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Global spatial distribution of natural riverine silica inputs to the coastal zone

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Abstract

Silica, SiO_2, in dissolved (DSi) and particulate (PSi) form, is both a major product of continental weathering as well as an essential nutrient in terrestrial and aquatic systems. Here we present estimates of the spatial distribution of riverine silica fluxes under natural conditions, i.e. without human influence, to ~140 segments of the global coastal zone. Focussing on the construction of the DSi budget, natural DSi concentration is multiplied with discharge of rivers for each segment for documented basins and segments. Segments with no documentation available are estimated using clustered information based mainly on considerations of local lithology, climate, and lake retention. We approximate fluxes of particulate silica in various forms (PSi) from fluxes of suspended matter, calculated from existing models. Results have been established for silica fluxes, concentrations and yields for drainage basins of the different continents, oceans basins as well as coastal segment basins. For the continental surfaces actually draining into the oceans (exorheic regions, representing 114.7 M km^2), 371 M t y^{-1} of DSi and 8835 M t y^{-1} of PSi are transported, corresponding to a mean concentration of 9.5 mg l^{-1} and 226 mg l^{-1}, and to a mean yield of 3.3 t km^{-2} y^{-1} and 77 t km^{-2} y^{-1}, respectively. DSi yields exceeding 6.6 t km^{-2} y^{-1}, i.e. >2× the global average, represent 17.4% of the global continental ice-free exorheic area but correspond to 56.0% of DSi fluxes. Pacific catchments hold most of the hyper-active areas (>5× global average), suggesting a close connection between tectonic activity and DSi fluxes resulting from silicate weathering. The macro-filters of regional and marginal seas intercept 33% and 46% of the total dissolved and particulate silica fluxes.

1 Introduction

Dissolved silica (SiO_2 or DSi, expressed as mg SiO_2 l^{-1} throughout this paper unless noted) is one of the major nutrients of continental aquatic systems (Schelske and Stoermer, 1971) and of marine systems (Tréguer et al., 1995), essential to the development of diatoms, radiolarians and sponges (Schlesinger, 1997). Silica is also a major component of the total dissolved solids found in continental waters resulting from the chemical weathering of soils and surficial rocks. As such, it provides information on weathering processes and rates (Wollast and Mackenzie, 1983) and has been analysed since the 19th century by European geologists and chemists. Perhaps the first comprehensive overview of silica in the environment (rock, soils, springs, rivers and the ocean) is provided by the German geologist Roth (1879). In the early 1900s, both geochemists, as the US Geological Survey pioneers (Clarke, 1924) and freshwater ecologists since the 1960s (Wetzel, 2001) enhanced the knowledge of silica in the environment. In the last 25 years there has been a growing evidence of another major silica cycle in the terrestrial vegetation, litter and soils through the uptake and storage of silica in phytoliths (Bartoli, 1983; Meunier et al., 1999; Conley, 2002). Part of the phytoliths is not recycled and may be eroded, as the soil organic matter, and carried by rivers. Freshwater diatoms, living and as detritus, are also considered as biogenic particulate silica (BSi). It can be identified and quantified through visual analysis, a long and tedious procedure. A chemical proxy for BSi has been proposed, using a soda extraction (Conley, 1998; Isaji, 2003; Saccone et al., 2006). The silica extracted by this method is referred to as amorphous silica (ASi).

In open ocean waters ASi and BSi are nearly identical as there is little non-biogenic amorphous silica. Exceptions may temporarily occur in case significant amounts of long-range atmospheric dust, containing fly ash, are deposited on surface waters, as for East Asia downwind regions (e.g. Hartmann et al., 2008). For riverine material ASi and BSi is not always identical as detrital amorphous silica can also originate from the mechanical erosion of sedimentary rocks and soils (e.g. chalk, cherts). Finally, there is an anthropogenic component of the silica cycle: either from diatomite earth mined from past lacustrine deposits, or artificially produced zeolith (Breese, 1994; van Dokkum et al., 2004). They are used in industries (pulp and paper production, water and waste water treatment, soil stabilization), pharmaceuticals and household products (mainly zeolith in detergents) and likely to reach the aquatic system either as dissolved or as particulate silica. The other impact of Humans on the silica cycle is the additional retention of BSi by reservoirs, mainly as diatoms detritus (Humborg et al., 2000; Straskrabova et al., 2003). This process is identical to the silica retention in natural lakes (Wetzel, 2001).

The dissolved silica fluxes are generally inferior to the particulate silica fluxes generated by the mechanical erosion of silica-containing minerals from soils and rocks (cf. Garrels and Mackenzie, 1971; Garrels et al., 1973; Martin and Meybeck, 1979). River inorganic particulates of non-biogenic origin are composed mostly by quartz, feldspar and clays (illite, chlorite, kaolinite, etc.) (e.g. Subramanian, 1980; Gölz, 1982; Gaiero et al., 2004). Minerals most resistant to chemical weathering are characterised by increased proportions in suspended matter, if compared to unweathered source rocks of a river catchment. Sometimes fine fragments of eroded rocks may contain amorphous detrital silica. All silica-containing components, including phytoliths and BSi, are part of the particulate silica (PSi), analysed after a complete digestion of river particulates.

There are therefore multiple ways to consider the riverine silica, from the analytical chemist, the ecologist, the geochemist, and the physical geographer (Fig. 1).

Since the first estimates of average dissolved silica concentrations in rivers by Roth (1879) and Clarke (1924), there have been few studies on this topic, compared to the ones on nitrogen and phosphorus (Livingstone, 1963; Meybeck, 1979, 1987, 1988; Probst, 1992; Tréguer et al., 1995, and the special issue of Global Biogeochemical Cycles, edited by Seitzinger et al., 2005). The budgets are not or little spatialized (e.g. Jennerjahn et al., 2006) while other nutrients and carbon budgets have been gradually spatialized over the last 15 years, first at the 2°×2° resolution, then at 0.5°×0.5° (Ludwig et al., 1996; Amiotte-Suchet et al., 2003; Green et al., 2004; Seitzinger et al., 2005). Many of these recent budgets are based on a general register of river inputs to oceans, GEMS-GLORI (Meybeck and Ragu, 1995) that lists about 500 individual rivers with various levels of documentation.

In the case of spatially explicit model budgets for dissolved and particulate matter, in general monitoring data of the ∼60–120 largest rivers draining to coastal waters are applied for model calibration and small catchments information is neglected. However, some studies provide evidence that regions characterised by small catchments draining to coastal zones in humid and warm climates may represent above average specific fluxes (Milliman and Syvitski, 1992; Hartmann et al., 2009a, b). In particular, the ring of fire, surrounding the Pacific Ocean, is characterised by small and steep catchments due to plate tectonics.

The only existing homogeneous global river data base on dissolved and particulate matter (Meybeck and Ragu, 1995) is also partly used here for the emphasized dissolved silica budget in order to

1. reach a global spatial distribution of natural – i.e. without human influence – river dissolved silica concentrations and fluxes at the regional level (one million square kilometres);
2. compare these with the particulate silica fluxes;
3. identify areas most contributing to the global budget;
4. discuss the net silica inputs to oceans, focusing on DSi.

We therefore consider the following steps:

1. collection and selection of individual DSi and PSi data for major and some minor rivers at the global scale;
2. extrapolation of documented data at regional resolution using a previously introduced coastal catchments delineation (COSCATs) (Meybeck et al., 2006), and calculation of silica river fluxes for each coastal catchment;
3. spatial analysis of silica fluxes from continents, for open oceans and regional seas, according to the methodology defined by Meybeck et al. (2007).

2 Data and methodology

2.1 Database for DSi and PSi in river waters and particulate matter

The dissolved silica found in continental waters originates from the chemical weathering of a great number of minerals, from the more easily weathered (e.g. volcanic glass, olivine) to the least (e.g. clays, quartz) (cf. Wollast and Mackenzie, 1983; Meybeck, 1987; Stallard, 1995):

The levels of silica transported from the terrestrial to the fluvial system depend on the relative proportions of these minerals in soils and rocks, on temperature, water residence time, drainage intensity, slope gradient and acids involved in weathering as e.g., carbonic, sulphuric or humic acids (Wollast and Mackenzie, 1983; Drever, 1994, 1997; Gaillardet et al., 1999; West et al., 2005; Jennerjahn et al., 2006; Hartmann et al., 2009b).

The retention of silica in river systems, e.g. in lakes and flood plains, is linked to their trophic state (for DSi), to lake abundance, expressed by the limnic index (% of lake cover in a given area, i.e. % of area covered by lakes with respect to the total catchment basin area – this value can attain up to 20% at the ~1 M km^2 scale regarded here) (Conley et al., 2000), and by deposition of ASi in alluvial plains (Admiraal et al., 1990). The commonly reported retention for DSi extends from 4 to more than 100 g SiO_2, with a median value of 20±10 g SiO_2, per year per m^2 of lake area (Campy and Meybeck, 1995). Apart from the formerly glaciated shields in Canada, Northern Europe and Taymir Peninsula (Siberia), where it commonly ranges between 5 and 20%, the limnic index rarely exceeds few percent in other parts of the world (Meybeck, 1995).

In order to construct the DSi database, dissolved silica concentrations are first selected from the Meybeck and Ragu (1995) catalogue of river inputs to oceans ("GEMS-GLORI", www.gemswater.org). They selected 1 to 3 average analyses for the same river, depending on authors and period of records, in which we generally took the earliest silica average. We also used another data set on pristine rivers of the world (PRISRI, unpublished), mentioned by Meybeck (2003), to determine the control factors of river chemistry in natural conditions. In this second data set numerous important references on river chemistry prior 1950/60 are given and reported here in our annexes, i.e. before the main development of large reservoirs on world rivers (Vörösmarty et al., 1997), as (i) works on US rivers from a dozen of US Geological Survey reports prior to 1940, most of them used and cited by Clarke (1924), (ii) former Soviet rivers analysed between 1940 and 1960 by Alekin and Brazhnikova (1960, 1962, and 1968) and (iii) J. Kobayashi's work on Asian rivers in the same period for Japan, Thailand, Indonesia, Sri Lanka (Kobayashi, 1959, 1960, and 1966). We also selected more recent analyses in regions with limited human impacts as in Alaska and Canada (Brunskill, 1986), Amazon and Orinoco basins (Lewis and Saunders 1989), Patagonia (Depetris and Paolini, 1991), in West and South Africa (de Villiers, 1962; Olivry and Noah, 1978; Orange, 1990). The detailed list of references is given in Annex 1A to F (http://www.biogeosciences-discuss.net/6/1345/2009/bgd-6-1345-2009-supplement.pdf) for each river.

Particulate silica (PSi) in rivers is not analysed within most water quality surveys as it is not listed as an indicator of contamination: it must be collected for each river from individual papers dealing with suspended particulate matter (SPM) chemistry. The total particulate silica obtained after complete digestion of filters or of dried deposited sediments is the most common element found in any SPM analysis although it is not much analysed in academic literature, instead heavy metals and rare earth elements (REE) are the most commonly analysed. In case of large proportions of carbonate rocks in the river catchment, most of the carbonate minerals are dissolved during chemical weathering and only the insoluble material – clays – is carried with SPM together with some fine carbonate detritus (e.g. Gölz, 1982). In the example case of France, the average SiO_2 content in limestone and dolomite draining streams is 3.6 and 4.0 mg l^{-1}, respectively, and can go up to 12.0 mg l^{-1} for chalk basins due to the presence of amorphous silica in this rock type; in gypsum marl DSi can also be high, between 8.0 and 9.6 mg l^{-1} (Meybeck, 1986, 2003). As a result, even carbonated river basins do export particulate silica. The coarse fraction of river particulates that transits as bed load consists of quartz with few percent of heavy minerals. As a result, in medium to large rivers silica is largely dominating all other elements in particulates (Martin and Meybeck, 1979; Canfield, 1997). A preliminary survey of hundreds of river analyses for major and trace elements (GLOMET, Meybeck, 2009) gives a PSi median content of 260 000 mg Si per kg (or ppm) of river particulates with interdecile values from 210 000 to 310 000 for individual rivers. The 260 000 ppm level for particulate silica is very close to the one of Martin and Meybeck (1979), 285 000 ppm, based on large rivers only (n=13, range 230 000 to 362 000 ppm). The major control factor of PSi export by unit river basin area (yield) is therefore the sediment supply that commonly ranges from 10 to 10 000 t km^{-2} y^{-1} in medium and large rivers (Milliman and Syvitski, 1992). Among more than 50 chemical elements analysed in river particulates, Si is the least variable, either under different climate conditions or due to rock lithology, for rivers exceeding 10 000 km^2. Therefore, we have considered here as a first approximation a constant PSi content of 260 000 mg Si kg^{-1}, i.e. 55.64 weight-% SiO_2, for each coastal catchment, i.e. at the one million km^2 resolution at which this budget is realised. In this first estimate the river bed load, which consists mostly of quartz sands and gravel, has not been considered. It is often considered as 10% of the river total sediment transport (Milliman and Syvitski, 1992).

2.2 Calculating silica budgets for coastal catchments

For spatial analysis of material fluxes the exorheic part of the continents can be segmented, as done by Meybeck et al. (2006), resulting in a mega-puzzle of ~140 pieces, the coastal catchments or COSCATs. These entities have been specifically designed to allow the reporting of global river fluxes of water, of dissolved and particulate materials as nutrients and carbon species, and of contaminants in a standardized way. Previous coastal segmentations are not applicable for river budget reporting, while COSCATs delineations are based on multiple criteria combining basin boundaries, coastal morphology, ocean dynamics, regional seas limits etc. (see a complete discussion in Meybeck et al., 2006). The COSCATs are related to the exorheic part of the ~6200 individual river basins that have been delineated at the 0.5°×0.5° resolution and can be fully described through many databases that have been developed over the last 10 years, in particular within the IGBP-BAHC programme (Vörösmarty and Meybeck, 2004) as the global river network (Vörösmarty et al., 2000a, b), the global scale relief typology (Meybeck et al., 2001), or lithology (Dürr et al., 2005). Of particular importance is the water runoff field at the same resolution, resulting from a global-scale model combined to data from the Global Runoff Data Center at WHO/UNESCO (Fekete et al., 2002).

As such, each segment has a maximum homogeneity in its coastal area. Fixed segment boundaries allow easy description and mapping at coarse resolution and all land to ocean fluxes can be reported in the same format, e.g. for application in Earth System models. The median length of coastline of the segments (at the 0.5°×0.5° resolution) is a little over 2000 km, and the mean reach of the segments inland is 360 km (median 150 km). Some of the COSCATs are quite large in area, from 2 to 7 millions (M) km^2, since the largest river basins cannot be split as for the Amazon or Congo. The median size of the COSCATs is 0.83 M km^2. Each COSCAT is associated to a river runoff ($mm\,y^{-1}$ or $km^3\,y^{-1}$) that can range from near zero (arheism) to >2400 $mm\,y^{-1}$ for very humid tropics (Meybeck et al., 2006). COSCATs have a 4 digit coding: the first two digits for individual continents, then for individual COSCATs numbered clockwise. COSCAT names are originating from oceanic and coastal morphological features (see original maps and details in Meybeck et al., 2006, and the auxiliary material pertaining to it).

For each COSCAT the DSi fluxes result from the following steps:

1. Product of documented DSi concentrations by the related natural river discharges (usually also available in Meybeck and Ragu, 1995; otherwise they are calculated from the Fekete et al., 2002, data set), and calculation of non-documented area and runoff.

2. If the river basin characteristics in the undocumented area are close to the documented ones then these known average concentrations are extrapolated to the

remaining part of the COSCAT.

3. If the undocumented area is much different, a specific river or tributary can be chosen as representative of this area. It may even originate from a nearby COSCAT or river where general basin characteristics are similar. This informational clustering is based on lithology, climate, relief, water drainage, and abundance of lakes, which are the main control factors of silica (Wollast and Mackenzie, 1983; Meybeck, 1995, 2003; Drever, 1997; Gaillardet et al., 1999; Hartmann et al., 2009b). This estimated DSi is then combined to the remaining runoff which can also be different from the one of the documented area (estimated DSi levels are given in Annex 1 for each COSCAT). For instance, for very large COSCATs where climate and runoff can be heterogeneous, as for the Ob, Yenisseï and Lena, the undocumented coastal basins have not been based on the known DSi in these major rivers, but on much smaller north Siberian rivers as Khatanga and Olenek, coupled with a much lower runoff.

4. Few COSCATs remain completely undocumented: here the DSi concentration is chosen from rivers or a group of rivers characterised by similar weathering conditions, including similarity in catchment properties, and attributed to the whole runoff of the undocumented COSCAT.

The resulting discharge-weighted silica concentrations DSi* (mg SiO_2 l^{-1}) and yields Y_{DSi} (t SiO_2 km^{-2} y^{-1}) are then calculated for each COSCAT (Eqs. 1 and 2):

$$DSi*_j = (\Sigma\ fluxes_{cij})/(COSCAT_j\ discharge) \quad (1)$$

$$Y_{DSi-j} = (\Sigma\ fluxes_{cij})/(COSCAT_j\ area) \quad (2)$$

With *ci* being the running index for catchments within a COSCAT j.

The fluxes and yields of particulate silica for each COSCAT have been calculated on the basis of SPM loads estimated from the Ludwig and Probst (1998) model which takes into account several control factors as relief, lithology, runoff, vegetation cover and is used to characterise the particulate inputs for each COSCAT. This spatialized model (0.5°×0.5°) does not include the sediment trapping in reservoirs which is believed to become more and more important (Vörösmarty et al., 2003; Syvitski et al., 2005), it is therefore compatible with our target of estimating the silica budget as close as possible to pre-anthropogenic conditions. SPM yields and loads are then combined to the median PSi content (260 000 mg Si kg^{-1}) to generate the corresponding PSi yields and loads re-converted into SiO_2 (Eq. 3) in order to facilitate the comparison between Y_{DSi} and Y_{PSi}, both expressed as SiO_2:

$$Y_{\mathrm{PSi}-j} = Y_{\mathrm{SPM}-j} \times 0.26 \times 2.14 \quad (3)$$

With:

$Y_{\mathrm{SPM}-j}$ = sediment yield in COSCAT j in t SPM $km^{-2}\,y^{-1}$
0.26 = constant factor for all COSCATs: 26% of Si in SPM or 260 000 ppm Si
2.14 = conversion factor from Si to SiO_2.
Example: $Y_{\mathrm{SPM}-x}$=100 t $km^{-2}\,y^{-1}$→$Y_{\mathrm{PSi}-x}$=55.6 t SiO_2 $km^{-2}\,y^{-1}$.

3 Results

The combination of COSCATs and their silica budgets allows for the calculation of various types of budgets: per continent, per ocean drainage basin, per latitudinal zones, and for different regional seas. It is common among geochemists and geographers to calculate riverine fluxes per continents (Berner and Berner, 1996; Gerasimov et al., 1964): this type of reporting is used in Table 1. In this table the exorheic catchment area of continents – i.e. the area facing the oceans – includes areas that are not presently characterized by active river runoff – i.e. arheic regions. This operational cut-off is set here at 3 mm y^{-1} (Vörösmarty et al., 2000a, b) which corresponds to an average of one flood occurrence every 10 years in desert regions. Presently glaciated areas as Antarctica and major parts of Greenland are not considered in our budget.

Endorheic regions – i.e. facing internal regions – as the Caspian Sea basin (Volga, Terek, Sulak, Kura Rivers), the Rift Valley (Omo River), Lake Chad (Chari and Logone Rivers) and Okawango (Okawango River) basins in Africa, the Lake Eyre Basin (Cooper River) in Australia, the Altiplano (Deseaguadero River) and the Great Basin (Sevier and Humboldt Rivers) in the Americas, the Caspian and Aral Sea basins and other regions of Central Asia, are not considered in our budget although they contribute to the weathering of continents at the global scale. The few major rivers with available data (Meybeck, unpublished report to WHO "*Water quality of endorheic basins*": Chari 19.2 mg $SiO_2\,l^{-1}$ for 24.2 $km^3\,y^{-1}$ discharge; Logone 19.3 mg $SiO_2\,l^{-1}$ for 15.8 $km^3\,y^{-1}$, Okawango 16.0 mg $SiO_2\,l^{-1}$ for 10.0 $km^3\,y^{-1}$; Omo 18.0 mg $SiO_2\,l^{-1}$ for 14.0 $km^3\,y^{-1}$; Sevier 38.4 mg $SiO_2\,l^{-1}$ for 0.02 $km^3\,y^{-1}$; Humboldt 32.0 mg $SiO_2\,l^{-1}$ for 0.42 $km^3\,y^{-1}$ discharge) have a discharge-weighted DSi average of 18.6 mg $SiO_2\,l^{-1}$ (1.2 M t total annual DSi flux for 64.5 km^3 of annual discharge, i.e. 7.1% of the total annual endorheic discharge for 6.1% of the total endorheic catchment area). Most of these regions are characterised by semi-arid to arid conditions (63% of the total endorheic area are arheic) with elevated DSi.

The exorheic parts of individual continents are characterized as follows:

Although North America has an average runoff of 268 mm y^{-1}, much higher than Africa (157 mm y^{-1}), their silica yields, in t $SiO_2\,km^{-2}\,y^{-1}$, are of the same order: 2.2 t $km^{-2}\,y^{-1}$ for North America, 2.0 t $km^{-2}\,y^{-1}$ for Africa. This is in part due to the silica retention by lakes observed in most of the Canadian rivers where the limnic index of lake occurrence is commonly between 5 to 20% (Meybeck, 1995; Lehner and Döll, 2004): most Canadian rivers have a DSi level between 1.1 and 3.6 mg $SiO_2\,l^{-1}$ (see Annex 1C, COSCATs #0815 to 0818) while Alaska and British Columbia rivers are characterised by much higher silica levels (COSCATs #0809, 0810, 0812, 0813) and much lower limnic index (Table 1).

European rivers have the lowest silica levels on average: 5.6 mg $SiO_2\,l^{-1}$ vs. 9.5 mg $SiO_2\,l^{-1}$ for the global exorheic average. This is probably due to several factors: cold to temperate climate, retention of silica in Scandinavian lakes (Conley et al., 2000), scarcity of (young) volcanic rocks and abundance of carbonate rocks (Dürr et al., 2005). Removal of DSi by plankton communities by elevated nutrient (N and P) levels may impact observed low concentrations, too. Despite our attempt to choose reported DSi concentrations with low anthropogenic impact in general, for Europe it remains difficult to cope with this objective, because of the strong anthropogenic influence since the 19th century. Roth (1879) reports nitrate concentration for the Rhine (1848), Seine (1848) and Thames (no date) of 3.8, 14.6 and 3.9 mg l^{-1}, respectively.

Africa silica concentrations are the highest (12.6 mg l^{-1} on average), despite the scarcity of volcanic rocks. This can be explained by the prevalence of hot climate conditions that favour chemical weathering of crystalline rocks abundant on this continent, for the exorheic regions.

South America silica yields are near twice the world average (6.1 vs. 3.3 t km^{-2} y^{-1}), with silica concentrations very close to the world average (9.0 vs. 9.5 mg l^{-1}). This is related to the very high runoff on this continent, 681 mm y^{-1} vs. 340 mm y^{-1} for the global average: the silica yield of river systems is predominantly controlled by their runoff (Meybeck, 1994). Most of the observed DSi fluxes originate in the humid regions of the Andes (Mortatti and Probst, 2003; Depetris et al., 2005; Jennerjahn et al., 2006), characterised by high proportions of volcanics (Dürr et al., 2005).

DSi fluxes from Asia are not easy to evaluate, because of the great heterogeneity of the continent. The very wet southern flanks of the Himalayan region are characterised by high fluxes due to intensive influence of the monsoon, whereas much drier central parts like Tibet are characterised by low fluxes (Galy and France-Lanord, 1999). Large endorheic areas are located in the centre of Asia and cold climate in the northern parts leads to low DSi fluxes.

The silica budgets for ocean drainage basins (Table 2) generate the following comments:

Due to its extended drainage area and water inputs (50% of world exorheic), the Atlantic ocean receives 45% of the silica inputs, with an average concentration (8.4 mg l^{-1}) very close to the world average (9.5 mg l^{-1}), despite a lower than average outcrop proportion of volcanic rocks (5.4% vs. 9.3% on average). The presence of the three world's major rivers in terms of discharge, Amazon (#1), Congo (#2) and Orinoco (#3), which are characterised by high runoff values and higher silica contents (45.5 M t, 12.4 M t and 7.2 M t SiO_2 flux per year, carrying alone 18% of the global exorheic DSi flux), compensates the limited inputs from the dry regions of the Atlantic Ocean basin.

The relatively high silica concentrations in the Pacific ocean drainage basin rivers (23.2 mg $SiO_2\,l^{-1}$ on average) are probably linked to its higher volcanic outcrops (22.9%) and are thus related to the tectonic activity of the ring of fire, surrounding the Pacific. Silica yields in this basin are also the highest, due to a runoff three times the world's average (1010 vs. 340 mm y^{-1}), but its drainage area is relatively small. As a result the absolute DSi flux to the Pacific Ocean is less than the one from the Atlantic drainage basin.

Arctic rivers are characterised by relatively low silica levels, 6.1 mg $SiO_2\,l^{-1}$ on average, for an average volcanic rock outcrop. Multiple factors can be invoked: the lower weathering rates due to colder climate, permafrost extent, and the abundance of lakes in Canada and Scandinavia, an order of magnitude more than in the other ocean drainage basins (Meybeck, 1995; Lehner and Döll, 2004), resulting from the occurrence of past ice caps in the Arctic drainage basin. The yield (1.2 t $km^{-2}\,y^{-1}$ vs. 3.3 for the world's average) is linked also to a lower runoff (199 mm y^{-1}). The absolute flux of DSi received by this ocean is only 5.4% of the world's river fluxes (371 M t $SiO_2\,y^{-1}$).

It is important to note that, when the DSi inputs are compared to ocean volumes and/or to ocean area, these relative inputs are ranked in a very different manner. Ocean volumes and area are those given by Kossinna (1921) and reported by Viglieri (1966) in Fairbridge (1966). Ocean coastline has been determined here for each COSCAT at the 0.5°×0.5° resolution (Meybeck et al., 2006) and may be somewhat lower than the actual coastline delineated at a finer resolution: it varies between 57 000 km for the Arctic Ocean and 149 000 km for the Atlantic Ocean (Meybeck et al., 2007). The Arctic Ocean is actually receiving the maximum DSi inputs with regards to its size and the relative silica inputs to the Pacific Ocean are more than one order of magnitude less

(Table 3).

The global estimate for river SPM fluxes to coastal zones is 16 billion tons per year (Ludwig and Probst 1998), corresponding to a mean concentration of 226 mg l^{-1} or about 9 billion tons of particulate Si, expressed as SiO_2, i.e. the DSi/PSi ratio at the global scale is 4.2% (371/8835=0.042). As the PSi concentration in SPM is nearly constant (26%±4% of Si), the distribution of PSi concentration per liter of water is nearly identical to the one of SPM which commonly varies between less than 10 mg l^{-1} to more than 10 000 mg l^{-1} in world rivers. We refer here to the large body of literature describing the characteristics of SPM yields and concentrations in world rivers (e.g. Milliman and Syvitski, 1992; Ludwig and Probst, 1998; Meybeck et al., 2003; Syvitski et al., 2005, and references therein).

The latitudinal distribution of the measured and/or estimated DSi from the ∼140 coastal segments is reported on Fig. 2, using the latitude of the COSCAT barycentre (or gravity centre). Maximum contents are found in the sub-tropical regions while the boreal regions have much lower contents: minimum contents of the sub-tropics (around 10 mg SiO_2 l^{-1}) are higher than maximum contents north of 50° N and south of 45° S. Due to the runoff minimum for the 20–30° N and 20–30° S belts, the DSi export rate is relatively low at these latitudes despite medium DSi contents. The maximum DSi is actually linked to the wet sub-tropics where both high DSi contents and runoff are encountered. With few exceptions, regions with high DSi yields correspond to high runoff values as well as high DSi concentrations, but this is a very general picture for all latitudes. For example, most COSCATs with DSi yields ≥2× the world exorheic average, i.e. $\geq 6.6\,t\,km^{-2}\,y^{-1}$, also have runoff values ≥2× the world exorheic average, i.e. $\geq 680\,mm\,y^{-1}$ (see discussion). The relative minimum in silica contents (concentrations) around the equator might be due to the often deeply weathered environments in the Brazilian and African shields located in the central tropics. For example, the two largest tropical rivers, i.e. the Amazon and Congo, both show low concentrations at their river mouth. They are characterised by large proportions of deeply weathered regolith in areas contributing large proportions of runoff and, in the case of the Congo river, also some proportions of carbonates are present (Probst et al., 1994; Stallard, 1995; Mortatti and Probst, 2003; Dürr et al., 2005). Low concentrations can thus be attributed to tectonic stability (≫100 M y) and further to the high precipitation in these wet tropical regions (compare Mortatti and Probst, 2003). The Northern Hemisphere is characterised by a strong latitudinal correlation of DSi concentrations and yields towards the equator and is probably indicating the influence of temperature and vegetation, pointed out by missing values in the lower concentration range in the subtropical and tropical zone.

4 Discussion

4.1 Global coverages and approaches to river silica budgets

For each coastal catchment we have determined the sum of documented silica fluxes vs. undocumented ones and their related areas and runoff. These area and discharge coverage rates are tabulated for individual continents and ocean drainage basins on Table 4, and in the Annexes for individual COSCATs. The resulting percentages of dissolved silica flux coverage range from 25% for Australasia – i.e. Australia, New Guinea and New Zealand – to 81% for the Arctic river runoff. The mean coverage rates are 56.7% for the continental area, 58.6% for the continental runoff, and 51% for the silica flux, i.e. half of the silica flux is based on actual water analyses combined with measured runoff, half has been extrapolated. This extrapolation has been realized by the product of estimated regional or local DSi concentrations and the river runoff over undocumented areas, now known from global models with a satisfactory accuracy (Fekete et al., 2002). If we assume that DSi analytical uncertainties and flux calculation uncertainties for documented rivers are negligible, the uncertainty induced by the frequency of regular river measuring campaigns results in errors around 10% for major ions as expressed by the electrical conductivity (Moatar and Meybeck, 2007). The maximum uncertainty will be somewhat higher: sometimes not many analyses are used for a certain value or no measurements over several seasons exist, or only arithmetic averages are available instead of discharge-weighted averages. As a rough approximation, we estimate that the additional uncertainty on extrapolated yields, using our method, yields in a total error probably not much greater than 30% and probably less in well-documented areas.

The hypothesis of constant PSi content in river particulates induces an uncertainty of ±15%, probably lower than the uncertainty of particulate matter fluxes. The total PSi flux of rivers depends on their suspended particulate budget. The inputs of PSi to oceans thus greatly depend on the estimates of SPM fluxes by rivers. Ludwig and Probst's (1998) estimate might underestimate some inputs, especially from the smallest basins (basin area $<10\,000\,\mathrm{km}^2$), particularly in South East Asia coasts (Milliman and Syvitski, 1992). Recent models give varying numbers (Vörösmarty et al., 2003; Syvitski et al., 2005, and references therein), due to the balance between enhanced inputs owing to land use changes on the one hand, and to enhanced retention by reservoirs on the other (see discussion in Vörösmarty and Meybeck, 2004).

As for any global river budget, it is very much dependant on the analyses of the largest rivers, i.e. Amazon, Congo, Orinoco, Ganges and Brahmaputra, Mississippi, Yangtze, and Great Arctic rivers which are surveyed by water quality authorities and/or by scientists. An error on the Amazon average concentration (15% of the world river discharge) may affect the whole budget. The use of a complex model linking all control factors to silica yields as developed by Probst (1992), although very much needed to explore past Earth System conditions (West et al., 2005) and future Global Change scenarios, would not have improved much this mode of extrapolation, since multi-regression models are globally not more accurate than 30%, as for carbon and nutrients (Global Biogeochemical Cycles, Special Issue on Global Nutrient Fluxes from Watersheds [Global-NEWS], edited by Seitzinger et al., 2005).

When comparing global average silica concentrations that have been proposed since Clarke's first estimate in 1924, these figures have not changed much: they range between 8.3 and 13.1 $\mathrm{mg\,l^{-1}}$ SiO_2 (Table 5). Clarke's figure (8.3 $\mathrm{mg\,l^{-1}}$ SiO_2) was an arithmetic average based on the silica content of dry residue from few major rivers, mostly located in the North temperate regions of Europe and North America. Livingstone made first an arithmetic average of DSi for each continent, then these means were weighted by the average runoff of the continents (six continents including Australia) in order to calculate the "global weighted DSi". He obtained a higher value (13.1 mg l^{-1} SiO_2). Since continents are generally heterogeneous, this approach is not very reliable (e.g. Asia average of 11.7 mg l^{-1} SiO_2, mostly based on tropical Asia since Livingstone's data set doesn't contain any Russian rivers). The first average made by Meybeck in 1979 (DSi=10.4 mg l^{-1} SiO_2) was based on 60 rivers distributed in most continents with less weight from the big Arctic rivers, and developed for the first time a simple typology linking silica yields with temperature and runoff to extrapolate the documented data set to unknown regions. The first multi-regression approach was made by Probst in 1992 on the same set of rivers, mostly large ones. It resulted in a 8.9 mg l^{-1} SiO_2 average, very close to the present average. A previous unpublished attempt for global silica budgets has been made by one of our co-authors in 1992 (Meybeck unpublished) on the basis of a new and larger data set (n=250), later published as the GEMS-GLORI register (Meybeck and Ragu, 1995). It was based on another typology, based on tectonics and global geomorphology: 9 morpho-tectonic types were defined, such as old and recent sedimentary basins, Hercynian, Caledonian and Alpine mountain ranges, active volcanism etc. The corresponding silica average by this approach was 9.2 mg l^{-1} SiO_2. A similar level (9.1 mg l^{-1} SiO_2) has been reached by Tréguer et al. (1995) on the basis of the GEMS-GLORI data that was communicated to these authors. The exorheic plus endorheic rivers have also been considered recently (Meybeck, 2003), also using exorheic rivers selected by Meybeck and Ragu (1995) plus major endorheic rivers, the corresponding world weighted average is 8.7 mg l^{-1} SiO_2.

It must be reminded that riverine budgets should either associate concentrations and discharges, or yields and area. Extrapolations are then carried out based on the hypothesis of constant concentration or of constant yields. The first hypothesis therefore greatly depends on the global water budget, which is now more and more addressed (Oki et al., 2001; Fekete et al., 2002) and has therefore been chosen here. Although the second one is easier to use, as drainage areas are well defined (e.g. in Meybeck's budget, 1979), it greatly depends on the sample of documented rivers, which should have representative average runoff, sediment yields and lithology (for a more detailed discussion see Meybeck, 1988).

4.2 Relations between dissolved and particulate silica exports and yields

Silica yields Y_{DSi} and Y_{PSi}, expressed in t $\mathrm{SiO_2}$ $\mathrm{km^{-2}\,y^{-1}}$, are calculated at the river mouths upstream of the land-ocean interface. Actually, there can be differences between whole river yields at mouth and those measured in headwaters, if retention processes of river-borne material are significant, as for particulates (Walling, 1983), organic carbon (Stallard, 1998), and nutrients, including dissolved silica, which can be processed and stored within the aquatic system (Sferratore et al., 2005).

The ratio between average Y_{DSi} and Y_{PSi} in COSCATs (Fig. 3) varies over more than three orders of magnitude, from 0.005 to 10. DSi export nearly matches PSi exports in few regions as in the Zaire-Congo river basin (COSCAT #0014) and in some Siberian COSCATs, due to the very limited river transport of particulates in downstream areas of these regions.

PSi export largely dominates in most regions and the $Y_{\mathrm{PSi}}/Y_{\mathrm{DSi}}$ can exceed 1000 for the Pohai Gulf (COSCAT #1325), which is dominated by the HuangHe (Yellow River) sediment inputs. Such an anomaly in the dissolved vs. particulate river material relationship has also been observed for the organic carbon (Meybeck, 1993). This observation is attributed to high physical erosion rates from the loess regions within the catchment. The observed weak positive relation between DSi and PSi yields (r^2=0.41 for the ∼140 log-log COSCAT couples) is partly due to their common control factor, runoff.

This general positive relationship between dissolved and particulate river matter has also been described for total dissolved solids and suspended particulates at the global scale, although in specific regions of the world opposite trends have been found as for the USA (see a complete discussion in Meybeck, 1994). The world weighted average DSi/PSi ratio of 4.2% is biased towards the particulate material. The median DSi/PSi ratio in COSCATs is slightly lower (4.0%). Regions in which the dissolved silica export is dominant (DSi>PSi) are very rare and correspond essentially to Hudson Bay drainage, i.e. to lake outlets where PSi is completely trapped (also Y_{PSi} is not measured in those areas, but estimated from the Ludwig and Probst (1998) model with many uncertainties in those lake-covered regions). In these environments PSi at lake outlets may be largely biogenic (diatoms).

4.3 Hot spots of river silica inputs to coastal zones

Export rates of silica by rivers vary over more than 3 orders of magnitude for particulates and 2 to 3 orders for the dissolved component (Fig. 3). After yields normalisation to the world average, the relative rates $Y_{\mathrm{DSi}}/\overline{Y_{\mathrm{DSi}}}$, scaled to the world's weighted average, can be compared for any type of river material. Meybeck et al. (2006) have proposed a general classification of relative rates in 7 classes, centred around the world average ($\overline{Y_{\mathrm{DSi}}}$):

- Hot regions have $10<Y_i/\overline{Y_i}$
- Hyper-active regions are characterised by $5<Y_i/\overline{Y_i}<10$
- Eury-active regions by $2<Y_i/\overline{Y_i}<5$
- Meso-active regions by $0.5<Y_i/\overline{Y_i}<2$
- Hypo-active regions by $0.2<Y_i/\overline{Y_i}<0.5$
- Oligo-active regions by $0.1<Y_i/\overline{Y_i}<0.2$
- Steno-active regions by $0.01<Y_i/\overline{Y_i}<0.1$

- Inactive regions have $Y_i/\overline{Y_i}<0.01$

For dissolved silica, at the spatial resolution of COSCATs, i.e. circa one million km^2, there are no true hot spots, but several hyper-active regions are found, as in wet tropical regions and/or wet volcanic regions (Fig. 4). Of particular interest is the Pacific Ocean drainage basin where most hyperactive COSCATs are found: they coincide with the dominance of volcanic outcrops related to the Pacific ring of fire from Kamchatka to Java, in Central America, and in the wet coast of South Chile.

In contrast, most of the northern COSCATs are hypo- to steno-active (e.g. West Hudson Bay). The Amazon and Orinoco regions and the Asian monsoon regions, from the Ganges to the Mekong, are eury-active, i.e. between 2 and 5 times the world average DSi yields. Maximum dissolved silica yields are found in subtropical and tropical, as well as in wet volcanic regions (Jennerjahn et al., 2006; Hartmann et al., 2009b) as in Japan: the Tokachi River (DSi=29.9 mg SiO_2 l^{-1}, runoff q=1240 mm y^{-1}) yield is 37 t SiO_2 km^{-2} y^{-1} on 8800 km^2 (Kobayashi, 1960). As silica concentrations are even higher in volcanic and hydrothermal regions as in Kamchatka (e.g. 41.9 mg l^{-1} SiO_2 for a spring close to Koryaksky volcanoe; Hartmann, 2006), and fresh unweathered ashes are capable to release large amounts of DSi, a maximum Y_{DSi}, exceeding 50 t km^{-2} y^{-1}, is likely at local scale (Hartmann et al., 2009b). Other hot spots of silica fluxes combine extreme runoff and active tectonics as for the Purari river (New Guinea) which exports 35.2 t SiO_2 km^{-2} y^{-1} (DSi=13.8 mg SiO_2 l^{-1} and q=2750 mm y^{-1}, data from Petr (1983), see also Annex 1F).

Similar mapping as for DSi can be made for PSi. As noted that particulate Si content in river SPM could be considered as constant ±26%, the pattern of PSi yield is identical to the one observed for SPM resulting from the Ludwig and Probst (1998) model which matches well the observations already made by Milliman and Syvitski (1992): most particulates originate from the erosion of the Himalayas, South East Asia island arcs and archipelagos, from Taiwan to New Zealand.

When the global silica budget is disaggregated for the 7 relative flux classes, from inactive to hyper-active regions (Fig. 5), the following observations can be made:

- 17.4% of the exorheic area contribute to 55% of the dissolved silica fluxes (eury- to hyper-active regions).
- 28.9% of the exorheic area contribute to only 2.3% of fluxes (inactive, steno- and oligo-active regions).

This skewed distribution of riverine fluxes is very general and has been observed for water, suspended matter and nutrients as total nitrogen (Meybeck et al., 2006).

4.4 Towards spatial estimates of net river inputs to oceans

At the beginning of global bio- and geochemical cycles studies, started by Garrels et al. (1973), the amount of data on world rivers was scarce, GIS did not exist nor global models. Therefore it was impossible to spatialize river inputs at global scale. The most recent global budget of silica (Tréguer et al., 1995) was also not spatialized. The first major improvement was the use of GIS and multi-regressions to build up spatialized models of river inputs to oceans at the basin scale (Probst, 1992; Ludwig et al., 1996; Amiotte-Suchet et al., 2003). These river material budgets were then used in regional ocean biogeochemical models as for organic carbon (Aumont et al., 2001). However, they did not take into account the natural filters between river basins and the open ocean as estuaries, shelves and regional seas.

The processing and retention of dissolved silica in estuaries and its potential impact on coastal food webs has been demonstrated since several decades (Nixon, 1987; Billen and Garnier, 1997; Rabalais and Turner, 2001). The retention of riverine silica and other nutrients on the shelf is also well documented (DeMaster et al., 1983; Rabouille et al., 2001, Dagg et al., 2004). However, none of these processes has been addressed at the global scale.

The main transformations occurring to silica in near-shore and estuarine environments are (i) its uptake by diatoms under its dissolved form to produce biogenic silica

(Roubeix et al., 2007, and references therein), (ii) the dissolution of the particulate pool within the water column or the upper layer of the sediment which regenerates dissolved silica (Yamada and D'Elia, 1984) and (iii) the permanent storage of the particulate silica through sediment accumulation which constitutes the sink term of the system and leads to long-term Si retention (Nixon, 1987). The importance of a proper representation of the particulate biogenic pool of silica was pointed out by several authors (Conley, 2002, and references therein). The fraction of PSi that is considered possibly dissolved and biologically available is currently not well known. Most of the PSi is in mineral form that will dissolve only very slowly and mainly be buried and re-mineralized in marine sediments. A small fraction of PSi is constituted of biological material (i.e. BSi), mostly phytoliths and diatom frustules. This BSi is considered orders of magnitude more easily soluble than the remainder of PSi, i.e. it can become bioavailable, and can thus contribute to algal growth (van Cappellen, 2003). The BSi fraction in PSi is difficult to estimate as it depends very much on the river basin considered and will be linked to control factors such as forest distribution, land use, water turbidity, or any factor likely to influence diatom productivity. Conley (1997) estimated the global BSi load to estuaries at 63±7.2 Mt SiO_2 y^{-1} (1.05±0.2 Tmol Si y^{-1}), i.e. 17% of the total DSi flux. This represents just 0.75% of the total PSi export from the rivers, and, considering the lithogenic fraction of the PSi as biologically inert, the available fraction might thus be <1% (see Table 1), due to the overwhelming mineral composition of PSi. This fraction can be seen as the maximum amount of PSi potentially recycled and biologically available at shorter timescales and is 5 to 6 times smaller than the pool of DSi.

However, direct measurements of BSi fluxes in budgets are still scarce and, for instance, BSi production in coastal environments is often deduced from primary production or DSi consumption (Beucher, 2003). Estimates of the net uptake of silica in estuaries deduced from estuarine mixing curves, i.e. DSi vs. salinity relationship from rivers to sea waters, are still the most common type of studies available in the literature and both excess and depletion patterns of DSi in estuarine environments have been observed, they vary seasonally and between stations. Net budgets to oceans, combining silica patterns and river discharges are very limited and/or biased (for example, summer profiles are much more common than profiles at river flood stage) (DeMaster, 1981; Aston, 1983; Balls, 1994; Rendell et al., 1997; Kimmerer, 2005; Chou and Wollast, 2006). However, primary production is a typically seasonal process driven by light and temperature conditions and varies greatly through the year as do river inputs. Hence, extrapolating an annual flux from these estimates is proving to be a difficult task which also does not account for the potential transient storage within the estuary itself (Webster et al., 2000). Moreover, the net uptake is a transfer from the dissolved to the particulate pool but does not indicate the real retention of silica within the system. For that matter, the work of DeMaster (2002) to quantify the accumulation of particulate silica within the sediment remains one of the only references at global scale but is essentially based on carbon measurements and molecular ratios. Recent studies also indicate that this retention can be influenced by “reverse weathering”, a process suggested by Garrels and Mackenzie (1967, and cited by Mackenzie and Kump, 1995), and describing rapid formation of new aluminosilicate minerals (clays) from BSi in marine sediment by chemical combination of elemental material from oceans and marine sediments (Michalopoulos and Aller, 1995; Michalopoulos et al., 2000). The quantity that is removed by reverse weathering reactions is assumed to be a small fraction of the total river input, but is currently not precisely known (Holland, 2005). Results for the Amazon delta suggest that ~90% of the biogenic silica originally present in deposits is converted to clay or otherwise altered and the deltaic storage of riverine Si is estimated to be ~22% of the Amazon River input (Michalopoulos and Aller, 2004). Further retention may result from the activity of benthic organisms that enhance benthic-pelagic coupling (Ragueneau et al., 2005) but large scale extrapolations remain to be calculated. One may also refer to the concept of proximal and distal limited filters for the coastal ocean (Rabouille et al., 2001), for the retention, particularly from river inputs.

Overall, this relative lack of specific data, combined with the heterogeneity of the coastal zone and the question of its precise definition (Smith and Hollibaugh, 1993), makes the quantification of global budgets a very difficult task and stresses out the need for a coastal typology of coastal systems especially for small to medium-sized systems. The world's largest rivers, however, often generate large plumes which consist in an "external" estuary dominating the biogeochemical transformations occurring in the adjacent continental shelf. Therefore, a good understanding of these River-dominated Ocean Margin (RiOMar, McKee, 2003) systems and their plumes would help significantly understanding and quantifying the fate of silica in the coastal zone (Johnson et al., 2006) and systems such as the Amazon (DeMaster et al., 1983; Michalopoulos and Aller, 2004), the Zaire/Congo (Chou and Wollast, 2006), the Mississippi (Rabalais and Turner, 2001) or the Danube (Ragueneau et al., 2002) should be regarded with greatest attention.

In addition to the silica retention in the coastal zone, one should also consider the retention in major regional seas of the world. They have been considered as mega filters within an Earth System analysis by Meybeck et al. (2007). Five types of mega filters have been defined: three types of regional seas, depending on their connection to the open ocean, plus extended platforms (e.g. Siberian seas) and coastal archipelagos (e.g. Canadian Archipelago and South Chile Coast). Their related drainage area and riverine fluxes have been tabulated using a specific re-aggregation of the COSCATs mega puzzle. On the basis of simple assumptions relating the retention of particulates to the morphology of these mega filters and the retention of nutrients to their theoretical river water residence time, which exceeds three orders of magnitude between the Saint Lawrence Gulf (fastest renewal) and the Red Sea (longest renewal), it has been estimated that (Meybeck et al., 2007):

1. Regional seas intercept 39% of the exorheic continental landmass (glaciated areas as most of Greenland and Antarctica excluded), and 35% of the exorheic river runoff.
2. Regional seas store about 80% of the incoming related particulate fluxes; this proportion will be similar for the riverine particulate silica.
3. Regional seas intercept 33% of the related dissolved silica of which about 75%

might not be exchanged with the open ocean.

Some examples of the river silica fluxes to regional seas as calculated by COSCATs aggregations are featured on Table 6. Their ranges in terms of average concentration (1.9 to 17.1 mg l^{-1}) and yields (0.4 to 9.9 t km^{-2} y^{-1}) are over one order of magnitude and illustrate the multiple control factors already presented.

For each individual ocean drainage basin the actual silica retention in regional seas should now be estimated; it may be quite different from these global figures (Meybeck et al., 2007):

The Southern Atlantic Ocean has no mega filter except for the Patagonia platform, therefore retention is very limited.

The North Atlantic Ocean is very different from the South Atlantic, as it is connected to many regional seas, often interconnected in nested basins as the Mediterranean plus Black Sea, the Gulf of Mexico plus Caribbean – also termed North American Mediterranean –, the Baltic Sea, Hudson Bay and St. Lawrence Gulf (see Table 6 for individual budgets). The potential silica retention is large (40% for PSi, 20% for DSi, applying the filter types proposed by Meybeck et al., 2007).

The Pacific Ocean is very much affected by regional seas: (i) its drainage area is already very limited (19.8 M km^2 drainage basin area/181.3 M km^2 Pacific Ocean area = 0.11), compared to the world average (114.7 M km^2 total exorheic basin area/362 M km^2 total ocean area = 0.32) or to the Arctic Ocean (16.7 M km^2 drainage basin area/12.3 M km^2 Arctic Ocean area = 1.4); (ii) a larger proportion of its western drainage area (83%) is actually linked to the West Pacific Mediterranean Regional Seas from Okhotsk to Banda and Sulu Sea (Meybeck et al., 2007); (iii) the Bering Sea, the British Columbia and S. Alaska coast archipelago type of mega filter may also retain an important share of the riverine dissolved silica from the Yukon River to the Fraser River. The net riverine inputs to the open Pacific, even without considering the estuarine and shelf retention, could therefore be lowered by half of the gross river inputs.

In the Arctic Ocean the mega filters consist mostly of the Siberian platform – a limited mega filter, also termed Siberian Seas, much more connected to the open ocean than the enclosed and semi-enclosed West Pacific regional seas. The consideration of mega-filters is therefore increasing the discrepancy between the Arctic Ocean, relatively well fed by river silica per unit volume of open sea – i.e. without the regional seas and other mega filters –, and the open Pacific Ocean, very much deprived of river silica.

The Indian Ocean has a limited connection to regional seas (e.g. Andaman Sea, Persian Gulf, Red Sea), which are often characterized by minimal river inputs, as for the Red Sea. To our knowledge, the retention of silica inputs from the Ganges-Brahmaputra-Meghna rivers in the Bay of Bengal remains to be established. If it is recognized, the open waters of the Indian Ocean might receive less silica than those of the South Atlantic.

Open oceans are generally deprived of DSi at their surface due to bioactivity when compared to deeper waters (Levitus et al., 1993). Only in some regions, where COSCATs characterised by high proportions of volcanic rocks drain to the open ocean (e.g. Indonesia, Hawaii, Kamchatka), some increases in surface water DSi concentrations can be observed (if Antarctica and northern Arctic waters are disregarded). Upwelling onto continental margins and subsequent storage due to sedimentation can be a sink for oceanic silica (Tréguer et al., 1995; Laruelle et al., 2009), but these 're-verse' fluxes of silica in the land-ocean continuum can currently only be estimated by ocean models and since they do not concern continental silica fluxes to the oceans, they are not discussed further here.

Besides riverine inputs, atmospheric deposition of DSi and PSi is the most important source of "new Si" to the surface oceanic system. Atmospheric PSi dust deposition ranges globally from 278–489 Mt yr^{-1} of dust, and 79 to 128 Mt yr^{-1} PSi from dust is deposited onto the oceans (Tegen and Kohfeld, 2006), with highest amounts reported for the North Atlantic and the western North Pacific. However, the contribution of atmospheric deposition to the oceanic DSi budget is difficult to estimate and can be attributed to large differences in DSi in atmospheric deposition as well as uncertainties in quantification of DSi from PSi dissolution (cf. Zhang et al., 2005; Hartmann et al., 2008). For example, it was found that the ratio of DSi deposition over suspended matter (SM) (DSi/SM) in a Japanese watershed close to the sea was higher for periods with increased abundance of dust storm events. Even more important is the observation that the DSi/SM deposition rate decreases with increasing suspended particulate matter (SM) deposition rate and in some cases both deposition rates are completely decoupled from each other. The overall observation range suggests a ratio of DSi/SPM concentration of about 8% in Japan. This high observed ratio can in part be attributed to influences of anthropogenic fly ash with high amounts of amorphous silica for the East Asian region (cf. Misran et al., 2007; Hartmann et al., 2008), but this amount is globally not equally distributed in aerosols. In general, reported Si-solubility from deposited particulate matter into surface waters ranges from 0.02–1.1% for aerosols from Saharan dust events deposited over the Atlantic (Baker et al., 2006a) to theoretical estimates of 5–10% (Harrison, 2000; Tréguer et al., 1995), leading to a suggested probable range of 1% to 5% of dust fallout PSi. However, these solubility rates are based on the assumption of different dust mineral compositions. For example, Saharan dust contains large amounts of quartz whereas Harrison (2000) uses kinetic considerations to derive potential solubility estimates and assumes that aerosol particles contain large quantities of feldspar. For global ocean models calculating at time scales ranging from years to decades, DSi input from dust is often neglected as it is assumed that deposited aeolian silica would be deposited as sand particles whose sinking speed wouldn't allow any dissolution resulting in a significant input of silicic acid (Johnson et al., 2006). In consequence, a fair estimate of DSi input via the atmosphere into the oceanic system can not be provided, except for the value provided by Tréguer et al. (1995) for DSi inputs via rain water (0.5 Tmol y^{-1}, i.e. 30 Mt SiO_2 y^{-1}; this results in an atmospheric flux of 25.8 Mt SiO_2 y^{-1} derived from the exorheic parts of the continents, taking into account the distribution of continental drainage from Vörösmarty et al., 2000a, b, and disregarding that probably a larger proportion is derived from endorheic parts as a larger proportion is arheic), which will be used here for our attempt of a global land-to-ocean budget (see below). However, estimated global DSi and PSi deposition on the ocean is much lower than the estimates for riverine DSi.

The amount of DSi retained in lakes and floodplains can be estimated as a rough first-order calculation as follows: from the work by Lehner and Döll (2004), lake surface can be calculated, plus a certain proportion of the share of a region covered by floodplains; swamps and wetlands. From the share in a given area that is covered by floodplains, swamps and wetlands, we assume 15% of this share to be permanently flooded – similar to the calculation proposed by Laruelle et al. (2009) for a global silica box modelling study. This calculation (classes 1, 3, and 15% of 4, 5, 9–12 in Lehner and Döll, 2004) results in a total surface area of 3.4 M km^2 of exorheic area occupied by lakes and permanently inundated floodplains, swamps and wetlands. If an average dissolved silica retention of 20±10 $g\,m^{-2}\,y^{-1}$ is considered (see above, Campy and Meybeck, 1995), this results in 69±35 Mt $SiO_2\,y^{-1}$ retained in continental areas connected to the oceans. This number corresponds to 1.2 Tmol Si and is somewhat lower than the 2.8 Tmol calculated by Laruelle et al. (2009) as preserved in sediments, but their number includes the volume of rivers, in addition to lakes and floodplains. Yet the average DSi retention in lakes should be confirmed with a larger data set.

Human impacts on the silica fluxes have not been targeted here. They can affect both sources and sinks. As diatomites and/or artificially produced zeoliths are often used in washing powders and other household products (2–3 million metric tons of SiO_2, Breese, 1994; van Dokkum et al., 2004), an increase of silica due to urban impacts is possible. Such inputs have been estimated to 780 g SiO_2 (for DSi) per capita per year (1 g of Si per capita per day) by Sferratore et al. (2006) on Paris megacity (10 million people). The extrapolation to 1 or 2 billions of similar users would correspond to a load of 0.78 to 1.56 Mt $DSiO_2$ per year, compared to a river flux of 371 Mt $DSiO_2\,y^{-1}$ to coastal zones. Based mainly on data from Europe, van Dokkum et al. (2004) estimate the total additional flux due to anthropogenic emissions to be <=2% of riverine DSi fluxes. These fluxes might thus be of local importance (e.g. Seine), and are very minor at global scale, but such extrapolation remains poorly constrained.

Additional sinks correspond to the 100 000 and more reservoirs already registered

(Vörösmarty et al., 2003). They correspond to at least 0.5 M km^2 area of registered impoundments, and have been globally estimated to a total area of 1.5 M km^2, if smaller and unregistered reservoirs are taken into account (St. Louis et al., 2000). Considering again, as for lakes, an average dissolved silica retention of 20±10 g m^{-2} y^{-1} (Campy and Meybeck, 1995), the total DSi retention would be of the order of 30±15 Mt SiO_2 retained each year in reservoirs. This number can be adjusted to 26.4±13.2 Mt SiO_2 if the distribution of 88% reservoir area to exorheic regions is taken into account, calculated using the database – containing major reservoirs only – by Lehner and Döll (2004). It must be noted that the retention rate of silica per unit lake or reservoir area considered is about seven times higher than the weathering rate of silica-bearing minerals. This retention has already been attributed to the decrease of silica in some large river basins as the Mississippi, where the N:Si ratio has widely fluctuated over the last 100 years (Rabalais and Turner, 2001). Other cases of silica-depleted coastal waters have also been reported for Swedish rivers and in the Danube River delta (Humborg et al., 1997, 2000, 2006), invoking also alternative human impact mechanisms such as reduced connectivity with usually DSi-rich aquifers due to hydraulic alterations, resulting in less exchanges with the riparian zone or lower natural water levels controlling silicon weathering rates (Teodoru et al., 2006). For suspended particulate matter (SPM), and thus detrital PSi, global retention in reservoirs is now estimated between 20% (Syvitski et al., 2005) and 30% (Vörösmarty et al., 2003). Additional retention of DSi can occur in main stems of rivers and is closely related to anthropogenic influence on nitrogen (N) and phosphorus (P) levels. Significant amounts of BSi resulting from plankton blooms can be sedimented in flood plains (Admiraal et al., 1990). As early data from European rivers suggests (see above), DSi retention due to N and P fertilization may occur since the middle of the 19th century (Roth, 1879). N and P fertilization might thus cause decreases in DSi levels in urbanized or agricultural catchments. When recent decreases of N and P in rivers are observed, it has been noted that DSi concentrations might eventually come back to nearly pristine levels, as observed for the Rhine River (Hartmann et al., 2007; Hartmann, 2008), at least in some catchments. It must be noted that long-term records of DSi in rivers are much less common than those for N and P.

Retention in lakes, floodplains, and human-built reservoirs is very much dependant on water residence times in these bodies, and our simple calculation should be verified by further studies. The assumed retention rate of 20±10 $g\,m^{-2}\,y^{-1}$ by Campy and Meybeck (1995) is a crude estimate that has been derived for lakes, and is probably lower for reservoirs and highly anthropised floodplains, due to lower residence times.

If our first-order back-of-the-envelope estimate, proposed here as a working hypothesis, is validated in forthcoming studies, the total amount of dissolved silica in headwaters, derived from weathering on the exorheic parts of the continents should be majorated by as much as 95 Mt SiO_2 per year (additional retention of 69±35 Mt SiO_2 as BSi in lakes, floodplains, swamps and wetlands for the natural situation, as well as human-built reservoirs, plus 26 Mt SiO_2 as DSi atmospheric input over oceans from rain), assuming that riverine DSi derived from re-dissolution of BSi ultimately also stems from weathering sources.

A schematic view on the silica transfers from land to ocean with the cascading filters, both natural and anthropogenic, and new anthropogenic inputs that characterize the Anthropocene (Crutzen and Stoermer, 2000) situation of river systems described by Meybeck and Vörösmarty (2005), is presented in Fig. 6. It is combined with the nested filters of river inputs to oceans: estuaries, shelf, regional seas and other mega filters.

5 Conclusions and perspectives

The spatialized distribution of riverine dissolved silica fluxes has been realised for ∼140 coastal catchments (COSCATs). The documented area and river runoff correspond to 56 and 58% of the globe, respectively, and the documented river DSi fluxes to 51%. The undocumented part is extrapolated on the basis of modelled runoff, and of regional similarities of dissolved silica based on lithology, climate and lake occurrence. Some of the COSCATs are still lacking analyses (e.g. Madagascar island and parts of Australasia), but the spatial coverage of the 250+ rivers used in this budget is not biased for any of the control factors. The resulting overall dissolved silica average (9.5 mg l^{-1}) is not much different from previous attempts of the last decade, but the spatialization of average concentrations and yields for each piece of the COSCAT puzzle is new.

At such resolution (ca. 1 M km^2), the average DSi concentrations for COSCATs range over one order of magnitude and a factor of 50 for DSi yields. The highly skewed distribution of yields results in a marked imbalance of riverine fluxes: at the global scale, 55% of dissolved silica fluxes originate from only 17.4% of the land area facing the oceans, while 28.9% of this area contribute to only 2.3% of fluxes. Similar skewed distributions have been found for many other river-borne materials. Higher fluxes originate from different COSCATs, encountered on many continents: they correspond to high to very high runoff rates, combined with medium and high relief, volcanic and/or highly active tectonic regions, the major control factors of silica sources. The occurrence of multiple lakes or of single large lakes (e.g. Saint Lawrence basin, COSCAT #825, with the Great Lakes, or Gulf of Finland basin, COSCAT #0406 with the Neva River showing one of the world's lowest silica yields due to the presence of Lake Ladoga close to its outlet, combined to a cold climate) is probably a major control factor of silica retention on continents.

Decomposing silica outputs from individual continents has little interest since they generally combine both high and low yields as demonstrated when considering individual COSCATs.

The riverine silica inputs to individual oceans, required by ocean biogeochemists, show great disparities when considering relative fluxes received per unit ocean area or volume: there is nearly one order of magnitude difference between the fluxes to the Arctic Ocean (silica over-fed) and the Pacific (silica-starving). This type of computation should now also take into account the nested filtering effects of estuaries, shelves and regional seas: the discrepancy between the silica fluxes received by the Pacific after the potential retention of DSi by regional seas may be even greater, compared to those received by the Arctic.

When comparing the riverine yields of dissolved silica (Y_{DSi}) and of particulate silica (Y_{PSi}) – at the COSCAT resolution, assuming a constant silica content around 55% $\mathrm{SiO_2}$ in river suspended matter – a weak positive correlation is found, with the Pohai Gulf (COSCAT #1325) including the HuangHe basin set aside. The $Y_{\mathrm{DSi}}/Y_{\mathrm{PSi}}$ ratio in COSCATs ranges from more than unity to 10^{-4} (HuangHe). A majority of COSCATs has a ratio between 0.005 and 0.5, compared to the global flux ratio ($\overline{Y_{\mathrm{DSi}}}/\overline{Y_{\mathrm{PSi}}}=0.042$). 9% of the COSCAT area (10.3 M km^2) are constituted by regions where the particulate transfers are very high ($\overline{Y_{\mathrm{DSi}}}/\overline{Y_{\mathrm{PSi}}}<0.01$), as for the Pohai Gulf.

Future development of ocean budgets should therefore aim at regional budgets in which river inputs are spatially distributed. These biogeochemical models combine all river nutrients (N, P, Si) and carbon species (Sferratore et al., 2005), including the retention impact of reservoirs that is not yet fully quantified at the global scale.

The improvement of the silica budget coverage, e.g. from the actual 50–60% coverage to 75%, will not be easily achieved. There are only few major rivers, such as the Salween and Irrawaddy, that remain undocumented in the database used here and the inclusion of hundreds of small and medium basins (0.01 to 0.1 M km^2) would be needed: the first 10 rivers, ranked by basin area, correspond to about 26% of the global exorheic area, the first 100 to 62% and the first 1000 to 74% only (Milliman and Syvitski, 1992; Meybeck and Ragu, 1995).

Further research should first estimate each of the components of the global silica cycle (Fig. 6), then establish these fluxes for individual regions and/or ocean basins and we have seen that major disparities exist in silica concentrations or yields.

A most promising approach is represented by biogeochemical models that are spatially distributed at very high resolution linking sources (weathering) and sinks (uptake, sedimentation of biogenic silica), as already developed for the Seine River (Sferratore et al., 2005) and the Red River (Hong) in Vietnam, in connection with N and P models (Quynh et al., 2005). This type of model is often data-limited and should now be validated in different types of river basins. Also the analysis of riverine particulate biogenic silica, either detrital or phytoliths, or autochthonous, should be further developed, particularly in highly eroded river basins, and compared to the particulate organic carbon. These models will be able to simulate the silica retention in reservoirs and explore Global Change scenarios on the riverine components of the silica cycle.

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Table 1. Average dissolved and particulate silica fluxes, concentrations (runoff weighted averages) and yields (area weighted averages) for the exorheic parts of the continents. Catchment surface area, discharge and runoff are given as well as % of volcanic rocks from Dürr et al. (2005). The fraction of PSi that possibly dissolves and becomes biologically available might be <1% (see discussion).

	Catchment area 10^6 km^2	Discharge km^3 y^{-1}	Runoff mm y^{-1}	Volcanic rocks (Vb+Va+1/2 Cl) %	DSi mean concentration mg l^{-1} SiO$_2$	DSi flux M t y^{-1} SiO$_2$	DSi yield t km^{-2} y^{-1} SiO$_2$	PSi flux M t y^{-1} SiO$_2$	PSi yield t km^{-2} y^{-1} SiO$_2$
Africa	26.2	4130	157	4.2	12.6	52.1	2.0	528	20.1
Europe[a]	8.4	2410	285	6.9	5.6	13.5	1.6	367	43.5
North America	21.9	5880	268	11.3	8.0	47.2	2.2	1713	78.2
South America	17.4	11 850	681	10.0	9.0	106.5	6.1	1633	93.9
Asia	34.0	12 900	379	12.8	10.0	129.4	3.8	3951	116.2
Australasia	6.7	1920	284	8.4	11.8	22.6	3.3	643	95.3
Total Exorheic	114.7	39 080	341	9.3	9.5	371	3.3	8835	77.0

[a] including a small non-glaciated fraction of Greenland.

Table 2. Average dissolved and particulate silica fluxes, concentrations (runoff weighted averages) and yields (area weighted averages) from catchments to coastal zones related to ocean basins. Catchment surface area, discharge and runoff are given as well as % of volcanic rocks from Dürr et al. (2005).

	Catchment area 10^6 km^2	Discharge km^3 y^{-1}	Runoff mm y^{-1}	Volcanic rocks (Vb+Va+1/2 Cl) %	DSi mean concentration mg l^{-1} SiO$_2$	DSi flux M t y^{-1} SiO$_2$	DSi yield t km^{-2} y^{-1} SiO$_2$	PSi flux M t y^{-1} SiO$_2$	PSi yield t km^{-2} y^{-1} SiO$_2$
Arctic	16.7	3310	199	8.3	6.1	20	1.2	122	7.3
Atlantic	57.5	19 950	347	5.4	8.4	169	2.9	2748	47.8
Indian	20.8	5200	250	7.9	12.0	62	3.0	2138	102.8
Pacific	19.8	10 620	1010	22.9	23.2	120	6.1	3826	193.5
Total Exorheic	114.7	39 080	341	9.3	9.5	371	3.3	8835	77.0

Table 3. Dissolved and particulate silica fluxes received by coastal zones related to ocean basins, rated to coastline length, ocean areas and ocean volumes. Retention of silica in estuaries, on shelves and in regional seas is not considered here. Coastline length, ocean area and ocean volume according to Meybeck et al. (2006, 2007).

	Arctic	Atlantic	Indian	Pacific	Global Ocean
t DSi silica received per km y^{-1} of coastline	353	1133	920	935	923
t per km^2 y^{-1} of ocean area	1.64	1.79	0.84	0.66	1.03
t per km^3 y^{-1} of ocean volume	1.47	0.50	0.22	0.17	0.28
t PSi received per km y^{-1} of coastline	2144	18 541	31 613	29 706	21 992
t per km^2 y^{-1} of ocean area	9.97	29.3	28.9	21.1	24.4
t per km^3 y^{-1} of ocean volume	8.92	8.18	7.51	5.36	6.55

Table 4. Percentages of documented area, discharge and corresponding dissolved SiO_2 fluxes for continents, regional seas and ocean drainage basins.

	% Area	% Discharge	% DSi flux
Africa	46.3	46.9	43.5
Europe[a]	53.0	47.0	44.3
North America	60.2	51.6	49.0
South America	69.4	78.3	70.1
Asia	63.1	54.6	44.7
Australasia	25.8	25.2	25.0
Regional Seas	53.6	48.5	42.2
Arctic	77.3	81.6	76.8
Atlantic	59.4	68.5	66.8
Indian	36.5	41.0	35.2
Pacific	53.0	41.4	33.1
Total Exorheic	56.7	58.6	51.1

[a] including a small non-glaciated fraction of Greenland.

Table 5. Existing global budgets and values of ranges for dissolved silica (DSi).

Reference	Global average concentration ($\mathrm{mg\,l^{-1}\,SiO_2}$)	Approach
Clarke (1924)	8.3	Extrapolated from few, big temperate rivers
Livingstone (1963)	13.1	As Clarke (1924)
Meybeck (1979)	10.4	Biomes typology, 60 rivers, Amazon included
Probst (1992)	8.9	Multiregression (Meybeck's data)
Meybeck (1992, unpublished)	9.2	Data later published as Meybeck and Ragu (1995); plus 9 morphotectonic types (lithological control)
Tréguer et al. (1995)	9.1	Meybeck and Ragu (1995) data
Meybeck (2003)	8.75	On the totality of the analyses from Meybeck and Ragu (1995) (~260 rivers and tributaries, exo- and endorheic)

Table 6. Dissolved silica fluxes, concentration and yield for selected regional sea catchments : North Atlantic Regional Seas and Japan Sea. Catchment surface area, discharge and runoff are given (from Meybeck et al., 2007) as well as % of volcanic rocks from Dürr et al. (2005) and lake density from Lehner and Döll (2004).

	Catchment area 10^6 km^2	Discharge km^3 y^{-1}	Runoff mm y^{-1}	Lake density %	Volcanic rocks (Vb+Va+1/2 Cl) %	SiO_2 flux Mt y^{-1}	SiO_2 mean concentration mg l^{-1}	SiO_2 yield t km^{-2} y^{-1}
Baltic Sea	1.6	390	240	6.4	2.8	1.5	3.9	0.9
Black Sea (incl. Azov)	2.4	410	170	0.78	8.7	2.1	5.1	0.9
Mediterranean Sea	8.3	800	97	1.3	6.0	3.3	4.1	0.4
Hudson Bay	4.0	850	210	10.5	2.4	1.7	1.9	0.4
St. Lawrence Gulf	1.6	630	402	19.4	2.4	3.3	5.2	2.1
N.American Med.Seas (Gulf of Mexico, Caribbean)	6.5	1875	290	0.95	6.9	22.7	12.1	3.5
Japan Sea	0.4	240	580	–	39.2	4.1	17.1	9.9

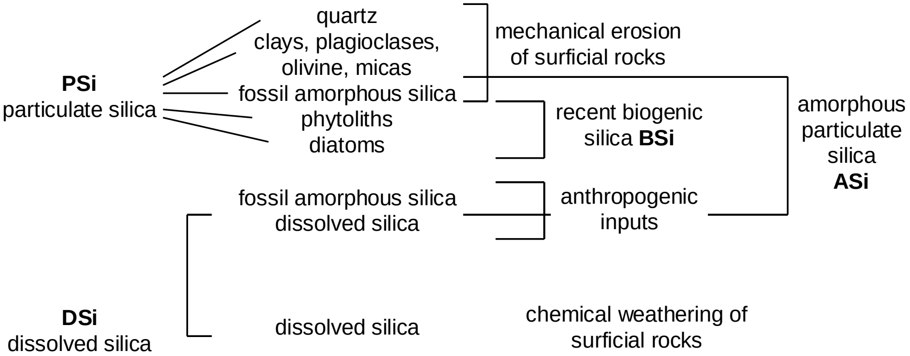

Fig. 1. Sources and forms of riverine silica.

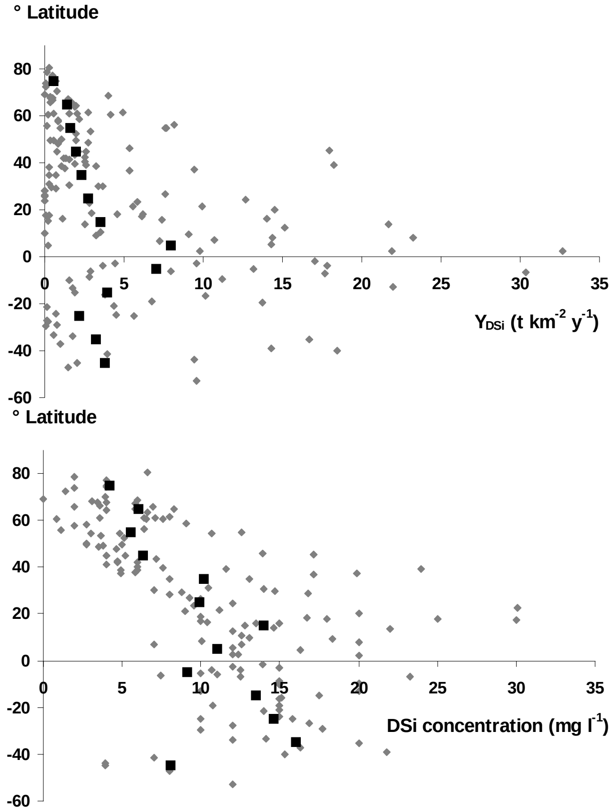

Fig. 2. Latitudinal distribution of dissolved silica inputs to coastal zones (at barycentre of the 140 COSCATs). Y_{DSi} in t SiO_2 km^{-2} y^{-1}, DSi concentration in mg SiO_2 l^{-1}. Grey dots: individual COSCATs, black dots: averages per 10° latitudinal bands.

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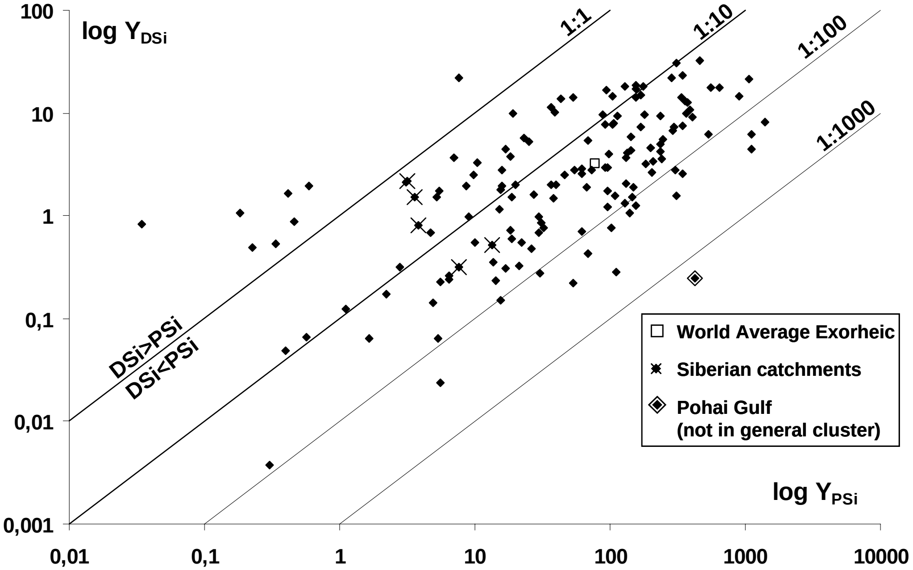

Fig. 3. General relation between dissolved (Y_{DSi}) and particulate (Y_{PSi}) silica yields in the 140 coastal catchments and in the global budget. Y_{DSi} and Y_{PSi} in t SiO_2 km^{-2} y^{-1}, log scales.

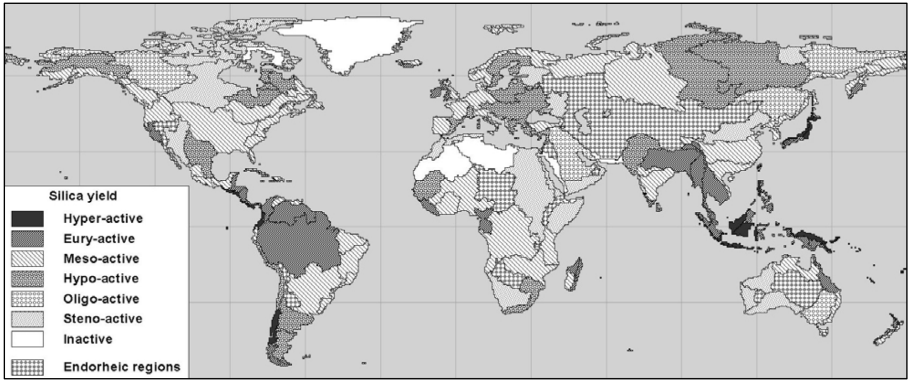

Fig. 4. Relative natural dissolved silica yield for coastal catchments (COSCATs) (115 M km^2, $n \approx 140$, global mean yield 3.3 t DSi km^{-2} yr^{-1}). Inactive areas 0–0.01× global mean yield, steno-active 0.01–0.1×, oligo-active 0.1–0.2×, hypo-active 0.2–0.5×, meso-active 0.5–2×, eury-active 2–5×, hyper-active 5–10×. No Hot spots (>10× global mean yield) are observed at this scale. Silica yield classes boundaries see also Fig. 5. Antarctica and glaciated parts of Greenland not considered. Endorheic regions are set apart.

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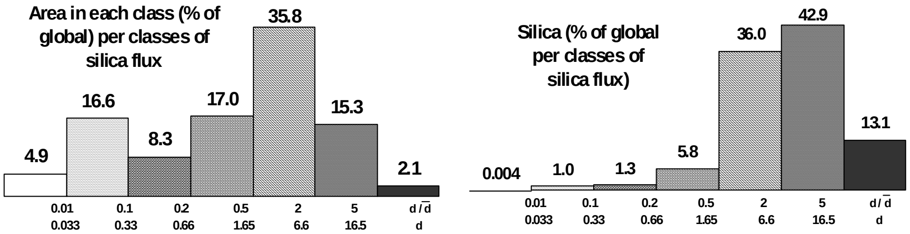

Fig. 5. Relative distribution of dissolved silica yields in exorheic basins (115 M km^2, $n \approx 140$). Classes are constructed after the mean yield of 3.3 t DSi km^{-2} yr^{-1} (see text). Antarctica and glaciated parts of Greenland not considered.

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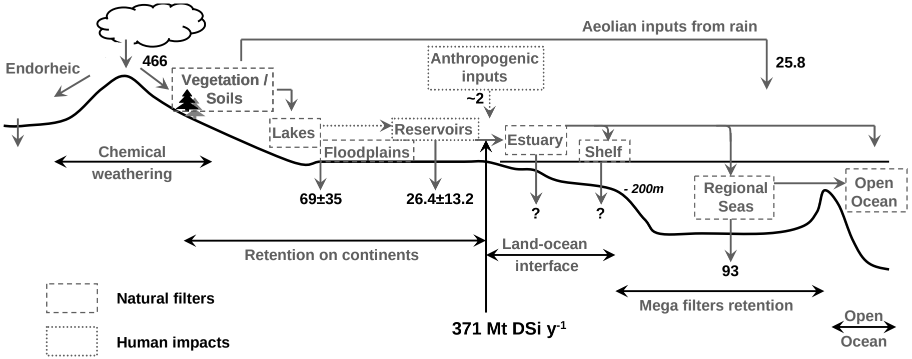

Fig. 6. Conceptual pathways of dissolved silica from land to oceans with cascading filters on land and nested filters at the land-ocean interface. Dotted: anthropogenic components. All numbers are in Mt DSi per year.