Dear Editor,

We thank the reviewer for his comments and suggestions, they will help to improve the manuscript. In the revised version (text parts in blue), we clarified the issues raised by the reviewers (in italics) to the best of our abilities, notably on the data sources, quality and accuracy, as well as on the control factors on silica fluxes. In the last year, substantial new literature on this subject has appeared, and we aim to cite the latest literature where appropriate, especially the works by Beusen et al. (2009), and the group of Hartmann et al. (several references). We provide specific answers to the
individual comments by the reviewers below.

Reviewer remark: The fluxes calculated are the natural ones because the anthropogenic impact of dissolved and suspended Si fluxes are taken into account, in particular because the data base contains Si concentrations prior to human perturbations.

Reply: This is why a clear focus on the earliest available data has been made, and not on the latest literature presenting new data (see the comment on more recent data sources). We will further clarify this in the revised manuscript.

Reviewer remark: Even if the first order estimates of Si fluxes to the ocean are not significantly different to those published before, this study is the first trying to spatialized fluxes.

Reply: Together with the pre-anthropogenic data, this is the main objective of this manuscript, and as such it is new, together with the study by Beusen et al. (2009), based on the data presented here.

Reviewer remark: This paper represents a lot of work for data collection and spatialization. I doubt of his interest actually and I have no opinion whether BGD should publish it or not. Because this is a new approach for calculating the Si input to the ocean and that Si of great interest for ocean chemistry and the global C cycle, this paper may have some interest for the global change community.

Reply: The results of our work, presented here, have now been used in several applications, proving its utility for the scientific community. Bernard et al. (2010, Biogeosciences Discussions) used the spatialized data as input for an OGCM. Beusen et al. (2009) used the data for a statistical approach on control factors. Laruelle et al. (2010) used the data for an assessment of the global biogeochemical silicon cycle. Also regional studies may benefit as they need spatialized data for comparison with other, similar regions (e.g., Hartmann et al. 2009, Jansen et al. 2010). We also identify here major regional seas as significant filters of land-ocean DSi-fluxes. The budget of DSi
reaching the open ocean is significantly different from the amount that is delivered at river mouths to the coastal zones. In the revised manuscript, the new references will be added, and we will clarify the potential use of this work. It should be noted that the compilation of data presented here has been used as input data for referenced work and we think that it is worth to discuss the characteristics of the data sets, assuring that the referenced works can be interpreted properly.

Reviewer remark: It is very difficult to have an idea of the data quality and accuracy. The way data base have been set up poses a number of problems with regards to data quality. If data quality is good when numbers are extracted from peer-reviewed papers of the scientific literature, this may not be the case for data derived from agencies with poor or no control. This included not only the measurement by itself but also the collection of water, conservation, filtration, and conservation processes. As the reader cannot make his own idea about this quality issue, this would be good if the authors could comment of that problem. This is a limitation to the present study.

Reply: Measuring dissolved silica is a very simple and standard colorimetric method, used since tens of years. Contrary to other substances (as ammonium) potential error sources are small. We will add some standard references (Robinson & Thompson 1948, Strickland et al. 1968, Koroleff 1983) to clarify this. Furthermore, the data used and the according sources were included in a substantial data quality control and standardization efforts, based on principles used in previous studies (see mainly Meybeck and Ragu 1995 and Meybeck 2003). For example, sufficient inter- and intra-annual data must be present to assure representative annual averages. Meybeck and Ragu (1995) have explained the detailed data quality requirements for the Gems-Glori database, which has been designed using a similar approach. The pristine river database used here follows the same data quality requirements (Meybeck 2003), with the additional requirement that as little human influence as possible can be detected, and hence often the oldest available data have been recognized as more appropriate to avoid as far as possible human influences due to the construction of dams or eu-
trophication. In the manuscript, we describe the origin of the data. Some carefully selected personnel communications were added. We did our utmost to track all data sources, and have been able to add a few to the revised manuscript, but this has not been possible for all data. Spatializing dissolved silica concentrations is the major focus of this manuscript, and most effort into data collection and preparation has been made here. As the documentation of all procedures for the data sampling, measurement, etc. is beyond the appropriate space and scope of this paper, we refer the reader (and reviewer) to the references provided.

Reviewer remark: In supplementary materials, the list of reference used to elaborate the data base contains a lot of “Meybeck, personal data”. This is a strange. Why not publishing this data in the present paper. The authors have to make data available. In addition, a number of important and recent contributions on river composition are missing. This is a severe drawback of this paper.

Reply: We are of course aware that some more recent data exists and we are tracking the recent literature continuously (as can be seen in the recent publications of the authors, see also new reference list here). However, the objective of the data collection for the presented manuscript was to identify data with as little human impact as possible and which are located in the vicinity of the coastal zone, within the freshwater part of rivers. As stated above, we have done our utmost to find additional references, which fulfil the above-mentioned criteria (especially for Arctic rivers). Due to this it was not our principal effort to find the most recent published data, but rather to find the most ancient ones (see above), in order to minimize influence of reservoirs. Most of the presented analyses thus have a date before 1980/1990. To our knowledge, no other effort has gone into such detail (at global scale) as our study.

Reviewer remark: Particulate Si data have been published in a number of papers that are not considered by the authors. This includes papers from various group, on large river systems (Ganges, Amazon, Congo, Niger, Mackenzie, Chinese River) and volcanic islands. A particular study in Iceland (Gislason et al.) addressed the reactivity...
of river particles once in the ocean. As this only reference for particulate Si data is GLOMET, Meybeck 2009 and that this reference is not given, I got the same “black-box” impression on the quality of data than I had for dissolved Si. It is very difficult for the reader to judge the quality, and representativity of data. Taking finally a mean average of 55.64% of SiO2 to calculate the Psi flux neglects the importance of grain-size (and quartz dilution), carbonate content, and organic matter content. It also gives a great important to the suspended matter fluxes.

Reply: We apologize for not giving the appropriate references. However, the work is containing published data. We agree that our approach is an estimate based partly on data that are not all published in peer-reviewed international journals (however, most are – see references below). The average silica in world rivers suspended particulate matter (SPM) in the GLOMET data base has been based on 62 major basins and tributaries from 5 continents and from latitudes ranging from 40°S to 65°N. The arithmetic average content is 260 000 ppm, it is also the average content weighted by the particulate loads. Silica is the most abundant element found in rivers SPM, and its range is very narrow, from 160 000 to 360 000 ppm. This represents the smallest range of contents observed for more than 40 elements. Silicium, or silica, is also not affected by human impacts in the GLOMET database. The only exception is noted for rivers with very low SPM contents due to reservoir settling of detrital material and to the presence of biogenic silica due to diatom growth. The related fluxes at the global scale are quite limited. The data base for silica analysis in river SPM and/or freshly deposited fine-grained sediments originates, among others, from the following sources: Martin and Meybeck (1979) (all rivers), Thomas and Martin (1982), Meybeck (1984) (all rivers), Churchman et al. (1988) (New Zealand), Snoussi (1988) (Morocco), CuiHui et al. (1990) (China), Orange et al. (1991) (W Africa), Qu et al. (1993) (China rivers), Chen et al. (2000) (China), De Vos et al. (1996) (European rivers, floodplain sediments and bed sediments), Dupré et al. (1996), Canfield (1997) (US rivers), Gaillardet et al. (1997), Négrel (1997), Singh and Hasnain (1998) (Indian rivers), Dekov et al. 1999 (Indian rivers), Elbaz-Poulichet et al. (1999) (Amazon and tributaries), Gaillardet et
al. (1999), Mc Lennan and Murray (1999) (carbonate-free shale), Olley and Caitcheon (2000), Haynes and Kwan (2002) (Papua rivers), Rosales-Hoz et al. (2003), Stefansdottir and Gislason (2005) (Iceland). Several world averages have been proposed for silica since 1979, they are very similar despite the growing data base: Gordeev and Lisitzin (1978) 255 000 ppm, Martin and Meybeck (1979) 285 000 ppm, Glazowsky (1990) 254 000 ppm. Viers et al. (2009) compiled a new global database on the chemical composition of suspended sediment fluxes, they found a quite similar value for Si content (25,4%), with little variation (11,7%). Their database contains all the rivers mentioned by the reviewer. In addition, we should note that the original GLOMET collection includes to a certain amount the same data.

Key references (as far as not yet cited in the manuscript):


chemical mapping based on overbank sediments in the heavily industrialised border area of Belgium, Germany and the Netherlands. Journal of Geochemical Exploration, 56, 91-104.


The silica content of river SPM also depends on the grain size: coarser bed sediments are more siliceous with contents around 300 000 ppm while SPM are mostly in the silt and clay fraction and have a lesser quartz content and a higher content in Al, therefore
a low content in Si. Viers et al. (2009) found low carbonate contents, also with very little variation. The stream bed sediments in European rivers are around 286 000 while river alluvial deposits are at 302 000 ppm (median values, De Vos et al. 2006).

The main objective of our manuscript is DSi. A large amount of literature exists, and we can not cite them all (most is aggregated in the references given above). We hope that this is in accordance with the reviewers understanding.

Addressing the remarks with respect to the work of Gislason et al.: If we identified the appropriate work “Gislason et al. (2006: Role of river-suspended material in the global carbon cycle)”, we found, that the scope of this publication is on Ca-Mg bearing silicates with a focus on Iceland. Furthermore, reactivity of river particles once in the ocean is outside the scope of this paper, although we discuss the influences on riverine DSi and BSi (the potentially bioavailable part of PSi) in estuarine environments (in short, uptake by diatoms, dissolution of the particulate pool, and net retention through sediment accumulation). Note that we have not focused on spatial BSi distribution here, because the bioavailable part of PSi (=BSi) is actually still under discussion, without a definitive emerging number and we found that the few available studies providing local data do not provide a large enough data base for an appropriate global spatalization (c.f. Conley 1997). We thank the reviewer for his critical view at this part of the manuscript and will modify it (specifically the discussion section) with respect to the findings named, incorporating the references named.

Reviewer remark: The suspended matter fluxes are taken from Milliman, which is probably the best data base so far. The anthropogenic impact on the modern sedimentary fluxes is not known and therefore, it may be that the Psi flux calculated by the authors could be completely be overprinted by the anthropogenic perturbation of sediment yields. This is not discussed by the authors. In what extent the measured suspended yields (even monitored on long time periods) represent the mechanical denudation fluxes?
Reply: While there is now a considerable amount of literature (e.g., Vörösmarty et al., Syvitski et al.) on the anthropogenic overprint of suspended matter fluxes, it is outside the scope of this paper to add to this discussion. We are mainly interested in comparing the natural DSi and available PSi fluxes, and we discuss only the potential changes of human influence on the DSi fluxes. To clarify the important issue addressed by the reviewer, we will add information on the anthropogenic overprint, which is considered to be around 30% retention (but partly balanced by increased deforestation leading to enhanced denudation). Because suspended sediment yields at the land-ocean transition zone do not represent mechanical denudation fluxes in the hinterland (please compare with some references of the classical literature on this subject; e.g., sediment delivery ratios in Walling 1983, reference already given in the main manuscript; Walling and Webb 1996), we do not discuss this issue here, especially as there exists more specific publications on this topic. We hope that this is in accordance with the understanding of the reviewer.

Reviewer remark: That would be interesting to have an idea of the main controlling parameters of Si concentrations or Si fluxes from catchments: runoff, temperature, elevation, lithology. The data base used by the authors should give this information quite easily. The first order control on the Si fluxes seems to be runoff actually, given the fact that Si concentration does not vary very much from one river to another (compared to runoff). If the data base contains such an information, it should be stated here.

Reply: We will provide a discussion on controlling parameters of DSi, including runoff, temperature, elevation and lithology. Recently, and partly also based on the data compiled here, the major control factors on local, regional and global DSi fluxes have been analysed using empirical techniques. Control factors are usually extracted by using small to medium size catchments (<10000 km2). Some of the factors mentioned have been identified for specific regions of the globe (Hartmann et al., 2010, for Japan; Jansen et al. 2010 for the USA), as well as globally (Beusen et al. 2009; using the database presented here). While correlations of DSi concentrations (not fluxes) with
temperature have been observed (Garnier et al. 2006), these do not always show in large-scale statistical models (Beusen et al. 2009, Hartmann et al. 2010). The spatial correlation between runoff, lithology and silica fluxes is very different between local scale and regional scale catchments. Comparing the references named it becomes clear that the findings about controlling factors from smaller catchments are not representative for large basins or the total global budget. The findings of the later studies confirm our results for the global scale. It should be mentioned that there is still an absence of entirely process-based models for global scale due to difficulties to globalize or regionalize important parameters (Sferratone et al. 2005). Because of this it seems appropriate to employ empirical and budget approaches for the global spatial representation of land-ocean DSi-fluxes. We will add this discussion to the manuscript and will update relevant references to elucidate more the control factors on DSi mobilization from the terrestrial-land system into river systems and the control factors on DSi concentration during transport in the river system.

Reviewer remark: This paper gives the impression that the controlling factors for silicate weathering (and hence Si concentrations in waters) are quite well known, which is far to be the case. Actually, most of the numerous papers aiming at establishing chemical weathering laws are not cited in this paper. This must be acknowledged by the authors that chemical weathering of silicates is a complicated problem and that, to date, no model is able to predict what should be the chemical composition of a given riverwater as a function of climate, mineral assemblages, residence time of soils, ecosystems.

Reply: Please see the reply in the section above. Along with the already mentioned references, we will add Bluth and Kump (1994) and Dessert et al. (2003), together with already present or mentioned references. Control factors at local scale are well known, but do not always show up in large-scale statistical relationships (see reply above). However, e.g. temperature could only be identified to show a correlation with DSi fluxes for basalt, if regionalised averages are applied, using data from tropical to cold regions (Dessert et al. 2003). Note that the latter study did not analyse a pos-
sible bias due to correlations with other control factors such as runoff, evaporation or precipitation, that are also influenced by temperature. There is still a discussion on how and to what extent this assumed temperature effect can be identified, its strength on DSi mobilization can be estimated robustly, and how it could be employed in regional and global scale models (cf. findings in Godderis et al. 2009 and Hartmann et al. 2010). We believe that the budget approach presented here, considering local and regional characteristics, is an appropriate tool for deriving global land-ocean flux estimates. This is supported by the outcomes of the work of Beusen et al. (2009), if compared with the results presented here.

Reviewer remark: The relation between fluxes of dissolved Si and particulate Si is interesting and close to the relationship reported by previous authors between physical and chemical fluxes of silicate weathering. No mention is made to these previous studies (Riebe et al., 2001, Millot et al., 2003, Gaillardet et al., 1999, West et al., 2005, Lyons et al. 2005).

Reply: We will acknowledge these references. However, it must be noted that these studies focus on chemical weathering rates and fluxes, and they do not distinguish DSi specifically. E.g., Gaillardet et al. do not report DSi fluxes in detail (with exception of the concentrations in Table 1 of their manuscript), but in the second part of their manuscript they describe the observable correlation between chemical weathering rate and physical erosion. The same holds true for Riebe et al. (2001), Millot et al. (2002) and West et al. (2005). While the work of Gaillardet et al. and West et al. are already referenced in our manuscript, we will reference to all this publications at the appropriate place in the revised manuscript, to address the issue of the correlation between physical and chemical weathering rates more clearly.

Long-term average dissolved silica mobilized into river systems ultimately origins from silicate mineral weathering, while particulate Si mostly concerns quartz and clay mineral particles 10 to 50 times less soluble than silicates. The ratio DSi (in mg/l) to PSi (in ppm) is thus essentially regulated by grain size and not the weatherability of silicates,
as they are rarely dominant on quartz and clay minerals in rivers (if this is the case the resulting rocks are arkoses). The ratio of DSi flux to PSi flux is very low as soon as the SPM fluxes increase (ex. Madeira) and much higher when SPM fluxes are low as in the Rio Negro where dissolved silica dominates (but this is a very rare case). In general, DSi / (DSi + PSi) is between 0.1 and 0.5, except for the Negro. For the Yellow River it is 0.001 or lower.

Reviewer remark: The end of the paper (section 4.4.) is very speculative. The fluxes of river dissolved and particulate Si are the input fluxes to the ocean because of number of transformation involving Silica can potentially occur in estuaries, river plumes. . . and because of atmospheric deposition. Our knowledge of reverse weathering reactions is so poor that we actually do not know how much silica is sequestered by reverse weathering reactions in the ocean.

Reply: We agree that this is currently very difficult to quantify at global scale (which we do not attempt). However, we feel that it is important for such a manuscript to mention all important processes. We will clarify our statements and rewrite the section addressing the reviewers concerns.

Reviewer remark: Final remark: Si exists in water as silicic acid not SiO2. This is quite disturbing.

Reply: This is true, but reporting as SiO2 is a classical expression used in the geochemical literature (in more chemically oriented papers mostly reporting as $\mu$mol Si is chosen).

Reviewer remark: In conclusion, the approach is interesting, but my feeling is that river Si concentrations are not well known so far (and their control) and that the fluxes proposed here still suffer from important uncertainties. A significant volume of new literature geochemical data are is not considered.

Reply: As discussed above, control factors at local scales are well known, and statis-
tical models start to appear at regional to global scales (e.g., Bluth and Kump 1994, Dessert et al. 2003, Hartmann et al. 2009, Beusen et al. 2009, Jansen et al. 2010). However, we still think this manuscript is valid as a consistent compilation of globally available data of pristine DSi fluxes, with an added global budget, and a discussion of other relevant parameters and processes concerning terrestrial to coastal silica fluxes. Clear focus is the global scale, reporting regional averages. Local process understanding can be applied to the COSCATs as they are specifically designed to represent homogeneous units (see discussion in the manuscript and in Meybeck et al. 2006).

We hope to have sufficiently answered all reviewer’s comment, and will incorporate as much as possible into the revised manuscript, specifically the additional references. We will update some missing references to data in the source table and will better discuss data quality criteria (which are the same as for the GEMS-GLORI data set, Meybeck and Ragu 1995, but with a focus on pristine data here). Recent references will be added to include the new knowledge that has emerged in the literature during the last year. In conclusion we think that this manuscript still has value as a data compilation of pristine river data, together with budget calculations, and in-depth discussion of processes and magnitudes of the different parts of the terrestrial to coastal silica cycle via rivers, which have not been discussed in the publications applying these data now.

Additional references (as far as not yet cited in the manuscript):


Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/6/C4893/2010/bgd-6-C4893-2010-supplement.pdf

Interactive comment on Biogeosciences Discuss., 6, 1345, 2009.