allen et al., 1998; the Baltic Sea: Rahm et al., 1996; the North Aegean Sea: Trianfyfyllou et al., 2001; the Chinese Bohai Bight: Zhang et al., 1994, 2004).

The role of damming and reservoir construction in these changes, although it is rather limited in the above examples of the Seine and Scheldt rivers, can have played a much more significant role in other, severely engineered basins, by increasing retention of biogenic silica (Conley, 1999; Humborg et al., 2006).

The recent trend of a re-increasing N:P ratio, resulting from the decrease of phosphorus release from point source while non-point sources of nitrogen remains high, is also apparent in the data from other river systems than the Seine and Scheldt (e.g. the Rhine, Behrendt, 1994; the Mississippi, Turner and Rabalais, 2003).

5. Conclusion

Comparing the balance of N, P and Si delivery by rivers from different geographical regions of the world, with different levels of anthropogenic perturbations reveals trends similar to those evidenced by retrospective reconstructions of the biogeochemical functioning of individual river basins. The nutrients exported by pristine watersheds are rich in silica and low in nitrogen and phosphorus, with N:P ratios above the Redfield ones. Agriculture in the watershed, even with traditional techniques, opens the nitrogen cycle, as well as that of phosphorus although to a lesser extent, leading to increasing N:P and decreasing Si:N ratios of the nutrient delivered. Urbanization, on the other hand, because it involves direct discharge of wastewater with low N:P and Si:N ratio, tends to decrease these ratios. The recent efforts of water authorities in industrialized countries devoted to phosphorus abatement from domestic wastewater in order to limit freshwater eutrophication problems, resulted in a shift toward higher N:P and higher Si:P values, as it used to be in the past, while nitrogen contamination remains at high level.

The nutrient limitation status of a given coastal system cannot be simply inferred from the elemental

ratios of the nutrient delivered by the concerned rivers, as many other factors may control the nutrient cycles within marine coastal ecosystems. The more rapid mineralization rate of phosphorus *versus* nitrogen recycling, the storage and recycling of nutrients at the benthic phase, the possible occurrence of nitrogen fixation or denitrification, the hydrodynamical circulation and local climatic conditions, etc... are other factors to be taken into account (DeMaster et al., 1996; Garnier and Billen, 2002; Cantoni et al., 2003; Cugier et al., 2005; Lancelot et al., 2005, 2007). Identifying which is the limiting factor of primary production in a particular coastal system is therefore difficult and often controversial (Smith, 1994; Taylor et al., 1995; Howarth and Marino, 2006).

The indicator of coastal eutrophication potential (ICEP) proposed in this paper simply refers to the new primary production of non-siliceous algae which can potentially be sustained by the nutrient fluxes delivered by a river system. It thus characterizes the river basin, and not directly the receiving marine water body. From this respect, we have shown that this indicator is a useful index, summarizing as one single figure the relevant information provided both by the absolute and relative values of the nitrogen, phosphorus and silica fluxes delivered by large river systems.

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