Modelling the transfer, transformation and retention of silica along aquatic continuums: an upgraded deterministic approach

by

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I recently went to the theatre to see the monologue “Merci” (“Thanks”), written and performed by Daniel Pennac, a famous French writer. He imagined himself being the winner of a literary award, and the whole representation concerned his reflections about the moment in which, after receiving the prize, he should say ‘thanks to…’. So he was wondering whom to acknowledge first… and why, and what to do not to forget any special friends, wondering if even the order of listing would be a reason of disappointment for the concerned people.

Well, I feel a certain relief in realizing that even people like Pennac, that shouldn’t have problems in formulating the right sentences at the right moment, thought a lot about what is the best way to acknowledge…

I decided to start ‘from the beginning’, and I would like to acknowledge first of all my supervisors, Josette Garnier and Gilles Billen, for having chosen my application among the others, for this PhD position. Working with them gave me the possibility to learn a lot of new things, especially about riverine ecology, allowing me to extend my background knowledge from coastal science to far upstream, where often are located the sources of coastal environmental problems. I am also grateful to my supervisors for their generous dedication concerning the time they spent in stimulating my curiosity, and for their patience and encouragement in the less easy moments that are also part of research life.

My gratitude goes also to Michel Meybeck, for helpful discussion and critical insights into biogeochemistry, especially for what concerns global environmental issues. I am also indebted to all the PhD commission members, Christoph Humborg, Christiane Lancelot, Marianna Pastuszak, Olivier Ragueneau, Alain Saliot, for having accepted to spend some of their time in revising this manuscript. It is a sign of generosity to my opinion, when senior scientists have the kindness to spend time to help younger researchers in developing their ideas and scientific approach.

Over the past three years I had the opportunity to travel, to take part to summer schools, workshops, and congresses, and this is also thanks to the EU funding of the Si-WEBS
Research Training Network (HPRN-CT-2002-00218). Such a network, where the rule is being a student in a country that is not yours, allows participants to learn or to improve a new language, to get in touch with other cultures, all things that I consider invaluable. Moreover, the strong scientific interactions among the network members, as well as the intense work and pleasant (but few!) spare time shared with other PhD students during summer school favour the creation of strong links among young researchers, which will be certainly a basis for future collaborations. I would like then to thank all the people I met within the Si-WEBS network, young researchers and senior scientists invited to our summer schools, for the beneficial discussions and exchange of ideas. As special thank to Olivier Ragueneau, for having coordinated and animated so successfully this programme. I am also indebted to Sibyl Seitzinger for having invited me to the Global NEWS (Nutrient Export from WaterSheds) workshops held at UNESCO, and to Lars Rahm and Christoph Humborg for having involved me in some meetings of the MARE (MArine Research on Eutrophication) project; these were great opportunities to get in touch with researchers using very different modelling approaches; the brainstorming issued from these workshops led for example to the articles presented in chapters 4 and 5.

But research is not only workshops or summer schools; most of the time it consists of everyday ‘lab life’, and I am grateful to the whole UMR Sisyphe group for their warm hospitality, for having stood my ungrammatical French at my arrival, for their sympathy and encouragement, especially during the last month of this Sisyphean challenge that is finishing a PhD thesis. I felt very enjoyable the time I spent in this lab, and this thanks to all the nice people that are part of it.

Finally, I would like to thank my parents, family and friends, for their constant support and wise advices in all occasions.
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FOREWORD

The core of this Ph.D is the implementation of the silica cycle in the deterministic biogeochemical model Riverstrahler. This model allows to relate land use and water quality, representing river functioning and taking into account major nutrients (N, P, Si...) in their various forms (particulate, dissolved). After an introduction to the silica cycle in general, and its importance at the global scale, the first chapter presents the Riverstrahler model, its modifications for what concerns silica, as well as the modelling results on the Seine River basin. Successively, diffuse and point sources quantification is detailed (chapter 2) and biogenic silica dissolution is discussed (chapter 3).

Since Riverstrahler has been mostly elaborated for the temperate oceanic Seine River basin, a major concern can be: is the model generic enough to be then applied to other climates and contexts? An answer to this question can be found in chapter 4, where Riverstrahler model is applied to two Arctic climate rivers in Sweden, one pristine and the other heavily dammed. A final work consisted in testing the model output sensibility to the quality and amount of input data; a comparison of Riverstrahler results for the Seine River Basin is presented (chapter 5).

I hope that these chapters will encourage the reader to go through two other papers that are in the annex, one on physiological ecology of diatoms along the land-ocean continuum, the other on modelling silica transfer processes in river catchments.

All the presented chapters are either published, in press or submitted for publication articles.
INTRODUCTION

One may ask why silica is important, and why the need for modelling it. I hope to provide you with some good reasons and explications in this introduction, first about the importance of the silica cycle and its connections to other issues, and then about modelling.

SILICA CYCLE
Silica is, after oxygen, the second most abundant element in Earth crust, and it can be found in the environment in two forms, as dissolved and particulate (amorphous or cristalline) silica. A generic non-perturbed silica is shown in Figure 1: under the influence of climate, i.e. atmospheric events such as wind and rain, and solar energy, implying temperature variations, the silica present in rocks is weathered or eroded.

Figure 1: schematic representation of unperturbed silica cycle along the land-ocean continuum. Processes occurring along the continuum are evidenced, and the waterscape sectors in which they dominate are covered by the extent of the corresponding arrows.
Chemical weathering of silicate rock is strictly linked to atmospheric CO₂ (Berner et al. 1983; Wollast and Mackenzie, 1986; Ittekkot et al., 2003), and can be summarised by the following reactions:

\[
2 \text{CO}_2 + 3\text{H}_2\text{O} + \text{CaSiO}_3 \rightarrow \text{Ca}^{++} + 2 \text{HCO}_3^{-} + \text{H}_4\text{SiO}_4
\]

\[
2 \text{CO}_2 + 3\text{H}_2\text{O} + \text{MgSiO}_3 \rightarrow \text{Mg}^{++} + 2 \text{HCO}_3^{-} + \text{H}_4\text{SiO}_4
\]

The dissolved silica (\(\text{H}_4\text{SiO}_4\)) issued from these reactions reaches the ocean via rivers, but while passing the system it can temporarily or permanently be involved into smaller - but not less important - cycles: it can be recycled by vegetation, or be uptaken by organisms requiring silica for their growth, such as diatoms, that can themeselves be trapped and buried in lakes, reservoirs or river bottom sediment. But dissolved silica can also reach wetlands, that are active sites of nutrient recycling, or estuaries, that are major biogeochemical filters and that according to their typology (delta, macrotidal estuary, fjord etc.; Perillo, 1995) and relative characteristics (as residence time, average depth, turbidity, salinity gradient) can be a site of silica trapping, recycling or algal production.

Physical weathering concerns mostly reliefs, and it also contributes to the alteration of silicate rocks (for ex. by freeze-thaw cycles, sheeting etc.), producing particulate silica that is susceptible of taking part in the smaller cycles cited above or transported to the ocean via wind or rivers. Nevertheless not all the particulate silica that reaches the coastal zone arrives at its final destination, i.e. the ‘global ocean’, since some can be trapped in regional coastal seas that, because of their morphology, do not export particulate matter to the open ocean (Meybeck et al., submitted).

Passing from such a generic description of silica cycle to relative importance of silica sources, a special attention should be paid to the time scale at which the silica-related processes occur. From this point of view, in fact, even though weathering processes are important (since they concern all the Earth crust) and have been for long time described as the main continental source of silica for aquatic environments (Garrels, 1967; Drever, 1988), it should be pointed out that these same processes take place on geological time scales, and that particulate silica of lithogenic origin has five order magnitude slower dissolution rates than biogenic origin silica (Hurd, 1983), which means that biogenic silica is more rapidly dissolved and thus available for biological processes. For that reason, and also because the direct application and aim of this thesis are to explore silica interactions with other nutrients as possible cause of coastal eutrophication at short time scale, the lithogenic silica cycle will not be detailed.
Introduction

further, even though it is taken into account in the modelling approach presented in the next chapters by the inclusion of silica diffuse sources issued of chemical weathering.

Since few years the importance of terrestrial biogenic silica cycle has been put in evidence (Bartoli, 1983; Alexandre et al., 1997; Conley, 1997; Meunier et al., 1999; Derry et al., 2005). Dissolved silica present in soil moisture is in fact absorbed by some plant species such as herbaceous phanerogams or arboreal taxa as palms (Piperno, 1988) that fix it in the form of amorphous silica in their tissues. These small biogenic silica particles are called phytoliths, and after plant degradation they enrich soils where they can dissolve (being thus available again for plant uptake) or from where they can be eroded and transported through the drainage network to ocean. A recent estimate of terrestrial silica delivery has shown that biogenic silica can account for more than 15% of the silica exported to the oceans (Conley, 1997; Conley, 2002), which is not negligible. Increasing evidence of the important presence of biogenic silica in soils has been achieved also, thanks to improving techniques (DeMaster, 1981; Mortlock and Froelich, 1989; Saccone et al., 2006) that allow to extract and estimate the biogenic silica fraction in particulate matter. In fact, the biogenic silica cycle was often neglected by geochemists, who by measuring silica flux at river outlet used to attribute its origin to weathering processes, bypassing the internal cycles described above, related to vegetation and diatom uptake, estuarine trapping/production. It should be noticed that silica-related processes along the land-ocean continuum can be either a source or a sink for silica (for ex. depending on the vegetation type, silica can be absorbed and thus trapped, or not); also it might occur in some cases depending on the time scale considered that the silica flux at a river outlet could correspond to what is issued just from lithology, meaning that the balance of all other processes is zero, but not that these processes do not take place as well. Thus in a comprehensive biogeochemical approach, all these temporal and spatial aspects should be taken into account, including silica cycling in vegetation. This is of particular importance now because increasing anthropogenic pressure is susceptible of being the major driving factor of changes in nutrient riverine export (Billen et al., 2001; Billen et al., in press; Cugier et al., 2005; Meybeck and Vörösmarty, 2005; Syvitsky et al., 2005); thus the understanding of all the main processes in which a nutrient is involved is of crucial importance in view of avoiding nutrient disequilibrium (Redfield et al., 1963) and consequent effects as eutrophication.
Introduction

Figure 2: schematic representation of silica cycle along a land-ocean continuum perturbed by human activity. The sectors in which the perturbations are dominant are covered by the extent of the corresponding arrows.

Human driven changes can directly affect silica cycle (Fig. 2); for example climate change can affect weathering rates (strictly dependent on temperature and rainfall), deforestation can imply increased erosion, artificial river regulation and dam building can cause particulate silica trapping, while new silica sources can be issued from urban runoff, being silica largely used in detergents and paper production processes (van Dokkum et al. 2004).

So silica is present along the whole land-ocean continuum, and its cycle is possibly perturbed by modifications of each internal cycle that takes place along this continuum. The reasons why silica cycle should be studied with particular attention, and why silica should be included in water quality monitoring programmes (which is recent and still not always the case) can be found from local to global scale. Considering the intermediate regional scale there can be a high variability in silica delivery to the coastal zone, due to the hydrology (wet versus dry years) but also to the balance of the several processes that can take place along the land-ocean continuum. A close look at the silica molar ratio to other nutrients such as nitrogen and phosphorus allows a better understanding of coastal eutrophication and harmful algal blooms (HAB) that has been shown to occur in case of silica limitation (Justic et al., 1995; Billen and
Garnier, 1997; Cugier et al., 2005; Lancelot et al., 1987; Lancelot et al., in press). This aspect will be widely treated in the next chapters, because Riverstrahler is a multi-nutrient regional model and thus one of its most immediate applications is the simulation of N, P and Si delivery to the coastal zone.

At the global scale, on the other hand, silica plays a crucial role in modulating atmospheric CO\textsubscript{2} concentration: it happens over geological times in chemical weathering reactions, where CO\textsubscript{2} is sequestered to allow silicate rock dissolution, but the modulation of carbon dioxide is even more interesting over the short time, as such a modulation takes place through the so-called ‘silica-driven carbon pump’ in the ocean. Dissolved silica available in the global ocean (either supplied by rivers, or by \textit{in situ} dissolution of particulate silica) is absorbed by diatoms and incorporated together with CO\textsubscript{2} through photosynthesis. This biological carbon pump reduces CO\textsubscript{2} content in the surface waters where diatom production takes place, and under such circumstances a compensation of CO\textsubscript{2} from the atmosphere to the ocean is needed to establish the equilibrium at the air-water interface, process that occurs on time scales of weeks or months (Smetacek, 1999). Dead or grazed diatoms sink to the ocean bottom, and thus organic carbon is buried in marine sediments (Ragueneau et al., 2000).

So there might be a positive feedback of this biological pump and human driven recent changes in CO\textsubscript{2} emissions, since siliceous phytoplankton in ocean might exert the same action that forests are considered to do in continental environments, contributing to diminish CO\textsubscript{2} in the atmosphere, and thus to act against global warming. Annual net primary production in the ocean was estimated to be about 50 Gtons of C (Falkowski et al, 1998; G, Giga = 10\textsuperscript{9}), which accounts for about half of all the carbon fixed (and hence oxygen released) through photosynthesis on global scale. However this simple statement that silica availability in the ocean enhances CO\textsubscript{2} sequestration is not as straightforward as it can seem, because diatom primary production itself is not only dependent on silica, but also on iron availability, local upwelling conditions, and several others factors. In addition to that, as Falkowski et al., (1998) pointed out, global warming trends are associated with increased precipitation, which would lead to alteration of oceanic circulation and production. Increased precipitation would reduce iron eolian inputs to the ocean, with a consequent reduction of primary production. So, many processes have to be better understood before determining an exact correlation between silica availability in the upper ocean layer and the organic carbon burial.
A help to better understand silica cycle, and its interactions with other cycles, can come from modelling. A model in fact is a ‘reproduction of reality’ by a simplified description of what occurs. Two main modelling approaches can be distinguished: deterministic and statistical modelling. In deterministic modelling, the internal structure of the model attempts to capture some processes (hydrological and biogeochemical in this case). Statistical models, on the other hand, are derived to assure that certain properties of the output are reproduced on the basis of statistical occurrence; the drawback is that prediction of such models are reliable only within the range of the observed statistical data, and cannot be extended or extrapolated further.

Nevertheless it would be incorrect to say that one modelling approach is better than the other. The type of model applied should rather be used according to the addressed questions. For local scale budgets, where the aim is to pinpoint what are the processes responsible of certain observed conditions or events, a deterministic approach might be more suitable, while for global budgets where it is more important to have an quantitative idea about average stocks and annual fluxes and, when there is no need of detailed representation of processes, then a statistical model might be appropriate.
SILICA BOX MODEL

Whereas the deterministic Riverstrahler model will be presented in the next chapter here I would like to describe the terrestrial section of a global silica box model developed during the second summer school of the Si-WEBS network (Natural and anthropogenic modifications of the Si cycle along the land-ocean continuum: Worldwide Ecological, Biogeochemical and Socio-economical consequences), with the objective of making an updated budget of silica cycle from available literature.

The global silica box model along the land-ocean continuum was divided into terrestrial, estuarine and ocean sections, that share the same state variables to allow a continuity of input and outputs (the output of the terrestrial section are used as input for the estuarine part, etc.). The whole model is the result of the work of the young scientists involved in the network, with the suggestions of senior scientists, and it will be object of a common publication (Laruelle et al., in preparation,). The silica cycle is represented schematically in Figure 3 is the outcome of the common work of the ‘terrestrial silica group’ composed by Hans Dürr, Loredana Saccone, Claudette Spiteri and myself.

Figure 3: schematic box model representing silica cycle in the terrestrial part of the land-ocean continuum. Silica stock values are in bold, expressed in Tmol Si, while fluxes are presented as arrows, and the reported values are in Tmol Si/year. Export fluxes atmosphere and estuaries are presented in red (T, Tera = 10^{12}).
Introduction

Boxes are the stocks of dissolved, biogenic and lithogenic silica (DSi, BSi and LSi respectively), present either on the continent (representing silica stored in rocks, soils, vegetation) or in continental freshwater (silica in rivers, exorheic lakes and flood plains).

The boxes are numbered, and the arrows between them indicate the processes/fluxes responsible for the silica transformation and transfer from one reservoir to the other (for ex. $\text{flux}_1$-$3$ is the flux from box 1 to box 3). Lithogenic silica is represented, but only its chemical weathering is taken into account, while other processes are neglected because they take place at a temporal scale, that is beyond the purpose of the model itself.

Silica stocks are estimated on the basis of available literature with some assumptions that are explained in details in table 1.

Table 1: silica stock sizes expressed in Tmol Si for dissolved, biogenic and lithogenic silica (DSi, BSi, LSi) as shown in Fig. 3. Details about how the stocks have been calculated, and corresponding references (Ref.), are provided as well.

<table>
<thead>
<tr>
<th>Si stock size (Tmol Si)</th>
<th>Details of Si stocks calculations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Box 1</strong>&lt;br&gt;<strong>Terr. LSi</strong></td>
<td>The average Si concentration in soils (330mg Si/g soil) is multiplied by the volume of the soil reservoir (110 $10^{18}$ g), assuming the silica rich soil being 1 m deep.</td>
<td>(1)</td>
</tr>
<tr>
<td>1290000</td>
<td>$330\text{g Si/g soil} \times 110\times 10^{18}\text{ g} / M(\text{Si})$</td>
<td></td>
</tr>
<tr>
<td><strong>Box 2</strong>&lt;br&gt;<strong>Terr. BSi</strong></td>
<td>The average value of 0.5g phytoliths per 100 g of soil is converted into Si, taking into account a 42% Si content in phytoliths. The obtained value of 0.21 g Si per 100g soil is then multiplied by the volume of the soil reservoir, assuming the silica rich soil being 1 m deep.</td>
<td>(2), (3)</td>
</tr>
<tr>
<td>8250</td>
<td>$0.005 \text{ g phytoliths/g soil} \times 0.42 \frac{\text{g Si}}{\text{phytoliths}} \times 110\times 10^{18}\text{ g} / M(\text{Si})$</td>
<td></td>
</tr>
<tr>
<td><strong>Box 3</strong>&lt;br&gt;<strong>Terr. DSI</strong></td>
<td>The average Si concentration in rivers is multiplied by the volume of groundwater and soil (1.53 $10^{19}$l)</td>
<td>(1), (2)</td>
</tr>
<tr>
<td>3073</td>
<td>$200\text{ umol Si/l} \times 1.53\times 10^{19}\text{ l}$</td>
<td></td>
</tr>
<tr>
<td><strong>Box 4</strong>&lt;br&gt;<strong>Aq. BSI</strong></td>
<td>The average BSI concentration in rivers is multiplied by the volume of rivers, exorheic lakes and 15% of flood planes (127.2 $10^{15}$l)</td>
<td>(1), (4)</td>
</tr>
<tr>
<td>3.6</td>
<td>$28 \text{ umol Si/l} \times 127.2\times 10^{15}\text{ l}$</td>
<td></td>
</tr>
<tr>
<td><strong>Box 5</strong>&lt;br&gt;<strong>Aq. DSI</strong></td>
<td>The average concentration of Si in rivers (9.3 SiO$_2$ mg/l) times the volume of rivers (1.7 $10^{15}$l) is added to the average Si concentration is lakes (5.0 mg/l SiO$_2$) times the volume of exorheic lakes and 15% of flood planes (127.2 $10^{15}$l)</td>
<td>(1), (5), (6)</td>
</tr>
<tr>
<td>10.8</td>
<td>$9.3 \text{ SiO}_2\text{ mg/l} \times 1.7\times 10^{15}\text{ l} + 5.0 \text{ mg/l SiO}_2 \times 127.2\times 10^{15}\text{ l}$</td>
<td></td>
</tr>
<tr>
<td><strong>Box 6</strong>&lt;br&gt;<strong>Aq. BSI sed.</strong></td>
<td>Surface of rivers + exorheic lakes and 15% flood plains (17.383 e12 m$^2$) multiplied by 0.1 m (supposed depth of reactive layer). The obtained value is multiplied by and average concentration of SiO$_2$ in the 10 cm layer of 50 mgSiO$_2$/g sediment=1416.7 Tmol Si</td>
<td>(1), (7)</td>
</tr>
<tr>
<td>1417</td>
<td>$17.383\times 10^{12}\text{ m}^2 \times 0.1\text{m} \times 50\text{ mg SiO}_2/\text{g sediment}$</td>
<td></td>
</tr>
</tbody>
</table>

Fluxes are either estimated from literature, if available, or calculated to balance the inputs/outputs from each box (Table 2); in fact not all the fluxes listed in Table 2 have been ever quantified in literature. Therefore such a box model, in which some fluxes can be deduced from others, is of particular interest, but with the drawback of a lack of validation. The model as presented here is considered at steady state, which means that the sum of incoming and outgoing fluxes to/from one reservoir equals zero. A first order rate constant \( (k) \) associated to each flux/process can be deduced as:

\[
k_{ij} = \text{Flux}_{ij} / \text{Reservoir}_i
\]

The soil stocks of biogenic and dissolved silica are connected by the processes of dissolution and uptake (by plants). The same processes take place in the aquatic sector, where the biogenic silica eroded from soils, together with BSi in the form of diatoms, can be dissolved, and where dissolved silica can be actively taken up by diatoms. The exported fluxes towards the estuaries are estimated to be equal to 1.1 Tmol/year for BSi, and 6.6 Tmol/year for DSi, biogenic silica constituting ca. 16% of the dissolved silica export.

Since the model as presented here is at steady state, fluxes related to a single reservoir are fixed -as already mentioned- in such a way that their sum is zero. But in reality some estimates for these same fluxes provide ranges of variations, because of the incertitude of indirect estimate techniques. For example, dissolved silica plant uptake from soils is here fixed at 81.2 Tmol Si/year, while Conley (2002) estimated the biogenic silica stored in plant in a range of 60-200 Tmol Si/year on the basis of i) the global terrestrial carbon production (and correspondent incertitude) and ii) the Si:C ratio in vegetation. What is remarkable, is that the order of magnitude of that flux is comparable to the corresponding biogenic silica oceanic gross production, estimated to 240 Tmol Si/year (Tréguer, 1995). Such a similitude of flux size supports the idea that biogenic terrestrial silica cycle might be as important as the oceanic cycle, and its relative importance is also confirmed by the size of the biogenic silica pool itself, which actually might be even underestimated. In fact extraction techniques to quantify the biogenic silica present in soils are constantly refined, and the latest results show that the acid based extraction methods commonly used until now in soil science might lead to an underestimation of biogenic silica content up to one order of magnitude in comparison with alkaline extraction techniques (Saccone, personal communication).
Table 2: fluxes (Tmol Si/year) of dissolved, biogenic and lithogenic silica (DSi, BSi, LSi). Details about flux calculations and corresponding references are provided as well.

<table>
<thead>
<tr>
<th>Flux label</th>
<th>Details about calculations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-atm</td>
<td>Published estimate</td>
<td>(1)</td>
</tr>
<tr>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-atm</td>
<td>Published estimate</td>
<td>(1)</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>calculated to balance steady state fluxes in reservoir (3)</td>
<td></td>
</tr>
<tr>
<td>13.2</td>
<td>( Flux_{3,2} + Flux_{3,5} + Flux_{3,est} - Flux_{2,3} )</td>
<td></td>
</tr>
<tr>
<td>1-est</td>
<td>Silica annual particulate load of 4418 E+6 ton/yr converted into mols</td>
<td>(2), (3), (4)</td>
</tr>
<tr>
<td>158</td>
<td>( 4418 \times 10^6 , \text{ton/yr} / M(\text{Si}) )</td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>92% of uptake</td>
<td>(5), (6)</td>
</tr>
<tr>
<td>74.7</td>
<td>92% of ( Flux_{1,2} )</td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>value taken within the published estimated range of 60-200 Tmol/year</td>
<td>(5)</td>
</tr>
<tr>
<td>81.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-5</td>
<td>The average world river DSi concentration in headwaters of 10 mg/l estimated by Hans Duerr (this value is higher than the 9.3 mg/l in world rivers, because headwaters are supposed to be slightly richer in silica) is multiplied by the surface world river discharge (95% of 40,000 km³/year, the remaining 5% being groundwater)</td>
<td>(7)</td>
</tr>
<tr>
<td>6.3</td>
<td>( 10 , \text{mg Si/l} \times 0.95 \times 40000 , \text{km³/year} / M(\text{Si}) )</td>
<td></td>
</tr>
<tr>
<td>3-est</td>
<td>the estimated global submarine groundwater discharge (5% of global river discharge, i.e. ( 0.05 \times 40 , 000 , \text{km³/year} )) is multiplied by the average SiO₂ concentration in soils and groundwater of 0.2mmol/L.</td>
<td>(8), (9)</td>
</tr>
<tr>
<td>0.4</td>
<td>( 0.05 \times 40 , 000 , \text{km³/year} \times 0.2 \text{mmol/L} )</td>
<td></td>
</tr>
<tr>
<td>2-4</td>
<td>Soil erosion is estimated to 80 e12 tons of eroded soil / year and is multiplied by the BSi concentration in soils (0.21 gSi/100g soil)</td>
<td>(10)</td>
</tr>
<tr>
<td>6.0</td>
<td>( 80 \times 10^7 , \text{tons soil/year} \times 0.21 , \text{g Si/100g of soil} / M(\text{Si}) )</td>
<td></td>
</tr>
<tr>
<td>4-5</td>
<td>BSi dissolution rate of 1 \times 10⁹/hour converted into rate/year (1.752/year) is multiplied by the stock of BSi aquatic, reservoir 4</td>
<td>(11)</td>
</tr>
<tr>
<td>6.3</td>
<td>( 1.752/\text{year} \times 3.6 , \text{Tmol Si} )</td>
<td></td>
</tr>
<tr>
<td>5-4</td>
<td>An average primary production value in rivers (0.037 g C/m²/day) is converted into g of Si (0.034 g Si/m²/day) by the Si/C ratio, then converted into mol Si per year gives 0.445 mols /m²/year. This value is multiplied by the world surface occupied by rivers, exorheic lakes and flood planes</td>
<td>(12)</td>
</tr>
<tr>
<td>7.8</td>
<td>( 0.037 , \text{g C/m²/day} \times \text{Si/C ratio} / M(\text{Si}) \times 365 , \text{days} \times 17.383 , \text{10² m²} )</td>
<td></td>
</tr>
<tr>
<td>4-est</td>
<td>BSi export estimated in 1.05 Tmol Si/year or range obtained considering suspended matter riverine export (15-20 Gt/year) multiplied by the Si content in s.m. (330mg/g s.m.)</td>
<td>(13), (14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1-2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-est</td>
<td>The average river DSi concentration (9.3 mg Si/l) is multiplied by the surface discharge of rivers (95% of 40,000 km³/year)</td>
<td>(15)</td>
</tr>
<tr>
<td>6.2</td>
<td>( 9.3 , \text{mg Si/l} \times 40000 , \text{km³/year} / M(\text{Si}) )</td>
<td></td>
</tr>
<tr>
<td>4-6</td>
<td>The amount of suspended solids retained in river systems (60 Giga tons/year) is multiplied by the BSi concentration in suspended matter (3mgSi/gSM)</td>
<td>(10)</td>
</tr>
<tr>
<td>6.4</td>
<td>60 Giga tons SM/year \times 3 , \text{mg Si/g SM} / M(\text{Si})</td>
<td></td>
</tr>
<tr>
<td>6-5</td>
<td>the k here is adjusted to get a flux of 1.4</td>
<td>(16)</td>
</tr>
<tr>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-diag.</td>
<td>calculated to balance steady state fluxes in reservoir (6)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( Flux_{4,6} - Flux_{5,6} )</td>
<td></td>
</tr>
<tr>
<td>In-1</td>
<td>calculated to balance steady state fluxes in reservoir (1)</td>
<td></td>
</tr>
<tr>
<td>180.7</td>
<td>( Flux_{1,atm} + Flux_{1,est} + Flux_{1,3} )</td>
<td></td>
</tr>
</tbody>
</table>

Another example of flux range uncertainty concerns the BSi riverine export, which is here fixed at 1.1 Tmol Si/year (see Fig.3) on the basis of the estimate published by Conley (1997). This value was obtained by multiplying an average BSi concentration in rivers being equal to 28 µmol Si/l by the global riverine discharge. However, it is also possible to calculate BSi export on the basis of sediment fluxes (Table 2); for example riverine suspended solids (SS) outputs can be calculated as the difference of eroded SS (80 Gt/year) and SS retained in reservoirs (60 Gt/year) (Meybeck et al., 2003), which gives 20 Gt/year of SS river output in agreement with the findings of Vörösmarty et al. (2003) who reported a range of 15-20 Gt/year. The mean value of this range, multiplied by the Si content in suspended matter (330 mg/g SS according to Berner & Berner, 1996) leads to a particulate silica export of about 2 Tmol Si/year, which is almost double if compared to Conley’s (1997) estimate; on the other hand in Berner & Berner (1996), it is not specified if the Si content in suspended solids refers to biogenic silica only, or includes also lithogenic silica, which might explain partly the difference (overall of the same magnitude) between these two estimates.

To sum up, it is evident that further investigations on silica sources and fluxes are needed, and that this need opens plenty of perspectives for researchers, about the understanding of silica cycle in terrestrial ecosystems, including improvements in extraction techniques, mass balance modelling, with either box and/or deterministic approaches.
BIBLIOGRAPHY


Billen et al. 2001


Cugier et al 2005


CHAPTER 1

Implementation of the silica cycle in Riverstrahler model:
the Seine case study

submitted to Ecological Modelling

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Implementation of silica cycle in Riverstrahler model

Abstract

The watershed-based deterministic model Riverstrahler, developed to simulate ecological river functioning and nutrient delivery at the river outlet, has been improved regarding algal dynamics and silica cycle representation. Silica is present in the model in two forms: dissolved (DSi) and particulate / biogenic (BSi). Three groups of diatoms are now considered, spring and late summer planktonic diatoms and benthic diatoms, in order to better represent dissolved silica uptake spatially (benthic diatoms develop mostly upstream) and temporally (the summer diatom bloom is composed of diatoms with different characteristics including those of the spring species). The diatom groups differ in their physiological parameters, such as growth rate, optimal temperature, etc., and the sensitivity of the model to these parameters is explored.

For biogenic silica, not only diatoms are represented, but phytolith inputs to the watershed are also included, as well as a comprehensive representation of BSi transport, dissolution, deposition and diagenesis.

A budget of silica delivery at the river outlet is established from the model results for two hydrologically different years (dry-1991 and wet-2001), showing the dependence of silica transfer on hydrological conditions. In fact, although silica specific fluxes are in the range of those typical of temperate regions, dissolved silica export from the Seine basin can vary from 552 kg Si/km²/year in 1991 to three times this amount in a wet year such as 2001 (1721 kg Si/km²/year). Biogenic silica in total silica export can vary from about 7% in the upstream network, to 29% at the river outlet as in 1991.

The integration of new silica-related processes in the model allows a synoptical simulation of multi-form (dissolved and particulate) and multi-nutrient (N and P being already represented) delivery to the coastal zone.
1.1 INTRODUCTION

The RIVERSTRAHLER model was developed to simulate the ecological functioning of the Seine River and the nutrient delivery at its estuary (Billen et al., 1994; Garnier et al., 1995; Billen et al. 2001). It was then applied to several other rivers, such as the Danube (Garnier et al., 2002a), the Scheldt (Billen et al., 2005) and the Red River in Vietnam (Garnier & Billen, 2002), proving to be a powerful tool to relate changes in the land use to the water quality in watersheds of various sizes and anthropogenic pressures. The model can simulate nutrient export (N, P, Si) on seasonal and long-term scales (Billen et al., 2001; Billen et al., 2005).

Nutrient ratios are of particular importance to evaluate eutrophication and to forecast algal successions during a given season. In fact, as indicated by Redfield et al. (1963) diatoms, which are silicified aquatic organisms, require Si in a special ratio to N and P for optimal growth (molar ratio C:N:P:Si = 106:16:1:16 for marine algae, 106:16:1:42 for freshwater diatoms, according to Conley et al., 1989). In case of silica limitation, non-siliceous algae dominate. In coastal marine systems, these algae are often undesirable because they produce either toxins (Cugier et al., 2005) or mucilage, escaping the normal grazing food web and leading to anoxic conditions at the decay of the bloom (Lancelot et al., 1994, Lalli & Parsons, 1993).

In river systems, silica originates mainly from diffuse sources, being strongly dependent on the lithology of the river basin (Meybeck, 1987). Silica is, in fact, the second most abundant element (after oxygen) in the terrestrial crust, and silicate minerals (olivine, pyroxene, amphibole, feldspar) are fundamental components of many rock types (igneous, metamorphic, sedimentary) (Berner & Berner, 1996). Rock weathering is a function of temperature and rainfall, which act as catalysts of silica dissolution. As a consequence the release of dissolved silica from rocks is modulated by climatic factors (Meybeck, 1979; Oliva et al., 2003; Justic et al., 2005). But climate also has an effect on vegetation, and recent studies (Oliva et al., 1999; Conley, 2002; Meunier, 2003; Derry et al., 2005) focusing on the role of opaline particles (phytoliths) that accumulate in some plants, have shown that these biogenic particles can be an important source of terrestrial silica reaching the ocean through rivers. Even if these natural silica inputs (lithogenic and biogenic) to rivers remain unchanged within a given basin (flux fluctuations being mainly due to the water discharge) the silica ratio shows dramatic changes with respect to other nutrients (Admiraal et al., 1990; Billen & Garnier, 1997; Turner et al., 2003), especially nitrogen due to the
change in land use which leads to, higher N fluxes (intensive use of fertilizers in agriculture) and phosphorus, mainly due to increasing incompletely treated domestic effluents that increase P fluxes (Officer and Ryther, 1980; Billen et al., 2001; Pastuszak et al., 2005; Garnier et al., 2005). Moreover, silica can be trapped as a sediment along the river continuum because of damming (Vörösmarty et al., 2003; Garnier et al. 1999; Humbort et al., 2000; Hunspreugs et al., 2002); if the residence time in the artificial reservoir is high enough to allow diatom development and sedimentation, then Si in its biogenic form (BSi) is temporarily or permanently sequestered, and does not reach the estuary (Garnier et al., 2002a; McGinnis, personal communication).

Although diffuse inputs of silica to surface waters largely dominate, urban point sources cannot be completely ignored, as the per capita silica load (g Si/inhab./day) is increasing (Garnier et al., in press; Sferratore et al., submitted).

The Riverstrahler model is able to simulate nutrient fluxes in relation to hydrology, meteorology, diffuse sources (from land use) and point sources (domestic and industrial inputs). The silica cycle representation is simple compared to the one of nitrogen and phosphorus, since there is only one dissolved form, DSi, i.e. orthosilicic acid, and one particulate form, biogenic silica, BSi. In the early version of the model (Garnier et al., 1995; Fig. 1a), dissolved silica originating only from diffuse sources was taken up along the river continuum by planktonic diatoms, which were possibly grazed by zooplankton or exported to the estuary and coastal zone as suspended biogenic silica. The BSi in this representation can only dissolve, and return to the dissolved silica pool. In the light of a Si budget, including DSi and BSi, at the scale of the whole Seine network, and at the scale of a key component - the reservoirs - it became necessary to refine the silica cycle in the modelling approach (Garnier et al., 2002b).

The initial simple representation did not take into account major features such as terrestrial BSi inputs (phytoliths), its sedimentation and temporary storage within the river sediments, uptake of dissolved silica by benthic diatoms in shallow streams. An improvement of the silica representation in the model seemed therefore necessary (Fig. 1b). The objective of this article is to mathematically formalize these additional pathways in order to better simulate and quantify seasonal variations of silica delivery to the coastal zone.
Implementation of silica cycle in Riverstrahler model

Figure 1: previous (a) and improved (b) silica cycle representation in the Riverstrahler model.
1.2 STUDY SITE

The Seine Basin (Fig. 2) is the third largest watershed in France, after the Rhône and the Loire, covering a surface area of 75,000 km² (estuary included). The Seine River has three main tributaries, the Marne, the Oise and the Upper Seine. The average discharge is 500 m³/s with a pluvio-oceanic regime. The summer low flow is sustained by three reservoirs (750 x 10⁶ m³ in total) built along the Marne and Upper Seine.

Figure 2: the Seine watershed; in grey the Oise River basin.
The basin is characterized by intense human activity, especially in the Paris area which accounts for 2/3 of the basin population (total population: about 16 million inhabitants) and contributes to the nutrient enrichment. In fact the water quality in the higher river orders is typical of eutrophicated rivers with algal blooms in spring (diatoms) and summer (diatoms and green algae).

The Seine River has been chosen as a case study site to test the improved version of the Riverstrahler model, since it is a basin with a well-known hydrological regime and for which a long time series of data is available on water quality and runoff, by which the model results can be validated.

To follow up the diatom variations and succession, the Poses water-quality station, located at the upstream limit of the Seine estuary, was chosen for this study. At that point the Seine is of the 7th order according to Strahler’s classification (Strahler, 1957) and the basin surface area is approximately 64 500 km².

In addition to that, some tests were made on the Oise River which joins the Seine at Conflans-Sainte-Honorine, about 65 km downstream of Paris on the right bank. The Oise accounts for 16900 km² (about 23 % of the Seine watershed) and is quite representative of the whole Seine river, but it is unregulated (no reservoirs, as opposed to the Marne and the Upper Seine), which allows a simplification in the forcing factors to be tested. Two hydrologically contrasted years, 1991 - a dry and 2001 - a wet year, were chosen for these simulations.

The input data to run the model are taken from various sources (Table 1).

1.3 MODELLING APPROACH AND IMPLEMENTATION

RIVERSTRAHLER results from the coupling of two models:

- HYDROSTRAHLER, which describes the hydraulic regime of a river, from the small orders in the headwaters to the river outlet. The discharge is the result of two components of the water flow, the base and the surface flow (for a detailed description: Billen et al., 1994; Garnier et al., 2002a) to which an average nutrient concentration is associated depending on the lithology and land use; the river network is represented as a regular scheme of tributary confluence with increasing stream order;
Implementation of silica cycle in Riverstrahler model

- RIVE, which integrates into the hydrologic model, a description of the dynamics of the main biological compartments and associated processes typical of lotic systems (Table 2): phytoplankton, zooplankton, benthic feeders, bacteria. The phytoplankton, in particular, includes green algae, diatoms and cyanobacteria.

A special feature of the model is that the same processes take place along the river continuum, modulated by the forcing factors that are or are not favourable to a certain process, so that the model outputs change according to external constrains (land use, lithology, climate, point and diffuse sources) and are not due to differences in the kinetics affecting the biological processes, since these kinetics remain unchanged from the headwaters to the downstream sectors.

### Table 1: sources of input and validation data.

<table>
<thead>
<tr>
<th>Data sources</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Climate &amp; hydrology</strong></td>
<td></td>
</tr>
<tr>
<td>Rainfall</td>
<td>Safran Database – Météo France</td>
</tr>
<tr>
<td>ETP</td>
<td>Safran Database – Météo France</td>
</tr>
<tr>
<td>Runoff</td>
<td>Calibrated (see text)</td>
</tr>
<tr>
<td>Discharge (validation)</td>
<td>AESN, Agence de l'Eau Seine-Normandie</td>
</tr>
<tr>
<td><strong>Morphology of the drainage network</strong></td>
<td></td>
</tr>
<tr>
<td>Morphology – stream ordination</td>
<td>PIREN Seine</td>
</tr>
<tr>
<td><strong>Diffuse Sources</strong></td>
<td></td>
</tr>
<tr>
<td>Lithology</td>
<td>European soil database version 2, European Environment Agency (EEA)</td>
</tr>
<tr>
<td>Land use</td>
<td>Corine Land Cover (CLC90), European Environment Agency (EEA)</td>
</tr>
<tr>
<td><strong>Point Sources</strong></td>
<td></td>
</tr>
<tr>
<td>Industrial sources</td>
<td>AESN, Agence de l'Eau Seine-Normandie.</td>
</tr>
<tr>
<td><strong>Water quality</strong></td>
<td></td>
</tr>
<tr>
<td>Validation data</td>
<td>AESN ; SNS (Service de la Navigation de la Seine); PIREN-Seine : Garnier et al., 1995; 1998; unpublished</td>
</tr>
</tbody>
</table>
Table 2: state variables and processes considered in the improved Riverstrahler model.

<table>
<thead>
<tr>
<th>State variables</th>
<th>Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended and deposited mineral material</td>
<td>Sedimentation, resuspension</td>
</tr>
<tr>
<td>Green algae</td>
<td>Primary production</td>
</tr>
<tr>
<td>Diatoms (spring, late summer, benthic)</td>
<td>Primary production, sedimentation of planktonic diatoms, erosion of benthic diatoms</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>Primary production</td>
</tr>
<tr>
<td>Heterotrophic bacteria</td>
<td>Organic matter degradation and remineralization</td>
</tr>
<tr>
<td>Nitrifying bacteria</td>
<td>Nitrification</td>
</tr>
<tr>
<td>Zooplankton (Rotifera and Cladocera)</td>
<td>Grazing and remineralization</td>
</tr>
<tr>
<td>Dissolved organic matter</td>
<td>Rapid or slow hydrolysis for the non-refractory fraction</td>
</tr>
<tr>
<td>Particulate organic matter</td>
<td>Rapid or slow hydrolysis for the non-refractory fraction, sedimentation</td>
</tr>
<tr>
<td>Ammonium and nitrate</td>
<td>Nitrification, denitrification, uptake, benthic recycling</td>
</tr>
<tr>
<td>O-Phosphate and adsorbed inorg. P</td>
<td>Uptake, adsorption-desorption, benthic recycling</td>
</tr>
<tr>
<td>Dissolved silica</td>
<td>Uptake</td>
</tr>
<tr>
<td>Suspended and deposited biogenic silica</td>
<td>Dissolution, sedimentation</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>Heterotrophic consumption, autotrophic production, reaeration</td>
</tr>
</tbody>
</table>

The model is watershed based and can be applied to a river basin considering it as one, or taking into account a main axis with branches (several sub-basins), reservoirs and other stagnant annexes (ponds, sand pit lakes, etc.). The resolution is chosen according to the questions of interest and to the availability of the data (Sferratore et al., 2005; Ruelland et al., submitted). The representation of the silica cycle in the RIVE model has been considerably refined on the basis of both published literature and field data collected in the Seine watershed. The improvements with respect to the previous version are described by compartments.

Algal dynamics

Diatoms dominate river plankton together with green algae, that have a peak of biomass in summer (Descy, 1987; Garnier et al. 1995; Gosselain, 1998; Wetzel, 2001). A significant reduction in DSi concentration appears not only in spring, but also in summer, due to a succession of diatoms with different characteristics, according to the optimal blooming season. Therefore, the single group of planktonic diatoms in the previous version of the RIVE model was split into a spring and a late summer diatom group to better represent the silica and algal dynamics within the river continuum. Their parameters such as growth rate (µ), optimal
temperature (Topt), dependence on light intensity ($\alpha$) have been drawn from literature on diatom assemblages typical of spring and late summer populations (Table 3).

The r-selected species (Margalef, 1978, Sommer et al., 1986) are dominant when the conditions of light and nutrients are optimal, i.e. in spring.

**Table 3**: list of freshwater diatom parameters as collected from the literature, and as used in Riverstrahler model.

<table>
<thead>
<tr>
<th>Species</th>
<th>Ecosystem</th>
<th>Seasonality</th>
<th>Growth rate $\mu$ or $\mu_{\text{max}}$ (d$^{-1}$)</th>
<th>Irradiance (µE/m2/s)</th>
<th>$T_{\text{opt}}$ (°C)</th>
<th>$T_{\text{range}}$ (°C)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Asterionella formosa</em></td>
<td>lake</td>
<td>n.d.</td>
<td>1.25 *</td>
<td>100</td>
<td>20</td>
<td>5-25</td>
<td>(1)</td>
</tr>
<tr>
<td><em>Aulacoseira</em></td>
<td>river</td>
<td>n.d.</td>
<td>0.418, 0.715, 0.779, 0.870</td>
<td>40</td>
<td>15, 20, 25</td>
<td>n.d.</td>
<td>(2)</td>
</tr>
<tr>
<td><em>Stephanodiscus hantzschii</em></td>
<td>pond</td>
<td>n.d.</td>
<td>1.25 *</td>
<td>100</td>
<td>25</td>
<td>10-30</td>
<td>(1)</td>
</tr>
<tr>
<td><em>Thalassiosira curviseriata</em></td>
<td>estuary</td>
<td>spring</td>
<td>0.65, 0.96, 1.50, 1.93</td>
<td>80 (sat), 80 (sat), 80 (sat), 70 (sat)</td>
<td>5, 10, 15, 20, n.d.</td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td><em>Thalassiosira eccentrica</em></td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.4</td>
<td>130</td>
<td>15</td>
<td>n.d.</td>
<td>(4)</td>
</tr>
<tr>
<td>Riverstrahler spring diatoms</td>
<td>river</td>
<td>spring</td>
<td>1.56 (sat)</td>
<td>14</td>
<td>$T_{\text{opt}} \pm 7-10$</td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>Riverstrahler Summer diatoms</td>
<td>river</td>
<td>summer</td>
<td>2.04 (sat)</td>
<td>28</td>
<td>$T_{\text{opt}} \pm 7-10$</td>
<td></td>
<td>(5)</td>
</tr>
<tr>
<td>Riverstrahler benthic diatoms</td>
<td>river</td>
<td>whole year</td>
<td>0.84 (sat)</td>
<td>11</td>
<td>$T_{\text{opt}} \pm 9$</td>
<td></td>
<td>(5)</td>
</tr>
</tbody>
</table>


These species are generally of small size, rapid growth rate, and form a large biomass. *Stephanodiscus hantzschii* and similar small centric diatoms, which are abundant in the spring bloom (Garnier et al., 1995), are typical of this group. In the text below, this group will be indicated as “SCDs”, small cell diatoms.

The k-selected species on the other hand, are able to exploit the summer conditions, when some resources can be limiting. They grow more slowly, building large cells; *Aulacoseira* is a typical example of these summer diatom groups and are referred to as “LCDs”, large cell diatoms.
The characteristics described above help to better understand the differences in the diatom parameters listed in table 4. For example, spring diatoms have a higher $\alpha$, indicating a higher capacity to use light, necessary in spring conditions.

Table 4: diatom parameters as in the improved version of Riverstrahler model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Spring diatoms (SCDs)</th>
<th>Summer diatoms (LCDs)</th>
<th>Benthic diatoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{\text{max}}$ (h$^{-1}$)</td>
<td>max growth rate</td>
<td>0.065</td>
<td>0.085</td>
<td>0.040</td>
</tr>
<tr>
<td>$T_{\text{opt}}$ (°C)</td>
<td>optimum temperature</td>
<td>14</td>
<td>28</td>
<td>11</td>
</tr>
<tr>
<td>$dT_i$ (°C)</td>
<td>temperature range</td>
<td>$T_{\text{opt}} + 7$, $T_{\text{opt}} - 10$</td>
<td>$T_{\text{opt}} + 10$, $T_{\text{opt}} - 10$</td>
<td>$T_{\text{opt}} + 10$, $T_{\text{opt}} - 10$</td>
</tr>
<tr>
<td>$K_p\text{Si}$ (umol Si l$^{-1}$)</td>
<td>mean half saturation constant for silica</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>$K_p\text{P}$ (µmol P l$^{-1}$)</td>
<td>mean half saturation constant for phosphorus</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$K_p\text{N}$ (µmol N l$^{-1}$)</td>
<td>mean half saturation constant for nitrogen</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$\alpha$ (h$^{-1}$ (µE m$^{-2}$ s$^{-1}$)$^{-1}$)</td>
<td>slope of the growth rate vs. irradiance</td>
<td>0.0024</td>
<td>0.0010</td>
<td>0.0012</td>
</tr>
<tr>
<td>$V_s$ (m s$^{-1}$)</td>
<td>Velocity of sedimentation</td>
<td>0.001</td>
<td>0.001</td>
<td>0</td>
</tr>
</tbody>
</table>
The greater growth rate of LCDs in comparison to SCDs at the respective optimal temperature may seem controversial. But, in reality, the optimal temperature for LCDs is never reached within the Seine temperature range (shaded area in Fig. 3): as a result, during the vernal season, the growth rate of SCDs is greater than that of LCDs.

Moreover, a benthic diatom compartment was identified as well (in the Seine: M. Coste, unpublished data; Garnier et al., 1995; Flipo et al., 2004) and is now explicitly integrated in the model (Table 4). The benthic diatom population, typical of small hydrological orders or shallow rivers (Sabater et al., 2000; Leira and Sabater, 2005), are the principal consumers of DSi in headwaters while, due to increasing depth and higher turbidity and a decreasing dilution rate, they leave room for planktonic species in larger rivers. This hypothesis is echoed by similar cases in literature where benthic diatoms are considered responsible for silica consumption in small streams (Casey et al., 1981; House et al., 2001; Bowes et al. 2005) and it is confirmed by a survey concerning DSi concentration in the upstream sector of the Seine watershed. The survey was performed in monolithological basins in order to minimize the effect of the lithology and shows a decrease of silica probably due to benthic diatom uptake in the spring and early summer (Fig. 4) since planktonic diatoms are known to develop further downstream from the 4th to the 5th orders (Garnier et al., 1995; Garnier et al., 2004).

Figure 3: temperature dependency of growth rate for the planktonic diatoms (spring: black line; summer: dotted line) and benthic diatoms (grey line) represented in Riverstrahler. The Seine water temperature range corresponds to the shaded area.
Implementation of silica cycle in Riverstrahler model

Figure 4: Seasonality of dissolved silica in the upstream sector (orders 1st–3rd) of the Seine watershed in 1991. Dissolved silica measured in January, April and July 1991 in small basins of uniform lithology a) calcareous, b) chalk and c) mixed lithology.

Whereas the two groups of planktonic diatoms change their biomass according to the balance of the processes of growth, mortality, sedimentation and grazing, benthic diatoms are regulated only by growth, mortality and erosion. The latter process is represented according to the following relationship, inspired by the work of Dufayt (2000):

\[
\text{Erosion (h}^{-1}) = a + b \times v^2
\]

where ‘a’ and ‘b’ are parameters calibrated on local data

- \(a (h^{-1}) = 0.00005\)
- \(b (m^{-1}) = 0.001\)

and where ‘v’ (m h\(^{-1}\)) is the current velocity.

The equation consists thus of two terms respectively representing permanent cells losses, and flow rate-dependent erosion. A similar distinction into permanent and flow-dependent losses is also found in Flipo et al. (2005), following the work of Biggs and Close (1989) that determined the relation between current intensity and periphyton losses, but a different formulation is here adopted.
**Sediment transport and dissolution**

To better simulate silica dynamics in the river network, a comprehensive representation of BSi transport, dissolution, deposition and diagenesis was established. Suspended BSi transported within the water column is associated with suspended matter. It is fed by planktonic diatom mortality, benthic diatom erosion and phytoliths from terrestrial sources; it is subjected to dissolution and sedimentation.

The BSi dissolution kinetics is represented in function of temperature, applying Arrhenius’ law as suggested by Rickert et al. (2002):

\[ kb_{Si} f(T) = kb_{Si} \times \exp(60000 / 8.314 \times (1 / 275 - 1 / (273 + temp))) \]

where

- \( kb_{Si} \) is the dissolution constant set at the beginning as 0.000003 h\(^{-1}\)
- \( temp \) is the surrounding environment temperature.

Since the solubility at equilibrium is also temperature-dependent, the saturation of Si as a function of temperature between 0 and 40 degrees C can be represented by the following relationship established by Van Cappellen and Qiu (1997):

\[ DS_{\text{isat}} = 10^{(6.44 - 968 / (273 + temp))} \]

Finally dissolution of Si can be considered as a function of the degree of undersaturation, so that the apparent dissolution constant \( kb_{Si\text{AP}} \) is:

\[ kb_{Si\text{AP}} = kb_{Si} f(T) \times (DS_{\text{sat}} - DS_{\text{concentration}}) / DS_{\text{sat}} \]

Once deposited on the river bottom, biogenic silica forms a pool of non-living benthic biogenic silica (BBSi) which can temporarily accumulate within the benthic phase. It is subjected to dissolution, erosion (together with deposited suspended matter, according to current velocity), and compaction. The latter process, characterized by a rate of 0.0005 h\(^{-1}\), represents a permanent burial of silica in the deeper, compacted layer of sediments.

**Diffuse and point sources of silica**

In addition to the diffuse sources of DSi originating from rock weathering, the new version of the model incorporates inputs of suspended BSi, corresponding to phytoliths accompanying soil erosion, based on measured values of BSi in arable soil samples from the Seine watershed (4.9...
mg BSi/g soil – ranging from 2.5 to 7.3 mg BSi/g, Sferratore et al., submitted.). Given the range of suspended-matter concentrations found in headwaters of the Seine basin (30 to 250 mg/l), this corresponds to a BSi content of 5 to 35 µmolSi/l, in good agreement with the value of 28 µmol/l BSi found as an average concentration in ‘world’ rivers (Conley, 2002).

Silica input from urban sources has been better quantified and is also incorporated in the model. Analyse of water from the Achères treatment plant that receives the sewage of about 6.5 \(10^6\) inhabitants show that the average incoming raw water has a silica concentration of 2.6 mg Si/l, while the outgoing treated water has one of 1.9 mg Si/l (the values are corrected by the tap water concentration). Thus, one can calculate a per capita load of respectively 0.8 and 0.6 g Si/inhab./day for raw and treated waters. These values are low compared to diffuse silica sources (Garnier et al., in press; Sferratore et al., submitted.).
1.4 RESULTS AND DISCUSSION

The spatial-temporal distribution of silica is simulated for two contrasted hydrological years, 1991 a dry year and 2001, a wet year. All simulations were run with adjusted discharges, to test only the performance of the ecological-process model (RIVE). The results of the runs for the Oise River and for the entire Seine Basin are shown from the upstream orders down to the Poses station, in order to better represent the river continuum. The model results show a good agreement with validation data available at the 6th and 7th orders both for total chlorophyll \( a \) and dissolved silica concentrations (Fig. 5).

The DSi depletion takes place from the first river orders (1st-4th), down to the Seine outlet, due not only to the planktonic diatoms (that develop mostly from the 5th order), but also to the benthic diatom bloom in the upstream network. Benthic diatoms develop throughout the spring and summer seasons, so that the upstream silica depletion is present during almost all this period. On the contrary separate spring and summer blooms of planktonic diatoms cause silica riverine concentrations to decrease both in spring and in late summer; the introduction of the summer diatom (LCDs) group is an improvement permitting a better simulation of the summer diatom development and the corresponding silica depletion in the downstream river sectors.

During the dry year (1991), a high diatom bloom is simulated in spring and shows a succession of SCDs to LCDs at the Poses station (Fig. 6a). In the very wet year (2001), both the bloom and the succession are simulated, but to a lesser extent, as the high discharge did not allow intensive diatom development (high dilution rate compared to the algal growth rate).
Figure 5: modelled development of benthic diatoms (a), planktonic diatoms (b) and corresponding silica uptake (c) from upstream to downstream in 1991. Observed data are given in comparison (dots).
Sensitivity tests

Several test were made to investigate the sensitivity of the model to some physiological diatom parameters at the Poses station (Fig. 6).

For the reference situation, the model shows a succession from SCDs to LCDs and back to SCDs (Fig. 6.a); the last SCDs autumn bloom is due to the fact that at that time of the year the SCDs find similar optimal temperature conditions as in spring.

The LCDs can completely disappear if a higher growth rate is attributed to SCDs instead of to LCDs (Fig. 6.b). On the other hand, if all the parameters are left unchanged but the optimal temperature of the SCDs is increased, the SCDs will grow faster, sometimes coinciding with the LCDs bloom (Fig. 6.c). With an optimal temperature of SCDs equal or very close to that of LCDs, the two groups would coexist, but in that case the summer diatoms would be more abundant because of their higher growth rate.

A last sensitivity test concerns the capacity to use light ($\alpha$). If a lower $\alpha$ value is assigned to SCDs, than to the LCDs, the latter will dominate during most of the year (Fig. 6.d).

Export budgets

In terms of dissolved silica export, discharge is a key factor, since the dry year export (710 kg of Si/km$^2$/year for the Oise, 552 kg of Si/km$^2$/year for the entire Seine) is much lower than that of the wet year (3694 kg of Si/km$^2$/year for the Oise and 1721 kg of Si/km$^2$/year for the entire Seine). This is mainly due to the greater diffuse inputs by the high discharge.

In streams the retention of silica can only result from long-term benthic storage of particulate biogenic silica on the river bottom, in the flood plain or the hydrological annexes, either in the form of phytoliths or diatoms.
Implementation of silica cycle in Riverstrahler model

\[ \mu_{\text{spring}} = 0.065 \, \text{h}^{-1} \]
\[ \mu_{\text{summer}} = 0.085 \, \text{h}^{-1} \]
\[ T_{\text{opt spring}} = 14 \, ^\circ\text{C} \]
\[ T_{\text{opt summer}} = 28 \, ^\circ\text{C} \]
\[ \alpha_{\text{spring}} = 24 \times 10^{-4} \]
\[ \alpha_{\text{summer}} = 10 \times 10^{-4} \]

\[ \mu_{\text{spring}} = 0.085 \, \text{h}^{-1} \]
\[ \mu_{\text{summer}} = 0.065 \, \text{h}^{-1} \]
\[ T_{\text{opt spring}} = 20 \, ^\circ\text{C} \]
\[ T_{\text{opt summer}} = 28 \, ^\circ\text{C} \]
\[ \alpha_{\text{spring}} = 10 \times 10^{-4} \]
\[ \alpha_{\text{summer}} = 24 \times 10^{-4} \]
\[ (\text{h}^{-1} \text{µE m}^{-2} \text{s}^{-1})^{-1} \]

**Figure 6:** sensitivity tests on diatom parameters in a dry and a wet year for the 6th order of the Oise river: reference run (a), sensitivity to growth (b), to growth optimal temperature (c) and to capacity to use light(d). SCDs in black and LCDs in grey.

If considered in an upstream-downstream perspective (Fig.7) in 1991, the specific dissolved silica flux decreases in the downstream direction, mainly because of the diatom uptake, which is highest at the 6th order. As the DSi is converted into the diatom biomass, the decrease in the exported DSi flux leads to an increasing biogenic silica flux, albeit unbalanced due to the
Implementation of silica cycle in Riverstrahler model

retention. Compared to the DSi specific flux the exported BSi can thus increase from 7% at the 4th order of the Oise, to 14% at the 6th order, to about 29% at the Seine at Poses, of order 7.
The balance between the BSi formation processes through diatom production and BSi dissolution is usually positive in favour of BSi production, with the exception of the budget for the Oise at order 4 since, as already mentioned, the development of planktonic diatoms occurs further downstream, and the benthic diatoms that develop upstream have a relatively lower uptake than the total dissolution of both diatoms and phytoliths.
The calculated specific export fluxes of dissolved silica from the Seine river for both dry and wet years (550-1720 kgSi/km²/yr respectively) are in the range of the values reported in the literature for other systems in temperate climates. Thus, for the Scheldt river system Billen et al. (2005) calculated a silica delivery between 500 and 2000 kg Si/km²/year over a period of 50 years (1950 – 2000) with variable hydrology. The Danube river basin has a lower specific silica export, ranging according to Cociasu et al. (1996) between 200 and 600 kg Si/km²/year. These values are comparable to the world river average yield (endorheic + exorheic) provided by Meybeck (2003) for more than 700 rivers, and to the average of 1430 kg of Si/km²/year calculated on the basis of several river basins (n= 67) at different latitudes by Turner et al. (2003). Note that these temperate river exports are all low compared to silica export in subtropical regions, e.g. the Red River in Vietnam, which exports about 3200 kg of Si/km²/year (Garnier et al., in press; Le Thi Phuong, 2005).
Finally, the silica budgets presented in this paper are an example of synoptic modelling of both dissolved and particulate (biogenic) silica, rarely found in nutrient budget literature.
**Figure 7**: silica export budget in 1991 from the Oise basin at order 4, order 6 and from the outlet of the Seine at Poses. All fluxes are expressed in kg of Si/km²/year.
1.5 CONCLUSIONS

Beside a deeper knowledge gained by this study, the silica cycle in the Riverstrahler model has been considerably improved, and the model seems to be very sensitive to changes in parameters with an influence on silica export and on diatom growth (temperature, discharge, light, growth rates). Additionally, there is evidence of an important influence of benthic diatoms on silica depletion along the whole river continuum, although these diatoms develop mostly in the upstream headwaters. This supports the hypothesis that large reservoirs are not necessarily preferential sites of silica retention, as in-stream processes may be equally important; such a result was shown for the Danube system within which the Iron Gate was not totally responsible for the decrease in silica delivery to the Black Sea (Garnier et al., 2002a), thereby diverging from what was previously reported (Humborg et al., 1997). The residence times, both in-stream and in the reservoirs, are determinant drivers for silica retention. The study of nutrient fluxes in a land-ocean perspective shows that such a deterministic watershed-based model is both useful and valuable since it can calculate local budgets, thus allowing the role of some locally active biological processes to be discussed when they might be by-passed if only the river outlet is considered.

Finally, in the ‘Anthropocene’ era in which humans might be the driving factor of environmental changes, the DSi trend will probably decrease because of damming but also because of other land use practices (Meybeck & Vörösmarty, 2005) and N and P point source management (Billen et al., 2001); it is therefore important to include silica in monitoring programs, because only a synoptic view of the major nutrient ratios (ex. N:P:Si) can allow an assessment of the water quality and of the possible structure of phytoplankton communities in the river and the coastal zone.
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Implementation of silica cycle in Riverstrahler model


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Safran Database - Météo France
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CHAPTER 2

Diffuse and point sources of silica in the Seine River watershed

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Diffuse and Point Sources of Silica in the Seine River Watershed

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Dissolved silica (DSI) is believed to enter aquatic ecosystems primarily through diffuse sources by weathering. Point sources have generally been considered negligible, although recent reports of DSI inputs from domestic and industrial sources suggest otherwise. In addition, particulate amorphous silica (ASI) inputs from terrestrial ecosystems during soil erosion and in vegetation can dissolve and also be a significant source of DSI. We quantify here both point and diffuse sources of DSI and particulate ASI to the Seine River watershed. The total per capita point source inputs of Si (DSI + ASI) were found to be 1.0 and 0.8 g Si inhabitant−1 d−1 in raw and treated waters of the AcheÁres wastewater treatment plant, in agreement with calculations based on average food intake and silica-containing washing products consumption. A mass balance of Si inputs and outputs for the Seine drainage network was established for wet and dry hydrological conditions (2001 and 2003, respectively). Diffuse sources of Si are of 1775 kg Si km−2 y−1 in wet conditions and 762 kg Si km−2 y−1 in dry conditions, with the proportion of ASI around 6%. Point sources of Si from urban discharge can contribute to more than 8% of the total Si inputs at the basin scale in hydrologically dry years. An in-stream retention of 8% of total inputs in dry conditions and 12% in wet conditions is inferred from the budget.

1. Introduction

Silica is found in water in two forms: as dissolved silica and in particulate matter. Dissolved silica (DSI) is an important nutrient for the growth of aquatic organisms such as diatoms, radiolaria, and siliceous sponges. These organisms take up DSI to build their frustule or skeleton, which is deposited as amorphous silica (also known as biogenic silica, BSI). Particulate matter containing Si is composed of two different operationally defined pools: mineral silicates and different forms of amorphous silica (ASI). While the largest pool of Si in suspended particulate matter in aquatic environments is as mineral silicates (1), they are unreactive on biological time scales (2) and will not be considered further here. Suspended particulate matter also contains various forms of ASI (3, 4), composed of phytoliths (5), e.g., ASI deposited in plants, and from the in situ growth of diatoms (1). DSI is essentially of diffuse origin and depends on basin lithology, but is also controlled by factors such as hydrology and temperature, i.e., climate in general (6, 7). In addition, biological processes, especially the cycling of Si through vegetation, exert a strong control on the rates of weathering (8, 9), with the biogeochemical cycling of Si through terrestrial ecosystems significantly affecting DSI in rivers (10, 11). In watersheds such as the Seine River Basin significant anthropogenic inputs of nitrogen and phosphorus, mostly originating from fertilizers and detergents, are present in excess relative to DSI, which can become a limiting nutrient in the river network (12), and in the coastal zone (16–19) even though DSI and ASI are found in point sources (detergents, paper production processes (13, 14), and in sewage inputs (15)). In addition, predicted future trends for the Anthropocene indicate that DSI concentrations and the ratio toward other nutrients might decrease due to the fact that more and more river basins are affected by human activities (20).

The objective of the present study was to determine the importance of different DSI and ASI inputs, both diffuse inputs and from point sources, to the highly anthropogenically impacted Seine River watershed. Furthermore, as diffuse and point sources are major constraints to the modeling approach developed on the Seine River, these results can be directly used by the version of the Riverstrahler model that includes improvements to the biogeochemical silica cycle (21).

Methods

Sampling Strategy and Databases. Sampling for DSI and ASI was carried out in 2001–2003 at major hydrological stations in the Seine River watershed (Figure 1): the outlet of Marne River at St. Maurice, the upstream Seine River outlet at Choisy, the Oise outlet Méry, and the lower Seine River at Poses (unpublished). However, the DSI and ASI measurements at Poses station only are used here.

In order to quantify diffuse source inputs, particulate ASI was measured in suspended matter collected by sediment traps and at different stations within the Seine basin. Soil samples from agricultural soils were collected during winter when the intensively cultivated surface was bare. Soil samples were sieved and the fraction less than 250 μm was analyzed for ASI. Diffuse inputs of DSI are calculated from the bedrock lithology on the basis of the lithological map of the Seine basin (22) and on the work initiated by Meybeck (23) assigning a specific DSI concentration for each rock type (6, 24).

Rainwater samples were collected in 2001 at five stations within the Seine watershed, from upstream to downstream: Le Der and Coulommiers at 300 and 100 km upstream from Paris respectively, Paris, and Rouen and Le Havre, at 250 and 350 km downstream from Paris (Figure 1). For groundwater, a database containing DSI data with more than 800 measurements was used for the Seine River basin. Most of the samples were from wells (44%) followed by bore wells (30%) and springs for tap water distribution (24%). Raw and treated waters of the AcheÁres wastewater treatment plant (WWTP) were analyzed for DSI and ASI to estimate the specific silica load (g Si inhabitant−1 d−1), as has been obtained already for nitrogen and phosphorus (26). Finally, DSI was measured in the Paris urban runoff. Most of the data are presented as averages ± confidence interval (of 90% confidence, which is considered acceptable in ecological sciences) unless otherwise stated.
Si fluxes were determined for the 2 years 2001 and 2003, with contrasting hydrology, the minimum and maximum respectively observed for the 10 last years (27); DSi and ASi concentrations measured at two week intervals and daily discharge measurements were used according to the procedure described by Verhoff et al. (28) with the flux calculated by multiplying mean discharge times the discharge-weighted mean concentration:

$$\text{flux} = Qm \times \Sigma(CiQi)/\Sigma Qi$$

where $Ci$ = instantaneous concentrations, $Qi$ = corresponding instantaneous water flux, and $Qm$ = mean water flux for the period considered (annual or summer).

**Determination of DSi and ASi.** Dissolved silica (DSi) was determined by spectrophotometry and analyzed from water samples filtered through Whatman GF/F filters and stored at 4 °C (29).

Amorphous silica (ASi) in riverine particulate matter which includes both biogenic silica as diatoms and phytoliths and inorganic forms of ASi (4), was determined using two different methods (30, 31) for which comparative results were obtained (32). ASi in soil was also measured using Demaster’s method (30), although the weak base used (Na2CO3) can underestimate soil ASi depending upon soil type (Saccone, L., personal communication). The DSi extracted was measured by spectrophotometry (29) on subsamples taken every hour during 5–6 h to reach a plateau, all BSi being assumed to be dissolved, while lithogenic silica, which has a much slower dissolution rate, remains in particulate form.

**Results and Discussion**

**Diffuse Sources.** *Dissolved Silica.* Rainwater DSi concentrations averaged 0.18 ± 0.07 mg Si L⁻¹. Lower DSi concentrations (0.1 mg Si L⁻¹) were found in samples upstream from Paris, while the Lower Seine rainwater was higher in DSi (0.2–0.3 mg Si L⁻¹), but due to large intra-sample variability (from a minimum of 0.02 to a maximum of 0.62 mg Si L⁻¹) no significant differences were found. Some of the variability can be attributed to atmospheric dust containing ASi, which can dissolve increasing the amounts of DSi in rainwater. The values found in the Seine River watershed are in the range of rainwater DSi concentrations found in other studies (0.03 mg Si L⁻¹ in France (33), or 0.07 mg Si L⁻¹ in Switzerland (34)).

DSi concentrations in groundwaters averaged 5.2 mg Si L⁻¹ (Figure 2), while the average concentration weighted by the lithology of the basin is estimated to 4.9 mg Si L⁻¹ (Table 1). DSi concentrations in riverine waters were also calculated on the basis of average lithology in the Seine River basin (22) using wintertime DSi concentrations in small unperturbed streams, so as not to be influenced by the strong biological uptake in rivers occurring in spring and summer. Riverine water DSi concentrations averaged 3.8 mg Si L⁻¹ (Table 1).

**Particulate Silica.** Soil ASi concentrations of the various land types ranged from a minimum of 2.5 mg Si g soil⁻¹ to a maximum of 7.3 mg Si g soil⁻¹. Winter ASi concentration in suspended matter (5.7 ± 0.9 mg Si g SM⁻¹) is not significantly different from the soil ASi concentration (4.9 ± 0.8 mg Si g soil⁻¹). Large differences in ASi concentrations of riverine suspended matter were observed among the winter
Basins. (from refs 6 network, are rich in DSi, especially after short (5 min). Paris and its suburbs averaged 4.1 mg Si L−1 urban runoff than in rainwater. Nevertheless, DSi concentrations are two times higher in rain events (Figure 3), confirming the fact that often 41% of DSi in the runoff, probably because of a ‘dilution’ effect. Impermeable urban surfaces are made of materials contain-

### TABLE 1. Influence of Watershed Lithology (According to ref 22) on Dissolved Silica (DSi) Concentrations (mg Si L−1) in Small Basins (from refs 6 and 42)

<table>
<thead>
<tr>
<th>Lithology</th>
<th>% aquifer lithology in the Seine watershed</th>
<th>groundwater Si, mg L−1</th>
<th>% surface lithology in the Seine watershed</th>
<th>riverine water Si, mg L−1</th>
<th>crystalline rock 2.96.333.36</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ante Trias sedimentary rock</td>
<td>14.7</td>
<td>n.d.</td>
<td>1</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>sand</td>
<td></td>
<td>4.6</td>
<td>8</td>
<td>4.76</td>
<td></td>
</tr>
<tr>
<td>clay and clayey sand</td>
<td></td>
<td>n.d.</td>
<td>5</td>
<td>3.78</td>
<td></td>
</tr>
<tr>
<td>clay and non gypsum marl</td>
<td></td>
<td>n.d.</td>
<td>5</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>calcareous sandstone and recent alluvium</td>
<td></td>
<td>n.d.</td>
<td>21</td>
<td>4.67</td>
<td></td>
</tr>
<tr>
<td>pure, non chalky, limestone</td>
<td>28.1</td>
<td>3.3</td>
<td>30</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td>chalk</td>
<td>33.8</td>
<td>4.9</td>
<td>22</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>other carbonate rocks</td>
<td>20.5</td>
<td>7.2</td>
<td>5</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>total % of watershed area</td>
<td>100</td>
<td>4.9</td>
<td>100</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>weighted mean for the Seine watershed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2. Amorphous Silica (ASi) Concentration in Soil and Suspended Matter Samples (mg Si g−1)

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Mean</th>
<th>Min−Max*</th>
</tr>
</thead>
<tbody>
<tr>
<td>cultivated soil</td>
<td>5.2</td>
<td>2.5−7.3</td>
</tr>
<tr>
<td>meadow</td>
<td>4.7</td>
<td>3.7−5.8</td>
</tr>
<tr>
<td>forest</td>
<td>3.9</td>
<td>3.9−4.0</td>
</tr>
<tr>
<td>all soils</td>
<td>4.9</td>
<td>2.5−7.3</td>
</tr>
<tr>
<td>suspended matter (winter)</td>
<td>5.7</td>
<td>3.8−7.7</td>
</tr>
<tr>
<td>suspended matter (summer)</td>
<td>18.4</td>
<td>9.1−48.2</td>
</tr>
</tbody>
</table>

* Due to the limited number of samples, confidence intervals were not calculated, and only minimum and maximum values are reported.

### FIGURE 3. Dissolved silica (DSi) concentrations in urban runoff from Paris, France (n = 30) during rain events (short rain ≤10 min, long rain > 10 min). The dotted line represents the DSi concentrations in rainwater and the error bars represent the 90% confidence interval.

and spring−summer samples, and spring−summer ASi concentrations were ca. 3-fold higher than those in winter (Table 2). Microscope observations of sediment trap samples showed that diatoms were also present in higher abundance than phytoliths in both winter and spring samples (Conley, unpublished data). The large difference in the amount of ASi between winter and summer suspended matter samples was probably due to diatom blooms that enrich summer samples (1).

**Point Sources. Si in Urban Runoff.** Urban runoff waters, collected together with domestic wastewaters to sewage network, are rich in DSi, especially after short (5−10 min) rain events (Figure 3), confirming the fact that often impermeable urban surfaces are made of materials containing weatherable Si. Longer rains lead to lower concentrations of DSi in the runoff, probably because of a “dilution” effect. Nevertheless, DSi concentrations are two times higher in urban runoff than in rainwater.

**DSi in Tap Water.** DSi concentrations from tap water from Paris and its suburbs averaged 4.1 mg Si L−1 (Table 3). The Montsouris reservoir, replenished with groundwater from springs, had higher DSi concentrations than the other reservoirs. About half of Paris tap water comes from spring sources and half comes from purified riverine water in which DSi is taken up during diatom blooms; for that reason river−origin water has lower DSi concentrations than groundwater, due to the combined effect of dilution of groundwater by surface water and due to uptake by diatoms in rivers. It was assumed that ASi concentrations in drinking water were not detectable since all particles in tap water are expected to be eliminated during purification.

**Si in Domestic Wastewater.** DSi and ASi have been measured in raw and treated waters of the Acheres treatment plant which collects and treats sewage from about 6.5 × 10^6 inhabitants per day. The specific Si load per inhabitant was calculated by taking into account the concentration of DSi in tap water (4.1 mg Si/L), the Si concentration in the Acheres WWTP (7.3 and 6.7 mg Si L−1 of DSi and ASi in raw and treated waters, respectively, with higher variability among treated than raw waters) and the daily volume of treated water (320 L per inhabitant). Calculated values of inhabitant equivalents are obtained equaling 1.0 and 0.8 Si inhabitant−1 d−1 for raw and treated waters, respectively, with a large proportion of ASi in both (Table 4). Estimated Si inhabitant equivalents are low compared to nitrogen and phosphorus which, for the Acheres WWTP have been estimated at 1 g inhabitant−1 d−1 for P and 10 g inhabitant−1 d−1 for N in treated waters (26). All these values, converted into moles and compared to the optimal environmental N/P/Si Redfield
ratios (16:1:16) show that Si point sources are still low compared to nitrogen or phosphorus, with a N/Si ratio of about 2:1 (instead of 16:16) and a P/Si ratio of about 1:1 (instead of 1:16).

These values should be considered specific for the Seine River basin, as values found in treatment plants effluents can differ because of the local land use, population load, industrial activity (pulp and paper production being a source of Si), and on the concentration of DSi in tap water, which differs depending upon its source. For example, Clark et al. (15) provide a figure of about 9 mg Si L⁻¹ in effluent water from a treatment plant in New York, while Van Dokkum et al. (14) report average values of 3.5 and 3.1 mg Si L⁻¹ for incoming and outgoing sewage water in six WWTPs in The Netherlands, where tap water concentration was 0.9 mg Si L⁻¹.

### Anthropogenic Emission: Si in Human Diet and Released with Detergent

Statistical data available for France in 1998 (INSEE, Institut national de la statistique et des études économiques) provide an average food consumption in kg per inhabitant per year. Using an exhaustive review paper on the Si concentration in food (35), combined with other reports (36, 37), it is possible to estimate a minimal and maximal Si intake in the average French diet (Table 5), and a correspondent Si release of 0.02 to 0.23 g Si inhabitant⁻¹ d⁻¹. Other published diet-dependent Si intake for U.S. (38), Finnish (39), and English (40) diets also fall within this range, and are mostly closer to the lower limit. The most common Si sources are grain products and beer, but the contribution of each depends on the consumption.

### Table 5. Si Minimal and Maximal Intake from Food on the Basis of an Average French Diet and According to Minimal and Maximal Silica Percentage in the Different Food Types

<table>
<thead>
<tr>
<th>Food</th>
<th>average consumption (kg inhabitant⁻¹ y⁻¹)</th>
<th>min (Si%)</th>
<th>max (Si%)</th>
<th>min (g Si inhabitant⁻¹ d⁻¹)</th>
<th>max (g Si inhabitant⁻¹ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>flour and semoule</td>
<td>5.5</td>
<td>0.0091</td>
<td>0.0185</td>
<td>0.0014</td>
<td>0.0027</td>
</tr>
<tr>
<td>rice</td>
<td>3.53</td>
<td>0.0034</td>
<td>0.0409</td>
<td>0.0003</td>
<td>0.0038</td>
</tr>
<tr>
<td>biscuits</td>
<td>11.92</td>
<td>0.0030</td>
<td>0.0030</td>
<td>0.0011</td>
<td>0.0011</td>
</tr>
<tr>
<td>pasta</td>
<td>7.39</td>
<td>0.0020</td>
<td>0.0060</td>
<td>0.0003</td>
<td>0.0011</td>
</tr>
<tr>
<td>bread</td>
<td>59.87</td>
<td>0.0017</td>
<td>0.0100</td>
<td>0.0027</td>
<td>0.0164</td>
</tr>
<tr>
<td>potatoes</td>
<td>65.78</td>
<td>0.0002</td>
<td>0.0020</td>
<td>0.0000</td>
<td>0.0036</td>
</tr>
<tr>
<td>fresh vegetables</td>
<td>91.33</td>
<td>0.0004</td>
<td>0.0439</td>
<td>0.0011</td>
<td>0.1099</td>
</tr>
<tr>
<td>frozen vegetables</td>
<td>6.69</td>
<td>0.0003</td>
<td>0.0439</td>
<td>0.0000</td>
<td>0.0079</td>
</tr>
<tr>
<td>dried vegetables</td>
<td>1.41</td>
<td>0.0030</td>
<td>0.0439</td>
<td>0.0000</td>
<td>0.0016</td>
</tr>
<tr>
<td>canned vegetables</td>
<td>24.34</td>
<td>0.0024</td>
<td>0.0439</td>
<td>0.0016</td>
<td>0.0293</td>
</tr>
<tr>
<td>fresh and frozen fruits</td>
<td>55.86</td>
<td>0.0002</td>
<td>0.0090</td>
<td>0.0003</td>
<td>0.0137</td>
</tr>
<tr>
<td>dried fruits (raisins and prunes)</td>
<td>1.3</td>
<td>0.0020</td>
<td>0.0140</td>
<td>0.0000</td>
<td>0.0005</td>
</tr>
<tr>
<td>jams</td>
<td>6.63</td>
<td>0.0002</td>
<td>0.0076</td>
<td>0.0000</td>
<td>0.0014</td>
</tr>
<tr>
<td>meat</td>
<td>84.89</td>
<td>0.0005</td>
<td>0.0020</td>
<td>0.0011</td>
<td>0.0047</td>
</tr>
<tr>
<td>eggs</td>
<td>14.85</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>fish and crustaceans</td>
<td>25.04</td>
<td>0.0005</td>
<td>0.0300</td>
<td>0.0003</td>
<td>0.0022</td>
</tr>
<tr>
<td>milk</td>
<td>68.65</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0000</td>
<td>0.0003</td>
</tr>
<tr>
<td>dairy products</td>
<td>68.03</td>
<td>0.0004</td>
<td>0.0040</td>
<td>0.0008</td>
<td>0.0074</td>
</tr>
<tr>
<td>oil &amp; margarine</td>
<td>14.25</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>sugar</td>
<td>11.16</td>
<td>0.0002</td>
<td>0.0062</td>
<td>0.0000</td>
<td>0.0019</td>
</tr>
<tr>
<td>chocolate &amp; sweets (candies)</td>
<td>6.14</td>
<td>0.0005</td>
<td>0.0110</td>
<td>0.0000</td>
<td>0.0019</td>
</tr>
<tr>
<td>honey</td>
<td>0.44</td>
<td>0.0007</td>
<td>0.0064</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>ice creams</td>
<td>6.81</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>wine &amp; cider</td>
<td>78.27</td>
<td>0.0007</td>
<td>0.0020</td>
<td>0.0014</td>
<td>0.0041</td>
</tr>
<tr>
<td>beer</td>
<td>37.4</td>
<td>0.0003</td>
<td>0.0061</td>
<td>0.0033</td>
<td>0.0063</td>
</tr>
<tr>
<td>sparkling drinks</td>
<td>40.06</td>
<td>0.0002</td>
<td>0.0006</td>
<td>0.0003</td>
<td>0.0005</td>
</tr>
<tr>
<td>mineral water</td>
<td>136.73</td>
<td>0.0011</td>
<td>0.0014</td>
<td>0.0038</td>
<td>0.0055</td>
</tr>
<tr>
<td>fruit juice</td>
<td>11.53</td>
<td>0.0000</td>
<td>0.0006</td>
<td>0.0000</td>
<td>0.0003</td>
</tr>
<tr>
<td>coffee</td>
<td>4.39</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>tea and infusions</td>
<td>0.29</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>total inhabitant equivalents for food</td>
<td></td>
<td></td>
<td></td>
<td>0.02</td>
<td>0.23</td>
</tr>
<tr>
<td>Detergents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>powder detergents</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>laundry</td>
<td>9.8</td>
<td>0.6</td>
<td>1.2</td>
<td>0.16</td>
<td>0.33</td>
</tr>
<tr>
<td>dishwashing</td>
<td>1.9</td>
<td>0.6</td>
<td>1.2</td>
<td>0.03</td>
<td>0.06</td>
</tr>
<tr>
<td>home care</td>
<td>0.4</td>
<td>0.6</td>
<td>1.2</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>other products</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>home care (liquid)</td>
<td>3.4</td>
<td>0.6</td>
<td>1.2</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>softener</td>
<td>3.0</td>
<td>0.6</td>
<td>1.2</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>laundry</td>
<td>3.0</td>
<td>0.6</td>
<td>1.2</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>dishwashing (liquid)</td>
<td>2.6</td>
<td>0.6</td>
<td>1.2</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>toothpaste</td>
<td>0.4</td>
<td>2.3</td>
<td>7.0</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>others</td>
<td>0.2</td>
<td>0.6</td>
<td>1.2</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>total inhabitant equivalents for detergents</td>
<td></td>
<td></td>
<td></td>
<td>0.43</td>
<td>0.89</td>
</tr>
<tr>
<td>Σ inhabitant equivalents</td>
<td></td>
<td></td>
<td></td>
<td>0.45</td>
<td>1.12</td>
</tr>
</tbody>
</table>

*Total consumption (kg Si inhabitant⁻¹ y⁻¹) and specific load inhabitant equivalents (g Si inhabitant⁻¹ d⁻¹) are also indicated.

D *ENVIRON. SCI. & TECHNOL. / VOL. xx, NO. xx, xxxx*
capita (Table 5), since detergents contain significant amounts of sodium meta-silicate (14). Powdered sodium meta-silicate readily dissolves in water forming DSi. Statistical information of sodium meta-silicate (Table 5), since detergents contain significant amounts and amorphous silica fluxes expressed in \(10^6\) kg Si y\(^{-1}\) to the total Si input in the watershed is higher, reaching up to 8% of the total Si inputs, and showing that point sources should not be systematically neglected in the investigation of the causes and consequences of coastal eutrophication.

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CHAPTER 3

Silica dynamics in the hydrographic network of the Seine River

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Silica dynamics in the hydrographic network of the Seine River

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Keywords: drainage network, dissolved and biogenic silica, dissolution rate, modelling

Abstract
In hydrographic networks, dissolved silica originates mostly from rock weathering and is not generally considered to be influenced by human activity. Eutrophication can however lead to increased retention in the upstream sectors of the drainage network and its stagnant annexes, through increasing diatom biomass (biogenic silica) under nutrient enrichment (N, P). More recently, the pools of biogenic silica, originating from both aquatic and terrestrial (phytoliths) ecosystems has been shown to be significant at a global scale.

In the framework of a comprehensive study carried out on the biogeochemical functioning of the Seine River, being dissolved silica limited in spring, we have undertaken to quantify the importance of biogenic silica vs. dissolved silica in the drainage network on the basis of Si budgets in key sectors. We have shown that biogenic silica flux represents

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about 10% of the total silica flux (dissolved silica + biogenic silica), and increases with biological activity, i.e. with diatom development within the drainage network. Retention in the reservoirs of the Seine River represents a small proportion in comparison with the total Si fluxes along the continuum. In order to better simulate the seasonal variations of dissolved silica concentration in the hydrographic network with the RIVER-STRAHLELM modelling approach, we have experimentally determined the rate of the dissolution constant of suspended matter containing biogenic silica and have explored the range of the values (2 × 10^{-4} to 2 × 10^{-5} h^{-1}) in the model. It appears that the response of the model to the dissolution constant is relatively small in this range, suggesting that more experimental work on dissolution rate of various types of biogenic silica material is needed. In addition, the results show the need for a better representation of diatoms in the model.

**Dynamique de la silice dans le réseau hydrographique de la Seine**

**Mots clés :** réseau hydrographique, silice dissoute et biogène, taux de dissolution, modélisation

**Résumé**

Dans les bassins fluviaux, la silice dissoute provient de la dissolution des roches, et sa concentration n’est en principe pas affectée par les apports anthropiques. Toutefois l’eutrophisation peut contribuer largement à sa rétention dans le réseau hydrographique et dans les annexes hydrauliques (réservoirs, chenaux, sablières...), à travers le stockage de la biomasse de diatomées (silice biogène), dont la production augmente avec l’enrichissement en nutriments (N, P). Plus récemment, il a été mis en évidence que le stock de silice biogène, issu du milieu aquatique mais aussi des écosystèmes terrestres (phytolithes), pouvait être quantitairement important à une échelle mondiale.

Dans le cadre de l’étude du fonctionnement biogéochimique du bassin de la Seine, comme la silice dissoute peut limiter au printemps le bloom des diatomées, nous avons entrepris de quantifier l’importance de la silice biogène à l’échelle du réseau hydrographique, en établissant des bilans de silice (dissoute vs. biogène) dans des secteurs clés du réseau. Il apparaît que le flux de silice biogène représente environ 10% du flux total de silice et que ce flux augmente de l’amont vers l’aval du réseau hydrographique, avec l’activité biologique (développement des diatomées). La rétention dans les réservoirs du bassin de la Seine représente une faible proportion du flux de silice à l’exutoire du système hydrographique. Afin de mieux simuler les variations saisonnières de la silice dissoute dans le réseau hydrographique avec l’approche de modélisation RIVERSTRAHLER, nous avons déterminé expérimentalement des valeurs de la constante de dissolution de la silice biogène contenue dans des matières en suspension. Ces valeurs (de 2 × 10^{-4} à 2 × 10^{-5} h^{-1}) ont alors
1. Introduction

Less attention has been paid to the fluxes of Si transferred from terrestrial systems to surface waters than is the case for phosphorus and nitrogen fluxes. Whereas values of phosphorus and nitrogen concentrations in surface water can be found in the literature or in the databases of Water Agencies for the last 30 years, dissolved silica concentrations are only found for the last 15 years, and even today remain scarce. Yet, dissolved silica is an essential nutrient for diatoms, since they use it to build their frustule (DeMaster, 1981; Anderson, 1986; Tréguier et al., 1995). Algae require nutrients in adequate ratios (Redfield et al., 1963; Brzezinski, 1985, C:N:P of 106:16:1:16, in atomic ratios). Since the 1970’s, inputs of nitrogen and phosphorus have significantly increased with the intensive use of fertilizers, especially for N, and with the increase of domestic and industrial waste water sources, especially for P. The flux of dissolved silica originates largely from rock weathering and is strongly dependent on hydrology, and dissolved silica concentrations are more stable over long time periods (Billen et al., 2001). As a consequence, due to the excess in N and P inputs, enhanced diatom blooms have been found to deplete dissolved silica concentrations in lakes and reservoirs (Conley et al., 1993; Garnier et al., 1999), and also in rivers despite the permanent water input (Garnier et al., 1995; Admiral et al., 1993). Dissolved silica can be immobilized under its biogenic form, more or less temporarily, both in small streams by benthic diatoms and in large rivers and reservoirs by planktonic species (Garnier et al., 1998a,b, 2002; Homborg et al., 1997). Such a Si retention in the aquatic river continuum can have great effects on coastal eutrophication (Lancelot et al., 1987; Méneguen et al., 1995; Billen & Garnier, 1997; Rousseau et al., 2002; Cugier et al., 2004) as it favors the occurrence of non-siliceous and often harmful algal blooms.

More recently, biogenic silica originating from aquatic and even terrestrial ecosystems has been considered significant as a Si stock at a global scale (Conley, 2002). Indeed, similarly to diatoms that use dissolved silica to build up their external skeleton (the frustule), terrestrial vegetation also incorporates dissolved silica as phytoliths (graminaceous, rice...). Although the occurrence
of phytoliths in plants were discovered with the origin of the microscope, their importance in Si-biogeochemical cycles was only recently quantified (BARTOLI, 1983; MEUNIER et al., 1999) and has been estimated to be significant at a global scale (CONLEY, 2002). Measurements of biogenic silica were first made in marine systems in the early 1980's (EGGIMAN et al., 1980; DEMASTER, 1981), but there are few measurements of biogenic silica for rivers (CONLEY, 1997).

In the framework of a comprehensive study carried out on the biogeochemical functioning of the Seine River the objectives of this paper are: 1. to quantify the importance of biogenic silica vs. dissolved silica in the drainage network on the basis of Si budgets in key sectors and 2. to explore with a model the sensitivity of drainage network Si retention to the dissolution rate of biogenic silica.

2. Sampling strategy and methodology

2.1. The Seine drainage network

The Seine River drainage basin, including the estuary, covers a surface area of 75,000 km². The population density averages 200 inhab. · km⁻², but it is unequally distributed from 50 inhab. · km⁻² in the upstream basin to 1000 inhab. · km⁻² in the urbanized zones. As a whole, population density is higher along the main tributaries (Marne, Seine, Oise), and in particular in the Parisian agglomeration that concentrates 2/3 of the population. Due to intense human activities in the whole basin, the Seine River is considerably enriched in nutrients (GARNIER et al., 1995; BILLÉN et al., 1998).

Dissolved and biogenic silica measurements along with other classical variables of water quality (not shown here) were made in 2001 at a seasonal scale (every two weeks) at the outlet of the Marne, Seine and Oise sub-basins, at the outlet of the Seine River (at Pois), and in the estuary (at Caudebec, the limit of the saline intrusion) (figure 1).

2.2. DSi and BSi measurements

Dissolved silica (DSi) was determined by spectrophotometry on waters filtered through Whatman GF/F and stored in the refrigerator (RODIER, 1984).

Biogenic silica (BSi) was determined according to two methods (RAGUENEAU & TRÉGUER, 1994; CONLEY & SChELSKA, 2001) that have been shown to lead to similar results (D’Ayguexvives et al., in prep.). Whereas RAGUENEAU & TrÉGUE (1994)’s method uses suspended matter gathered by centrifugation, the method by CONLEY & SChELSKA (2001) is based on suspended matter.
collected on a polycarbonate membrane of 1 μm pore size. The extraction of biogenic silica in both cases was made by alkaline digestion at 85 °C in Na₂CO₃ with subsamples taken through time (every hour during 6 h) followed by acidic neutralization. The extracted DSi was measured by Rodier's method (1984). DSi concentrations plotted as a function of time tend to a plateau indicating a decreasing solubility of the remaining Si, which is considered as non-biogenic (lithogenic silicate). The y ordinate-intercept with the plateau line, i.e. the fraction of the particulate Si rapidly dissolved, is considered as an estimate of biogenic silica (Ragueneau & Tréguer, 1994; Conley & Schelske, 2001). Biogenic silica can be expressed in content of the suspended matter or in concentration.
2.3. Experimental dissolution of biogenic silica

The value of the dissolution rate has been investigated experimentally in batch reactors at 60 °C on suspended matter of the Seine River collected during two different seasons, one with low biological activity and high water fluxes in January, the other during spring diatom development in April (D’Ayguessvives et al., in prep). This experiment was based on the measurement of dissolved silica appearing as a function of time at 60 °C in a shaker bath: for each batch reactor 1.67 g of freeze-dried suspended matter, homogenized with a mortar and a pestle, were placed in polypropylene centrifuged tubes with 50 ml of 0.7 M NaCl buffered solution (Tris) at pH 8.0 ± 0.1 (Ragueneau, pers. comm.). During the experiment, aliquots of 0.2 ml were collected after centrifugation for DSI analyses (Rodier, 1984). Initial BSi concentration (BSi₀) was measured according to Conley & Schelske (2001) equalling 4.80 and 4.22 mg BSi·g⁻¹ of suspended matter in January and April respectively. DSI concentrations show a rapid increase in concentration as a function of time during the first 30-50 hours and the rate of increase slowed down during the next 8-10 days. The initial slope ln(BSi₀ – DSi) = f(t) is considered as the dissolution rate of biogenic silica (h⁻¹) (figure 2). Decreasing dissolution rates as a function of time can be explained by a saturation of the solution and/or a decrease in the reactive surface of the particle (Van Cappellen, 1996; Dixit et al., 2001).

![Figure 2](image_url) - Variation of dissolved silica (DSI), in function of time, from suspended matter containing biogenic silica in batch experiments, at 60 °C. Experiments at two periods of the season, April and July 2002.
Dissolution rates obtained at 60 °C can be calculated for any other temperature according to Arrhenius’s equation: \( k = A e^{-E_{\text{app}}/RT} \) (Rickert et al., 2002)

where:

- \( A \) is a constant factor
- \( E_{\text{app}} \) is the energy of apparent activation (60 000 J·mol\(^{-1}\))
- \( R \) is the constant of perfect gas (8.314 J/(K·mol))
- \( T \) is the temperature in kelvin (1 K = 273 + T °C).

### 2.4. Hypothesis for budget calculations

Budget calculations for the year 2001 are mainly based on water fluxes data and DSi and BSi measurements. Calculations were made at various spatio-temporal scales: (i) an annual budget of Si at the scale of the Seine basin, including that in the reservoirs (Garnier et al., 1999, 2000), was estimated for the years from 1993 to 1995, (ii) a summer budget for the sub-basins (in particular the Marne), and (iii) budgets in the lower Seine branch (from Paris to Poses) as well as in the freshwater sector of the estuary (Poses-Caudebec).

DSi fluxes in the headwaters (upstream from any in-stream biological processes) were calculated on the basis of the water fluxes at Caudebec, the outlet of the basin, and on a DSi concentration characterizing the lithology of the considered sub-basins (Thibert, 1996; Billen et al., 1998; see also Garnier et al., 2002). The composition of the water at the head of the basins is mainly the result of rainwater interactions with the watershed rocks. The rock types in the basin and their chemical weathering, whatever the vegetation cover, determine the DSi content of the runoff (Billen et al., 1998). Feldspars, contained in crystalline rocks as well as in marine clay in sedimentary rocks, are weathered by the action of carbonic acid in rainwater and release DSi. Sedimentary rocks such as chalk or marl contain amorphous silica of biological origin (diatoms, sponges or other fossil siliceous micro-organisms) which, when dissolved, also enriches the drainage water. The different levels of DSi concentration in the water draining the small monolithological forest-covered watersheds in the Seine basin reflect these mechanisms (table 1). For the whole Seine watershed, an average concentration of 4.5 mg Si · l\(^{-1}\) can be calculated taking into account the lithology of the basin.

BSi fluxes of the upstream basins were calculated on the basis of suspended matter fluxes at Caudebec multiplied by the content of BSi characterizing terrestrial suspended matter, without BSi originating from in-stream algal growth. This value is assumed to be represented by the background level of suspended matter (SM) at high suspended matter load, obtained by plotting observed BSi content (mg BSi · g SM\(^{-1}\)) against suspended matter concentration (mg · l\(^{-1}\)), gathering all samples analysed from 1999 to 2001 at the outlet of the Marne
Table 1 — Influence of the watershed lithology on the median dissolved-silica content of small forested French basins, including the Seine (from Meybeck, 1986; Levêt, 1991; Thibert, 1996).

<table>
<thead>
<tr>
<th>Lithology</th>
<th>% area in the Seine watershed</th>
<th>SiO₂, mg · l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cristalline rock</td>
<td>3</td>
<td>7.2</td>
</tr>
<tr>
<td>Ante Trias sedimentary rock</td>
<td>1</td>
<td>5.4</td>
</tr>
<tr>
<td>Sand</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Clay and clayey sand</td>
<td>5</td>
<td>8.1</td>
</tr>
<tr>
<td>Clay and non gypseous marl</td>
<td>5</td>
<td>5.4</td>
</tr>
<tr>
<td>Calcareous sandstone and recent alluvium</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>Pure, non chalky, limestone</td>
<td>30</td>
<td>3.6</td>
</tr>
<tr>
<td>Chalk</td>
<td>22</td>
<td>12</td>
</tr>
<tr>
<td>Gypseous marl</td>
<td>1</td>
<td>9.6</td>
</tr>
<tr>
<td>Calcareous marl</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Gaize</td>
<td>1</td>
<td>19</td>
</tr>
</tbody>
</table>

100% of the surface area
Mean concentration for the Seine watershed: 8.75 mg · l⁻¹

River (figure 3). A background value of 1.5 mg BSi · g SM⁻¹ is derived from this analysis.

2.5. The RIVERSTRAHLER modelling approach

The RIVERSTRAHLER model (Billen et al., 1994, 2001; Garnier et al., 1995, 1998b, 2002; Billen & Garnier, 1999; Billen et al., submitted) is a generic model of the biogeochemical functioning of large drainage networks. It is based on the idea that the kinetics of the basic ecological processes in the functioning of the aquatic ecosystem are the same from headwater to downstream sectors, while the controlling factors, i.e. the hydro-meteorological and morphological constraints as well as the point and non-point sources of material from the watershed, modulate their expression. The RIVERSTRAHLER model thus results from coupling of a unique model of processes (RIVE) and a hydrological model (HYDROSTRAHLER), describing in an idealised way the water fluxes in the drainage network represented by a regular scheme of confluence of tributaries of increasing stream order with mean characteristics. This model simulates 22 variables for the water quality at the outlet of any
Figure 3 — Relationship between the biogenic silica (BSi) content of suspended matter (mg BSi · g SM⁻¹) and the concentration of suspended matter (mg · l⁻¹). The full horizontal line indicates the estimated background BSi content of SM.

sub-basin considered, here the upstream Seine, the Marne, the Oise and the Eure, and at every km of the main branch, from the Seine and Marne confluence (immediately upstream from Paris) to the outlet of the freshwater estuary (Caudebec). Its application to the description of the dynamics of diatoms and DSi at the scale of the whole Seine basin has been published earlier (GARNIER et al., 1995).

3. Budgets of Si transfer

Unless stated otherwise, the budgets presented below were established on the basis of data collected in 2001. It is important to mention that this year was very wet compared to the period of the ten last years 1993-2002 (figure 4).

3.1. Annual budget at the scale of the Seine hydrographic network and in the 3 main reservoirs

DSi and BSi fluxes at Caudebec, including the freshwater sector of the Seine estuary show a clear dominance of DSi (112 kT Si · yr⁻¹) compared to BSi (19 kT Si · yr⁻¹): BSi represents 15% of the total silica fluxes (figure 5). The comparison of DSi and BSi deliveries at Caudebec with the fluxes in the headwaters shows a clear retention of 14 kT Si · yr⁻¹ within the aquatic continuum, representing approximately 10% of the total silica (DSi + BSi) influxes.
The fraction retained in the reservoirs is relatively small, 0.42 kT Si \cdot yr^{-1} for the years 1993-1995, contrary to the results reported in the literature for other reservoirs (Officer & Ryther, 1980; Humborg et al., 1997), and can be explained by their upstream position in the drainage network and by their hydrological functioning (Garnier et al., 1999, 2000). The reservoirs are supplied by diverted water, filled in winter and spring and emptied in summer and autumn to sustain low river waters, leading to a residence time of half a year (Garnier et al., 1998a). Their shallowness leading to homogeneity of the water column does not help sedimentation of diatoms and sequestration of Si. The average value of 0.42 kT Si \cdot yr^{-1} obtained in 1993-1995 can even represent an overestimation of the retention in 2001, taking into account the high water fluxes and the lower residence time. Si immobilization within in the drainage network of the river Seine seems therefore to be the dominant process of Si retention at the scale of the basin.

Ecological processes studied in detail in one of the reservoirs (Marne Reservoir) contribute to a better understanding of the circulation and the transformation of Si in this stagnant system (see Garnier et al., 2000, and figure 6). Internal recycling appears to be mainly driven by primary production (^{14}C method) and benthic recycling (bell jar measurements). Retention, which is low at the scale of the whole drainage network, represents 30% of the input at the local scale of the reservoir.

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3.2. Summer budget in the Marne River

Similar calculations of the budgets at the scale of the Marne River for the summer period (July-September) show that retention can reach 35% of the influxes compared to the 10% obtained at the annual scale for the whole basin (figure 7). The largest Si retention by sedimentation of the planktonic diatoms is expected in spring on the basis of the classical seasonal succession of algae observed in rivers (Garnier et al., 1995). However, due to the high water fluxes in 2001, phytoplankton development was delayed to early summer (not shown). Periphytic algae (benthic diatoms) building high biomass in the small streams may participate in the temporary immobilization of DSi in the river bed (Flopo et al., 2003). At an annual scale, BSi contained in the biomass may be partly recycled as DSi, the remaining stock being flushed in autumn at the beginning of the high water period.

3.3. Summer silica budget in the lower Seine and its freshwater estuary

Besides the DSi and BSi inputs to the main branch of the Seine River by the tributaries (upstream Seine, Marne, Oise and Eure rivers), we have to consider those by the direct watershed as well as the input by the effluents of the Achères waste water treatment plant.
The DSi from the direct watershed was calculated on the basis of the water flux (obtained by difference between the value at Caudebec and the sum of water fluxes of the sub-basins) and DSi concentrations (those of the headwaters). Regarding BSi fluxes, except for the Marne River for which direct measurements have been carried out at the seasonal scale, the calculations were based on the suspended matter (SM) fluxes and on a mean BSi content of the SM calculated for the Marne River (see figure 4).

Along the fluvial course of the lower Seine River, an increase from 10% (Paris) to 17% (Caudebec) of total silica flux is observed (figure 8). The budget shows significant dissolution of BSi between Paris and Poses, that can be explained by the suspended matter that accumulates during summer in that sector (figure 8). On the basis of the studies on particulate storage by BONTÉ & MOUCHET (2002), who estimated a stock of suspended matter of about 100-200 × 10⁶ kg SM in this sector and on a BSi content of 1.5 mg BSi · g⁻¹ SM, a dissolution coefficient in the range of 3 × 10⁻³ to 1 × 10⁻² h⁻¹ is needed to balance the budget in the lower Seine River. Note that the value used in the model was initially set at 1 × 10⁻² h⁻¹.

In the freshwater estuarine sector (Poses-Caudebec), retention is relatively low, and can be explained by the high water fluxes observed in 2001 (figure 9). The calculations of the Si budget in this sector from 1993 to 2001 indeed
show that the retention is higher at low water fluxes; 6% (in 2001) to 47% (in 1993) of the DSi can be immobilized depending on the hydrological conditions; at high residence time in summer, phytoplankton maximal development can occur at various places in the river continuum, generally at the outlet of the sub-basins and in the freshwater estuary (GARNIER et al., 1995).

4. Dissolution rate of biogenic silica and exploration with the RIVERSTRAHLER modelling approach

4.1. Range of BSI dissolution rates

On the basis of 5 experiments, values of the dissolution rate constant, \( k_{\text{BSI}} \), calculated for a temperature of 20 °C, averaged \( 0.85 \times 10^{-4} \text{ h}^{-1} \) (standard deviation = \( 0.63 \times 10^{-4} \text{ h}^{-1} \)) for the suspended matter collected in winter and \( 1.39 \times 10^{-4} \text{ h}^{-1} \) (standard deviation = \( 0.65 \times 10^{-4} \text{ h}^{-1} \)) for the one collected in spring. As no significant difference can be shown between these two samples of suspended material, the extreme values of the range can be taken, i.e. \( 2 \times 10^{-4} \text{ h}^{-1} \) and \( 2 \times 10^{-3} \text{ h}^{-1} \) (table 2; D’AYGUESVIVES, 2002, D’Ayguesvives, unpublished). At this stage of the study, these values appear
Figure 9 — Si retention (% DSi) in the upstream estuary as a function of water fluxes (m$^3$·s$^{-1}$). The summer period is from July to September from 1993 to 2001.

much lower than the one previously assumed in the RIVERSTRAHLER, namely $1 \times 10^{-2}$ h$^{-1}$.

4.2. Sensitivity of the RIVERSTRAHLER model to the value of BSi dissolution rate

New runs of the RIVERSTRAHLER model have been carried out for the hydrological conditions of the years 1996 and 1997 with a range of BSi dissolution rates from $1 \times 10^{-2}$ to $2 \times 10^{-5}$ h$^{-1}$. Results are shown at the outlet of the Marne River (St Maurice) and the Seine River (Caudebec), and compared with observed DSi concentrations and chlorophyll data (figures 10 & 11).

A rather good agreement is found between the simulations and the observations of the water fluxes. Regarding DSi, the value initially used in the model ($10^{-2}$ h$^{-1}$) makes simulations that better fit to the observations than the experimentally obtained values (figure 10). On the contrary, the values found experimentally ($2 \times 10^{-4}$ h$^{-1}$ to $2 \times 10^{-5}$ h$^{-1}$) lead to a better agreement at Caudebec (figure 11) and it is interesting to note that the model is not sensitive to this range of variation. The results by the model do not invalidate the one found with the budget approach, i.e. a high dissolution of biogenic silica in the downstream sector of the Seine River.

Whatever values of dissolution rates are tested, phytoplankton biomass simulations are not affected. The comparison between the phytoplankton biomass simulations and the observations lead, however, to the conclusions that the representation of DSi could be not only improved by further determination of the dissolution constant but also by refining diatom dynamics in the model.
Table 2 — Value of the dissolution rate of biogenic silica \( k_{BSi} \), \( 10^{-4} \) h\(^{-1} \) as obtained from winter and spring suspended matter

<table>
<thead>
<tr>
<th></th>
<th>Winter suspended matter</th>
<th>Spring suspended matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{BSi} ), ( 10^{-4} ) h(^{-1} )</td>
<td>0.85 (SD = 0.63, ( n = 5 ))</td>
<td>1.39 (SD = 0.65, ( n = 5 ))</td>
</tr>
<tr>
<td>Average</td>
<td>( 1.2 \times 10^{-4} ) h(^{-1} )</td>
<td></td>
</tr>
<tr>
<td>Extreme values</td>
<td>( 2 \times 10^{-5} ) h(^{-1} ) to ( 2 \times 10^{-4} ) h(^{-1} )</td>
<td></td>
</tr>
</tbody>
</table>

At Caudebec especially, the model underestimates diatom biomass in summer, as shown by the depletion of DSi. A split of the diatom group into two compartments, one growing preferentially in spring, a second more adapted to summer or late summer conditions, would probably improve the simulations of both phytoplankton and DSi. It is well known that during the seasonal succession the diatom community is composed essentially of small rapidly growing species in spring, whereas larger species with a slower growth rate and low half-saturation constant are favoured in summer (Sommer et al., 1986; Tilman et al., 1982; Conley & Malone, 1992).

5. Conclusions

Our Si budgets, including both dissolved silica (DSi) and biogenic silica (BSi), are the first ever reported in a drainage network. Budget calculations can be considered as a way to test the coherence of the data gathered at different time and space scales, using various approaches (observations and modelling). Besides an evaluation of the Si fluxes at the scale of the basin, we have been able to calculate these fluxes at various scales, providing an overview of Si dynamics in the basin. BSi represents as a whole 10% of the total Si flux at the outlet of the basin, but this percentage could be much higher for a dry hydrological year, due to higher diatom production. Budget calculations have also shown that retention in the reservoirs is relatively low compared to the retention that can occur in the drainage network itself. Such a retention can be due to the uptake either by benthic diatoms in the headwaters or by planktonic diatoms in the large rivers. Depending on the residence time of the water and on the associated organic matter forming aggregates, BSi can be immobilized more or less temporarily, material being re-suspended or flushed at storm events and during the rainy season.
It is interesting to mention here the results obtained for the Danube River by a modelling approach according to which, and contrary to HUMBOERG et al.’s findings (1997), the greatest retention of Si did not occur within the Iron Gate reservoir, but in the drainage network itself (GARNIER et al., 2002; TRIFU, 2002). The short residence time of the water in the Iron Gate reservoir does not allow diatoms to build up high biomass that would be then lost by sedimentation.

A large range of values in the rate of Si dissolution has been tested by the model. The response differs according to the place in the drainage network, so that further studies are necessary to understand the controlling factors of BSi.
dissolution. In addition to refining the rates of BSi dissolution, it appears that we have to reconsider the representation of diatoms, by including more than one type of diatoms as state variables of the model.

As a whole, we will continue to use these complementary and interactive approaches to better understand Si dynamics, with Si being considered as an important nutrient similarly to phosphorus and nitrogen, with the aim of understanding and combating eutrophication in the aquatic continuum from headwaters to the coastal zone.

Figure 11 — Simulations of the seasonal variations of the water fluxes (m$^3$·s$^{-1}$), dissolved silica (DSi, mg Si·l$^{-1}$) and of phytoplankton (Phyto, μg Chl·a·l$^{-1}$) at the outlet of the fluvial estuary (Caudebec) in 1996 and 1997 for 3 values of the rate of BSi dissolution.
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CHAPTER 4

Modelling nutrient fluxes from sub-arctic basins: comparison of pristine vs. dammed rivers

submitted to the Journal of Marine Systems

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ABSTRACT

The deterministic Riverstrahler model of river functioning is applied for the first time to sub-arctic catchments. Seasonal nutrient (N, P, Si) deliveries to the coastal zone are simulated, and nutrient annual fluxes are established for the nearly pristine Kalixälven and the heavily dammed Luleälven rivers, both located in Northern Sweden and draining into the Baltic Sea. For Kalixälven river simulations are performed with a runoff calculated from precipitation, evapotranspiration and temperature data for the period 1990-1999, using an original hydrological model calibrated on observed monthly discharges at the river outlet. The same hydrological parameters are used to calculate specific runoff for the Luleälven basin in absence of dam regulation. Reservoir filling and emptying are simulated using a simplified representation of their management rules. The simulated trends are within the range of observed data, in particular for discharge, dissolved silica and total organic carbon. Specific runoff is 50 % higher in the Luleälven than in the Kalixälven watershed due to higher altitudes and precipitations. Average silica concentrations are much lower in the Luleälven (35 µmol/l) than in the Kalixälven (73 µmol/l) river and the overall total silica delivery is slightly lower in Luleälven (812 kg Si/km²/yr) than in Kalixälven (850 kg Si/km²/yr).

Comparisons of model results for the Luleälven river with and without dam show a reduction of about 23% and 80% in dissolved and biogenic silica delivery respectively. The model results suggest that this reduction should be attributed both to reservoir trapping of biogenic silica coming from erosion of the upstream watershed and/or produced in the reservoir by diatom growth, and to changes in the vegetation induced by flooding the formerly forested valley.

Keywords.
Silica, deterministic modelling, damming, arctic pristine rivers, Kalixälven, Luleälven.
1. INTRODUCTION

Nutrient fluxes from land-based sources to the ocean play an important role in the ecological and biogeochemical functioning of both the open ocean and the near-shore environment. An important scientific challenge is understanding how riverine delivery of nitrogen, phosphorus and silica to the sea is dependent i) on land cover and land use of the watershed, ii) on processes occurring during the downwards travel of these nutrients through the drainage network, and iii) on the human management of the river systems. More attention has been devoted in that challenge to investigate the role of nitrogen and phosphorus rather than silica, although the ratio of this element with respect to the others plays a crucial role in the coastal eutrophication problems (Officer & Ryther, 1980, Conley et al., 1993; Conley, 1999; Turner & Rabalais, 1994; Justic et al., 1995; Billen & Garnier, 1997; Turner et al., 1998; Cugier et al., 2005).

Several studies have focused on the effect of river damming on silica retention and delivery. Budget and modelling studies have shown that reservoirs are often a favourable site for diatoms to grow, taking up dissolved silica to incorporate it into their frustules which sediment within the reservoirs and are thus permanently buried (Garnier et al., 1999a; Hungspreugs et al. 2002; Garnier et al., 2002a, b; Meybeck and Vörösmarty, 2005; Humborg et al., 2006). However, the role of reservoirs has been sometimes overlooked, because these processes of uptake, sedimentation and burial strongly depend on the residence time of water within the reservoirs, so that reservoirs with too low residence time would not be the site of significant silica trapping (Garnier et al., 2002b; Friedl et al., 2004). It thus appears that generalization is not possible, and that very often the causes of silica depletion at the coastal zone are site-specific, and require a close examination of the mechanisms potentially involved. This is particularly true for (sub)-arctic rivers which represent a significant part of the global water discharge to the ocean, while their biological and geochemical functioning are not yet fully understood. Beside silica trapping, Humborg et al. (2003, 2004, 2006) have stressed the possible importance of the modifications brought by damming on rock-water-vegetation interactions in cold climatic conditions, that would lead to a reduction of rock weathering in certain areas of the watershed and hence to a decrease in silica supply and fluvial silica delivery.

In this study we try to quantify the magnitude of these different possible effects by the application of the deterministic Riverstrahler model to two neighbouring sub-arctic river systems, one representing a nearly pristine river (Kalixälven), the other being heavily
dammed (Luleälven). Several studies have already shown a significant difference in the mean silica concentration in the water from the two watersheds, silica delivered from the dammed Luleälven being lowered because the hampered role of vegetation in silica dissolution (Humborg et al., 2003, 2004, 2006). However, the role of reservoir as silica trap because of the increased residence time leading to possible algal development and subsequent sedimentation cannot be ruled off.

In this paper we gather the information required to apply the Riverstrahler modelling approach to these two systems characterized by a climatic context completely different from all previous applications (Continental climate; Garnier et al., 2002c; Trifu, 2002; Temperate oceanic climate: Garnier et al., 1999b; Billen et al., 2001; Billen et al., 2005; Sub-tropical climate: Garnier et al., 2002a; Le Thi Phuong, 2005). Once validated, i.e. once the calculated nutrient concentrations and mass-balance budgets are in agreement with the observations, the model can be a precious tool to help to the understanding of what factors are responsible for the observed differences in N, P and Si delivery from the two systems.

2. STUDY SITE

The Kalixälven and Luleälven River Basins are located in northern Sweden, across the Arctic Circle, between 66°30’ and 68°00’ (Figure 1). The Kalixälven watershed sensu-stricto covers an area of 17 818 km². However, about 57% of the adjacent Torne river basin drains into the Kalixälven river through a bifurcation at Tarendo (Dalhqvist et al., 2004), so that the ‘total’ Kalixälven watershed represents an area of 23 600 km² (Kalixälven will refer to this last surface area throughout the text). The Luleälven watershed area is 25 110 km². Figure 2 compares the morphology of both basins in terms of altitude distribution and characteristics of their stream order (Strahler, 1957) properties (drainage density, steepness): the Luleälven watershed is steeper, with 25 % of the basin area higher than 700 m, the average upper limit of forest (Humborg et al., 2004), while for Kalixälven only 10 % of the watershed lays over such altitude. However, the main difference between the two watersheds consists in the fact that the hydrographic network of the Kalixälven river is pristine while the Luleälven river is one of the most heavily regulated rivers in Europe (Dynesius and Nilsson, 1994), its dams being able to retain up to 70% of its natural discharge (Humborg et al., 2006).
Not less than 11 reservoirs are operated for electric power generation in the Luleälven basin. The largest reservoir is Akkajaure which receives water from its own watershed (4 650 km$^2$) and an additional discharge through a tunnel coming from another reservoir, Sitasjaure, located upstream. The dam is located at 453 m above sea level, and the maximum oscillation allowed for water is of 30 m, even though the reservoir is deeper than 90 m (Sahlberg, 2004). Collectively all reservoirs represent a total maximum storage volume of $11 \times 10^9$ m$^3$ covering an area of 900 km$^2$ and are entirely located along the 4$^{th}$ and 5$^{th}$ order tributaries, the fluvial corridor of which can be considered either completely flooded or deeply perturbed by these hydraulic works.
Figure 2. Morphological characteristics of the Kalixälven (black) and Luleälven (grey) drainage networks and basins.

Although these two rivers are not discharging into the Arctic Sea, but into the Gulf of Bothnia in the northern Baltic, they can be considered as arctic-type because of their hydroclimatalogical characteristics (Nijssen et al., 2003). The annual average air temperature in the Kalixälven during the considered period (1980-2000) is of -0.5°C with extreme values of -39.4°C and +22.6°C. In the Luleälven watershed the average air temperature is of -0.1 °C within a range between -34.0°C and +21.4°C. Annual average precipitations are of 538 mm/year and 618 mm/year for Kalixälven and Luleälven respectively. The yearly average discharge equals 320 ± 295 m³/s for Kalixälven, while the snow melt discharge peak
occurring in May or June averages $955 \pm 199$ m$^3$/s. Another discharge peak is often present in autumn, due to rain. Since Luleälven river is regulated no such difference between its average discharge of $538 \pm 140$ m$^3$/s and its snow-melt season discharge ($680 \pm 157$ m$^3$/s) appears. The number of days with snow cover usually ranges from 175 to 225 days (Carlsson, 1999), the two watersheds not being within the permafrost region. Lakes and reservoirs also present an ice cover which lasts for about 6 months (Eklund, 1998).

About 65% of the Kalixälven basin area is covered by forest, mostly coniferous trees, while flooded wetlands represent 20%, herbaceous areas 7.1%, bare rock 3.5%, lakes 2.5% and cultivated areas 1.2%. Only 0.1% of the watershed is urbanized. About 60 000 people live in the Kalixälven catchment, mostly located at the river mouth with the exception of the city of Kiruna (24 000 inhab.), situated in the Torne catchment connected to Kalixälven at approx. 67 52' N and 20 15' E and the inland city of Gällivare (19 000 inhab.) in the Kalixälven catchment itself, at 67 10' N and 20 40' E. The Luleälven watershed is less inhabited than the Kalixälven, with a total population of 28 910 inhabitants. Forests constitute 48% of the area, flooded wetlands 14.6%, herbaceous areas 14.5%, bare land 13.3% and lakes 7.4%, the rest being either cultivated or urban areas.

Bedrock in both basins is constituted mostly of Caledonides and Precambrian basement, and dominant soil type is till with podzol profiles (Fromm, 1965), while glacial and post-glacial river sediments occur close to river and small stream stretches (Land et al., 1999).

### 3. SIMULATION OF HYDROLOGY

The Riverstrahler model, in its previous versions developed for temperate or sub-tropical river systems (Billen et al., 1994; Garnier et al.; 2000; Billen et al., 2001), rests on the calculation of the specific runoff as the sum of two components, namely (sub)-surface runoff and base flow, resulting from the dynamics of two hydrological pools in the watershed, respectively soil water, with short residence time, and groundwater, with long residence time. In the case of arctic mountainous river systems like those studied here, snow represents an additional pool, and snow melt is a major process determining the hydrological regime. The calculation of water flow from precipitation and evapo-transpiration data by the Hydrostrahler model has therefore been modified, according to the conceptual scheme represented in figure 3.
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Figure 3. Conceptual model for the calculation of specific discharge from daily precipitation, evapo-transpiration and temperature.

Precipitation is considered to be deposited as snow when air temperature is below zero. When temperature is above zero, snow is considered to melt at a rate proportional both to temperature and to the stock of accumulated snow. Snow melt and liquid precipitation feed the pool of soil water. When some saturation level ($solsat$) is reached, all this water flows as surface runoff. Soil water flows as sub-surface runoff, at a rate proportional to the size of its pool and infiltrates to groundwater, which generates the base flow. The three pools involved in the hydrological dynamics of the watershed are split into 20 classes of altitude, from 0 to 2000 m, in order to take into account the altitudinal gradients of temperature and precipitation (air temperature lapse rate of 0.98 °C/100 m, Richardson et al., 2004). The five parameters involved (snow melt rate, soil saturation level, sub-surface runoff rate, infiltration rate, base flow rate) are considered the same over the whole watershed area.

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The parameters were determined by optimization on the observed values of daily precipitation, potential evapo-transpiration, temperature and monthly runoff of the Kalixälven watershed for the period 1990-1999 (Table 1); the database was provided by the Department of Applied Environmental Science in Stockholm. Figure 4 shows a comparison of the simulated to observed discharges; the Nash criterium (Nash & Sutcliffe, 1970) for the ten years series is above 0.66.

### Table 1: Values of the hydrological parameters adjusted on data from the Kalixälven watershed on the time series 1990-1999.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>units</th>
<th>Adjusted value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil saturation level</td>
<td>mm</td>
<td>200</td>
</tr>
<tr>
<td>Snow melt rate</td>
<td>day(^{-1}).°C(^{-1})</td>
<td>0.008</td>
</tr>
<tr>
<td>Sub-surface runoff rate</td>
<td>day(^{-1})</td>
<td>0.05</td>
</tr>
<tr>
<td>Infiltration rate</td>
<td>day(^{-1})</td>
<td>0.03</td>
</tr>
<tr>
<td>Groundwater runoff rate</td>
<td>day(^{-1})</td>
<td>0.004</td>
</tr>
</tbody>
</table>

For the Luleälven river a direct calibration of the hydrological parameters cannot be achieved due to the regulation by dams; we thus used exactly the same values of the parameters as for Kalixälven to calculate the specific runoff components, from the precipitation, evapo-transpiration, temperature and altitude data of the basin. From this reconstructed hydrology of the unregulated Luleälven basin, the cumulated curve of filling and emptying of the Luleälven reservoirs was calculated, assuming rules that simulate its management for electric power generation.

![Figure 4](image-url)  
**Figure 4.** Observed and simulated discharge at the outlet of the Kalixälven River basin.
The ‘collective reservoir’ receives the runoff of a total upstream unregulated watershed of 24000 km². The outflow represents a constant discharge of 485 m³/s, except when the total stored volume reaches twice the minimum level; in that case the output is decreased proportionally to the distance from the minimum level. On the other hand, when the total volume reaches the maximum level, the output represents 1.5 times the input flow. Figure 5 represents the calculated inter-annual variations of the Luleälven discharge and of the stored water volume in the reservoirs, as simulated by this model over the period from 1990 to 1999. Although the idealised formulation of the hydraulic management rules of the reservoir does not allow to reproduce all observed small discharge variations, the general trend is correctly simulated, with a rather constant discharge most of the time and some events of abrupt increase in the period of reservoir filling.

**Figure 5.** Observed and simulated discharge at the outlet of the Luleälven River basin, and simulated volume of water stored in the reservoirs.
4. QUANTIFICATION OF DIFFUSE AND POINTS SOURCES

Diffuse sources of nutrient are taken into account by associating to each three flow components a concentration of nitrogen (nitrate and ammonia), phosphorus (total inorganic P, TIP), silica (dissolved, DSi, and particulate biogenic silica, BSi), suspended matter (SM) and organic carbon (dissolved, DOC, and particulate, POC). The concentrations associated to each flow component (see Table 2) depend on the land cover of the catchment of each stream order, and are based on concentrations measured in headwater streams within the Kalixälven and Luleälven basins (Humborg et al., 2004) or on other data reported in literature for similar regions.

The land-cover distribution by stream order has been established for the Kalixälven and Luleälven basin on the basis of the overall land cover distribution mentioned in section 2, and the consideration that 1st and second stream orders entirely englobes the area of the basin above the tree line and are too steep to develop wetlands, while all agricultural and urban land is located within the 5th and 6th stream order basin (Table 2 a.).

For what concerns dissolved diffuse nutrients (nitrate, ammonia, dissolved silica and carbon) a zero concentration is assigned to melt flow, assuming that snow or ice melting generates a rapid surface runoff which does only marginally acquire some nutrient load. On the other hand melt flow, because of its eroding capacity, is rich in suspended matter. The levels of suspended matter assigned to the three flow components for the different land use types is based on values observed in rivers under temperate conditions (Garnier et al., 2005; Billen et al., in press). Once suspended matter values are assigned, several particulate nutrient concentrations are deduced from them, based on the following general relationships. Particulate organic carbon is considered to represent between 0.5 and 1% of suspended matter, while a concentration of 180 µmol BSi/g SM (Sferratore et al., submitted) is assumed for biogenic silica. For total inorganic phosphorus, we assumed the same general Langmuir relationship between dissolved inorganic phosphorus (oPO₄) and mobile adsorbed forms (PIP) as found in the Seine watershed for non agricultural soils (Garnier et al., 2005; Némery et al., 2005):

\[
P/IP = Pac * oPO_4/(oPO_4 + KP),
\]

with KP = 22 µmol and Pac = 0.1 µmolP/mgSM

As ortho-phosphate concentration measured in small headwater streams in the Kalixälven, Luleälven and Torneälven basins are reported always around 0.13 µmol/l, we considered this value representing the equilibrium dissolved phosphate concentration, and we assumed a
mean exchangeable P content of suspended matter issued from soil erosion equal to 0.6 \( \mu \text{mol P/g SM} \).

Dissolved silica concentration (DSi, \( \mu \text{mol/l} \)) in headwater streams has been shown to be closely related to total organic carbon (TOC, mgC/l) (Humborg et al., in press), indicating the prominent role of the biota on the process of rock weathering. Analysing data from a number of Nordic small rivers (basin area from 30 to 4000 km²) published by Humborg et al. (2004) and Smedberg et al. (2006), we found a very significant relationship of both DSi and TOC with the percent watershed area covered by forest and wetland (Figure 6).

\[
\text{DSi} = 0.9 \times + 24 \\
r^2 = 0.80
\]

\[
\text{TOC} = 0.072 \times + 0.25 \\
r^2 = 0.96
\]

**Figure 6.** Observed relationship between DSi and TOC in small Nordic headwater streams and the fraction of their watershed occupied by forest and wetlands. (Data from Humborg et al, 2004; Smedberg et al., 2006).

We used this relationship to assign the DSi and TOC concentration to the discharge component draining forest or wetlands on the one hand, herbaceous and bare rock on the other hand (Table 2b), using the seasonal minimum and maximum observed values to differentiate between surface sub-runoff and base flow.

Nitrate and ammonium concentrations are assigned to the different land cover classes on the basis of observed values in headwater streams as well as on small agricultural rivers in Sweden (Ulen and Jakobsson 2005). The Riverstrahler model assumes that a part of nitrate originating from soil leaching of the watershed might be denitrified in the riparian wetlands before it reaches surface water (Billen & Garnier, 1999).
Table 2a. Distribution of land cover classes by stream order direct catchments in the Kalixälven and Luleälven basins.

<table>
<thead>
<tr>
<th>Land cover type</th>
<th>Watershed average %</th>
<th>% Land cover type in stream order direct catchments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>order 1</td>
<td>order 2</td>
</tr>
<tr>
<td>Kalixälven</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forest</td>
<td>65.1</td>
<td>83.8</td>
</tr>
<tr>
<td>Herbaceous</td>
<td>7.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Wetlands</td>
<td>20.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Water/snow/bare</td>
<td>6.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Cultivated soil</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Urban</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Luleälven</td>
<td>48.0</td>
<td>39.7</td>
</tr>
<tr>
<td>Herbaceous</td>
<td>14.5</td>
<td>20.5</td>
</tr>
<tr>
<td>Wetlands</td>
<td>14.6</td>
<td>0.0</td>
</tr>
<tr>
<td>Water/snow/bare</td>
<td>12.5</td>
<td>26.1</td>
</tr>
<tr>
<td>Cultivated soil</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Urban</td>
<td>0.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2b: Concentrations of nitrogen (nitrate and ammonia) phosphorus (total inorganic P), silica (dissolved and particulate biogenic silica), suspended matter (SM), organic carbon (dissolved and particulate) associated to base flow, surface flow and melt flow according to the land use type.

<table>
<thead>
<tr>
<th>Diffuse source concentrations</th>
<th>Forest</th>
<th>Herbaceous</th>
<th>Wetland</th>
<th>Water/snow/bare</th>
<th>Cultivated soil</th>
<th>Urban</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃, µmol*</td>
<td>Melt</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>4</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>9</td>
<td>9</td>
<td>0</td>
<td>4</td>
<td>700</td>
</tr>
<tr>
<td>NH₄, µmol</td>
<td>Melt</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>2.5</td>
<td>2.5</td>
<td>10</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>Phosphorus</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIP, µmol</td>
<td>Melt</td>
<td>0.19</td>
<td>0.21</td>
<td>0.13</td>
<td>0.18</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>0.16</td>
<td>0.17</td>
<td>0.13</td>
<td>0.14</td>
<td>0.80</td>
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<tr>
<td></td>
<td>Base</td>
<td>0.14</td>
<td>0.14</td>
<td>0.13</td>
<td>0.13</td>
<td>0.2</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DSi, µmol</td>
<td>Melt</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>35</td>
<td>15</td>
<td>35</td>
<td>1.3</td>
<td>44</td>
</tr>
<tr>
<td></td>
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<td>50</td>
<td>150</td>
<td>25</td>
<td>114</td>
</tr>
<tr>
<td>BSi, µmol</td>
<td>Melt</td>
<td>18</td>
<td>25</td>
<td>0.9</td>
<td>14</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>9</td>
<td>12.5</td>
<td>0.9</td>
<td>1.8</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>2.5</td>
<td>3.6</td>
<td>0.35</td>
<td>0.9</td>
<td>4.5</td>
</tr>
<tr>
<td>Susp.Matter</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM, mg/l</td>
<td>Melt</td>
<td>100</td>
<td>140</td>
<td>5</td>
<td>80</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>50</td>
<td>70</td>
<td>5</td>
<td>10</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>15</td>
<td>20</td>
<td>2</td>
<td>5</td>
<td>25</td>
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<td>Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC, mgC/l</td>
<td>Melt</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Base</td>
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<td>1.5</td>
<td>4</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>POC, mgC/l</td>
<td>Melt</td>
<td>0.5</td>
<td>0.7</td>
<td>0.05</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>0.5</td>
<td>0.7</td>
<td>0.05</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>0.15</td>
<td>0.2</td>
<td>0.02</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>TOC, mgC/l</td>
<td>Melt</td>
<td>8.5</td>
<td>0.7</td>
<td>0.05</td>
<td>0.1</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>surf.</td>
<td>4.5</td>
<td>2.7</td>
<td>6.05</td>
<td>0.1</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>Base</td>
<td>4.15</td>
<td>1.7</td>
<td>4.02</td>
<td>0.05</td>
<td>1.13</td>
</tr>
</tbody>
</table>

* Riparian nitrate retention factor: 1.75*% watershed occupied by wetlands
In the present application, we considered a riparian retention proportional to the part of wetlands in the direct catchment of each stream order.

Point sources of organic carbon, nitrogen and phosphorus are calculated from the population data, assuming that wastewater is treated with a classical activated sludge process, and using corresponding per capita loadings cited by Billen et al. (1999), Servais et al. (1999) and Garnier et al. (in press). A per capita load is also considered for silica, equalling 0.8 g Si inhab\(^{-1}\) day\(^{-1}\) (Sferratore et al., submitted).

5. MODEL SIMULATION OF THE RIVER ECOLOGICAL FUNCTIONING

For the Kalixälven river system, the Riverstrahler model has been run for the hydrological conditions calculated for each year from 1990 to 1999 (Fig. 4), as well as using average, minimal and maximal runoff. The average (or minimum or maximum) hydrological scenarios correspond to the mean (or min or max) values for each ten days period of the whole 10 year series. The same was done for the Luleälven river, ignoring the presence of reservoirs, thus simulating a pre-dam situation. For the dammed situation, the filling/emptying curve of the ‘collective’ reservoir corresponding to the years 1994, 1995 and 1998 were associated respectively to these average, minimum and maximum scenarios, because these year represent indeed the average and extreme amplitude of filling and emptying of the reservoirs, according to our simulations (Fig. 5).

Beside the morphology and hydrology of the two rivers described in sections 2 and 3, and diffuse and point nutrient sources from the watershed discussed in section 4, the forcing functions to the model include the seasonal variations of light intensity, photoperiod and water temperature, which were represented by simple sine functions:

\[ \text{Photoperiod (hours)} = 12 \left[ 1 - 0.95 \cos \left( 2\pi \frac{t}{365} \right) \right] \]

\[ \text{Mean light intensity over the photoperiod (\(\mu\text{E/m}^2/\text{s}\))} = 400 \left[ 1 - 0.9 \cos \left( 2\pi \frac{t}{365} \right) \right] \]

\[ \text{Water temperature (°C)} = 4 - 4 \cos \left( 2\pi \frac{(t-30)}{365} \right) \]

where \(t\) is the time in julian days.

The kinetics parameters used for the simulation were taken identical to those used in previous applications of the Riverstrahler model to temperate rivers (see e.g. Garnier et al., 1999; 2002b; 2005; Sferratore et al. 2005, subm.). Only the parameters of the relation between planktonic organisms physiology and temperature were adjusted in order to take into account arctic algal populations. This relationship is classically expressed by a sigmoid function:
Activity (T) = Activity (Topt) \exp\left(-\frac{(T-\text{Topt})^2}{(T-\sigma ti)^2}\right)

with an optimum temperature (Topt) of 8°C and \( \sigma ti \) set at 8°C.

The results of model runs with average, minimal and maximal discharge are presented in Figure 7 and compared with the observations available for the period 1990-1999. In addition, results of the model for each year in particular allowed to calculate average nutrient fluxes for the decade that can be compared to the observed fluxes at the river outlet (Table 3).

For both the Kalixälven and the Luleälven without reservoirs a peak of discharge appears in late spring, related to the snow melt. The increased melt flow component of the average runoff is poor in dissolved nutrients (see Table 2) and the effect of this dilution can be seen in the decrease of nitrogen and silica concentration in the period of maximal average discharge. This high discharge during melt flow (coinciding with the optimal period for diatom blooms) does not allow intensive diatom development, as shown by the chlorophyll a simulations (Fig 7). In general, the average, minimal and maximal simulated values for the Kalixälven river are during most of the year within the envelope of observed data for discharge, dissolved silica, total inorganic phosphorus and total organic carbon. This agreement is also true for the simulations at 4\textsuperscript{th} order, which fit to the available observations in headwater streams of the Kalixälven basin (Fig. 8), confirming that the diffuse sources of nutrients are correctly taken into account in the model. Luleälven simulated discharge, silica and TOC fluxes are also in agreement with observed data; a much lower silica average concentration appears in Luleälven river (about 35 \( \mu \text{mol Si/l} \)), either with respect to Kalixälven, and to Luleälven in the ‘no dams’ scenario (Fig. 7).

The specific annual discharges calculated for Kalixälven and Luleälven (Table 3) show a good agreement with observed data, confirming the correctness of the hydrological model. Total inorganic nitrogen export flux is overestimated by the simulations, as well as total phosphorus for the Luleälven river, while silica export is within the range of the observations. Luleälven river exports more silica despite its low riverine water silica concentration (Fig. 7) because of its higher discharge. More, a decrease of about 23% in dissolved silica export appears when comparing the Luleälven with and without dams.
Figure 7: results of simulations of discharge, chlorophyll a, dissolved silica, total inorganic phosphorus, nitrate and total organic carbon for Kalixälven River (left column) and Luleälven River (with dams, middle column; without dams, right column). Black lines indicate results corresponding average hydrology simulations, light grey to minimal hydrology and dark grey to maximal hydrology. Dots and error bars indicate observations and their respective standard deviation.
Table 3: Specific annual N, P, Si export fluxes for Kalixälven and Luleälven (with/without dams) rivers.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Scenario</th>
<th>Kalixälven</th>
<th>Luleälven no dams</th>
<th>Luleälven</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>average specific fluxes ± standard deviation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge (l/km²/s)</td>
<td>simulated</td>
<td>11.7 ± 1.3</td>
<td>21.2 ± 3.1</td>
<td>23.6 ± 2.8</td>
</tr>
<tr>
<td></td>
<td>observed</td>
<td>13.7 ± 2.0</td>
<td>n. d.</td>
<td>22.0 ± 2.3</td>
</tr>
<tr>
<td>Tot-inorg N (kg/km²/y)</td>
<td>simulated</td>
<td>76.9 ± 9.2</td>
<td>98.7 ± 9.1</td>
<td>85.7 ± 7.5</td>
</tr>
<tr>
<td></td>
<td>observed</td>
<td>36.0 ± 5.0</td>
<td>n. d.</td>
<td>29.3 ± 4.3</td>
</tr>
<tr>
<td>Tot-P (kg/km²/y)</td>
<td>simulated</td>
<td>8.4 ± 0.9</td>
<td>12.4 ± 2.0</td>
<td>10.7 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>observed</td>
<td>8.9 ± 2.6</td>
<td>n. d.</td>
<td>6.6 ± 1.0</td>
</tr>
<tr>
<td>DSi (kg/km²/y)</td>
<td>simulated</td>
<td>740 ± 101</td>
<td>1019 ± 91</td>
<td>786 ± 60</td>
</tr>
<tr>
<td></td>
<td>observed</td>
<td>912 ± 187</td>
<td>n. d.</td>
<td>760 ± 162</td>
</tr>
<tr>
<td>BSi (kg/km²/y)</td>
<td>simulated</td>
<td>110 ± 5</td>
<td>114 ± 15</td>
<td>26 ± 4</td>
</tr>
<tr>
<td>Total Si (kg/km²/y)</td>
<td>simulated</td>
<td>850</td>
<td>1133</td>
<td>812</td>
</tr>
</tbody>
</table>

Figure 8: results of simulations for discharge and dissolved silica at order 4th of Kalixälven river. Dots indicate validations, while lines represent simulation results for the average (black), minimal (light grey) and maximal (dark grey) hydrology.
6. DISCUSSION

The application of the Riverstrahler model to Kalixälven and Luleälven rivers is a first attempt to test the model in sub-arctic climates. The introduction of a snow melt flow component to the Hydrostralher module was necessary to correctly simulate the late spring discharge peak and the correspondent nutrient dilution.

The differences between the pristine Kalixälven and the dammed Luleälven river nutrient concentrations, are pronounced for the three nutrients (silica, phosphorus, and nitrate) and have been correctly reproduced by the model. How these differences are generated in the model results requires further discussion in connection with previous hypotheses, namely the role of retention within the reservoir and the role of the changes in rock-water-vegetation induced by damming.

First of all, the model application forced us to carefully examine the differences in altitude, hydrology, meteorology and land cover between the two neighbouring basins. These factors already determine significant differences in both runoff and nutrient diffuse sources, which are illustrated by comparing Kalixälven results to the model reconstructed behaviour of Luleälven without dams (Fig. 7).

Further, the comparison of the Luleälven results with and without dams allows to quantify the role of damming. Because of the long water residence time in the reservoirs, the most obvious effect is a smoothing of the seasonal nutrient concentrations at the outlet, but this in itself does not prove any nutrient retention (Fig. 7). Budget calculations (Table 3) indicate a significant reduction of phosphorus (12%) and total silica (30%) fluxes in the model results. A part of this reduction can be attributed to the change in land cover induced by flooding the fluvial corridor of the 5th order river (and a part of the 4th order): the formerly forested valley has been inundated, becoming bare rock bottom of huge reservoirs. In addition, most of the water flows from one reservoir to the other through underground channels, which also contributes to reduce the soil-water contact. This is taken into account in the model by suppressing the nutrient input contribution from about 2000 km² wetlands and forest area. Wetlands and forests have been shown to be among the most active producers of silica, particularly in high latitude watersheds, because of the vegetation control of weathering rates (Gaillardet et al., 1999; Humberg et al., 2003; Humborg et al., 2004; Humborg et al., in press), and this is reflected in the relationship we used to define nutrient diffuse sources (Table 2b). However, the areas destroyed by damming represents hardly one tenth of the total
forested area of the basin, thus limiting the effect of its suppression to about 10% of the overall silica delivery. Incidentally, the disappearance of wetlands from the 5th stream order direct watershed, also resulted in a lack of riparian retention of nitrates in the model results of the dammed Luleälven scenario, explaining the slightly higher nitrogen flux compared to the no-dam scenario (Table 3).

Nutrient retention in the reservoir on the other hand is quite evident in terms of particulate biogenic silica, since its export decreases from about 114 kg Si/km²/yr in the Luleälven no-dam scenario to about 26 kg Si/km²/yr in the dammed case. The effect is less pronounced in the case of dissolved silica, because the model does not simulate significant diatom growth in the reservoir. In spite of the long residence time, the depth, and, principally, the very low phosphorus loading would limit algal development in this reservoir. A few available measurements of total chlorophyll pigments carried out in early June 2000 in four dams of the Luleälven system revealed concentrations between 1 and 2.5 µg/L, in good agreement with the values predicted by the model. The predicted annual primary production in the reservoir is evaluated by the model to 7 g C/m²/yr, close to the value of 6 gC/m²/yr cited for similar lake systems in the regional literature (Karlsson et al., 2001). With a Si:C ratio of 0.92 by weight (Conley et al., 1989), this primary production corresponds to a retention of 5800 10³ kg Si/yr in the 900 km² reservoir, assuming total sedimentation of the diatoms, and no re-dissolution. This calculation sets to a maximum of 230 kg Si/km²/yr, i.e. about 20% of the total specific diffuse silica inputs from the basin, the possible silica retention which could result from the diatom growth and sedimentation in the Luleälven reservoir.

The model results thus suggest that both the effects of vegetation modifications (destruction of wetlands and forests by flooding alluvial valleys) and direct trapping in the reservoir can play a role in the retention of silica after damming the Luleälven river.
REFERENCES


Modelling nutrient fluxes from sub-arctic basins: pristine vs. dammed rivers


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CHAPTER 5

Modeling nutrient (N, P, Si) budget in the Seine watershed:
Application of Riverstrahler model using data
from local to global scale resolution

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Modeling nutrient (N, P, Si) budget in the Seine watershed: Application of the Riverstrahler model using data from local to global scale resolution

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The deterministic Riverstrahler model that simulates nutrient transfer from land-based sources to the sea through the drainage network has been successfully applied to a number of large watersheds ranging from 20,000 to 800,000 km². In order to assess the feasibility of upscaling such a model in view of its worldwide application based on global databases of hydrology, climate, population, land use, and lithology, a sensitivity analysis has been carried out. The response of the model to differing scales of input data, both high-resolution local data and low-resolution global data, is examined, applying the model to the well-documented Seine River basin. The results show that the evaluation of the overall annual fluxes of nutrients delivered at the outlet of a basin can be correctly predicted even from low resolution input data, provided that (1) the total discharge and seasonal hydrological regime are correctly simulated; (2) the drainage network description does not neglect tributaries that drain more than approximately 4000 km² watershed area; and (3) the total point sources of nutrients as well as their distribution between the different stream orders are estimated (phosphorus being the most sensitive among the considered nutrients to point sources distribution). Diffuse sources of nutrients can be assessed from low-resolution land use and lithological data. As a result of this study, the capacity of statistical/empirical formulas to assess annual fluxes of nutrient delivery appears comparable to that of deterministic drainage network models, but the latter are particularly suited to predict seasonal variations of riverine nutrient delivery and its elemental ratios.


1. Introduction

Human activities have produced dramatic changes to the environment over the last century [Howarth et al., 1996; Billen et al., 2001; Justic et al., 2002; Billen et al., 2005; Schernewski and Neumann, 2005]. Changes such as urbanization, industrialization, intensification of agriculture, impoundment of artificial reservoirs, have direct consequences on nutrient export to coastal zones, many of which are particularly sensitive to eutrophication. Further, the formation of the coastline at the global scale creates many regional or semi-enclosed seas, preventing direct dilution of a major fraction of riverine dissolved and particulate fluxes into the global ocean [Meybeck et al., 2005]. In particular, alteration of the molar ratios of nutrient riverine delivery to the coastal zone [Redfield et al., 1963], either at the seasonal or at the annual timescale, can affect the succession of diatoms and non-siliceous algae, leading to harmful phytoplanktonic blooms and causing damage to fisheries and tourism [Anderson et al., 2000; Kirkpatrick et al., 2004]. Coastal marine eutrophication, with its locally very diverse manifestations, has thus become a widespread symptom of anthropogenic alteration of the global nutrient cycles [Turner et al., 2003]. All these issues justify current efforts devoted to evaluate and model nutrient fluxes (C, N, P, Si) from land-based sources to the coastal ocean at the global scale, as a function of land use changes. Predictive tools are indeed required to assess the possible consequences of current trends of human population and activities as well as the improvements that could be achieved from environmental protection measures.

Among the models developed for simulating nutrient delivery to the coastal zone, two basic approaches can be distinguished: (1) the “statistical approach,” which consists of calibrating the parameters of a simple mathematical relation between explanatory variables and nutrient delivery on a sample of documented world river systems [Smith et al., 1993; Alexander et al., 2001; Seitzinger et al., 2002; Galloway et al., 2004]; and (2) the “mechanistic or deter-
ministic modeling approach,” which is based on an a priori view of the processes involved in the transfer and retention of nutrients from land-based sources. The model consists of a description of the kinetics of the major processes involved, with independently determined values of the parameters. If available, a set of documented variables taken into account in the model, that is, nutrient concentrations and/or delivered fluxes, can be used to validate the model rather than to calibrate it. Examples of this approach are the Riverstrahler model, used here [Billen et al., 1994; Garnier et al., 1995; Billen and Garnier, 1999; Garnier et al., 1999], the INCA model [Whitehead et al., 1998], and the Potamon model [Everbeq et al., 2001].

[4] In practice, most approaches lie somewhere in between these two extreme types. The choice of pertinent explanatory variables, as well as the formalism of the mathematical relations in statistical models, reflect, to some degree, a conceptual vision of the processes involved, by stating variable dependencies [e.g., Caraco and Cole, 1999; Howarth et al., 1996]. On the other hand, most mechanistic models incorporate some statistical relations for processes that have not been described in detail, and parameterization and calibration are used to bypass the precise description of some complex processes.

[5] In the last 10 years much effort has been devoted to the development of the mechanistic Riverstrahler model of nutrient transfer in large regional river systems [Billen and Garnier, 1999; Garnier et al., 1999; Billen et al., 2001; Garnier and Billen, 2002; Garnier et al., 2002; Billen et al., 2005]. This model incorporates the knowledge gained since the 1980s on the kinetics of ecological and biogeochemical processes in aquatic environments. The model, together with others based on similar approaches, is based on the detailed calculation of a mass budget of material in drainage networks. Starting from the information about the land-based sources of nutrients to the surface water, deterministic models explicitly calculate the various processes affecting nutrients during their transport through the complex structure of streams, rivers, ponds and lakes, and the possible resulting retention or immobilization. Therefore these models can be thought to be better adapted than statistical ones to provide realistic responses of river systems to major and combined changes in their morphology, hydrology or loading.

[6] An important assumption of these mechanistic models is the uniqueness of the processes; it implies that the basic biological, physical and chemical processes involved in the functioning of the river system are the same from headwaters to downstream reaches. However, the hydrologic and morphologic constraints controlling the expression of the processes differ largely along an upstream-downstream gradient as well as the constraints exerted by the inputs of terrestrial material. The particularity of the ecological structure and function of the different sectors that succeed each other along the river continuum [Vannote et al., 1980] therefore is determined by the controlling factors rather than by the basic nature of the processes involved. This principle in the case of Riverstrahler also applies to gradients of climatic or morphologic river system types (Subtropical [Garnier and Billen, 2002; Quynh et al., 2005]; Cold (A. Sferratore et al., manuscript in preparation, 2005); Continental [Garnier et al., 2002; Trifù, 2002]; Temperate oceanic [Garnier et al., 1999; Billen et al., 2001, 2005]). Therefore a model applicable to such a wide range of climates and river types appears to be generic enough to be upscaled to global level applications. In practice, the major difficulty lies in the fact that such mechanistic models require high spatial resolution input information on watershed and drainage network morphology, land use and human activities, which are not fully available at the global scale. Recently, however, much progress has been made in gathering global databases relating to pertinent aspects of hydrology and human pressures [Meybeck and Ragù, 1997; Seitzinger et al., 2000; Vörösmarty et al., 2002; Bouwman et al., 2002; van Drechter et al., 2005].

[7] In this paper we examine to what extent that global scale information can be used as input variables to provide realistic estimates of the nutrient budget of the Seine River basin in France using the Riverstrahler model. The Seine watershed (75,000 km² in total, and about 65,000 km² if not taking into account the estuarine sector starting at Poses, the outlet of the fluvial non tidal part of the basin), has been chosen for this study because it offers a good example of a highly perturbed river system, with both a large urban agglomeration (Paris, 10 million inhabitants) and intensive agriculture.

[8] Our approach consists of examining the sensitivity of the simulations to the spatial and temporal resolution of the input data. Starting from a well-validated application of the model to the regional watershed of the Seine, supplied with high spatial resolution input data as available from local studies and specific databases, we have gradually substituted these high-resolution data by coarser information extracted from available global databases, and analyzed the response of the model in terms of nutrient delivery at the outlet of the basin. The ability of the model to simulate the seasonality of the nutrient fluxes, an important feature driving eutrophication of coastal zones, is also examined.

2. Description of the Riverstrahler Model

[9] The generic Riverstrahler model describes the biogeochemical functioning of whole river systems and is applicable at various scales, from 100 to greater than 100,000 km².

[10] The model describes the drainage network as a combination of three components: (1) upstream basins which are idealized as a regular scheme of confluence of tributaries of increasing stream order [Strahler, 1957], each characterized by mean morphological properties; (2) branches which are represented more realistically, with a spatial resolution of 1-km stretches; and (3) ponds or reservoirs which are connected either to branches, at a defined position, or to any stream-order river in an upstream basin with a statistical distribution and are taken into account as mixed reactors [Garnier et al., 2000].

[11] According to the spatial resolution required, the drainage network can either be considered as a single basin or as a collection of connected basins and branches. A recently developed new version of the model (Seneque 3-Riverstrahler) [Ruelland, 2004; D. Ruelland et al., Seneque 3: A GIS interface to the RIVERSTRAHLER model of the
biogeochemical functioning of river systems, submitted to Ecological Modelling, 2005], embeds Riverstrahler within the Seneque GIS interface and allows the user to run the model with various structures of basins and branches, selected online according to the geographical resolution required for the study. In the present application, this new version has been used for an easy extraction of the data required for the separate runs of Riverstrahler. We use a data set that represents the Seine as a single basin, a geographical scale that seemed more suitable in the context of a global upscaling.

[12] The model couples water fluxes routed through the defined tributary structure, with a detailed description of biological, microbiological and physical-chemical processes occurring within the water bodies. The module representing the kinetics of the processes is known as the RIVE. It has recently been improved for a better representation of the processes involved in phosphorus exchanges [Némery et al., 2005; Garnier et al., 2005b] and silica transfers [Garnier et al., 2003; A. Sferratore et al., manuscript in preparation, 2005]. The state variables and major processes considered in the present version of the model are listed in Table 1. In-stream nutrient retention within the drainage network is explicitly calculated as the result of biological (algal uptake, denitrification) and physical-chemical processes (adsorption, sedimentation).

[13] The water flowing at any point of the hydrologic network is calculated from specific discharges generated in the watershed of the various upstream basins and branches considered. These specific discharges can be calculated either from pluviometry and potential evapotranspiration (ETP) by a simple two-compartment rainfall-discharge model (the Hydrostrahler model [Billen et al., 1994] (see also J. Garnier et al., Drainage basin use and nutrient supply by rivers to the coastal zone. A modelling approach to the Seine River, in Drainage Basin Nutrient Inputs and Eutrophication: An Integrated Approach, edited by P. Wassmann K. Olli, pp. 60–87, 2004. E-book, available at http://lepo.it.da.ut.ee/~olli/eutr/html/htmlBook.html), or from a more complex model of surface and groundwater hydrology. In both cases, the discharge in any stream order river or branch is the sum of two components, surface/subsurface and groundwater flow.

[14] In addition to morphological and meteorological data, required information on diffuse and point sources are other major constraints to the model (Figure 1 and Table 2). In order to calculate the diffuse sources of nutrients, a constant mean composition is assigned to surface and groundwater flows, according to land use distribution within the watersheds. For surface water flows, the composition in nitrate, for example, can be calculated by empirical relations between land use and water composition in the sub-root zone, as deduced from lysimeter experiments [see Billen and Garnier, 1999]; it can also be derived from other agronomic models (i.e., STICS [Gomez et al., 2003]). For groundwater flows, the nutrient composition can be determined from an inventory of concentrations in aquifers, or can be deduced from groundwater models [Gomez, 2002]. Riverstrahler model also takes into account a riparian retention term, which is calibrated from the river water nitrate concentrations, to represent the role of the riparian zones, known to affect the nitrate flow of the sub-root and groundwater before it enters surface water. Point sources of nutrient from wastewater discharge constitute another required input data. When detailed census of wastewater discharge points is not available, point sources are deduced, with some estimation of the specific load [Servais et al., 1999], from general data on population and industrial activity, the contribution of the latter being extremely difficult to evaluate [Le Thi Phuong et al., 2005].

In developing countries, reliable data on pollution fluxes generated by industries and handicraft activities in villages in general are not readily available, leading to underestimation of N and P load.

### 3. Reference Simulations With High-Resolution Data

[15] We first run the Riverstrahler model with all the input data available from high-resolution local databases. In order to examine the role of interannual hydrological variability on nutrient transfers, two hydrologically contrasting years were chosen: 1991, a dry year (mean annual discharge 340 m³/s at Poses) and 2001, a wet year (900 m³/s). These two reference simulations are run with (see Table 2) (1) mean values per 10 day-periods of specific surface and base flow runoff rates, calculated by the Hydrostrahler model from pluviometry and evapotranspiration data and adjusted to measured daily dis-

### Table 1. State Variables and Processes Included in the Riverstrahler Model

<table>
<thead>
<tr>
<th>State Variables</th>
<th>Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended and deposited mineral material</td>
<td>sedimentation, resuspension</td>
</tr>
<tr>
<td>Green algae</td>
<td>primary production</td>
</tr>
<tr>
<td>Diatoms (spring, late summer, benthic)</td>
<td>primary production, sedimentation of planktonic diatoms, erosion of benthic diatoms</td>
</tr>
<tr>
<td>Cyanobacteria</td>
<td>primary production</td>
</tr>
<tr>
<td>Heterotrophic bacteria</td>
<td>organic matter degradation and remineralization</td>
</tr>
<tr>
<td>Nitrifying bacteria</td>
<td>nitrification</td>
</tr>
<tr>
<td>Zooplankton (Rotifer and Cladocera)</td>
<td>grazing and remineralization</td>
</tr>
<tr>
<td>Dissolved organic matter</td>
<td>rapid or slow hydrolysis for the non-refractory fraction</td>
</tr>
<tr>
<td>Particulate organic matter</td>
<td>rapid or slow hydrolysis for the non-refractory fraction, sedimentation</td>
</tr>
<tr>
<td>Ammonium and nitrate</td>
<td>nitrification, denitrification, uptake, benthic recycling</td>
</tr>
<tr>
<td>O-Phosphate and adsorbed inorganic P</td>
<td>uptake, adsorption-desorption, benthic recycling</td>
</tr>
<tr>
<td>Dissolved silica</td>
<td>uptake</td>
</tr>
<tr>
<td>Suspended and deposited biogenic silica</td>
<td>dissolution, sedimentation</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>heterotrophic consumption, autotrophic production, reaeration</td>
</tr>
</tbody>
</table>
charge at the Poses station; (2) mean values per 10 day-period of observed water temperature and light intensity; (3) a description of the morphology of the river network (length, slope, number of tributaries and watershed size per stream order); (4) estimates of point discharges of wastewater (in terms of inputs of total suspended solids, organic carbon, nitrate, ammonium and phosphates) aggregated by stream order, constructed from the census of the 1750 sewers and purification plants recorded by the Watershed Authorities (Agence de l’Eau Seine Normandie, AESN) with their measured loading and the exact location of their release point; and (5) estimates of diffuse nutrient sources, including the concentration of suspended solids, nitrate, ammonium, total phosphorus, dissolved and biogenic silica in surface runoff and groundwater. This information is derived from a GIS file of land use in the Seine watershed extracted from the European Corine Land Cover database (Corine Land Cover (CLC90), available from the European Environment Agency (EEA) at http://dataservice.eea.eu.int/dataservice/metadetails.asp?id=188). A mean nitrate concentration is assigned to arable land, grassland, forest and urban areas, on the basis of empirical data obtained from lysimeter experiments for the surface runoff, and direct measurements in the major aquifers for groundwater base flow [Billen and Garnier, 1999]. The diffuse sources input data also include a calibrated factor which accounts for riparian nitrate retention. For silica concentration, a similar approach is applied based on lithology (adapted from Albinet’s map, 1967) instead of land use. Following the work initiated by Meybeck [1986], a silica concentration in headwaters is associated to each rock type [Garnier et al., 2005a]; then by estimating the percentage area of the main rock types within the Seine basin, it is possible to determine an average silica concentration in the surface and groundwater. Dissolved ortho-phosphate concentrations are assigned as function of land use, varying from 0.04 mgP/L for forests or meadows to 0.10 mgP/L for arable land. Suspended solid concentration and associated particulate phosphorus in surface runoff are derived from a relation between total suspended solids and land use in the watershed at high water, while a constant value is assigned to the base runoff [Garnier et al., 2005b].

[16] The results of simulations of the seasonal variations of discharge, nutrient concentration and phytoplankton (as chlorophyll a concentrations) at the outlet of the basin are generally in good agreement with the observations carried out at a bi-monthly frequency (Service de la Navigation de la Seine, SNS) for both 1991 and 2001 (Figure 2). Major discrepancies are found for phytoplankton biomass that is
Table 2. Description of the Input Data Required for Running the Riverstrahler Model and Origin of These Data Either From Local Fine Resolution Databases or From Global Low Resolution Databases

<table>
<thead>
<tr>
<th>Data Sources</th>
<th>High Resolution</th>
<th>Global Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rainfall</td>
<td>Safran Database – Météo France</td>
<td>Legates and Willmott [1990]</td>
</tr>
<tr>
<td>ETP</td>
<td>Safran Database – Météo France</td>
<td>Vörösmarty et al. [1998]</td>
</tr>
<tr>
<td>Runoff</td>
<td>calibrated (see text)</td>
<td>Federer et al. [1996]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fekete et al. [2002]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Water Balance Model (WBM)</td>
</tr>
<tr>
<td>Morphotogy of the Drainage Network</td>
<td>PIREN Seine*</td>
<td>PIREN Seine*</td>
</tr>
<tr>
<td>Lithology</td>
<td>European soil database version 2b</td>
<td>Dürr et al. [2005]</td>
</tr>
<tr>
<td>Land use</td>
<td>Corine Land Cover (CLC’90), European Environment Agency (EEA)</td>
<td>Hansen et al. [2005]</td>
</tr>
<tr>
<td></td>
<td>(Seine-Normandy Water Agency)</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*Available at http://www.sisyphe.jussieu.fr/Internet/riverstrahler septem./*.  
**Available at http://dataservice.eea.eu.int/dataservice/метадетал.asp?id=196.

underestimation during summer in the dry year; such an underestimation is likely due to nonsiliceous organisms, since the corresponding silica simulation is in agreement with the observations. Whereas phosphorus trend is fairly well represented by the model, ammonium is overestimated (Figure 2).

[17] The simulated annual fluxes are in quite good agreement with those calculated from measured data (Table 3). Ammonium flux is overestimated, but it should be noted that its measurement can have large imprecision if not performed immediately after sampling, as is often the case in monitoring programmes; these discrepancies have limited effect on total nitrogen flux, nitrate fluxes being at least four fold higher than ammonium fluxes (see Table 3). Total phosphorus on the other hand was underestimated in the wet year.

[18] The interannual comparison for both simulated and measured nutrient fluxes delivered to the sea in 1991 and 2001 shows that silica and nitrate fluxes (both nutrients originating essentially from diffuse sources) were much lower (by a dilution factor greater than 2) in the dry compared to the wet year (Table 3). The phosphorus and ammonium loads, in contrast, were less dependent on the hydrology as they are mainly originating from point sources (Table 3).

[19] Redfield N:P ratio shows an accentuated P limitation during the wet year, whereas Si:N and Si:P ratios are associated with higher silica limitation in the dry year (Table 3). As a whole, these results are in agreement with the hypothesis that the risk of harmful (not diatoms) algal blooms in the Seine Bight is particularly high during dry years [Cugier et al., 2005].

4. Sensitivity to Data of Lower Resolution

4.1. Hydrology

[20] Hydrological data, such as those used for the reference simulations on the Seine do not exist for all river systems worldwide. At the global scale it is conventional to either use monthly meteorological data (including rainfall and evapotranspiration) averaged over several years to calculate runoff, or to extract data directly from runoff databases. To test the effect of a “global scale” hydrology on the Seine we used both approaches: (1) meteorological data (rainfall [Legates and Willmott, 1990]; evapotranspiration [Vörösmarty et al., 1998; Federer et al., 1996]) were entered into the Hydrostrahler model, to estimate mean ‘low resolution’ specific runoff for the Seine watershed area; (2) on the other hand, runoff data for the Seine basin were obtained from the Water Balance Model of Fekete et al. [2002].

[21] The results obtained with the first approach, using mean global scale hydrological input data, all other input files being the same as in the reference simulations, fall within the interannual variability of nutrient fluxes in the Seine basin. This is because the average global hydrology is itself in between the average discharges of 1991 and 2001, a very dry and wet year, respectively, that represent extreme situations in the studied region. The use of long-term average meteorological data does not allow to correctly represent the seasonality of the river system (Figure 3), but the calculated nutrient fluxes (Table 3) do capture long-term trends, since the hydrology itself is issued from long-term meteorological averages.

[22] For the second approach, using the runoff simulated by the Water Balance Model, the average specific discharge (4.7 L/s/km²) is lower than the average long-term Seine discharge (6.4 L/s/km² [Guerrini et al., 1998]), leading to nutrient fluxes more typical of a dry year. This underestimation of the average Seine nutrient export is, however, closer to the measured data than the scenario run with the average meteorological data. The results of these two approaches that use global hydrology can be also compared to the results obtained running the model with the not adjusted hydrology at high resolution (see the hydrology section in Table 2).
4.2. Morphology

[23] The Seine is a seventh-order river at its outlet (Figure 4a) and, in the reference simulations presented (see Figure 2), the Riverstrahler model requires a description of the Seine drainage network as a single idealized confluence scheme of streams of increasing orders, with average characteristics. For example, the model requires the number of streams for each order (from 1 to 7), as well as their respective mean values for length, width, slope and watershed area. These data were extracted from the GIS coverage of the drainage network digitized from topographical maps (1:50 000), combined with a refined 100 m x 100 m digital elevation model (AESN).

Figure 2. Validation of the Riverstrahler model: calculated (line) and observed (circles) seasonal variations of discharge, phytoplanktonic biomass, and nutrient concentration at the outlet of the Seine Basin conditions in 1991 (dry) and 2001 (wet).
Table 3. Calculated Nutrient Delivery to the Estuarine Zone at the Outlet of the Seine Fluvial System for Different Sets of Input Data by the Riverstrahler Model

<table>
<thead>
<tr>
<th>Hydrology</th>
<th>Observations or Scenario</th>
<th>Mean Annual, Discharge, L/s/km²</th>
<th>Specific Nutrient Fluxes Delivered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>SO₄²⁻, kgSi/km²/yr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry</td>
<td>1991 reference (hydrology, point and diffuse sources)</td>
<td>5.1</td>
<td>510</td>
</tr>
<tr>
<td>wet</td>
<td>2001 reference (hydrology, point and diffuse sources)</td>
<td>12.0</td>
<td>1480</td>
</tr>
<tr>
<td>dry</td>
<td>1991 reference (hydrology not adjusted)</td>
<td>5.1</td>
<td>578</td>
</tr>
<tr>
<td>wet</td>
<td>2001 reference (hydrology not adjusted)</td>
<td>12.0</td>
<td>1527</td>
</tr>
<tr>
<td>dry</td>
<td>average global hydrology for the Seine basin</td>
<td>9.0</td>
<td>1069</td>
</tr>
<tr>
<td>wet</td>
<td>average global hydrology for the Seine basin</td>
<td>9.0</td>
<td>1069</td>
</tr>
<tr>
<td>dry</td>
<td>WBM runoff for the Seine basin</td>
<td>4.7</td>
<td>559</td>
</tr>
<tr>
<td>wet</td>
<td>WBM runoff for the Seine basin</td>
<td>4.7</td>
<td>559</td>
</tr>
<tr>
<td>dry</td>
<td>limited to fourth order</td>
<td>5.1</td>
<td>681</td>
</tr>
<tr>
<td>wet</td>
<td>limited to fifth order</td>
<td>5.1</td>
<td>699</td>
</tr>
<tr>
<td>dry</td>
<td>reconstructed</td>
<td>5.1</td>
<td>562</td>
</tr>
<tr>
<td>wet</td>
<td>limited to fourth order</td>
<td>12.0</td>
<td>1074</td>
</tr>
<tr>
<td>wet</td>
<td>limited to fifth order</td>
<td>12.0</td>
<td>1072</td>
</tr>
<tr>
<td>wet</td>
<td>reconstructed</td>
<td>12.0</td>
<td>1513</td>
</tr>
<tr>
<td>dry</td>
<td>1991 ref. load uniform distribution</td>
<td>5.1</td>
<td>554</td>
</tr>
<tr>
<td>dry</td>
<td>1991 ref. load on seventh order</td>
<td>5.1</td>
<td>653</td>
</tr>
<tr>
<td>dry</td>
<td>GS load actual distribution</td>
<td>5.1</td>
<td>560</td>
</tr>
<tr>
<td>dry</td>
<td>GS load uniform distribution</td>
<td>5.1</td>
<td>537</td>
</tr>
<tr>
<td>dry</td>
<td>GS load on seventh order</td>
<td>5.1</td>
<td>637</td>
</tr>
<tr>
<td>wet</td>
<td>2001 ref. load uniform distribution</td>
<td>12.0</td>
<td>1532</td>
</tr>
<tr>
<td>wet</td>
<td>2001 ref. load on seventh order</td>
<td>12.0</td>
<td>1548</td>
</tr>
<tr>
<td>wet</td>
<td>GS load actual distribution</td>
<td>12.0</td>
<td>1494</td>
</tr>
<tr>
<td>wet</td>
<td>GS load uniform distribution</td>
<td>12.0</td>
<td>1477</td>
</tr>
<tr>
<td>wet</td>
<td>GS load on seventh order</td>
<td>12.0</td>
<td>1338</td>
</tr>
<tr>
<td>dry</td>
<td>GS 1991</td>
<td>5.1</td>
<td>517</td>
</tr>
<tr>
<td>wet</td>
<td>GS 2001</td>
<td>5.1</td>
<td>1402</td>
</tr>
<tr>
<td>GS</td>
<td>Global hydrology, diffuse and point sources (uniform distribution) on a river network limited to fourth order</td>
<td>9.0</td>
<td>996</td>
</tr>
<tr>
<td>GS</td>
<td>Global hydrology, diffuse and point sources (on the last order) on a river network limited to fourth order</td>
<td>9.0</td>
<td>1044</td>
</tr>
</tbody>
</table>

*a*Atomic stoichiometry relative to phosphorus. The optimal Redfield molar ratio of Si:N:P for diatoms is 16:16:1.
Such drainage network data may be unavailable for watersheds in remote areas of the world, where only the largest streams are represented on low resolution maps. Alternatively, any drainage network can be derived from digital elevation models (DEM), for example, that of 90 m × 90 m grid cells from U.S. National Geospatial-Intelligence Agency and National Aeronautics and Space Administration (Void-filled seamless SRTM data VI, 2003, International Centre for Tropical Agriculture (CIAT), available from the CGIAR-CSI SRTM 90m Database at http://srtm.csi.cgiar.org). Using DEMs it is possible to estimate a drainage network that has limited resolution and may not be representative of all stream orders.

For the present study the Seine River network has been thus reduced, limiting the resolution to stream orders from fourth to seventh in one scenario, and by taking into account only orders from fifth to seventh in another case (Figure 4b). Considering a river network composed of orders fourth to seventh, for example, it is also possible to extrapolate the logarithmic relationships between the different morphological characteristics of tributaries and their respective stream orders, and to reconstruct the “missing” upstream part of the drainage network (Figure 4c).

In the Seine limited to the representation of orders from the fourth, the drainage network accounts for only 15% of the actual cumulative length of tributaries, and begins with “apparent first order” streams of about 900 km² mean watershed area, while reconstructed drainage network represents a drainage density quite similar to the actual one. For the Seine limited at orders from fifth to seventh, the smallest basins (corresponding to orders first to fourth) have an average area of 4200 km², a size more easily available in global databases.

Using hydrological, and point and diffuse sources identical to those of the reference simulations, the Riverstrahler model was run with the morphological files of these three above presented cases (1) Seine limited at orders ≥ fourth, (2) Seine limited at orders ≥ fifth and (3) reconstructed Seine drainage network from the fourth order.

Surprisingly, the nutrient fluxes obtained at the outlet of the basin do not differ substantially from the reference simulations, either for the wet or the dry situations (Table 3). In particular, the seasonal variations of phytoplankton, hence of dissolved silica, are not significantly affected by the difference in drainage network morphology among the three explored cases (Figure 5).

This remarkable robustness of the model with respect to the representation of the drainage network comes from the fact that the dynamics of phytoplankton, the main in-stream factor affecting silica transfer, is greatly concentrated in stream orders fourth and greater, where the hydraulic dilution is low enough for phytoplankton to grow [Billen et al., 1994; Garnier et al., 1995], whereas only benthic diatoms occur in lower stream orders and have a less significant biogeochemical role. Similarly, benthic denitrification has probably a more limited impact on in-stream nitrogen retention in low-order streams than in larger river stretches. The Riverstrahler model calculates benthic denitrification all along the river continuum, as the result of diagenetic processes occurring in anoxic layers formed by
an important sedimentation of particulate organic matter [Billen and Garnier, 1999]; these conditions occur more often in higher river orders, with high organic contamination and low flow velocity.

Further, riparian nitrate retention, which is a more significant retention process than in-stream denitrification [Billen et al., 1989; Sebilo et al., 2003], is expressed as a percentage of diffuse inputs. Therefore nitrogen flux is not affected by the modification of the drainage network description in the model, as in the case of silica.

4.3. Point Sources

The reference simulations for the Seine River basin used point source data calculated from a detailed census of wastewater treatment plant releases. At the global scale, available information on point sources is limited. For

Figure 4. (a) Map of the Seine Basin indicating all stream orders; (b) surface of the watershed corresponding to the orders 1–3 (dark gray) and to order 4 (light gray); and (c) criteria for extrapolation of morphological constraints according to the stream order: experimental (dots) and extrapolated (crosses) values for length, slope, and number of tributaries.

Figure 5. Sensitivity of seasonal variation of (a) phytoplanktonic biomass and (b) dissolved silica to the morphology of the river network for the reference year 1991: detailed fine-scale morphology (thick light gray line), only orders greater or equal to fourth (thin dark gray line), only orders greater or equal to fifth (thin light gray line), or reconstructed morphology (thin black line).
example, using the global database of large cities WCPD [Rhind, 1991] to estimate the total population in the Seine watershed yields a value of 2.5 million inhabitants, considerably underestimating the real population (the Seine basin population is 16 million inhabitants, with 10 millions in Paris). This underestimation results from the fact that only municipalities with more than 100 000 inhabitants are listed in the database, so that many suburban municipalities are not included in the census.

[32] Another global population database [Klein Goldewijk and Battjes, 1997; Klein Goldewijk, 2001] provides population density at 0.5 degree resolution and the total population of the Seine watershed can be estimated to be about 14 million inhabitants, underestimating the actual population by 13%. From such population data, point nutrient discharges can be evaluated, according to a standard estimation of the specific domestic load and of the extent of wastewater collection. For untreated effluents, the French “official” definition of the “inhabitant equivalent” loading of 50 g orgC/inhab/day, 13 gN/inhab/day, 4 gP/inhab/day (Journal Officiel, 1991, available at http://www.journal-officiel.gouv.fr/accueil.php) can be used. Regarding the sewage treatment, world statistics by country [United Nations, 2000] (see also U.N. wastewater statistics at http://unstats.un.org/unsd/ environment/wastewater.htm) provide for France a figure of 90% wastewater collection. Note that industrial point sources of nutrients are not taken into account in this low resolution approach. Nevertheless, this low-resolution point source estimates provide about 40% higher nitrogen and threefold higher phosphorus inputs than in the case of the reference fine-scale estimates.

[33] Once the overall point sources of nutrients are estimated for the whole basin, they need to be distributed among stream orders. For this we tested three cases. As first case, the point sources were uniformly distributed among stream orders, according to their respective importance in terms of direct watershed area; this hypothesis largely favors the lower order tributaries that collectively drain the largest part of the total watershed (84% on orders 1–3, 11% on orders 4–5, 5% on order 6–7). In a second case, a relative distribution of the wastewater discharge among stream order tributaries similar to the one actually observed was adopted (i.e., 24% on orders 1–3, 8% on orders 4–5, 68% on orders 6–7). In a last case, all point loadings are concentrated on the highest stream order.

[34] We tested these three cases for both the detailed reference load and the one obtained from the global population database (Table 2). In both cases the most striking effect of point source distribution can be seen on the phosphorus flux at the basin outlet (Figure 6): Phosphorus delivery is much lower when the sources are uniformly distributed, allowing retention to act from the upstream river network, contrarily to the case when all point sources are discharged along the last stream order. This trend is observed for both dry and wet years.

4.4. Diffuse Sources

[35] The data on diffuse sources used in the reference simulations were derived from high resolution maps of land use (Corine Land Cover database, http://dataservice.eea.eu.int/dataservice/metadata
details.asp?id=188) and lithology [Albinet, 1967]; these data, together with a calibration with empirical data permitted the assessment of concentrations of nitrogen, phosphorus and silica in surface runoff and base flow from each of the land use (arable land, grassland, forest and urban areas) and lithological classes considered.

[36] To characterize the Seine land use by global-scale data we used a global land use database at the resolution of 1 km [Hansen et al., 2005]. The mean data extracted for the grid cells covering the Seine watershed provide an estimate of 67% arable land, 28% forest, 3% grassland and 2% urban area. Compared to the values extracted from the Corine Land Cover data (http://dataservice.eea.eu.int/dataservice/metadata
details.asp?id=188), 57% arable, 25% forest, 13% grassland and 5% urban, these global scale data overestimate arable land by 10% and underestimate both grassland and urban areas. Considering these distributions, we have calculated a nitrate concentration in both surface and groundwater runoff applying the general formula of Billen and Garnier [1999] adapted for inclusion of urban area by Billen et al. [2005].

\[
\text{NO}_3 = f \times 0.4 + g \times 3 + a \times (15 + 0.01 \\
\times \text{fert} + 0.1 \times i \times (\text{fert} - 130)) + a \times 10,
\]

where NO₃ is the nitrate concentration (mgN/l) in surface (and groundwater) runoff; f, g, a and u are respectively the forest, grassland, arable and urbanized land fractions of the watershed area; fert is the amount of nitrogen fertilizers, applied to arable land (kgN/ha/yr) and i is an indicator variable equal to zero if fert < 130 kgN/ha/yr and 1 if fert ≥ 130 kgN/ha/yr.

[37] The fine-scale nitrogen fertilizer application rate given in details per subbasin by the French Agriculture Chamber accounts for an average of 150 kgN/ha/yr. The mean value given for France by the FAO statistics (125 kgN/ha/yr), available for all countries in the world,
has been used in this context, and reported to the arable land fraction (67% of the Seine basin, according to global scale data). The resulting average concentration of nitrogen in surface runoff is of 11.3 mgN/L for the global scale scenario, while average values of 11.5 and 13.2 mgN/L were used for 1991 and 2001 respectively. In global scale diffuse sources calculation approach the fact that groundwater usually has a lower nitrate concentration is not taken into account, contrarily to the fine-scale approach.

[38] For phosphate diffuse sources, the same hypothesis as in the reference scenario was applied, and thus the phosphate flux is almost the same as in the reference Riverstrahler scenario for the same year. In addition, phosphate export mostly originates from point sources, which are left unchanged in this scenario. For silica, we used a global scale lithological map [Duerr et al., 2005; Duerr, 2003], instead of the Albinet’s map, to determine the percentage area of the main rock types within the Seine Basin. We adopted the same approach used for the silica concentration in the reference scenarios for the corresponding lithological classes [cf. Garnier et al., 2005a].

[39] The simulation by the Riverstrahler model using the “low-resolution” diffuse sources, together with the reference hydrological, morphological and point source data, produces nitrate specific fluxes very similar to the measured nitrate export in the wet year, and 30% higher in the dry year; this increase only in the dry year is probably due to the high fraction of base flow that, as already mentioned, is not benefiting of lower nitrate concentrations as in the reference scenario. Regarding silica, the specific flux is very close to the measured export, being from 10 to 15% lower than the one at fine-scale resolution (Table 3). No substantial differences are found for phosphorus and ammonium fluxes at the outlet.

4.5. Overall Low Resolution

[40] To complete this study, we have run the Riverstrahler model with all input data constructed from low-resolution global databases, instead of the high-resolution local ones used in the reference simulations (see Table 2). For global hydrology the average runoff issued from meteorological data has been used, and the river network has been considered limited to the orders ≥ fourth. Regarding the nutrient sources, in addition to the diffuse source file issued from global resolution, two distributions of the population by stream order for the point sources, either uniform or entirely located on the last order, have been tested.

[41] Whereas fluxes of silica and nitrogen, nutrients of rather diffuse origin, are within the range of the dry and wet reference years (Table 3), ammonium and phosphate fluxes are much higher when the population is concentrated on the last order. This is likely because the ammonium and phosphate fluxes are more influenced by point sources than by hydrology. This approach using all the coarse resolution data available is valid to reproduce long-term trends but, as already shown when testing only the global hydrology (see section 4.1), it seems of limited value for a fine analysis of eutrophication processes at the coastal zone, which depend closely on the seasonality and year-to-year variations (dry versus wet) of riverine inputs [Cugier et al., 2005].

5. Comparison of Nitrogen Fluxes Calculated by Global Models

[42] Last we applied to the Seine Basin two multiregression statistical models of nitrogen delivery to the coastal zone (for nitrate [Seitzinger et al., 2002]; for total nitrogen [Galloway et al., 2004]), using either fine-scale data (for 1991 and 2001) or global low resolution data. The input data required to run the models correspond to those already used for the Riverstrahler fine-scale and global scale simulation; the only additional data required was nitrate atmospheric deposition. A recent study [Garban et al., 2004] has estimated the total nitrogen atmospheric deposition in the Seine basin as 1100 kg N/km²/yr, 55% of which is in the form of nitrate. On a global scale we use a value of 1122 kg N/km²/yr (i.e., about the double of the high-resolution deposition data for nitrate) provided for the Seine by the database of NOy deposition [Galloway et al., 2004] at 1 degree resolution.

[43] The nutrient fluxes calculated with these empirical models are consistent with the ones obtained by Riverstrahler model and fall in the observed nutrient flux range, even if the annual variability due to hydrology is smoothed (Table 4). The major disadvantage of such an approach is that it is not suited to explore seasonal trends which are important to analyze problems such as eutrophication of the coastal zone. In addition, a comparison of the molar nutrient ratios (Si:N:P) in the system, to the Redfield optimal ratios (16:16:1) required for diatom growth, is of fundamental importance to explore how human activity changes in the watersheds affect eutrophication of coastal zones [Officer and Ryther, 1980; Nixon et al., 1996; Conley et al., 1993; Billen and Garnier, 1997; Lancelot et al., 1997; Cugier et al., 2005]. This limit of single element statistical models can be solved by applying several single variable models in order to provide multimutrient exports. Silica in particular is often neglected, especially in global models, despite its great importance for assessing the balance of nutrient ratios [see Billen and Garnier, 1997; Rousseau et al., 2002].

6. Conclusions

[44] The simulations carried out in this study demonstrate the possibilities and the limits of upscaling a deterministic drainage network model like Riverstrahler from a regional to the global scale, using low-resolution data available at the global scale. The point was not to assess the quality of the global scale data available (which are certainly issued from higher resolution surveys for western Europe and North America than for some other parts of the world), but rather to evaluate, on a well-documented river system, the robustness of the deterministic Riverstrahler model, when it uses different scales of input data.

[45] A major finding from this study is that the evaluation of the overall annual fluxes of nutrient delivered at the outlet of a basin can be correctly predicted by this deterministic model from low-resolution input data, provided...
that a number of conditions are met. First, the hydrological data should represent interannual variations of the time period considered, as the discharge represents a major determinant of nutrient delivery. For this reason, in fact, in order to test the correct simulation of nutrient export without the bias of hydrology, most of the scenarios (unless stated otherwise) were run with adjusted discharge. Second, the description of the drainage network is not a crucial factor for the accuracy of the annual flux estimation, provided that rivers with a watershed area of more than about 4000 km$^2$ are explicitly taken into account. Third, the nutrient point sources should be well estimated, and can be easily derived from population figures. The point source distribution among different stream orders is a factor for the accuracy of the annual flux estimation. Statistical models are nevertheless starting to be used to perform seasonal simulations on the basis of major driving factors for the considered nutrient (e.g. nitrogen export with discharge-apportioned method [Green et al., 2004]) and several single nutrient models are used in cooperative networks (as in the case of the Global NEWS network) to allow multielement (C, N, P, Si) and multiform (particulate, dissolved, organic, inorganic) simulations.

[47] We have shown by the present study applied to the well known pilot case study of the Seine basin (U.N. Education, Scientific, and Cultural Organization, 2003), at which conditions deterministic models as Riverstrahler can be upscaled for global scale applications.

[48] Acknowledgments. We would like to thank the Global NEWS network for having provided some of the databases, and in particular Sybil Seitzinger, for having stimulated exchange of ideas about modeling approaches and John Harrison for his help and suggestions concerning the global databases. We are also grateful to Hans Dier for having provided lithological data from the database submitted in this special section, and to Shannon Sterling for a helpful English revision of the manuscript. The Seine high-resolution databases have been developed in the framework of the PIREN-Seine and Seine-Aval programmes supported by several French Institutions (Rouen Port Autonome, AESN, DIREN, SIAAP, etc.). Agata Sferratore’s Ph.D grant has been funded by European Union project Si-WEBS (HPRN-CT-2002-00218).

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| Table 4. Nitrate and Total Nitrogen River Observed Export or Calculated by Three Models* |
|-----------------------------------|---|---|---|---|
| Source | Model/Data | 1991 | 2001 | GS |
| 1 | calculated from observations | 763 | 1262 | 2194 | 2712 |
| 2 | Riverstrahler | 712 | 1205 | 2220 | 2713 |
| 3 | Garban et al. [2004] | n/a | 1804 | n/a | 2714 |
| 4 | Seitzinger et al. [2002] | 927 | n/a | 1533 | n/a |

*All values are kg N/km$^2$/yr, and refer to observations or to simulations based on fine scale data (in a dry and wet year, 1991 and 2001) and data available on global scale (GS).


Conclusions

This Ph.D thesis has been developed in the framework of the EU Research Training Network Si-WEBBS (Natural and anthropogenic modifications of the Si cycle along the land-ocean continuum: Worldwide Ecological, Biogeochemical and Socio-economical consequences) and probably the existence of such a R.T.N. is a sign of growing attention towards the element ‘silica’, often neglected in environmental research programmes and in hydrological water quality surveys, despite its great ecological role (Officer & Ryther, 1980; Van Bennekom & Salomons, 1981; Cushing, 1989; Smayda, 1990; Justic et al., 1995; Ragueneau et al., 2002; Turner et al., 2003). In fact, even though nitrogen and phosphorus are considered macronutrients, by the definition of macronutrients as those elements that constitute more than 0.1 % of phytoplankton biomass, silica as a micronutrient appears of crucial importance to tune aquatic ecosystem community structure towards successions of either harmful algal blooms or other more desirable species (Sommer et al., 1986, Turner et. al., 2006).

The amount of silica delivered to the coastal zone depends on several factors, some of which have been explored in this Ph.D, and the described achievements have been used to implement Riverstrahler model, as presented in the previous chapters.

Dissolved and particulate silica sources have been quantified for the Seine watershed, showing a consistent proportion of biogenic silica (about 10%) to total silica export (Chapter 1: Sferratore et al., submitted; Chapter 3: Garnier et al., 2002). But silica (biogenic vs. dissolved) proportion from headwaters to the river mouth can change, depending on the primary production, retention in reservoirs and in the river bed, soil vegetation cover (Officer & Ryther, 1980; Humborg et al., 1997; Garnier et al., 2002; Humborg et al., 2006). A possible silica enrichment from urban point sources is scarcely considered. In fact, despite what is generally believed, i.e. that urban sewage delivers, besides ammonium, mostly phosphate pollution, silica can be present in urban wastewater as well, and in this study silica point sources have been shown to contribute to more than 8 % of the total Si inputs in the Seine watershed (Chapter Sferratore et al., 2006 in press).

Silica delivery in general has been shown to be dependent on hydrological conditions (Cugier et al., 2005; Billen et al., in press), and biogenic silica can be particularly high during hydrological
dry years, when a greater diatom bloom can be expected, and a ‘dilution effect’ is not enhanced (Chapter 1: Sferratore et al., submitted). Diatom development can be a sink for dissolved silica, but a source of biogenic silica for the coastal zone, if diatoms are not trapped in reservoirs along the river continuum.

The use of modelling tools such as Riverstrahler is of particular help to explore the link between nutrient inputs from land, and what happens to these nutrients once they are in the aquatic environment (see Billen et al., 1994; Garnier et al., 2002 for a complete description of the concepts, except for silica compartment detailed in Chapter 1). What is remarkable in Riverstrahler is the fact that this model allows multinutrient (N, P, Si) and multiform (dissolved, particulate) synoptic simulations, since all the nutrients reaching the river are susceptible of taking part in the ecological processes represented in the model. In addition, modelling results are available on seasonal scale, which is of particular use to explore Redfield molar nutrient ratios that can be in disequilibrium in some periods of the year: such a temporary perturbation would not be detected through annual budgets (Billen et al., 2001). The representation of more than one diatom group (Chapter 1: Sferratore et al., submitted) is thus a considerable improvement to the model, because it allows a better representation of silica uptake in space (from upstream benthic diatom activity, to downstream stretches where planktonic species are dominant) and in time (seasonal silica variations are finely represented thanks to spring and summer diatoms bloom simulations). Also other models, as for ex. the Potamon model (Everbecq et al., 2001), represent more than one algal compartment, since this seems to be the most appropriate approach to simulate riverine phytoplankton successions and their longitudinal and temporal changes.

Further improvements concerned silica dissolution, that is now included as a function of the water temperature and the degree of undersaturation of the environment. Silica dissolution rate is positively correlated with temperature (Van Cappellen and Qiu, 1997; Rickert et al., 2002), what is shown at the global scale by a gradient of silica concentrations from polar to tropical waters (Meybeck, 1988), independently from the lithology, which is an additional source of variation (see annexed, Garnier et al., in press). In the modelling approach here presented, to a temperature rise corresponds a direct increase in silica export, if all other conditions are left unchanged.

The implemented version of Riverstrahler has been tested not only on the Seine, but also on two sub-arctic Swedish rivers, Kalixälven and Luleälven, one pristine, and the other heavily dammed (Chapter 4: Sferratore et al., submitted.). These two rivers, in addition to the possibility
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of testing the influence of artificial regulation on nutrient export and particulate matter trapping, offer also challenging perspectives of understanding the role of the climatic context and of vegetation change in particular. In fact even though silica dissolution is lower in cold climates, the large percentage of forest in Nordic catchments enhances silicate rock weathering by the action of organic acids and microbial activity associated to vegetation (Humborg et al., 2004). Thus relatively high silica exports can be expected from high latitude pristine catchments, despite their cold climate, showing that natural systems cannot be described only by very straightforward hypotheses (for ex. decreased temperature = decreased dissolution rate = decreased silica export) if other factors, as vegetation in this case, may play an important role. At this stage of Riverstrahler implementation the relation of silica to vegetation has been imposed as a constraint, by a positive correlation between silica and total organic carbon, TOC, which can be considered a proxy of vegetation cover, according to recent literature estimates (Humborg et al., in press); but an interesting future perspective could be to refine the way in which the model takes into account vegetation cover changes, assigning for example a diffuse particulate silica input according to main vegetation types.

Even though Riverstrahler can be still improved for aspects discussed above, this new version of the model has been shown to be generic enough to be applied on rivers in different climatic contexts (Chapter 5: Sferratore et al., 2005). In addition, provided that certain conditions are met, i.e. hydrology is correctly simulated, point source distribution is well known, and sub-basin larger than 4000 km² are taken into account, the model has been shown to provide good estimation of observed nutrient budgets even when using global scale coarse input data.

One of the interesting and challenging aspects of modelling is of course the possibility of improving the model itself, but also of testing the constraints one by one, while in natural systems to separate processes that happen at the same time or that are responsible of the same effect is often difficult. Through a model it is possible to test for example the effect on silica delivery of a temperature change only. Although many scientist still argue that the recent temperature rise maybe due to a natural oscillation of Earth temperature as it already happened in previous geological eras, there is evidence of the fact that global warming is in phase with men-driven growing polluting activities. As suggested by Meybeck and Vörösmarty (2005), we are probably living in the ‘Anthropocene’ era (Crutzen and Stoermer, 2000; Meybeck 2001), where anthropic
activity is the driving factor that affects and causes changes in the environment. A temperature rise of 3.5° C in Antartica since 1945 is a fact of the matter, and global warming IPCC scenarios for 2100 forecast a temperature rise in higher latitudes of 1.5° to 6° C. Over France a simple rise of 0.9° C, would equal shifting meteorological conditions of 150 m higher, or 180 km northward implying a possible vegetation shift in the Seine Basin region, now dominated by oaks and chestnut trees; in addition, with a temperature rise of just 2° C there would be a dramatic shift to Mediterranean vegetation like maritime pine (Loustau et al., 2004).

Realistic scenarios of climate change would imply not only changes in temperature, but also in natural processes as erosion rates, weathering, or human activities as agricultural practices etc. (Ducharne et al., in press). The model at this stage is not able to simulate climate change directly, but it is possible to induce the needed constraints one by one.

To answer the question ‘how temperature changes might affect nutrient delivery at the coastal zone?’ three final scenarios of temperature change are applied to the Oise river basin. This tributary of the Seine River has been chosen as a case study because it has no artificial reservoirs, so the results of the simulations depend only on the change in the temperature conditions applied in each scenario.

Since Riverstrahler model has already been applied to subtropical and arctic rivers, the Red river in Vietnam and China (Le Thi Phuong, 2005) and the Kalixälven and Luleälven rivers in Northern Sweden (Chapter 4; Sferratore et al., submitted), in addition to the realistic Mediterranean climate scenario, also subtropical and arctic scenarios are here presented to show the possible impact of extreme changes in temperature. The only constraints that are modified in these simulations are temperature, light regime, precipitation and evapotranspiration. As the temperature change has an effect on silica dissolution, the input diffuse sources have a different silica concentration according to the average temperature imposed to the simulation. The scenarios consider different discharges, while erosion, lithology, land use, etc. are as presented in chapter 1, where the reference year chosen for Oise simulations is the dry year 1991.

All the input data used to run the scenarios are represented in figure 1, as well as the reference situation (temperate oceanic climate) for the Oise in 1991. For the Mediterranean scenario a typical regime is considered, with very limited precipitation in summer, a temperature range from 3° to 29° C, and a low discharge during all the year. For the sub-tropical scenario the average
Conclusions

temperature considered is of $22^\circ \pm 8^\circ$ C, and the hydrological regime presents a peak of high discharge in the wet season. For the sub-arctic climate scenario the temperature range is of $0^\circ \pm 17^\circ$ C, with a rise of discharge in spring, when the snow melts (Fig. 1). The light variations during the day are much less marked in the tropics that in the cold simulations.

Figure 1: Variations in temperature (yellow bars), precipitation (blue bars), light intensity (light blue line), evapotranspiration (red line) and discharge (black line) in the reference, Mediterranean, sub-tropical and arctic scenarios.
The results show dramatic differences in discharge, diatom development and silica delivery (Fig. 2). For what concerns diatoms (Fig. 2b), their bloom is present in spring in the Mediterranean scenario, while it is inhibited in the tropical scenario due to the high discharge. In the cold scenario there is development of small centric diatoms (SCDs), since they are more adapted to cold temperatures.

The differences in silica export are stressed by temperature and discharge variations (Fig. 2c), temperature enhancing silica dissolution, and discharge enhancing export. Thus the calculated silica export is 710 kg of Si/km$^2$/year for the reference Oise in 1991, while 622 kg of Si/km$^2$/year are delivered in the Mediterranean scenario, 7749 kg of Si/km$^2$/year in the sub-tropical exploration and 1052 kg Si/km$^2$/year in the arctic one. These explorations show the enormous consequences of water and temperature regime on the Si deliveries to the coastal zone; further, the modification of Si cycle derived from diffuse source inputs and erosion rates can have effects on the molar ratios (Si:N or Si:P) and thus on the phytoplankton succession (either diatoms, or harmful planktonic blooms in case of silica limited environment).

Figure 2: results of the simulations for the Oise River in the Mediterranean (left column), sub-tropical (middle column) and arctic (right column) scenarios for discharge (a), chlorophyll a (b) and dissolved silica (c).
This preliminary study on climate scenarios of the Oise basin opens future perspectives for testing the response of the model to the change of constraints other than temperature, such as rainfall, changes in land use, hydrological regulation etc. which may result in different erosion rates, diffuse sources inputs from the considered watershed. In addition, as already mentioned diffuse inputs of biogenic silica might be differentiated by vegetation type; for this note that a special attention is given to results of biogenic silica extraction techniques, since the most recent experiments show that the actual silica measured in biogenic samples is probably underestimated of one order of magnitude (Loredana Saccone, personal communication, Si-WEBS Ph-D).

All those aspects are a call to promote and enhance interdisciplinary studies, because even though silica could be seen simply as a chemical element, to understand its cycle, as important on the continent as in the oceans, a transversal approach, as being carried out in the Si-WEBS network, seems to be the most appropriate to enhance exchange of ideas between scientists of research domains that for too long time have been considered separated (terrestrial biogeochemistry, oceanography...). A land-ocean perspective is a way of looking at nutrient fluxes in the ‘right flow direction’ (since very often ecological problems at the coastal zone are a consequence of land use practices far upstream); there is also a need to establish strong interaction with Human Sciences, as changes in Si:N and Si:P nutrient ratios are typically human-induced. Although these aspects were beyond the work presented here, a goal of the Si-WEBS network is to "provide end-users with Si based tools that can be used for coastal ecosystem management in a perspective of sustainable development". Thus, a nearby perspective suggested by this work is to use Si:N and Si:P molar ratios as "Early Warning Indicators (EWI)" of dysfunction in coastal ecosystems.
Bibliography


ANNEX 1

Physiological ecology of diatoms along the river-sea continuum

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Physiological Ecology of Diatoms Along the River–Sea Continuum

Pascal Claquin, Aude Leynaert, Agata Sferratore, Josette Garnier, and Olivier Ragueneau

This chapter is a synthesis of diatom ecology and physiology along the river–sea continuum, where diatoms are ubiquitous and specifically adapted to various environmental conditions. Instead of an exhaustive literature review, we focus on the major factors that influence the growth characteristics of diatoms and their elemental composition, with special emphasis on the Si. We discuss the aspects of major changes observed in diatom assemblages, the Si sources, the physiological regulations (i.e., metabolisms, uptakes) and their effects on growth and stoichiometry, the bloom developments, and the successions of populations.

Diatoms, from Freshwater to the Marine Ecosystem

Diatoms are unicellular algae belonging to the Heterokontophyta clade. There are 285 known genera (Round et al. 1990) and 10,000–12,000 recognized species according to Norton et al. (1996), but many of them remain to be described. Diatoms occur as single cells or chains; individual cells are in the size range of 5–500 µm, and multicellular chains can reach several millimeters in length. Diatoms occurring in the sea and freshwater can be planktonic, benthic, periphytic, or epizoic (Graham and Wilcox 2000), and few species also occur in terrestrial moisture, aerial habitats, or soils.

Literature about river diatoms is scarce. Most studies are on phytoplankton physiology and dynamics in lakes and oceans. Among freshwater phytoplankton, some main differences occur because of the prevailing conditions: Rivers are permanently mixed, and nutrients are replenished from headwaters (soil leaching and anthropogenic sources). Also, water residence time is shorter (Garnier et al. 1995). Stream communities of diatoms usually are benthic and epiphytic species; planktonic genera are rare (Ruth 1977). The diatom flora differs greatly along a stream. In headwaters, species are
generally cool adapted, whereas downstream, where the current is stronger, rheophil diatoms such as Achnanthes and Cocconeis can grow on substrates, and when the flow is reduced, many species are found in the sediments (Ruth 1977). Only predators that have a short lifespan (e.g., Rotifera) have enough time to develop as they move along the river, before they reach the estuary (Pourriot et al. 1982; Testard et al. 1993). In some way the dynamics of plankton in a river may be comparable to that in shallow lakes with wind-induced mixing (Reynolds 1988). Important biomass of epipelagic communities consists of many species of Gyrosigma, Navicula, Nitzschia, Pleurosigma, and Amphora, which are adapted to the brackish water in the estuaries.

**Sources of Dissolved Silica**

Generally rock and soil weathering are considered the major source of dissolved silica (DSi) in rivers (Chapter 2, this volume). Wastewater treatment plants have been shown to be another source, although not a major one (Chapter 10, this volume). Few studies have been carried out on the biogeochemical cycle of silicon (Bartoli 1983), particularly on the role of biogenic silica (BSi) as a possible source of DSi. Plants absorb Si from soils and precipitate it in their tissues as phytoliths (opal particles), in a proportion that varies between a few parts per million to 15 wt% (Alexandre et al. 1997; see also Chapter 3, this volume). It is well known that gramineous species (such as oat) contain ten to twenty times more Si than leguminous species (Russell 1961) and that Si helps keep the plants erect, counteract manganese toxicity, and ward off fungal and insect attacks (Jones and Handreck 1967). Silicon is also present in pastoral plants, which are grazed by ruminants. Most of the Si ingested comes back to the soil unchanged, so the BSi stock present in the soil, coming from animal feces or directly from plant decomposition, is available for dissolution.

Rain forests are among the most efficient vegetation types in recycling Si (Lucas et al. 1993; Oliva et al. 1999). In particular, research in a small watershed in Cameroon studying the effect of organic matter on chemical weathering shows that DSi concentration in the waters of the swamp zone is well above quartz saturation; this excess of DSi (to the expected equilibrium with quartz) is attributed to the dissolution of phytoliths (Oliva et al. 1999) and confirms the important role of BSi (in addition to the lithogenic Si) as a source of DSi.

Although DSi is abundant in freshwater, it can become a limiting factor during spring diatom blooms in rivers enriched with N and P (Garnier et al. 1995). Seawater is everywhere undersaturated in DSi (Tréguer et al. 1995), and limitation of diatom silification rates has been observed at least once in almost every ocean environment examined, whether in fertile coastal waters or oligotrophic open ocean gyres (Brzezinski and Nelson 1996; Brzezinski et al. 1997; Martin-Jézéquel et al. 2000; Leynaert et al. 2001). Consequently, DSi availability has important effects on the distribution and abundance of diatoms (Egge and Asknes 1992).
Silicon Metabolism and Diatom Stoichiometry

A particular feature of diatoms is their silicified cell wall, called a frustule, which consists of hydrated amorphous silica. As a consequence, silicon metabolism plays a fundamental role in diatoms; vegetative division cannot occur without the formation of the valves of the daughter cells, and cell growth cannot occur without girdle band formation (Volcani 1981). Growth condition can strongly affect the Si metabolism and consequently the Si content per cell. Silicon metabolism in diatoms is strictly linked to the cell cycle (Martin-Jézéquel et al. 2000).

The cell cycle is classically divided into four phases: G1, S, G2, and M. The DNA is replicated during the S phase, M corresponds to the period of mitosis and cell division, and G1 and G2 refer to gaps in the cycle during which most cell growth takes place (Mitchison 1971). Silicon uptake and deposition appear to be associated with the formation of new siliceous valves just before cell division and thus to be confined mainly to the G2 and M period between cytokinesis and daughter cell separation (Hildebrand 2000). It has been suggested that an increase in G2 phase length should entail an increase in Si uptake (for example, Martin-Jézéquel et al. 2000), a hypothesis confirmed by Claquin et al. (2002) on a continuous culture of the marine diatom *Thalassiosira pseudonana*. They observed that the increase of the G2 phase length, which was caused by a decrease in the growth rate under light or nitrogen or phosphorus limitation, entailed an augmentation of cell silicification (Figure 9.1).

Thus it appears that the cellular Si content and frustule thickness (i.e., BSi per cell surface) are regulated by the total amount of Si uptake, directly driven by the length of the cell cycle (i.e., the growth rate). Consequently, the Si content variation appears to be linked not to the type of limitation but rather to the intensity. Under Si limitation, these results cannot be obtained, and the cellular amount of BSi decreases with the growth rate (Martin-Jézéquel et al. 2000).

Other factors such as salinity, pH, or metals (aluminium, germanium) can also influence the Si metabolism and deposition (Gensemer 1990; Vrieling et al. 1999a, 1999b). Recently, Milligan et al. (2004) proved the influence of pCO$_2$ on Si metabolism and content. They showed an increase of Si content with low pCO$_2$, which results in lowering of the Si losses (i.e., efflux and dissolution). Moreover, the basic pH of seawater is corrosive to BSi. The frustule of diatoms is protected by an organic coating that prevents a direct exposure to seawater (Martin-Jézéquel et al. 2000). If the organic covering is removed by chemical, enzymatic, or bacterial attacks, the rate of BSi dissolution increases because of the greater surface area exposed to the water (Bidle and Azam 1999, Van Cappellen et al. 2002).

DSi uptake does not require photosynthetic energy, but it does require energy from respiration (Sullivan 1980; Raven 1983); consequently, DSi uptake can occur in the dark or in the presence of light (Chisholm 1981; Martin-Jézéquel et al. 2000). The strict link between Si metabolism and the cell cycle associated with a low respiratory energy need independent of photosynthesis (Raven 1983; Martin-Jézéquel et al. 2000).
explains in part the uncoupling between C and Si metabolisms (Claquin et al. 2002). This controls the frequently observed variations of Si:C or Si:N ratios in response to changes in growth conditions caused by light intensity, temperature, or nutrient limitation (Paasche 1980b; Brzezinski 1985; Claquin et al. 2002).

A linear and positive correlation between Si content and diatom biovolume has been determined for both freshwater and marine diatoms (Conley et al. 1989). In marine species, one order of magnitude less BSi per unit of biovolume (0.00050 ± 0.00047 pmol/µm³) is present than in freshwater ones (0.00558 ± 0.00400 pmol/µm³). Similar findings emerge from studies on the species Cyclotella meneghiniana (Tuchman et al. 1984) and Thalassiosira pseudonana (Olsen and Paasche 1986), where cells growing at high salinity have lower Si contents than the ones growing at low salinity. A Si:C molar ratio of 0.79 ± 0.43 has been found for twelve freshwater species (Sicko-Goad et al. 1984), whereas a value of 0.13 ± 0.04 is reported for twenty-seven marine species (Brzezinski 1985).

Several possible reasons have been suggested for the difference in Si content between marine and freshwater diatoms (Conley et al. 1989). They include the following:

Figure 9.1. BSi content per cell surface as a function of the growth rate under light (E-lim), nitrogen (N-lim), and phosphorus (P-lim) limitations. Linear regression for the 3 limitations, \( y = 2.87 - 3.52x, r^2 = 0.78, p < .001 \) (from Claquin et al. 2002).
• Sinking strategy. A lower Si content in the frustule allows marine diatoms not to sink rapidly out of the photic zone (resuspension from great depths is unlikely). On the other hand, sinking is a strategy adopted by freshwater diatoms under nutrient limitations (Sommer and Stabel 1983); resuspension in this environment is generally possible.

• DSi availability. DSi concentration is higher in rivers than in the ocean. This may have led to selection of the species present in the two environments: Species with highly silicified frustules live in rivers, where DSi is more available, whereas marine diatoms are adapted to the ocean, where DSi is less abundant.

• Salinity. Although there is a relationship between salinity and Si content in diatoms, it is not yet clear whether this results from a direct interaction with salt or from other factors such as osmotic pressure (Olsen and Paasche 1986). Salinity can also affect valve morphology (Paasche et al. 1975). These authors showed on the brackish water plankton diatom Skeletonoma subsalsum that the valve faces were flat and the connecting processes much shorter at 3 psu or less, whereas at 5 psu or more the valves had a dome shape, and the connecting processes were longer. They obtained the same results by replacing salt with sucrose; therefore, they concluded that the morphological changes were caused by osmotic pressure variations and not directly by salinity. Vrieling et al. (1999b) found the same type of regulation on Thalassiosira weissflogii and Navicula salinarum. They observed that the decrease in salinity entailed an increase in BSi per cell and showed that the concentration of salts is an important factor that affects the Si polymerization.

Dissolved Silica Uptake and Growth Rate Parameters

Numerous studies have shown that specific rate of DSi uptake (V) and the specific Si-dependent cell division rate (µ) of natural communities and diatoms in culture fit reasonably well to Michaelis-Menten saturation functions. Typically, the half saturation for growth (Kµ) is less than that for uptake (Ks). This can be explained by the fact that to determine the growth rate, the increase in cell numbers is used most often. But diatoms are able to decrease the Si content of their frustule when extracellular Si(OH)4 concentrations limit Si uptake (Brzezinski et al. 1990). Thus, a doubling of the number of cells does not necessarily imply a doubling of the biomass.

Physiological parameters for growth (Kµ and µmax) are determined from batch or continuous culture of a given species. They have been measured for many marine diatom species (review in Martin-Jézéquel et al. 2000). For freshwater species, data are scarce, making any comparison difficult. However, there is a large range of variation, from 0.02 to 8.60 µmol/L and from 0.6/d to 9.3/d, respectively.

Uptake parameters can be determined either in culture for a specific species (such as the parameters for growth) or in situ for short-term experiments (a few hours) by using a radiotracer of silicon (32Si). In this latter case, they do not refer to a specific species (except in the case of a monospecific bloom) and can be biased by the fact that not all
the cells actively take up Si during an experiment. In this context, Brzezinski (1992) argues that the Si uptake systems of diatoms could have lower affinity and greater maximum capacity than some current kinetic parameters indicate. However, these parameters still give interesting information on the functioning of the natural community that is present at the time of sampling.

$K_s$ and $V_{max}$ for Si uptake have been measured for many species and in many environments. Martin-Jézéquel et al. (2000) summarize the parameters obtained in culture for specific diatom species, and Table 9.1 reports data from in situ natural diatom assemblages.

As mentioned earlier, along the river–sea continuum large changes in environmental conditions, such as hydrodynamics, salinity, temperature, and nutrient availability, control the structure and elemental composition of phytoplankton communities. One of these factors that may influence D Si uptake directly is the D Si concentration in situ, which varies by more than an order of magnitude between rivers and the open ocean. We could expect the affinity to be higher when ambient D Si concentration is low. However, even if the highest $K_s$ values usually are found in areas where D Si concentrations are high, the plot of $K_s$ as a function of ambient D Si concentrations does not show any obvious relationship (Figure 9.2).

A relationship between $K_s$ and ambient D Si concentrations probably would become visible if we take into account only data from systems in a quasistationary state (i.e., when physical, chemical, and biological parameters show very low variability at the time of sampling). In the equatorial upwelling, for example, because of a quasistationary upwelling driven by trade winds and associated with the surface divergence, the system works like a chemostat (Frost and Franzen 1992). The D Si uptake parameters measured in this region indicate that in situ diatom populations are able to regulate their uptake rate at about half the maximum, with a half saturation constant close to the ambient D Si concentration (Dugdale and Wilkerson 1998; Leynaert et al. 2001). However, the coastal environment is very dynamic, with important variation in D Si concentration on a very short time scale. The D Si concentration measured at a given time is the result of the difference between supply (e.g., dissolution, benthic, or river fluxes) and uptake. For instance, diatoms could use D Si released from BSi dissolution before we are able to measure an increase in water column concentration.

Thus, not only the concentration but also the patchiness of the nutrient may influence phytoplankton succession and community structure. The physiological differences in nutrient uptake ability between the different assemblages allows optimal use of the limiting nutrient in a particular patchy regime. Turpin and Harrison (1979) demonstrate that optimization in a patchy environment takes place through an increase of the maximal uptake rate (high $V_{max}$), whereas optimization in a homogeneous environment appears to take place through an increase in substrate affinity (i.e., low $K_s$). In this context, it is obvious that the relationship between $K_s$ or $V_{max}$ and the ambient D Si concentration cannot be straightforward.

Extremely high values for $K_s$ sometimes are reported (Brzezinski et al. 1998; Nelson
Figure 9.2. $K_s$ and $V_{\text{max}}$ values reported from the literature (see Table 9.1) for natural diatom assemblages, measured in situ in different environments as a function of ambient DSi concentrations.
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<td>3.20</td>
<td>0.6</td>
<td>0.040</td>
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<td>Del Amo 1993</td>
</tr>
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<td>0.041</td>
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<td>0.044</td>
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</tr>
<tr>
<td>Site</td>
<td>Si(OH)$_4$ (µmol/L)</td>
<td>$K_s$ (µmol/L)</td>
<td>SE</td>
<td>$V_{max}$ (per h)</td>
<td>SE</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------</td>
<td>----------------</td>
<td>----</td>
<td>-------------------</td>
<td>----</td>
<td>-------------------</td>
</tr>
<tr>
<td>Central North Pacific</td>
<td>2.33</td>
<td>1.97</td>
<td>0.008</td>
<td></td>
<td></td>
<td>Brzezinski et al. 1998</td>
</tr>
<tr>
<td></td>
<td>2.09</td>
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<td>0.010</td>
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<td></td>
<td>0.55</td>
<td>0.26</td>
<td>0.008</td>
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<tr>
<td>Southern Ocean</td>
<td>1.56</td>
<td></td>
<td>0.013</td>
<td></td>
<td></td>
<td>Nelson et al. 2001</td>
</tr>
<tr>
<td>Average</td>
<td>2.48</td>
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<tr>
<td>SD</td>
<td>1.93</td>
<td>0.025</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
et al. 2001), usually when the relationship between the specific uptake rate ($V$, per h) and $\text{Si(OH)}_4$ fits poorly to the Michaelis–Menten hyperbola or when the kinetics are assessed at very high $\text{Si(OH)}_4$ concentrations. This suggests that some other mechanism may exist. A new hypothesis proposes that uptake is controlled by the ratio of bound to unbound Si inside the cell (Thamatrakoln and Hildebrand 2005). When intracellular Si binding components are in excess, uptake occurs, and when levels of unbound Si are higher than bound Si, uptake is inhibited or efflux is induced. As D Si concentrations outside the cell rise, increasing surge uptake would occur, increasing the levels of unbound intracellular Si and inducing efflux to a greater extent. If this hypothesis is confirmed, the definition of physiological parameters for D Si uptake should be clarified.

Another variable, salinity, is especially important along the river–sea continuum. It does not affect the growth rate but can influence the Si metabolism. Indeed, salinity seems to play a major role in D Si uptake and Si content. Paasche (1980a) showed that marine diatoms have a half saturation constant for D Si that is one order of magnitude lower than that of freshwater diatoms. Olsen and Paasche (1986) observed a variation of D Si kinetic parameters in *Thalassiosira pseudonana* (Bacillariophyceae) in response to changes in the chemical composition of the growth medium. Half saturation constant for growth increased from 0.04 µmol Si/L to 8.6 µmol Si/L in *Thalassiosira pseudonana* grown at high salinity (marine medium) and at low salinity (freshwater medium), respectively. The overall means for these parameters are 2.48 ± 1.93 µmol/L and 0.63 ± 0.60/d, respectively.

It is interesting to note that $K_s$ values used in biogeochemical models usually are in the higher range for river and lake models, whereas they are in the lower range for coastal biogeochemical models (Table 9.2). All values used for $\mu_{max}$ are clearly above the calculated average for $V_{max}$.

**When Does the Bloom Occur? The Diatom Succession**

The development of diatom blooms in coastal waters and more generally in seawater is linked to light availability (i.e., opposite of turbidity) (Cloern 1987), water temperature, hydrodynamics (Cloern 1996), salinity (Kirst 1995), and nutrient availability (Egge and Asknes 1992). Other parameters such as trace elements (i.e., Fe), grazing rate, and $p\text{CO}_2$ can also play a role (Kirst 1995; Gobler et al. 2002). The interactions between these factors are responsible for the growth and succession of diatoms and other phytoplankton taxa. In rivers, phytoplankton blooms are controlled by the roughly same parameters (Lalli and Parsons 1993) as in seawater, but there is some specificity. Several authors have pointed out a negative correlation between discharge and phytoplankton bloom in spring. This phenomenon has been reported for the Sacramento River (Greenberg 1964), the Thames River (Lack 1971), the Loire River (Champ 1980), the Seine River (Garnier et al. 1995), and others, where a bloom has been observed just after the spring discharge. Depending on the hydrological conditions (wet or dry), the occurrence of the diatom bloom can shift from early to late spring. The bloom usually takes place not in
In the case of the Seine River, diatom blooms develop from fifth-order streams downward, with increasing biomass toward the estuary. This is essentially true for both spring and summer blooms, when diatoms constitute up to 76 and 51 percent of total phytoplankton biomass, respectively. However, whereas spring blooms are controlled from the bottom up (hydrology, nutrients, light, and temperature), summer blooms experience an intermittent decline in the seventh-order stretch because of biological top-down control (zooplankton grazing, virus lysis) before redevelopment toward the estuary (Garnier et al. 1995).

**Conclusion**

DSi availability along the river–sea continuum is not homogeneous. In contrast to marine diatoms, which are often limited by Si, river diatoms might occasionally be limited under high anthropogenic P and N inputs. Physiological differences between marine and freshwater diatoms appear to reflect the abundance of DSi in the two environments. However, few studies have analyzed the relationship between Si content, Si metabolism, and the role of environmental factors such as salinity, pH, and osmotic pressure. In general, phytoplankton blooms along the continuum are controlled mainly by similar factors. In rivers, discharge is an important additional factor controlling the development of blooms. Diatom successions have been widely studied in marine environments, and there is a lack of data concerning in situ river diatom assemblages. More physiological experiments are needed to better explain the link between environmental factors and Si metabolism and to elucidate the cellular regulations involved in these processes.

**Literature Cited**


---

**Table 9.2.** Diatom physiological parameters used in ecological models.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\mu_{\text{max}}$ (per d)</th>
<th>$K_s$ (µmol Si/L)</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnier et al. (1995)</td>
<td>1.2</td>
<td>4.2</td>
<td>River</td>
</tr>
<tr>
<td>Chen et al. (2002)</td>
<td>1.2–1.6</td>
<td>5.0</td>
<td>Lake</td>
</tr>
<tr>
<td>Chai et al. (2002)</td>
<td>3.0</td>
<td>3.0</td>
<td>Ocean</td>
</tr>
<tr>
<td>Dugdale and Wilkerson (1998)</td>
<td>3.0</td>
<td></td>
<td>Ocean</td>
</tr>
<tr>
<td>Le Pape and Menesguen (1997)</td>
<td>0.6 at 0°C</td>
<td>1.0</td>
<td>Coast</td>
</tr>
<tr>
<td>Lancelot et al. (2002)</td>
<td>3.7</td>
<td>1.0</td>
<td>Coast</td>
</tr>
</tbody>
</table>


Del Amo, Y. 1993. Dynamique et structure des communautés phytoplanctoniques en écosystème côtier perturbé; cinétique de l’incorporation de silicium par les diatomées. Université de Bretagne Occidentale, Brest, France.


ANNEX 2

Modelling silica transfer processes in river catchments

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“The Silicon Cycle. Human Perturbations and Impacts on Aquatic Systems”
SCOPE series 66, Island Press

Edited by V. Ittekkot, D. Unger, C. Humborg and N. Tac An.

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Modeling Silicon Transfer Processes in River Catchments

Josette Garnier, Agata Sferratore, Michel Meybeck, Gilles Billen, and Hans Dürr

Less attention has been paid to the fluxes of Si transferred from terrestrial systems to surface waters than is the case for P and N fluxes (Howarth et al. 1996; Nixon et al. 1996). Although river dissolved silica (DSi) has been analyzed by geochemists for decades (Clarke 1924), it was not included in water quality surveys until very recently. As a result, whereas P and N concentrations in surface water can be found in the literature or in the databases of water agencies for the last 30 years, DSi values are found only for the last 15 years and even today remain scarce.

DSi inputs to surface water originate mostly from rock weathering and generally are considered not to be influenced by human activity or land use. However, eutrophication can lead to increased retention in the upstream sectors of the drainage network and its stagnant annexes (from small ponds to deep lakes), through increasing diatom biomass production (and the associated uptake of DSi and the formation of biogenic silica [BSi]) under nutrient (N, P) enrichment (Schelske 1985; Schelske et al. 1985; Conley et al. 1995; Campy and Meybeck 1995). More recently, the pools of BSi originating from both aquatic and terrestrial (phytolith) ecosystems have been shown to play a significant role on a global scale (Conley 2002). Redfield ratio (Si:N, Si:P) changes are known to be major indicators of ecological changes in coastal ecosystems (Officer and Ryther 1980; Conley et al. 1993; Billen and Garnier 1997; Humborg et al. 1997; Rabalais and Turner 2001).

A number of recent modeling approaches are devoted to the representation of nutrient transfer through the aquatic continuum (see Vannote et al. 1980), taking into account input from the terrestrial systems of the watershed and the biological uptake and transformation processes in the river system. The RIVERSTRAHLER model (Billen et al. 1994, 1998, 2001, 2005; Garnier et al. 1995, 1998, 2002a, 2002b, in press; Billen and Garnier 1999; Garnier and Billen 2002) is one example of such an
approach. The RIVERSTRAHLER model offers a general framework for the study of the biogeochemical functioning of river systems and is used here to compare silica behavior in river networks that differ in their hydrological regime and climate and in the human activities in their watersheds. The rivers Seine and Danube in Europe and the Red River in Vietnam are the case studies chosen here. Special attention is paid to the factors controlling diffuse sources of silica to surface water. Following the previous work by Meybeck (1984, 1986, 1987, 2003), we investigated factors such as lithology, temperature, and latitude within a gradient of conditions represented by our three case studies. Once validated, the model has been used to explore a range of scenarios differing in the constraints imposed by land use and urban population.

Contrarily to multiregression models leading to annual or pluri-annual means (Kroeze and Seitzinger 1998; Green et al. 2004), the RIVERSTRAHLER model calculates seasonal fluxes delivered to the coastal zone and Redfield ratios. The model takes into account in-stream processes along the aquatic continuum, such as nutrient cycling and retention, and major hydrological features (i.e., reservoirs, canalization). The modular structure and resolution of the model allow us to explicitly consider the nutrient inputs (point or diffuse source) in a realistic way.

**RIVERSTRAHLER: A Modeling Approach at the Basin Scale**

**Description**

RIVERSTRAHLER is a generic model of the ecological functioning and nutrient cycling of large drainage networks as a function of the properties of their watersheds, taking into account the geomorphological characteristics of the watershed, land use, and urban effluent distribution. It is based on the idea that kinetics of the basic ecological processes in the functioning of the aquatic ecosystem are the same from headwaters to downstream sectors, and the hydrometeorological and morphological constraints and the point and nonpoint sources of material from the watershed modulate their expression. The RIVERSTRAHLER model thus results from the coupling of a unique model of processes (RIVE, Figure 10.1) and a hydrological model (HYDROSTRAHLER), describing in an idealized way the water fluxes in the drainage network, represented by a regular scheme of confluence of tributaries of increasing stream order with mean characteristics (see Strahler's concept of stream order; Strahler 1957).

The constraints necessary to build the hydrological model therefore are of geomorphological type, which with the rainfall–discharge relationship (Bultot and Dupriez 1976) are the basis for calculating the discharge in each stream order (Billen et al. 1994; Figure 10.2).

Discharge comprises two components; the surface and base flows are simulated at a ten-day step. This model simulates twenty-two variables for the water quality at the outlet of any subbasin considered, including the major biological compartment (phytoplankton, bacteria, and zooplankton) and the main nutrients (N, P, and Si). Ecological
Figure 10.1. Representation of the RIVE model showing the complex interactions between the main biological compartments in the water column, the water interface sediment, and the stocks of nutrients (PIP = particulate inorganic phosphorus, $\text{PO}_4$ = adsorbed orthophosphates, $\text{NH}_4$ = ammonium, $\text{NO}_3$ = nitrate), suspended matter (SM), oxygen (OXY), and organic matter ($\text{HD}_{1,2}$, $\text{HD}_3$ = dissolved organic carbon under 3 classes of biodegradability; $\text{HP}_{1,2}$, $\text{HP}_3$ = particulate organic carbon under 3 classes of biodegradability; MS = molecular substrates). Biological compartments are phytoplankton (GRA = green algae, DIA = diatoms, Cyanobact. = cyanobacteria), heterotrophic bacterioplankton (heterotr. bact. or BAC) as large and small bacteria, nitrifying bacteria (NIT), and zooplankton (ZOO) as microcrustaceans, rotifers-, and/or ciliates. Processes taken into account are sedimentation of suspended matter (sedim.), nitrification of ammonium (nitrif.), BSI dissolution (dissol.), photosynthesis (photos.), of small metabolites (S) and large molecule reserves (R) respiration (resp.), protein synthesis (growth), lysis and excretion of phytoplankton, exoenzymatic hydrolysis (exoenz. hydrol.), mineralization, growth, and respiration (resp.), mortality of bacteria, and grazing. All compartments are submitted to sedimentation (sedim.) as particulate organic matter ($\text{HP}_{1,2,3}$) at the sediment interface is degraded (org. matter degrad.), $\text{NH}_4$ is nitrified in the oxic layer (nitrif.), and $\text{NO}_3$ is denitrified (denit.) in the anoxic layer.
processes are calculated at less than 1 hour resolution and averaged over 24 hours. Taking into account silica as a state variable, similarly to N or P, implies quantifying silica inputs from point and diffuse sources. Although silica is contained in domestic effluents, it is principally of diffuse origin, from surface and base flows. Siliceous algae, the diatoms, represent one of the major groups in rivers (Garnier et al. 1995; Everbecq et al. 2001) that consume DSi in a ratio to P and N, defined by their physiology (Redfield 1958; Redfield et al. 1963; Conley and Kilham 1989). Dissolution of particulate BSi, both in the water column and in the sediments after deposition, is also taken into account, on the basis of experimental studies (Garnier et al. in press).

Field of Application

Although the RIVERSTRAHLER model was first developed on the Seine (Billen et al. 1994; Garnier et al. 1995), it was conceived as a generic model and was soon applied to several other rivers that offered a gradient of basin area, hydrological regime, and human pressure. The Seine, the Danube, and the Red River, selected here as case studies, differ mainly in their hydrological regimes and climates (Table 10.1). Population density is a good indicator of human activity within the watershed, as well as of land use (percentage in arable land, forest, and meadow).
Whereas the constraints are river specific and must be analyzed for the case of each investigated river, the kinetics of the processes and the corresponding parameters have been shown to be valid for any of the systems (Billen and Garnier 1997, 1999; Garnier et al. 1999b, 2001a, 2002a; Trifu 2002; Billen et al. in press). Although the RIVERSTRAHLER model is designed to represent the whole of the drainage network as a simplified scheme of confluences, where all tributaries of the same stream order are considered identical, the geographic resolution can be much improved by splitting of the drainage network into several homogeneous subbasins, characterized by different sets of morphological, land use, and human discharge constraints. Thus, the Seine and Red rivers are divided into four and three subbasins, respectively, connected to one main branch, whereas the Danube is divided into nine main subbasins connected to one very long major branch.

The Seine River, down to the entry of its estuarine zone at Poses, has a drainage area of 65,000 km$^2$ (77,000 km$^2$ when the estuarine part is included). It is characterized by a pluvio-oceanic regime, with mean annual flow around 500 m$^3$/s (at Poses the limit of the estuary for the last 10 years) and minimum summer flows of 120 m$^3$/s. The construction of three large reservoirs (725 Mm$^3$) in the upstream part of the basin sustains summer flow above 100 m$^3$/s. Upstream from Paris, the main subbasins considered are the upstream Seine, issued from the Langres Plateau, and the Marne. Downstream from Paris, the Seine receives the Oise and 150 km downstream the Eure, immediately downstream from the Poses station, where a sluice lock separates the lower Seine from the freshwater estuary. The results of the RIVERSTRAHLER model are given within

<table>
<thead>
<tr>
<th>Rivers</th>
<th>Seine</th>
<th>Red River</th>
<th>Danube</th>
</tr>
</thead>
<tbody>
<tr>
<td>Watershed surface (km$^2$)</td>
<td>65,000</td>
<td>169,000</td>
<td>817,000</td>
</tr>
<tr>
<td>Annual average and specific discharge (m$^3$/s [L/s/km$^2$])</td>
<td>500 (7.7)</td>
<td>4,000 (23.7)</td>
<td>6,400 (7.8)</td>
</tr>
<tr>
<td>Climate type</td>
<td>Temperate (oceanic)</td>
<td>Subtropical and monsoon</td>
<td>Temperate (continental)</td>
</tr>
<tr>
<td>Population density (inhabitants/km$^2$)</td>
<td>195</td>
<td>180</td>
<td>90</td>
</tr>
<tr>
<td>Land use (% forest, meadow, arable land)</td>
<td>35, 10, 55</td>
<td>34, 24, 21*</td>
<td>45, 15, 45</td>
</tr>
</tbody>
</table>

*Including 8% rice culture.
the estuary at Caudebec, where the limit of the saline intrusion is found. Upstream from Paris, the river and its tributaries drain intensive agricultural areas, causing heavy nitrate load. Most of the population of the watershed is concentrated in the central Parisian area, and the associated wastewater discharges, treated at the Achères wastewater treatment plant (6.5 million inhabitant equivalents), are responsible for a severe increase in organic matter, phosphates, and ammonium loadings (Garnier et al. 2001b). Forests and meadows occupy a small part (35 percent and 10 percent, respectively) of the upstream Seine subbasins, and arable land occupies 55 percent of the basin.

The Red River originates in Yunnan Province, in the mountainous region of South China. The river comprises three main subbasins: the Lo, Da, and Thao rivers, joining at Viet Tri. From this confluence, the main branch (called Huong River) reaches the China Sea at Ba Lat through a large delta (Dang Anh Tuan 2000). The basin area is of 169,000 km$^2$, of which 82,400 km$^2$ (about 48.8 percent) is in China, 85,100 km$^2$ (about 50.3 percent) in Vietnam, and 1,500 km$^2$ (0.9 percent) in Laos. The total length of the Red River is approximately 1,140 km (910 km from headwater to Viet Tri). The results of the RIVERSTRAHLER model are given immediately upstream the delta, at Hanoi, and do not include the impact of the city, which discharges its effluents into a branch of the delta. The discharge is maximal in July, during the monsoon rainy season, and averages 4,000 m$^3$/s. Occasionally, discharge values greater than 30,000 m$^3$/s can be observed in the flood season (37,800 m$^3$/s in 1971, the maximum for the last 100 years). Forests and meadows occupy the majority of the upstream Red River subbasins (34 percent and 24 percent, respectively), 8 percent for the rice culture and 13 percent for industrial crops; the remaining part is occupied mainly by rocky mountain terrain.

With a catchment basin of 817,000 km$^2$ and a main course 2,860 km long, the Danube River flows through many different geological facies and types of land cover. From its source in the Black Forest (in Germany) to its mouth on the Black Sea, the Danube River receives on its right bank the alpine tributaries (Inn, Drava, and Sava) and the Velika Morava, flowing from the Balkans. On the left bank, the major tributaries are the Morava and the Tisza, which drain a large area of the Hungarian plain, and the Olt, Siret, and Prut rivers, which originate in the Carpathians. To achieve a compromise between fine spatial resolution and model flexibility, we divided the Danube network into the nine subbasins corresponding to the main tributaries and the main branch of the Danube, from its junction with the Inn to its mouth. The average discharge of the Danube River into the delta amounts to 6,400 m$^3$/s, with values ranging from 2,000 to 12,500 m$^3$/s. The results of the RIVERSTRAHLER model are given at Reni, immediately upstream from the three main branches of the delta. Because of high precipitation in the upstream alpine sector, discharge is already high in Vienna. The snow cover on the watershed lasts from more than 200 days in the highest mountain regions to only about 10 days on the Black Sea coast. Arable land occupies large areas of the Hungarian plain in the middle of the basin and represents nearly half of the total watershed area. Large forests exist in the southwestern part of the basin and in the Transylvanian Alps and Carpathian regions. Grassland represents about 15 percent of the whole watershed;
whereas forest occupies a larger part of the upstream subbasins (45 percent), cultivated soils dominate in the downstream subbasins (45 percent).

**Sources of Silica from the Terrestrial Systems of the Catchment**

**Lithology-Based Diffuse Dissolved Silica**

Quartz, amorphous silica, and silicate minerals are the only sources of DSi in pristine rivers. Physical denudation and chemical weathering of silicate minerals are associated with the presence of DSi in freshwater, which varies according to the rock type, temperature, and runoff in a basin (Meybeck 1986; Berner and Berner 1996; Drever 1997; Gaillardet et al. 1999). General surface water DSi values for more than 1,000 rivers in pristine condition are 0.5 and 10 mg DSi/L for 1st and 99th percentiles, respectively (Global Environment Monitoring System–Global Registration of Land–Ocean River Inputs [GEMS-GLORI] database: Meybeck and Ragu 1997), and 3 and 23 mg/L in groundwater (Davis et al. 2002), although cases with higher values of silica concentration are reported, particularly under hydrothermal influence.

The review by Meybeck and Ragu (1997) showed that the sixty largest rivers in the world drain about 80 percent of the water from continents; therefore, the large watersheds approach may be enough to estimate major element fluxes to the ocean (Meybeck 1986).

**Table 10.2.** Average DSi concentrations calculated per ocean basin from the Global Environment Monitoring System–Global Registration of Land–Ocean River Inputs database (250 rivers) and the associated documented area.

<table>
<thead>
<tr>
<th>Ocean</th>
<th>DSi (mg/L)</th>
<th>Documented Area ($10^6$ km$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arctic Ocean</td>
<td>1.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Black Sea</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Hudson Bay</td>
<td>0.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Indian Ocean</td>
<td>5.2</td>
<td>7.0</td>
</tr>
<tr>
<td>Mediterranean Sea*</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>$\sum$ North Atlantic Ocean</td>
<td>3.3</td>
<td>16.3</td>
</tr>
<tr>
<td>$\sum$ South Atlantic Ocean</td>
<td>5.5</td>
<td>9.2</td>
</tr>
<tr>
<td>$\sum$ Pacific Ocean</td>
<td>4.1</td>
<td>10.6</td>
</tr>
<tr>
<td>Global discharge-weighted average</td>
<td>4.25</td>
<td>63.4</td>
</tr>
</tbody>
</table>

*With natural Nile discharge.
On the basis of the GEMS-GLORI database, average DSi concentrations per ocean basin can be determined (Table 10.2).

The ocean and regional sea drainage basins display a large variation of DSi, by more than a factor of six, which reflects the overall controls on DSi at such a scale. Cold, lake-covered glaciated shield regions as the Arctic, Baltic, and Hudson show minimum DSi, whereas warm, humid, and volcanic regions have the maximum values.

To determine the diffuse source characteristics for each of the chosen basins or sub-basins, a small watershed approach that combines the effect of lithology and homogeneous climatic conditions (Meybeck 1987; White et al. 1998; Oliva et al. 1999, 2003; Miretzky et al. 2001; Asano et al. 2003) is more appropriate. The global scale lithology map recently developed by Dürr (2003) has allowed us to determine the percentage area of the main rock types in each of the case studied and, following the work initiated by Meybeck (1987), a silica concentration of the headstream waters (without in-stream river cycling) was associated with each rock type (Table 10.3).

In addition, DSi surface flux is positively correlated with temperature (Meybeck 1979; White and Blum 1995), which directly enhances Si mineral dissolution (Stallard 1995; Berner and Berner 1996; Van Cappellen and Qiu 1997) or has an indirect influence through latitudes or altitudes. The importance of silica fluxes at tropical latitudes was reported by Meybeck (1979) and White and Blum (1995) (Figure 10.3).

On the basis of the studies by Schelske (1985) and Schelske et al. (1985) on the increase of permanent sedimentation in the Great Lakes, DSi deliveries at the outlet of large watersheds must take into account such in-stream retention. The effect of a lake

![Figure 10.3. Relationship between DSi concentrations in world rivers (Global Environment Monitoring System–Global Registration of Land–Ocean River Inputs [GEMS-GLORI] database) and latitude (average and SD for each 20° latitude class).]
Table 10.3. Lithological characteristics of the Seine, Danube, and Red River watersheds as determined from the lithological world map (Dürr 2003): percentage of surface area in each watershed occupied by lithological types and DSi concentration found for a monolithological basin with an average annual temperature of 10°C (based on Meybeck 1986).

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Seine (%)</th>
<th>Danube (%)</th>
<th>Red River (%)</th>
<th>DSi Concentration (mg DSi/L) at 10°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polar ice and glaciers</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plutonic basic-ultrabasic</td>
<td>0.6</td>
<td>2.6</td>
<td>1.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Plutonic acid</td>
<td>2.9</td>
<td>2.6</td>
<td>1.7</td>
<td>3.9</td>
</tr>
<tr>
<td>Volcanic basic</td>
<td>2.1</td>
<td></td>
<td></td>
<td>6.7</td>
</tr>
<tr>
<td>Volcanic acid</td>
<td></td>
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<td>5.0</td>
</tr>
<tr>
<td>Shield and basement</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Precambrian)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Metamorphic rocks</td>
<td>16.9</td>
<td>3.4</td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>Complex lithologies</td>
<td>13.5</td>
<td>34</td>
<td></td>
<td>3.9</td>
</tr>
<tr>
<td>Siliciclastic sedimentary</td>
<td>11.3</td>
<td>15.1</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>consolidated</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Mixed sedimentary</td>
<td>15.2</td>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>consolidated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate rocks*</td>
<td>66.6</td>
<td>12.6</td>
<td>17.1</td>
<td>2.2*</td>
</tr>
<tr>
<td><strong>Quaternary evaporites</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semiconsolidated to unconsolidated sedimentary</td>
<td>30.5</td>
<td>28</td>
<td>2.8</td>
<td></td>
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<tr>
<td>Alluvial deposit</td>
<td>13</td>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>Loess</td>
<td>16.3</td>
<td></td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>Dunes and shifting sand</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*When carbonate rocks are chalk with microfossils, a DSi concentration of 5.6 is taken into account (case of the Seine Basin).

or reservoir is not important in any of these catchments in terms of permanent retention because of their low residence time, ranging from days to months.

As a result of lithology and temperature dependence (Figure 10.4), DSi concentrations of 4.7, 2.6, and 7.6 mg Si/L were found as an annual river average for the two components of discharge, surface and base flow, for the Seine, Danube, and Red River, respectively.

Where data are available, these values are refined on the basis of the lithology spe-
specific to each subbasin considered within any watershed. In addition, DSi concentrations of aquifers, generally slightly higher than those of surface waters, can be taken into account in base flow when such data are available.

Finally, Oliva et al. (2003) show that besides the role of temperature in chemical weathering in granitic environments, high runoff (particularly when greater than 1,000 mm/yr) favors silica dissolution by increasing the effective contact time and exchange area of minerals with water. Because runoff is less than 1,000 mm/yr for the three rivers (240, 280, and 750 mm/yr for the Seine, the Danube, and the Red River, respectively), it is not explicitly considered here.

Anthropogenic Input of Dissolved and Biogenic Silica

Silica in present domestic raw and treated effluents has been measured in the Achères wastewater treatment plant, which serves 6.5 million inhabitants per day in the Parisian region. On the basis of a silica concentration of 4.5 mg Si/L in tap water and values of 7.1 and 6.4 mg Si/L in raw and treated water, respectively, a specific (per capita) additional Si load is estimated at 0.8 and 0.6 g Si/inhabitant/d (raw and treated), half in biogenic form (measured according to Conley and Schelske 2001). This new source of silica may result partly from the replacement of polyphosphates in household detergents by new additives containing silica. The value of 0.8–0.6 g Si/inhabitant/d fits well with the data obtained by Billen et al. (2001) from statistics on the domestic consumption of synthetic detergents over a 50-year period (Figure 10.5).

Thus, compared with the Redfield ratios (Si:N = 5.5 and Si:P = 41 (g/g), this new

\[
\begin{align*}
y &= 0.1x + 2.6 \\
R &= 0.54, n = 60
\end{align*}
\]

Figure 10.4. Relationship between DSi concentrations in world rivers (GEMS-GLORI database) and temperature.
specific (per capita) silica load is low compared with per capita loads in treated sewage of 1 and 10 g/inhabitant/d for P and N, respectively (Garnier et al. in press). For raw wastewater, the Si:P and Si:N ratios would be even lower, with P and N specific load amounts of 2 and 12.5 g/inhabitant/d, respectively, for raw domestic wastewater. This very low silica load from wastewater led us to neglect silica point sources in the model.

Modeling Nutrient Dynamics (Si, N, P) in the Drainage Network

Hydrology and Nutrient Concentration

As seen in Table 10.1, the Seine River, with low discharge in summer and high discharge in winter, has a typical oceanic regime, whereas the Danube, influenced by snowmelt,
has a maximum discharge in spring (Figure 10.6). The Red River (of monsoon type) experiences flooding in summer.

Because of differences in watershed size, comparisons are made between specific N, P, and Si fluxes (i.e., fluxes per square kilometer).

The model simulation of discharge and of the main variables of water quality shows a good agreement with observations. Although the seasonal variations in water quality variables are not always phased with the observations, the level of the concentrations is (Figure 10.6). Discrepancies may result from limitations in the quality of observations and constraints on data such as domestic and industrial point sources.

Among the three rivers, particularly striking are the differences in the concentrations

Figure 10.6. Observed and simulated seasonal variations of discharge, nitrates, phosphates (mg P/L), D Si, and phytoplankton biomass, expressed as chlorophyll-a concentrations, in the Seine River (in 1996), Danube River (in 1995), and Red River (average of 1995–1998 and additional observations in 2001).
of nitrates, much higher for the Seine by a factor four to eight compared with the Danube and the Red rivers, respectively, because of intensive agriculture in the French watershed and the use of fertilizers characteristic of Western European countries (Figure 10.6). Phosphate concentrations are about ten times higher in the Seine, and such high values result mainly from point sources at the outlet of the whole basin, although diffuse sources are equally important in the upstream basins (Némery 2003; Garnier et al. 2005; Némery et al. 2005). It is interesting to note that the levels of silica for tropical waters are twice those of the temperate countries, in accordance with the general tendency observed on a world scale. Important variations observed in the Seine are a typical response to eutrophication (Figure 10.6). In a nonlimiting phosphate environment, diatom blooms exhaust silica concentration, mainly when dry hydrological conditions and a high residence time allow the algae to build high biomass (Garnier et al. 1995, 2002b). The poor simulation of D Si in summer calls for more studies both on the timing of algal dynamics and species succession and on silica dissolution rates (Garnier et al. 2002b).

The model has been run on the Seine River, the most eutrophic of the cases studied, for a scenario of drastic abatement of P by wastewater treatment plants (a further 85 percent reduction beyond the abatement of 65 percent that has already been observed in the last 10 years; Garnier et al. 2005). Under these conditions, phytoplankton growth is reduced, and silica is less depleted (Figure 10.7).

![Figure 10.7](Image)

**Figure 10.7.** Response of the RIVERSTRAHLER model, in terms of D Si concentrations, to a reduction in phosphorus in the Seine River at the limit of saline intrusion in the estuary (Caudebec).
The seasonal variations in the molar ratio N:P:Si, calculated by the model for each watershed, reveal great seasonal changes for the Seine River, shifting from P limitation in spring to N limitation in summer, with Si limitation invariably observed in regard to either P or N (Figure 10.8).

For the Danube, silica limitation is also observed, with the N:P ratio being close to the Redfield value of algal requirement. With concentration of silica about twice those of the other rivers, silica generally is not limiting in the Red River compared with P or to N. The Red River nutrient load appears to be low in N rather than in P, which is explained by the large amount of diffuse P, whereas N fertilizers are not used as much as in European countries, at least in the upstream basins.

Silica Retention in Reservoirs

Silica retention in the reservoirs of all three river systems considered here is taken into account in the model. We already demonstrated that silica retention in the diverted reservoirs of the Seine River (residence time of 0.5 year) is low on an annual scale, amounting about 3 percent of the total retention in the drainage network and 0.3 percent of the silica flux at the outlet of the fluvial estuary (Garnier et al. 1999b, 2000, 2002b). Diverging from Humborg et al. (1997), we found silica retention in the large reservoirs of the Danube (Iron Gates) to be low because of the short residence time of the water masses (a few days). Our studies suggested a greater retention in the drainage network itself (Garnier et al. 2002a; Trifu 2002). Similarly, for the Red River, comparing the model results before and after damming showed that only low silica retention occurred in reservoirs (Garnier and Billen 2002).

Exploring Human Impact on N, P, Si Fluxes

The N, P, and Si specific fluxes calculated at the outlet of the three watersheds on the basis of the simulation presented in Figure 10.6 are compared in Figure 10.9.

In addition to the reference situations, two hypothetical scenarios have been tested for each river system: a “pristine” scenario considering the watershed entirely covered with natural vegetation (e.g., forest), without any point source of wastewater and without hydrological regulation, and a scenario called “no population,” corresponding to the present land use and hydrological regulation but without wastewater release.

Specific fluxes of N are much higher for the Seine River than for the other two basins (Figure 10.9). The smaller difference between the reference and the no-population scenario than between the reference and pristine scenarios indicates that, for all three watersheds, total N is mostly of diffuse origin and related to agriculture.

Regarding P, the highest specific fluxes are observed in the tropical Red River (Figure 10.9). The results of the scenarios indicate the predominantly diffuse origin of P fluxes in this basin. Erosion of agricultural soils in tropical regions and even of forested
areas is known to be a major source of suspended matter to which P is associated (Meybeck 1982); diffuse P sources are taken into account in the model (Garnier and Billen 2002). In the temperate systems, on the other hand, P fluxes are much lower and mainly of urban origin at the outlet of the watersheds because population is concentrated along the lower, larger rivers. For the Seine and the Danube the majority of domestic and industrial effluents is collected but only partially treated in wastewater treatment plants, usually without P removal.

Because Si is not directly related to human activity, there are no notable differences for the various conditions explored. Particularly striking are the much greater specific Si fluxes in the Red River (Figure 10.9). This is explained both by the lithology of the upstream Red River basin, composed of very heterogeneous Si-rich formations (e.g., volcanic rocks, sedimentary rocks), and by the wet tropical climate conditions (higher runoff) enhancing rock weathering.
Conclusion

Modeling the silica biogeochemical cycle at a multiregional scale, explicitly taking into account the mechanisms of the transfer and transformation processes within the catchment area and in the drainage network, is an original approach that needs further development in order to correctly simulate the absolute and relative value of the nutrient fluxes delivered to the coastal zones. Such a deterministic approach is needed if realistic scenarios are to be established for preventing or reducing coastal eutrophication, which closely depends on the ratios of riverine N, P, and Si inputs to the coastal environment (Cugier et al. 2005). Until now, most modeling approaches of riverine N and P delivery to the coastal ocean at a multiregional or global scale have been based on statistical regression approaches (Cole and Caraco 2001; Seitzinger et al. 2002a, 2002b; Green et al. 2004) instead of on a mechanistic representation of the biogeochemical processes involved.

The approach suggested in this chapter is still imperfect. In particular, it takes into

![Diagram of silica transfer processes](image)

Figure 10.10. Future representation of Si in the RIVERSTRAHLER model, taking into account diffuse particulate BSi associated to suspended solids (BSiSS) and additional compartments of planktonic diatoms (DIA 1 and DIA 2) and benthic diatoms (periphyton). The processes of silica uptake and dissolution (dissol.) as well as diatom grazing, mortality (mort.), sedimentation (sedim.) and erosion/washing (wash.) are also represented.
account only the diffuse sources of DSi, and particulate sources as BSi are neglected (Figure 10.10).

Although BSi input from the watershed represents only a small fraction (less than 2 percent) of total diffuse DSi and BSi sources in the Seine Basin (Garnier et al. in press), such a proportion could be much higher in low-relief regions where the terrestrial silica cycle and the vegetation silica uptake are more active (e.g., in tropical soils). The importance of phytoliths (opal particles) was first shown by Bartoli (1983). However, it was well known that gramineous species (e.g., oat) contain ten to twenty times more Si than leguminous species (Russell 1961) and that silica helps to keep the plants erect, counteract manganese toxicity, and prevent fungal and insect attacks (Jones and Handreck 1967). More recent works mention that plants absorb DSi from soils and precipitate it in their tissues as phytoliths, in a proportion up to 15 wt% (Alexandre et al. 1997).

From another point of view (river chemistry), the role of vegetation in DSi inputs to surface water could also be better represented in the model, which takes into account only the direct role of lithology; indeed, Humborg et al. (Chapter 5, this volume) showed a clear positive correlation between DSi and total organic carbon in small rivers draining differently vegetated catchments for the same lithology and climate.

A better representation of the aquatic biological uptake of silica (Figure 10.10) would be another improvement to the model. At present, one group of planktonic diatoms is considered. In analysis of the seasonal evolution of diatom successions in the Seine River (Garnier et al. 1995) and the pattern of seasonal successions in freshwater ecosystems (Sommer et al. 1986), at least two groups of diatoms should be taken into account, one for spring bloom and another one for late summer. This would probably improve the simulation of both seasonal phytoplankton and DSi variation levels. In addition, because the RIVERSTRAHLER model is more suited to simulating eutrophication in large rivers, development of benthic diatoms in small upstream rivers is not yet represented, although it could influence the silica biogeochemical cycle in headwaters (Flipo et al. 2004). Benthic algal development can be a sink for DSi in spring in headwaters but also can be a source of BSi by washing out at high discharges (Dessery et al. 1984; Barillier et al. 1993). To our knowledge the role of macrophytes in silica sequestration is not well documented, but it should not be excluded.

In the three river systems studied in this chapter, we found limited silica retention in reservoirs. On a global scale, however, damming is known to influence silica fluxes to the ocean because most of the reservoirs have much higher residence times than those studied here; for example, residence times in river channels can reach 3 months, compared with 20–30 days in natural conditions (Vörösmarty et al. 1997, 2003). But as silica retention in both reservoirs and hydrographic networks increases with eutrophication, short-term silica retention, not significant in an annual budget, can damage the ecological functioning of the coastal zone of temperate systems, when silica depletion in late spring leads to a shift from diatoms to blooms of undesirable nondiatoms (e.g., Phaeocystis, Lancelot 1995; or Dinophysis, Cugier et al. 2005). Silica transformation and retention in estuaries and deltas are much less documented, but, as in reservoirs, the
intensity of the transformations depends on residence time. For example, in the Seine estuary, BSi content of suspended solids (SS) is much higher in the turbidity maximum (residence time of a few months at low summer discharge), compared with the BSi content of headwaters (20 mg BSi/g SS and 5 mg BSi/g SS, respectively).

Although Si has long been studied by geochemists as a major ion, studies of its combination with the nutrient cycle and its importance in water quality date back only to the 1980s, so Si studies do not sufficiently cover various aspects of its cycle (e.g., transformations such as dissolution rates of BSi and lithogenic silica). Its circulation or retention along an aquatic continuum, from land to sea, are still poorly understood, especially under human impact. The “Anthropocene” Si cycle should be affected by changes in climate (temperature, runoff, and vegetation) and in N, P, and Si inputs (increase of fertilizers, improvement of N and P treatment, new use of Si in detergents)

Figure 10.11. “Anthropocene” Si transfers from land to sea. Routing of riverine Si and Si cycling and retention along the aquatic continuum. (a) Strahler ordination of the headwater and diffuse Si sources, (b) reservoir Si transformation and retention, (c) large wetland Si retention, (d) large city input of D Si and BSi, (e) estuarine Si transformation and accumulation of BSi in the turbidity maximum, and (f) D Si limitation in the coastal zone, BSi recycling at the sediment interface, and redistribution within the water column.
and by impoundments (increase retention time of surface waters), necessarily leading to a redistribution of coastal nutrients (Figure 10.11).

Our study shows that regional specificities (i.e., climate, lithology, human impact) should be considered explicitly to elucidate the present river Si transfers at the global scale.

**Literature Cited**


Modelling the transfer, transformation and retention of silica along aquatic continuums: an upgraded deterministic approach

Agata Sferratore

Abstract

Riverstrahler is a watershed based deterministic model that allows simulating nutrient fluxes from the land to the ocean on a seasonal scale. Silica cycle representation in the model has been improved in the framework of this Ph.D for what concerns:

- **algal dynamics**: three groups of diatoms are now considered, spring and late summer planktonic and benthic diatoms, in order to better represent dissolved silica uptake spatially and temporally. The diatom groups differ in their physiological parameters, and the sensitivity of the model to these parameters is explored.

- **diffuse and point sources**: dissolved and particulate silica sources from lithology, agriculture, urban runoff, rainwater are quantified and a budget for the Seine watershed is established.

- **sediment dissolution and transport**: a comprehensive representation of particulate biogenic silica transport, dissolution, deposition and diagenesis is presented.

The new version of the model has been applied to rivers differing for their climatic context and anthropogenic impact, such as the Seine in France and Kalix and Lule rivers in Sweden. Silica fluxes are compared to those of nitrogen and phosphorus and discussed in terms of molar Redfield ratios. Finally, another aspect of the work concerns the sensitivity of the model to the quality and amount of input data, in view of the application of Riverstrahler to river basins for which only global scale resolution data are available.

**Keywords**: deterministic Riverstrahler modelling, silica cycle, diatoms, diffuse and point sources, nutrient ratios.