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Riverine silica flux to the ocean – a model study

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Contribution of riverine nutrients to the silicon biogeochemistry of the global ocean – a model study

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Abstract

Continental shelf seas are known to support a large fraction of the global primary production. Yet, continental shelf areas are mostly ignored or neglected in global biogeochemical models. A number of processes that control the transfer of dissolved nutrients
from river to the open ocean remain poorly understood. This applies in particular to dissolved silica which drives the growth of diatoms that form a large part of the phytoplankton biomass and are thus an important contributor to export production of carbon.

Here, the representation of the biogeochemical state along continents is improved by coupling a high resolution database of riverine fluxes of nutrients to the global biogeochemical ocean general circulation model MPI-OM/HAMOCC5. Focusing on silicon (Si), but including the whole suite of nutrients – carbon (C), nitrogen (N) and phosphorus (P) in various forms – inputs are implemented in the model at coastal coupling points using the COSCAT global database of 156 mega-river-ensemble catchments from Meybeck et al. (2006). The catchments connect to the ocean through coastal segments according to three sets of criteria: natural limits, continental shelf topography, and geophysical dynamics.

According to the model the largest effects on nutrient concentrations occur in hot spots such as the Amazon plume, the Arctic – with high nutrient inputs in relation to its total volume, and areas that encounter the largest increase in human activity, e.g., Southern Asia.

1 Introduction

Continental shelf seas play a crucial role in biogeochemical fluxes from the continents to the open ocean; they are known to support a large part of the global primary production (Conley et al., 1993; Rabouille et al., 2001), only 8% of the ocean surface but 25% of the ocean primary production (Ver et al., 1999). They are also highly sensitive to human perturbations (Ver et al., 1999). The high level of production is supported by

complex dynamics including interplay of riverine supply of nutrients with coastal processes such as tidal currents or upwelling. Our perception of the functioning of the biogeochemical cycles in the global ocean requires a better understanding of the processes taking place on the continental margins. Global biogeochemical models partly
5 fail to integrate processes taking place on the continental margins; they reproduce only crudely the nutrient enrichment supported by coastal upwelling.

The riverine contribution is in the best case represented by a couple of main rivers, in most cases riverine inputs are ignored, neglected or distributed along the continental limits as one uniform mean global value. However, riverine inputs to coastal
10 zones show a high diversity and range over several orders of magnitude (Meybeck et al., 2006). Often, relatively small proportions of the continental area draining to the oceans (i.e. exorheic parts) contribute major parts of material fluxes. As shown by Dürr et al. (2008, this volume) for the example case of dissolved silica (DSi), yields exceeding $6.6\,t\,km^{-2}\,y^{-1}$, i.e. >2× the global average, correspond to 17.4% of the global
15 continental ice-free exorheic area but contribute 56.0% of DSi fluxes from the continents to the coastal zones. Pacific catchments hold most of the hyper-active areas (>5× global average), probably due to a close connection between tectonic activity and DSi fluxes resulting from silicate weathering.

Taking into account this context, continental margins should be considered as a com-
20 plex but essential interface between land and ocean, a contributor to global oceanic biogeochemical cycles and not just as passive boundaries.

In the open ocean, biogeochemical cycles follow a relatively simple scheme: plankton takes up nutrients, dies and sinks to the deep ocean. The sinking organic matter is progressively remineralised and only a very small fraction reaches the sea floor and
25 is buried in the sediments. The euphotic layer where plankton growth takes place is then fuelled by the currents that bring back the nutrients to allow plankton growth. The system is more complex on the continental shelf: first the sinking process is highly modified by eddies, then interaction of bathymetry with waves and tidal currents can lead to the resuspension of deposited organic matter, wind along the shore creates up-

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welling that brings nutrient rich waters rapidly back to the surface. Furthermore, many coastal waters receive continuous fluxes of nutrients from the rivers. The riverine inputs are difficult to take into account in models because of the lack of data for thousands of smaller rivers, which, however in total contribute a significant amount of nutrients. and
5　it is not reasonable to expect data for each river in the world. A comprehensive work of data integration is necessary to build up a database covering the entire world, and not only limited to the major rivers. This new generation of database is now made available: Dürr et al. (2008), Meybeck et al. (2006), the Global-NEWS project (Seitzinger et al., 2005).
10　Detailed regional models succeed in describing the progressive transfer of nutrients from estuarine areas to the adjacent sea (Rabalais et al., 1996; Kroeze and Seitzinger, 1998), but only little effort, mostly through global box modelling (Ver et al., 1999), has been made to study the land/ocean coupling at the global scale (Da Cunha et al., 2007). Satellite derived estimates of the chlorophyll concentration give evidence of
15　high primary production in coastal areas, while global models still fail to reproduce the belts of high chlorophyll concentration along the continents. Regional studies have tried to show the link between the reduction/increase of primary production and changes in nutrient ratios as for example in the East China Sea after the Three Gorges Dam across the Yangtze River was built (Gong et al., 2006). An increasing number of regions of
20　the world (e.g. Chesapeake Bay, northern Adriatic Sea, Gulf of Mexico) have seen their jellyfish biomass increased, supported by an increasing riverine nutrient load due to human activity (crops fertilization and urban sewage) (Graham, 2001;Purcell et al., 1999).

As shown by Humborg et al. (2000), changes in N:Si and P:Si alter biogeochemistry
25　and aquatic food webs in coastal marine environments since diatoms need silica to build up their siliceous frustules, and, in many coastal ecosystems, diatoms are the dominant phytoplankton species and the basic element of the food web.

The insufficient integration of the rivers contribution masks part of the potential of continental shelf seas productivity. In this work we demonstrate the importance of

riverine inputs of dSi to the global biogeochemical cycles on the global scale by adding the riverine fluxes of nutrients to a global scale BGCM. The regionalized inputs allow showing the importance of dynamics in the export of the nutrients to the open ocean and how long these nutrients are available to support the plankton production before being exported out of the system. The riverine inputs of silica are necessary to balance the burial of opal in the sediments (Treguer et al., 1995) the high resolution database (Fig. 1) of riverine fluxes illustrates the spatial heterogeneity of the riverine contribution to the marine silca cycle.

2 Model and data base

2.1 Model and forcing

This work is based on simulations with two numerical models, the ocean model MPI-OM (Marsland et al., 2003) and the biogeochemical model HAMOCC5 (Maier-Reimer, 1993; Maier-Reimer et al., 2005). The two models are coupled on-line and are running with the same vertical and horizontal resolution and the same time step.

The general circulation model MPI-OM grid is an orthogonal curvilinear C-grid with an average resolution of 3°. To optimize calculations, the North Pole is artificially located over Greenland and the South Pole over Antarctica. The resulting resolution is from 29 km in the Arctic to about 390 km in the Tropics. The water column is divided vertically into 40 vertical levels whose thickness gradually increases with depth, from 12 m in the surface layer to a maximum of 600 m in the deep ocean. The time step of the calculations is 0.1 day.

The biogeochemical model HAMOCC5 is based on the work of Maier-Reimer (1993) Six and Maier-Reimer (1996). The version used here is essentially identical with the one used by Wetzel et al. (2005) and Wetzel's PhD thesis (2004). We will only discuss the features relevant for the study presented here, a complete description of HAMOCC5 and MPI-OM are available on internet. For a detailed description see the

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Technical description of the HAMburg Ocean Carbon Cycle model (Maier-Reimer et al., 2005).

HAMOCC5 is a NPZD (Nutrient Plankton Zooplankton Detritus) model with one phytoplankton and one zooplankton box, photosynthesis is co-limited by N, P and Fe (Aumont et al., 2003), and is driven by the same radiation values as the MPI-OM. Temperature and salinity from MPI-OM are used to calculate chemical transformation rates and constants. HAMOCC5 simulates processes of denitrification and N-fixation, formation of calcium carbonate due to coccolithophorides as well as foraminifera and opaline shells from diatom growth, sinking of detritus and marine snow, uptake and release of dissolved iron by biogenic particles, as well as atmospheric dust deposition and sinking (Maier-Reimer et al., 2005). It is assumed here that there is no aeolian input of dissolved silica (only iron and clay). The atmospheric compartments allowed the computation of gases such as CO_2, O_2 and N_2 and their fluxes at the air-sea surface interface. In this version atmospheric carbon concentration is set to its preindustrial concentration.

Phytoplankton growth depends on the availability of light and nutrients. The local light supply is calculated from the temporally and spatially varying solar radiation at the sea surface. Beneath the surface, light intensity decreases with depth due to attenuation by sea water and chlorophyll.

Nitrate (NO_3) in the surface layer is computed simply following the phosphate dynamics, multiplied by a constant stoichiometric ratio, $R_{N:P}$. There is no variation of the internal N:P ratio of particulate or dissolved constituents from surface layer processes.

The phytoplankton growth is assimilated to an amount of organic phosphorous (P) and is driven by the light availability and the limiting nutrient, Eqs. (1) and (2), which is defined as the least available nutrient (phosphate, nitrate, or iron). Assuming that phytoplankton takes up P, N, and Fe in constant proportions determined by the Redfield ratios, the potential limiting effect of each nutrient correspond to the concentration of

each nutrient multiplied by a stoichiometric coefficient: $1/R_{N:P}$ and $1/R_{Fe:P}$, Eq. (2).

$$\text{Photosynthesis} = \text{Phy} * L(z,t) * \frac{X}{K_{Phy}^{PO_4} + X} \tag{1}$$

With

$$L(z;t): \text{ light availability } X = \min\left([PO_4], \frac{[NO_3]}{R_{N:P}}, \frac{[Fe]}{R_{Fe:P}}\right) \tag{2}$$

The predation of zooplankton on the phytoplankton transfers a part of the organic matter produced by the photosynthesis into the zooplankton biomass. During the ingestion of this organic matter, a fraction is immediately release in water (as faecal pellets) and forms the detritus fraction (det). The remaining fraction supports zooplankton growth. The metabolism of zooplankton and phytoplankton produces waste that is excreted in the form of dissolved organic matter (DOM). The zooplankton and phytoplankton mortality returns organic matter to the water column and forms the detritus fraction that will sink to the deep ocean. To summarise, the detritus originates from dead phytoplankton, dead zooplankton and faecal pellets from the zooplankton predation on phytoplankton. At this step the model calculates the opal and the calcium carbonate production as the two fractions of the non living part of the detritus, the shells.

It is assumed that phytoplankton consists of diatoms, coccolithophorids, and flagellates. As diatoms are known to be the fastest competitors (Egge and Aksnes, 1992), opal production by diatoms is computed first in the time loop if silica is available.

The siliceous fraction of the detritus is computed as:

$$\Delta\text{sil} = \min\left(\frac{\Delta\text{det}}{\Delta t} R_{Si:P} \frac{[SI(OH)_4]^{SI(OH)_4}}{K_{Phy}} + [SI(OH)_4], 0.5[SI(OH)_4]\right) \tag{3}$$

Where:

$R_{Si:P}$: required Si:P ratio by diatoms $K_{phy}^{Si(OH)_4}$: half-saturation constant for silica uptake

The calcium carbonate fraction is computed after as shown in Eq. (4).

$$\Delta car = R_{Ca:P} \frac{\Delta det}{\Delta t} \frac{K_{PHY}^{SI(OH)_4}}{K_{PHY}^{SI(OH)_4} + SI(OH)_4} \qquad (4)$$

Opal production (Δsil) consumes silica ($Si(OH)_4$). Dissolution of opal is temperature (T) dependant with a constant ratio, $\lambda_{opal;Si(OH)_4}$.

$$\frac{\Delta opal}{\Delta t} = \Delta sil - \lambda_{opal:Si(OH)_4} * 0.1 * (T+3) * Opal \qquad (5)$$

$$\frac{\Delta SI(OH)_4}{\Delta t} = -\Delta sil + \lambda_{opal:Si(OH)_4} * 0,1 * (T+3) * Opal \qquad (6)$$

The flux of particles through the water column redistributes phosphorous, silica and associated tracers along the sinking part enriching the deep waters in nutrients. In the default version of the code, particles have constant sinking speeds, w_{DET}, w_{CaCO}, w_{Opal} and w_{Dust} for organic detritus, $CaCO_3$, opal and clay respectively. The export production is computed as the material leaving the euphotic layer, i.e. 90 m depth of the surface ocean, separately for opal and $CaCO_3$. Remineralisation of opal and $CaCO_3$ occurs all along the sinking of particles after they left the euphotic layer. Fluxes from the bottom layer in each grid cell provide the boundary condition for the sediment module that includes 4 sediment weight fractions and 12 layers following Heinze et al. (1999). The sediment module computes the accumulation of the deposited material on the sea floor as well as processes of remineralization in the sediments and the release of redissolved tracers to the lowest level of the water column.

The model is forced with NCEP based climatology (National Centers for Environmental Prediction). Dust deposition was generated by the National Center for Atmospheric Research's Community Climate System Model for the current climate, they have been shown to be consistent with present day satellite and deposition data (Mahowald et al., 2006).

2.2 Initial conditions and model spin-up

The model was run for a 2400 years spin-up from a homogeneous distribution of the 18 tracers in the water column after 600 years of spin-up of the global circulation model. After 2400 years the simulated distribution of tracers is consistent with observed sur-
5 face map concentrations and cross sections of the Pacific, Atlantic and Indian Oceans. The coupling of the riverine fluxes of nutrients to the HAMOCC5 model is then inte- grated on a 100 years time period (900 CPU h per run). The MPI mode of the model currently runs on a distributed shared-memory system of IBM p575+ nodes intercon- nected with a high-bandwidth low-latency switch network (HPS). Each simulated year
10 takes 35 min running on 16 processors for a total of 9 CPU h per simulated year.

2.3 River nutrient databases

Here we take into account the current state-of-the-art datasets for riverine nutrient ex- ports in different forms (Table 1), as established for the reference year 1995 (for C, N, P except DIC) by the Global-NEWS project (Seitzinger et al., 2005); we used the merged
15 and slightly adapted dataset as made available to us by the group in January 2008), and for pre-industrial conditions for silica as established by Dürr et al. (2008, this vol- ume). For DIC, we used the alkalinity flux data as calculated by Suchet (2003). Global- NEWS established the datasets at a 0.5 degree resolution for the ~6200 river basins available from the STN-30 dataset of Vörösmarty et al. (2000a, b). They have been
20 aggregated here to the resolution of ~140 mega-river-catchments (COSCATs) corre- sponding to homogeneous coastal segments with fixed segment boundaries as estab- lished by Meybeck et al. (2006). These segments have a median length of ~2000 km and were specifically designed for standardized spatial analysis and reporting of ma- terial fluxes – water, dissolved and particulate material such as nutrients and carbon
25 species – from the exorheic (i.e. draining to the oceans, as opposed to the endorheic parts draining to internal end points) parts of the continents (see also Dürr et al., 2008, this volume and a complete discussion in Meybeck et al., 2006). The silica flux dataset

is directly available at the COSCAT resolution. The DIC data has also been directly calculated summing up the 1 degree original data set to the COSCAT resolution. Injection points are calculated as the central coastal point for each COSCAT, and adapted to the ocean model resolution (see Fig. 1).

2.4 Coupling

The coastal segments (COSCATs) are defined as the coastline between two geographical locations. The riverine fluxes of nutrients are released in the near-shore model grid cells located in between both ends of a given segment. Due to the low resolution of the model grid, some of the 156 original segments were merged, resulting in 129 segments used here. Coupling of the database, fluxes of nutrients are computed at each time step; 10 times a day (Si, N, P and C). The flux is released homogeneously all along the coast line in the corresponding grid cells in the upper layer (first 12 m). The fluxes are assumed to be constant over time; the river discharge does not yet take into account the seasonal cycle or interannual variability. However, such information progressively becomes available and will be incorporated in later versions of the model.

The model code relies on the Redfield Ratio, i.e. nutrient uptake occurs according to a 122:16:1 C:N:P ratio. The same applies to the remineralisation process.

The data of riverine nutrient fluxes included dissolved organic nitrogen, phosphorous and carbon (DON, DOP and DOC). The dissolved organic matter (DOM) was regarded as the least available organic element (either phosphate or carbon):

$$DOM = \min\left(DOP, \frac{DON}{16}, \frac{DOC}{122}\right) \tag{7}$$

The dissolved organic element in excess with regard to the Redfield ratio was added under its inorganic form, for example in the case P is the least available nutrient (either phosphate or nitrate, see Eqs. 7 and 8).

$$F_{DIN} = DIN + (DON - 16 * DOP) \tag{8}$$

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While,

$$F_{DIC} = DIC + (DOC - 122 * DOP) \tag{9}$$

The same approach was applied to particulate matter.

3 Global results, silicic acid concentration

Mapping the silicic acid concentration of the ocean surface shows four major hotspots when comparing the run with riverine silicon loads to the run without: the Arctic Ocean, the eastern Gulf of Guinea (coast of Cameroon, Gabon, Congo and Angola), the Amazon plume and South Eastern Asia (Fig. 2). The total flux is 6.2 teramoles of silicon per year (or 371 Mt SiO_2 per year) is in agreement with earlier estimates of 6.1±2.0 teramoles of silicon per year (Treguer et al., 1995).

In the Arctic Ocean, the largest effect of the riverine silica occurs along the Siberian coast where rivers that drain the Siberian plateau annually release 0.25 teramoles Si (15 Mt SiO_2), this results in a 15 μmol l^{-1} increase of the dissolved silica concentration (Fig. 2). In the Eastern Gulf of Guinea, the largest river in Western Central Africa, the Congo River (21 Mt SiO_2 yr^{-1} or 3.5 teramoles Si yr^{-1}) contributes to a 5 to 10 μmol l^{-1} increase of the silicic acid concentration all along the 1000 km coastline from its mouth to the coast of Cameroon, extending the silica supply from the Benguela upwelling system. Across the Atlantic Ocean, at the same latitude, the Amazon releases 0.94 teramoles Si per year, more than 15% of the global land-ocean flux of silica, 1.1 teramoles Si per year with the Orinoco River (0.16 teramoles Si per year). Combined with the Orinoco, the Amazon load is the strongest input of silica to the open ocean and can be traced all along its plume drifting North West sustaining a 10 μmol l^{-1} excess concentration into the Caribbean. The plume of the Amazon drifts North West along the north coast of South America and mixes in the Gulf of Mexico with the waters from the Mississippi. The time series in Fig. 4 show the annual cycle of nutrients,

photosynthesis, opal and calcium carbonate production together with the carbon export at a few hundreds kilometres from the Amazon mouth. Despite the distance from the coast, the comparison of the 2 runs with/without rivers clearly shows the shift in calcium carbonate production. The riverine silica input maintains the dissolved silica concentration higher than 8 μmol/l, which sustains the opal production, as shown in Figs. 2 and 4. If the riverine input of silica is switched off, the dissolved silica concentration drops below 1 μmol l^{-1}, promoting the calcium carbonate production by limiting diatom growth.

The calcium carbonate production benefits from the low dissolved silica concentration through the silica limitation of opal production. Here only the Amazon plume is represented as the other hot spots show the same scheme.

The major hotspot of dissolved silica release to the ocean is located in South Eastern Asia (Fig. 2). The Ganges River and its neighbouring smaller rivers support an annual input of 0.4 teramoles Si (or 23.32 Mt SiO$_2$) to the Bay of Bengal. Not as strong, but on a larger spatial scale, the Indonesian archipelago's coastline receives in total the equivalent of the Amazon's load; with the Mekong River (21 Mt SiO$_2$ or 0.35 teramoles Si per year), Indonesia and Malaysia (21.4 Mt SiO$_2$ or 0.36 teramoles Si per year). The dissolved silica concentration raises about 20 μmol l^{-1} Si in the Java Sea, between Indonesia, Sumatra and Java, these numbers should be considered with caution as this sea basin doesn't account for more than a few cells. Therefore a weak advection of tracer could artificially increase the accumulation process locally.

The open ocean benefits as well from the riverine input of silica. The Fig. 2 shows an increased silicic acid concentration of a few μmol l^{-1} on large surface of the Equatorial East Pacific Ocean and in the North Pacific Ocean. The Congo raises the eastern South Atlantic surface silicic acid concentration by 2 μmol l^{-1}, which is significant for such a low Si concentration area.

The silica concentration shows local accumulation processes but opal production better describes the utilisation of the silica provided by the continent through weathering of rocks. Delivery of silica by rivers increases the concentration; phytoplankton

utilization decreases the concentration; where these two processes are not in balance there is either accumulation either depletion of the dissolved silica. As shown on Fig. 3, there is no photosynthesis in the Arctic Ocean because of sea ice. The photosynthesis is not responding to changes of the riverine inputs of silica for the simple reason

5 that if diatom growth is limited by silica availability it is replaced by calcium carbonate production which leaves the annual primary production unchanged. In the code, the photosynthesis only depends on light availability, phytoplankton and the limiting nutrient (phosphate, nitrate or iron). It is therefore interesting to note that hotspots of riverine silica inputs (Fig. 2) are mainly located in highly productive areas (Fig. 3) for two differ-

10 ent reasons; the nutrient availability supplied by the river itself (Amazon plume, Fig. 4) and in some cases the vicinity of coastal upwelling (Southwest coast of Africa). In this case the riverine silica mixes with the silica enriched waters of the upwelling, and both contributions work in synergy to maintain a high level of silica concentration. The situation is slightly different in the Indonesian archipelago; despite a large riverine input

15 of N and P, the iron limitation driving the photosynthesis of most of the Pacific Ocean (Behrenfeld et al., 1996) maintains photosynthesis below a few moles of $P\,m^2\,yr^{-1}$.

The opal export production is the flux of opal that exits the euphotic layer (set to 90 m depth in the code). Two main areas of the global oceans show a significant increase of the vertical export of silica via opal export; the Amazon plume including

20 the Caribbean Sea and the Gulf of Mexico and South-eastern Asia. The strongest increase of opal export production is the Amazon and Orinoco Rivers; these two rivers alone contribute to maintain an annual opal export of up to a $0.8\,mol\,Si\,m^{-2}$ along the north coast of South America (Fig. 5). This large input of silica (1.1 teramoles Si per year) enhances Diatoms growth and opal export as far as the Caribbean Sea,

25 and mixes its signal with the input of the Mississippi River in the Gulf of Mexico. The second area where riverine silica significantly increases opal export covers a large part of the East Indian Ocean between Australia and South-eastern Asia. The annual opal export production is enhanced by $0.2\,mol\,Si\,m^{-2}$ all around Indonesia. The riverine contribution reaches its maximum along the coast of India and Burma where the annual

opal export production locally increases by $0.5\,\mathrm{mol\,Si\,m^{-2}}$.

4 Discussion

Rivers are the most significant input of silicic acid for the global ocean (Treguer et al., 1995), thus also in our model and are assumed to balance the burial/redissolution of opal in the sediment. Atmospheric silica inputs such as dust deposition and dissolved silicic acid in rain are here considered negligible. We assume here that deposited aeolian silica would be deposited as sand particle whose sinking speed wouldn't allow any dissolution resulting in a significant input of silicic acid (Johnson et al., 2006). Riverine supply contributes to enrich the euphotic layer in addition to the upwelling systems. In a steady state ocean, rivers balance the burial of Silica into the sediments (Treguer et al., 1995).

Riverine input of silicic acid occurs at the same time as the other limiting nutrients supporting a vigorous primary production (Figs. 2 and 3), except on the Pacific side of the South Eastern Asia witch is limited by iron. The conditions are then favourable to a local use of the available silicic acid that explains the relative low export of the silica from the marginal seas. For that reason a large part of the opal is buried on the continental margins (Treguer et al., 1995). The situation is different for the Arctic region that receives a large flux of silicic acid in relation to the shallowness of the basin and its volume (Dürr et al., 2008) and where sea ice doesn't allow the plankton growth as shown on Fig. 3. This combined factors lead to the accumulation of silicic acid in the Arctic basin.

The maps of the surface silicic acid (Fig. 2) and opal export production (Fig. 5) point out the strong spatial heterogeneity of the riverine silica contribution to the oceanic biogeochemical cycle of silica. This is not surprising given the enormous heterogeneity in the spatial distribution of riverine silica inputs, indeed, 56% of Silica flux to the coastal zone are concentrate on 17% of the coastline where the flux is twice as large as the average flux (Dürr et al., 2008).

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Riverine inputs of silica do have a stronger effect on the ocean distribution of silica as they often occur in areas that encounter no major input from upwelling (Amazon, South-eastern Asia, Arctic rivers as shown on Fig. 2). The silica delivery in these areas is dominated by riverine flux. Remobilisation of opal shelf sediments would not compensate for a large decrease of the riverine silica input. It is also interesting to point at the general climate impact on the regionalization of total input of silica to the euphotic layer. Both riverine and upwelling supply depend on climate. The precipitation on the continents drives the weathering of rocks and the transport of silica to the ocean while winds drive the upwelling processes along the shore. Any changes in the atmospheric circulation could thus spatially redistribute the riverine silica inputs to the sea surface of the ocean.

The effect on the surface silica concentration depends on the location of the river mouth; in fact the effect of the silica inputs from the Amazon appears to be small as compared to the Siberian Rivers. The Siberian COSCATs combined contribute to raise the surface silica concentration by $15\,\mu\text{mol}\,\text{l}^{-1}$ with an annual input of 0.26 teramoles of Si. Despite the 1.1 teramoles Si per year released by the Amazon River and Orinoco River, the surface silica concentration just raises by $6–8\,\mu\text{mol}\,\text{l}^{-1}$. First, one must take into consideration the size of the oceanic regional domain. Accordingly, the Arctic Ocean is the region of the global Ocean that encounters the highest silica input in relation to its size. Second, the depth of the oceanic regional domain determines the efficiency of the removal of silicic acid by the silica pump described by Dugdale (1995). The Si export to the deep ocean has been shown to be more efficient than for N and P (Bidle and Azam, 1999), recycling of opal remains slower than for N and P. The narrowness of the continental shelf determines the efficiency of the opal export. The shallowness of the continental shelf shorter the sinking time of opal, most of which reaches the sediments before being redissolved. The slow remineralisation of opal sediments promotes then its storage on continental shelf for a long period (Ragueneau et al., 2002). If the opal export takes place further out in the open ocean, the longer sinking time promote the dissolution of a larger fraction of the exported biogenic silica,

the redissolved silica will sooner or later be reexported to the euphotic layer (by advection or diffusion). This process is illustrated by the case of the Amazon contribution, whose large scale plume is correctly captured by the model if compared to the study of Nikiema (2007). As shown in Figs. 2 and 5, the north-westward Amazon plume input
5   is so powerful that it exports its load up to a few hundreds of kilometres from the coast, supporting opal production far outside the continental shelf. The silica taken up by diatoms to build up their silicic shells is directly exported to the deep ocean after diatoms die. In the case of the Arctic Ocean, the sea ice prevents plankton growth and silica uptake, which causes an accumulation.
10   Riverine silica input shows high sensitivity to land use and human activity in general (Conley et al., 1993; Humborg et al., 2000). River damming and artificial reservoirs trap part of the riverine silica and as DSi only originates from natural weathering of rocks (Meybeck, 1998), measurement have shown a decrease of the riverine DSi during the last decades (Justic et al., 1995b). In parallel, human activity had the opposite
15   effect on N and P (agriculture, industry or urban sewage increased N and P emission. The combined results is a general decrease of the riverine SI:N and Si:P ratio (Justic et al., 1995a, b). In addition, the increased input of N and P stimulates the primary production fuelling the silica pump. Sediment beneath the Mississippi River plume showed an increased accumulation of biogenic silica over the last decades (Rabalais et
20   al., 1996). It is therefore interesting to note that South Eastern Asia, which receives one of the most significant inputs of riverine silica, is the region of the world that encounters the strongest population growth, urbanization and development. It is therefore logical to expect a large change in the land/ocean nutrient flux. The expected shifts in the plankton population with an increase in the occurrence of and intensity of toxic algal
25   blooms are the major problem the local fisheries will have to deal with in the future.
     Iron was not initially part of the land to ocean fluxes of nutrients as it is assumed that on the continental margins iron originates from the remineralisation taking place in the sediments. Not shown in this paper, the dissolved iron availability showed to interact with the utilisation of the riverine silica through its potential control of the photosynthe-

sis, the iron/nitrogen limitation boundary shifts after coupling of the complete set of river inputs. The model generates an iron limitation in the coastal zone due to the high use and export of the original iron caused by the high supply of nutrients. The model fails to reproduce the iron recycling from the shelf's sediments. The primary source of iron in the continental shelf seas is resuspension of particles and redissolution of deposited iron in the benthic boundary layer, followed by upwelling of this iron-rich water, rather than direct riverine input (Johnson et al., 1999). The generated artificial iron limitation masks part of the potential of the continental margins primary production potential. It probably artificially decreases the opal production of the marginal seas. In the model, iron is supplied by aeolian dust deposition.

The complex pattern of iron during its transfer to the ocean does not allow a direct flux from the rivers (Wells and Mayer, 1991; Poulton and Raiswell, 2002). Iron aggregates and sediments in the estuary when freshwater and sea waters mixes (Poulton and Raiswell, 2002). A large part remains trapped in the estuary. The input of iron is assumed to be mainly supported by dust deposition and remineralisation in the sediment pore waters of the coastal sediments before advection to the surface (Johnson et al., 1999). The active recycling of iron on the continental margins prevents iron limitation on the continental margins but in coastal upwelling regimes (Hutchins and Bruland, 1998). To use riverine iron concentration from the literature would rather generate an iron fertilization experiment than give a better picture of the marginal seas productivity. A realistic approach would consist in getting a better simulation of the iron return from the coastal sediments to the surface on continental margins as suggested by Wells and Trick (2004). This might be the reason why the model fails to reproduce the high production belt along the continents even when riverine nutrient input is taken into account.

To better simulate the land-ocean interface it is necessary to enhance the implementation of coastal processes, taking into consideration regional patterns of the estuarine and near-shore retention of riverine nutrients. The idea is to overcome the coarse resolution of the OGCM by using a box model that will prescribe the riverine flux for each

coastal segment of the COSCATs database, with a specific parameterisation for each segment.

The coupling of the model to the database of riverine nutrients will allow running scenarios with changes in the fluxes; it will be based on scenarios built by Global-NEWS models currently under development according to the Millennium Scenarios. Ongoing projects of damming majors rivers such as the Three-Gorges Dam already shown changing nutrient concentrations and ratios in the coastal zone and the East China Sea (filling phase started in June 2003). Investigations carried out by Gong et al. (2006) have shown that the Si:N ratio in the river-affected region changed from 1.5 in 1998 to 0.4 in 2004. All over the world, all nutrients are expected to be impacted, Kroeze's model predicted that between 1990 and 2050 the dissolved inorganic nitrogen (DIN) export by rivers more than doubles to 47.2 Tg N in 2050 (Kroeze and Seitzinger, 1998). Whatsoever riverine N and P stabilized or not, all observations show a general decrease of the Si:N and Si:P ratio. The decreasing riverine DSi concentration is probably due to enhanced reservoir retention effect similar to the Iron Gate (McGinnis et al., 2006). In addition Rabalais suggested that a larger amount of silica would be buried in the continental shelf due to an increased coastal primary production supported by the increased rinverine N and P input. The silica in sediments beneath the Mississippi River plume increased during the past two decades (Rabalais et al., 1996) despite a decrease of the Mississippi supply in silica.

The recent development of the river biogeochemical states is different depending on the regional level of economical development. In a few developed countries, due to a political will of reduction of eutrophication (wastewater treatment, denitrified and diphosphorilated) and sustainable land use changes, the riverine load of N and P stabilised. In some rare cases the load of N and P tends to decrease. For example, in Poland, economical changes in the early 1990s, led to a drastic decrease in fertilizer consumption (Eriksson et al., 2007). Water quality management policies and rehabilitation of aquatic habitats forced to a limitation of the release of nutrients in the rivers to limit eutrophication impacts on the environment. Nevertheless, this local improve-

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ment is little compare to the global increase of river load in the rest of the world and its resulting decrease of the Si:N and Si:P ratio.

5 Conclusions

Regionalisation of silica inputs highlights the heterogeneity of land waters contribution to the marine cycle of silicon. The fate of the riverine silica input is largely depending on the input location and local level of productivity. The hot spots are mainly located in areas where there is little support of the marine ecosystem through upwelling; it makes these areas dependant on the riverine fluxes and sensitive to the human activity that affect the riverine transport of nutrients. The uniform distribution of riverine silica at the surface of the ocean commonly used in global models to balance opal burial in the sediments can no longer be used if one plans to properly describe the biogeochemical cycle of silica, especially for models taking into consideration the competition between calcifiers and diatoms. We take here the first steps to a full integration of nutrient cycling, including the continental shelf seas and land/ocean coupling, in an Earth System modelling context.

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Table 1. Data sources for nutrient forms used here as riverine inputs.

Nutrient form	Acronym	Method	Data format used	Reference
Dissolved silica	DSi	Extrapolation from river catchments to COSCATs using characteristics like lithology, climate, lake occurrence	Data directly available at the COSCAT resolution of ~140 mega river-ensemble catchments	(Dürr et al., this volume)
Dissolved inorganic nitrogen	DIN	Spatially explicit regression models linking basin	Data originally developed for the STN-30 v.6 river	(Dumont et al., 2005)
Dissolved inorganic phosphorus	DIP	characteristics at 0.5 degree resolution plus human influence to	basins, merged data set used here and aggregated to the	(Harrison et al., 2005b)
Dissolved organic nutrient forms	DON, DOP, DOC	nutrient export	COSCAT resolution	(Harrison et al., 2005a)
Dissolved inorganic carbon	DIC	Data originally calculated at 1 degree resolution, regression model using methodology derived from monolithologic watersheds	Fluxes are used as aggregated at the COSCAT resolution	(Amiotte-Suchet et al., 2003)
Particulate nutrient forms	PP, PN, PC	Spatially explicit regression model for suspended sediments (same model strategy as for DIN, DIP and organic matter), the nutrient partitioning is derived from known relationships resulting in fractions of suspended matter flux	Data originally developed for the STN-30 v.5 river basins, merged data set used here (adapted for STN-30 v.6) and aggregated to the COSCAT resolution of ~140 mega river-ensemble catchments	(Beusen et al., 2005)
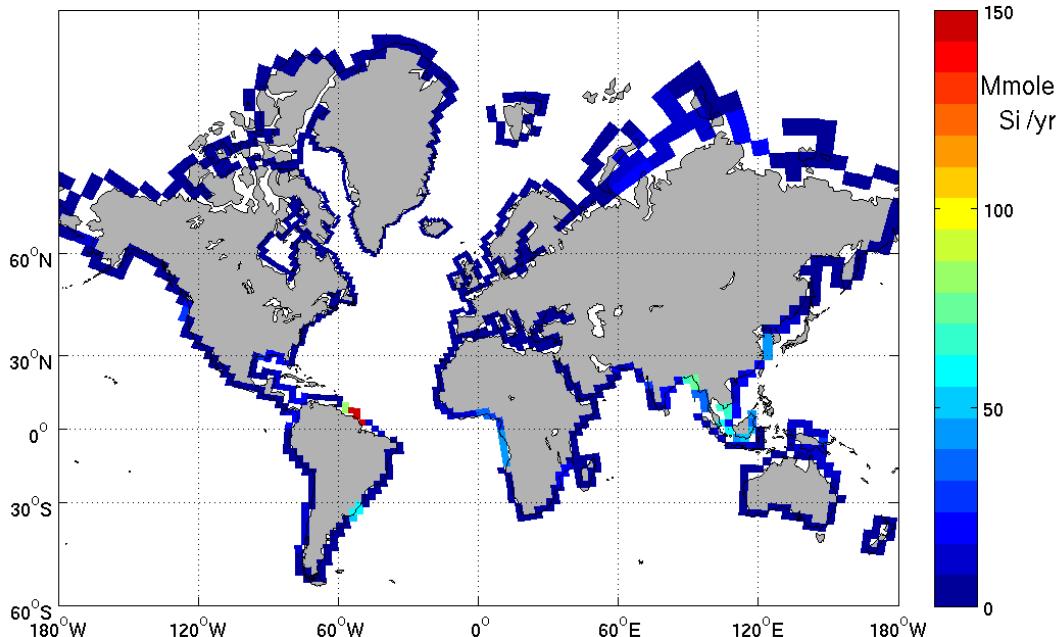
Fig. 1. Integrated annual flux of silica as added in the model grid, according to the 129 coastal segments from the COSCAT approach. Riverine silica inputs are given in megamoles Si per year.

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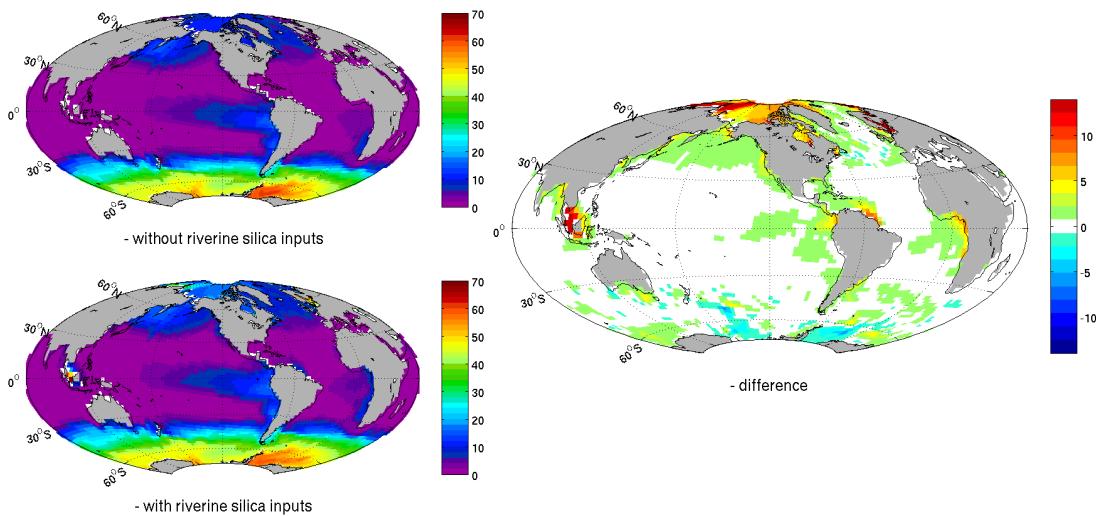
Fig. 2. River contribution to the surface silicic acid concentration. (Left) Sea surface map concentration of the silicic acid in μmol l^{-1}: without riverine silica inputs (top) – with riverine silica inputs (bottom) and the computed difference with/without riverine silica inputs (right).
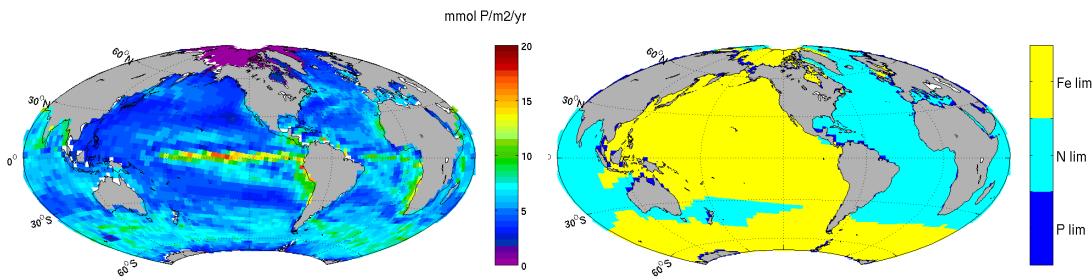
Fig. 3. Left, annually integrated photosynthesis in the euphotic ocean layer, the photosynthesis is expressed in mmol P m^2 yr^{-1}. Right, limiting nutrient driving the photosynthesis in the surface layer.
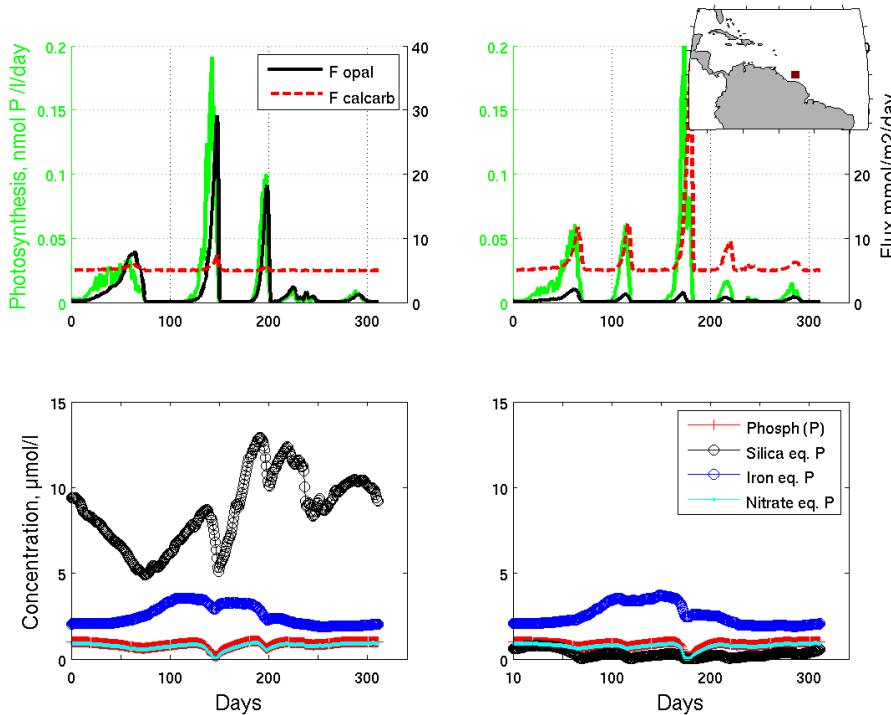
Fig. 4. The seasonal cycle of nutrient limitation (element equivalent phosphorous) in the Amazon plume, (lower panels) with (left) and without (right) riverine silica inputs. Opal and calcium carbonate export (F opal and F calcarb) at 10m depth in response to photosynthesis (upper panels). Nutrient limitation is expressed as the concentration adjusted to the necessary stoichiometric concentration of nitrogen and iron relative to phosphate. The limitation of photosynthesis is driven by the lowest concentration equivalent phosphate (iron, nitrate or phosphate). Opal and calcium carbonate competition is driven by the silica concentration.

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- without riverine silica inputs

- with riverine silica inputs

- difference

Fig. 5. Rivers contribution to the Opal export production in mol Si m^{-2} year^{-1} – without silica riverine inputs (top-left) – with silica riverine inputs (bottom-left) and the computed difference with/without riverine silica inputs (right).