

## ***Interactive comment on “The fate of riverine nutrients on Arctic shelves” by V. Le Fouest et al.***

**V. Le Fouest et al.**

lefouest@obs-vlfr.fr

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We gratefully thank referee #2 for her/his constructive comments with respect to our manuscript results, discussion and conclusion. In order to improve the manuscript with respect to these comments, we amended the manuscript as suggested by the referee wherever it was possible. Note that, when needed, comments were merged together to bring more clarity in the answer:

1) “It is not described where most of the data originate from.”

“The standard deviation of the monthly data is extremely high. Therefore it is important to know more about the origin of the data, e.g., how many data are from Russian stations and from the databases.”

“It is also questionable if it is worthwhile to use all the historical data, and it is important

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to know if these data are responsible for the huge variations.”

“Since the data are not used to calculate trends over the last 60 years the quality of the data should be carefully checked. It might be better to focus on the recent data from the databases.”

We fully agree on the need to detail the sources of nutrient data. A new table providing the source and number of data for each sampling station of all 9 rivers is given in the PDF file providing supplementary material. Note that we corrected accordingly small errors on the total number of data (n):

Page 13401 (line 8): “We compiled riverine nitrate (n = 2436), SRP (n = 1618), silicate (n = 1683), DOC (n = 509), DON (n = 380), POC (n = 160) and PON (n = 160) data for 9 large Arctic rivers, the Yenisey (Kara Sea; at Igarka (67.4°N, 86.5°E) and Dudinka (69.2°N, 86.1°E)), Lena (Laptev Sea; at Zhigansk (66.8°N, 123.4°E), Kyusur (70.7°N, 127.4°E) and Stolb (72.37°N, 126.80°E)), Ob (Kara Sea; at Salekhard (66.6°N, 66.6°E)), Mackenzie (Beaufort Sea; at Tsiigehtchic (67.46°N, 133.7°W)), Yukon (Bering Sea; at Pilot Station (61.93°N, 162.88°W)), Pechora (Barents Sea; at Oksino (67.6°N, 52.2°E)), Northern Dvina (White Sea; at Ust’Pinega (64.1°N, 41.9°E) and Arkhanggelsk (64.3°N, 40.3°E)), Kolyma (East-Siberian Sea; at Kolym-skoye (68.7°N, 158.7°E) and Cherskii (68.4°N, 161.2°E)) and Indigirka (East-Siberian Sea; at Chokurdakh (70.4°N, 147.6°E)).”

To illustrate the fact that differences amongst datasets are not systematic, we compared monthly-binned concentrations of SRP in the Yenisey River (at Dudinka) using two different sets of data: one with all data including the OGSNK/GSN (1985-1995; n=56) and more recent A-GRO (2009-2010; n=56) databases, and another one only with data from the A-GRO database. Figure 1 given in the PDF file providing supplementary material shows the mean SRP concentrations and related standard deviations for both cases. On the first hand, it can be shown that removing older data does not necessarily translate into lower standard deviations. On the other hand, restricting the

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data to the more recent datasets may strongly limit the temporal coverage. This issue can, however, be overcome by using all the historical data.

2) "The finding that the discharge of riverine nitrate to the Arctic Ocean is only small is a well known fact."

In this study, we linked the removal of riverine nitrate by phytoplankton to that of riverine phosphate and silicate. To our knowledge, this was not done in recent studies hence making the originality of our work. In addition, we inferred the contribution of riverine nutrients with respect to nutrients of marine origin on marine biogeochemistry, which is an original contribution to the recent publication effort made on that topic.

3) "I don't believe that photoammonification of refractory DON is an important process in contributing nitrogen. More important is a discussion about microbial decomposition of PON and DON which is discussed rather vague?"

In our physical-biological coupled modeling study in the Beaufort Sea (this issue; Le Fouest, V., B. Zakardjian, H. Xie, P. Raimbault, F. Joux, and M. Babin (2012a), Plankton ecosystem functioning and nitrogen fluxes in the most oligotrophic waters of the Beaufort Sea, Arctic Ocean: a modeling study, *Biogeosciences Discuss.*, 9, 14751-14793), we showed that the photochemical production of ammonium from refractory DON supported directly (through phytoplankton uptake) and indirectly (through food-web remineralization) 60% of the total pelagic primary production within the top 10 meters of the water column. Without the inclusion of the photoammonification process in our biogeochemical model, the observed vertical shape and levels of primary production could not have been achieved. In summer, photoammonification contributes substantially to the supply of nitrogen within the nitrogen-limited waters of the Beaufort Sea.

With respect to the microbial decomposition of riverine DON, Letscher et al. (2013) estimate that  $10.2 \times 10^9$  mol N yr<sup>-1</sup> of dissolved inorganic nitrogen (ammonium + nitrate) could be produced from the degradation (including photochemical and microbial pro-

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cesses) of terrigenous DON. This rate was obtained by using terrigenous DON decay constants and river water residence time. By subtracting the authors' value from our estimate of photochemically produced ammonium in July-August (ca.  $4 \times 10^9$  mol N), we would obtain a microbial contribution of  $6.2 \times 10^9$  mol N yr<sup>-1</sup>. This coarse calculation suggests that photo-chemical and microbial processes would fairly compare in their contribution to the production of dissolved inorganic nitrogen from riverine DON.

The text was hence modified as follows:

Page 13410 (line 3): "Applying this rate to this flux, rivers could indirectly supply  $3.9 \times 10^9$  mol N in the form of photochemically produced ammonium, which is fairly comparable to the dissolved inorganic nitrogen that could be produced through microbial degradation of riverine DON (e.g. Letscher et al., 2013). This photochemically produced ammonium exceeds the riverine nitrate flux in summer for the same 5 rivers (ca.  $2.6 \times 10^9$  mol N for the June-August period from the monthly flux estimates). For comparison, the June-August riverine ammonium flux summed up for the same 5 rivers is only  $0.6 \times 10^9$  mol N. Photoammonification of refractory riverine DON is potentially a greater source of nitrogen for phytoplankton production than the direct combined supply of nitrate and ammonium by rivers. In the Beaufort Sea, the photochemical production of ammonium from refractory DON would support directly (through phytoplankton uptake) and indirectly (through foodweb remineralization) 60% of the total pelagic primary production within the top 10 meters of the water column (Le Fouest et al., 2012)."

4) "The manuscript is unfortunately neither a review nor a really new research paper. For a review it is too superficial. A lot of similar information is already published, e.g., by McClelland et al. (2012)."

"The concluding remarks should summarize the most important new findings. However, they mostly support only our present knowledge. The future perspectives are also mainly citations of other publications but are not based on the results of this study."

In the present study, we compiled historical nutrients data to infer the fate of riverine

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nitrogen, phosphate and silicate within the Arctic Ocean. As mentioned above in our reply to comment #2, the link between the removal of riverine nitrate by phytoplankton and that of riverine phosphate and silicate, as well as the contribution of riverine nutrients with respect to nutrients of marine origin on marine biogeochemistry, were not the focus of recent studies. To that respect, we consider that this work is an original contribution to the recent publication effort made on that topic. By providing monthly-binned concentrations of riverine nutrients, we also provide the Arctic Ocean modeling community with data that could further be used to constrain rivers biogeochemical models.

5) “Results and discussion Is there any statistical significance between the monthly concentrations of the rivers and between the different rivers? The huge variation of the data may probably prevent any significance. This should be written somewhere. I am missing any statistics.”

Statistical analyses were performed on nutrients data to compare the monthly averages of nutrient concentrations. The results generally corroborate our statements, but in some cases differences were not statistically significant. We hence modified the text accordingly:

Page 13403 (line 9): “With regards to SRP, no significant seasonal trend can be drawn from the monthly-binned concentrations (Kruskal-Wallis test,  $P > 0.05$ ; R Core Team, 2012; Felipe de Mendiburu, 2012) except in the Pechora, Ob and Northern Dvina rivers (Kruskal-Wallis test,  $P < 0.05$ ), where concentrations drop during the freshet along with those of nitrate and silicate. Large differences in concentration can be found between rivers. For instance, wintertime silicate concentrations are significantly higher in the Yukon River (ca. 200 mmol Si m<sup>-3</sup>) than in any other river (Kruskal-Wallis test,  $P < 0.05$ ), and the seasonal variations are large (130 mmol Si m<sup>-3</sup>) compared with the Mackenzie River (ca. 25 mmol Si m<sup>-3</sup>), for example. Greater silicate concentrations in the Yukon River can be explained by the higher dissolved silica yield in the Yukon catchment (Dürr et al., 2011). Regarding SRP, wintertime concentrations are generally significantly higher in the Ob, Pechora and Northern Dvina rivers than in North-American

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rivers (Kruskal-Wallis test,  $P < 0.05$ ). The Ob River shows the highest SRP concentrations (up to 3 mmol P m<sup>-3</sup>) prior to and after the seasonal peak discharge in July. Apart from the Ob River, Eurasian rivers exhibit significant differences in DOC and DON concentrations throughout the year (Kruskal-Wallis test,  $P < 0.05$ ) but comparable maximum values in spring (ca. 1000 mmol C m<sup>-3</sup> and 20-30 mmol N m<sup>-3</sup>) (Kruskal-Wallis test,  $P < 0.05$ ). In August and September, the concentrations of DOC and DON in the Ob River are significantly higher than those of its North-American and Eurasian counterparts (Kruskal-Wallis test,  $P < 0.05$ ). The concentrations of PON and POC are also significantly higher than those of its Eurasian counterparts (Kruskal-Wallis test,  $P < 0.05$ ), but not significantly different from those of its North-American counterparts (Kruskal-Wallis test,  $P > 0.05$ ).”

6) “I propose to discuss ranges of PP calculated from the extremely variable nutrient data used for the mean concentrations.”

In order to account for the overall uncertainty on interpolated riverine nitrate concentrations, we computed monthly averages of nitrate  $\pm$  standard deviation for each river sampling location. Note that the calculations account for the data interpolation procedure on monthly-binned concentrations, as suggested by referee #1. We thereafter introduced a range of contribution of riverine nitrate to marine primary production in Table 2. The new Table 2 is given in the PDF file providing supplementary material. The text was hence adapted accordingly:

Page 13406 (line 24): “On an annual basis, the mean riverine nitrate contribution to AO PP<sub>new</sub> (<0.83%, Table2) is small relative to that of the Bering Strait inflow (<41.2%), in accord with previous studies (Gordeev et al., 1996; Tank et al., 2011). However, large differences are found across shelf seas (Fig. 7). Rivers contribute the least to PP<sub>new</sub> in the Barents Sea (0.04%), the Bering Shelf (0.11%) and the East-Siberian Sea (0.4%), and the most in the White Sea (6.7%). The Kara and the Beaufort seas show intermediate values (2.7-4.7%). Accounting for the higher range of uncertainty relative to nitrate concentrations makes this contribution to PP<sub>new</sub> rise to 6.7-8.3% in

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the White, Kara, Laptev and Beaufort seas. However, the 9 most important rivers taken into account in this study only represent a fraction of the total continental freshwater flow into shelf seas. Using total (i.e. river and groundwater) freshwater discharge estimates from literature, and assuming a proportional relationships with the mean nitrate flux given in Table 1, we can provide a coarse estimate of how much PPnew might be supported in shelf seas if all continental inputs of freshwater were accounted for. The total discharge (river + groundwater) is estimated to 1630 Km<sup>3</sup> yr<sup>-1</sup>, 802 Km<sup>3</sup> yr<sup>-1</sup>, and 267 Km<sup>3</sup> yr<sup>-1</sup> in the Kara, Laptev and East-Siberian seas, respectively (Gordeev et al., 1999). This is respectively 38%, 60% and 57% more than the freshwater discharge by the Ob and Yenisey rivers, the Lena River, and the Kolyma and Indigarka rivers. In the Beaufort Sea, the Colville River, second most important river after the Mackenzie River (285 Km<sup>3</sup> yr<sup>-1</sup>), has a discharge of ca. 15 Km<sup>3</sup> yr<sup>-1</sup> (source: USGS). Accounting for the total freshwater discharge in shelf seas, the mean riverine nitrate contribution to PPnew would rise to 3.8% (Kara Sea), 5.4% (Laptev Sea), 0.8% (East-Siberian Sea) and 5.3% (Beaufort Sea) but would still remain relatively low. Nevertheless, it could be much larger at local scale. Based on ocean color data, PPnew close to the mouth of Mackenzie River would reach up to 0.24 Tg C yr<sup>-1</sup> (S. Bélanger, pers. comm.). Here, riverine nitrate would meet, in average, 37% of phytoplankton nitrogen requirements. Note, however, that this contribution to PPnew is probably be less than estimated here as potential biological uptake in the estuarine transition zone (e.g. Emmerton et al., 2008) is not included in the calculation.”

7) “You may also mention the coastal nutrient input which should be as high as the riverine one.”

Coastal erosion plays a key role at local scale in the Arctic Ocean carbon cycle, representing an annual flux of organic carbon to the ocean of ca. 5.6x10<sup>6</sup> t C (Vetrov and Romankevich, 2010; Anderson et al., 2009). With respect to dissolved inorganic nutrients, there are, to our knowledge, no published studies providing fluxes resulting from coastal erosion for the Arctic Ocean. We only report a study from Savelieva et

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al. (Nutrients Seasonal Variability and Carbonate System Dynamics in the Laptev Sea coastal zone (2010), EGU General Assembly 2010, 2-7 May, 2010, Vienna, Austria, p. 13380, 2010EGUGA..1213380S), which suggests coastal productivity is enhanced by the supply of inorganic nutrients through coastal erosion.

8) “Introduction Page 13400, from line 7: This is a very simple definition of the origin of the nutrients. Rivers are partly more than 4000 km long and there are a lot of nutrient sources during the transport to the Arctic Ocean.”

The text was modified accordingly:

Page 13400 (line 12): “Riverine nitrate is derived from soil leaching (i.e. moved or dissolved and carried through soil by water) and terrestrial surface run-off (i.e. transported over land in the excess water when soil is infiltrated to full capacity). Soluble reactive phosphorus (SRP) originates from the weathering of crustal minerals (e.g., aluminium orthophosphate, apatite) and silicate from weathering of silicate and aluminosilicate minerals. Along the river path, the specificity of the lithological substrate and permafrost, and the terrestrial vegetation are important factors governing the riverine nutrients flux. Glacial or thermokarst lakes also control the nutrients transport from the soil to the river. Around delta lakes, inorganic nutrients can be enhanced via processes involving floodwater percolation among flooded vegetation and soils (e.g. Emmerton et al., 2008). Human activity may also provide nitrate and SRP in the White Sea, which has one of the most industrialized Arctic coastlines.”

9) “Table 1: I cannot find any data by Gordeev and Kravchishina (2009) listed as reference in Table 1. There are, for example, data for DIN (mostly nitrate) and phosphate in Dittmar and Kattner (2003) but because this is a review data may originate also partly from other authors like Holmes et al. (2000). You have to be more careful in compiling data in Table 1.”

Careful attention was paid to the source of the data used in this study. Note that we indicated no data for nitrate and SRP from Dittmar and Kattner (2003), because as

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specified in the authors' Table 1 (page 107) data were taken from Holmes et al. (2000, 2001), who used the same OGSNK/GSN dataset that we used in our study. We used annual export estimates given by Gordeev et al. (1996) in their Table 8 (page 683) for nitrate, SRP and silicate, whereas we used annual export estimates given by Gordeev and Kravchishina (2009) in their Table page 150 for DOC and POC. The two references will be separated in our Table 1.

10) "The manuscript is not carefully prepared. There are a lot of major and minor flaws in the text and the figures. Chemical definitions are sometimes incorrect. Figure legends are partly incorrect or not detailed enough, etc. The figures are not in a style for publication."

"Figures You are mixing SiO<sub>2</sub> and SiO<sub>4</sub> in the figures. Both are not the correct chemical formulas. The better term is silicate because there is no unequivocal formula; it exists in different chemical forms. The NO<sub>3</sub>:SRP molar flux ratio as well as other flux ratios are certainly also N:P (or Si:N) molar flux ratios and not nitrate to phosphate molar ratios."

"Figures are difficult to view. They are too small. The names of the rivers (only 2 for the Alaskan rivers) at the right side of the graphs should be placed somewhere else to increase the size of the graphs. The river names can be presented once on top of the graphs."

"Fig. 1-4 legends: There are sometimes only 4 Eurasian rivers, not always 7! I don't like the word "climatology" (here and throughout the ms). It is a big word just for simple concentrations. The same with "time course". This is a monthly flux estimate. No bar: no data or zero? Fig. 2: What means "month 2 to 14" for PON?? Fig. 3-5: Add g per month or year to the axis legend. I propose to add a map which shows the locations of the origin of the data used. Some locations are pretty far away from the river mouths."

According the referee's comment, NO<sub>3</sub>:SRP and SiO<sub>2</sub>:NO<sub>3</sub> molar flux ratios were replaced by their correct formulation, respectively N:P and Si:N molar flux ratios. Terms

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SiO<sub>2</sub> and SiO<sub>4</sub> in the figures were also replaced by silicate. In the text, mentions to NO<sub>3</sub>:SRP were replaced by N:P in pages 13405 (lines 27 and 28) and 13406 (line 3). Mentions to SiO<sub>2</sub>:NO<sub>3</sub> were also replaced by Si:N in page 13407 (line 4).

The term "climatology" will be either replaced by a more appropriate description such as "monthly binned nutrients concentrations" in legends and throughout the text or simply removed (e.g. page 13400, line 29).

Figures have been improved according to the referee's suggestions on plots size, errors on axis and labels. Legends have been also modified to account for referee's comments. New legends are given in the PDF file providing supplementary material.

The latitude and longitude of each sampling site is given in the Material and Method section (page 13401, lines 8-18) hence providing the reader information on its geographical location.

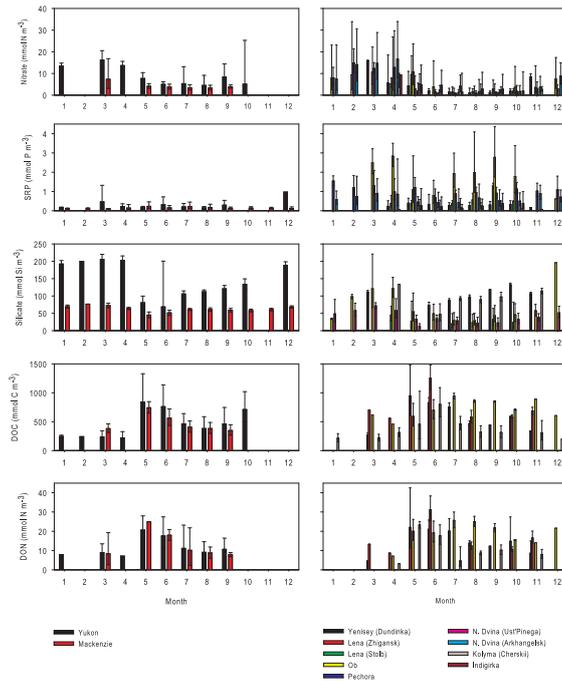
Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/9/C7720/2013/bgd-9-C7720-2013-supplement.pdf>

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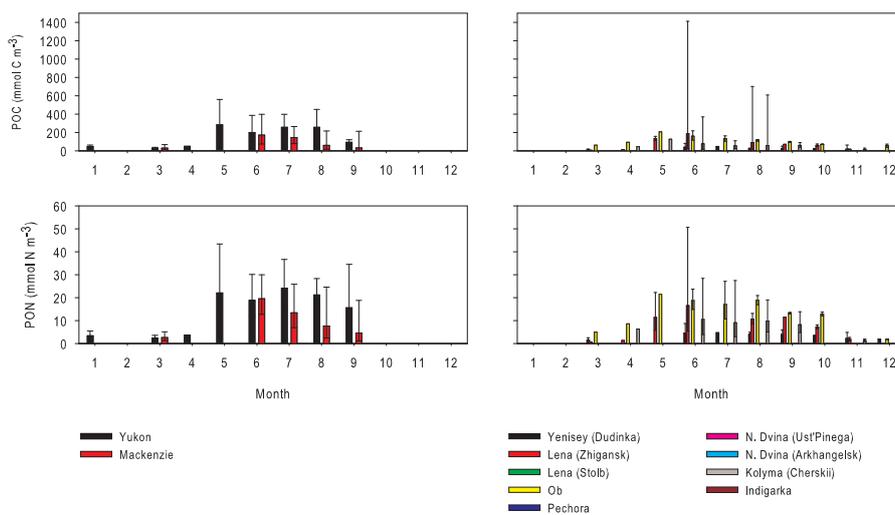
Interactive comment on Biogeosciences Discuss., 9, 13397, 2012.

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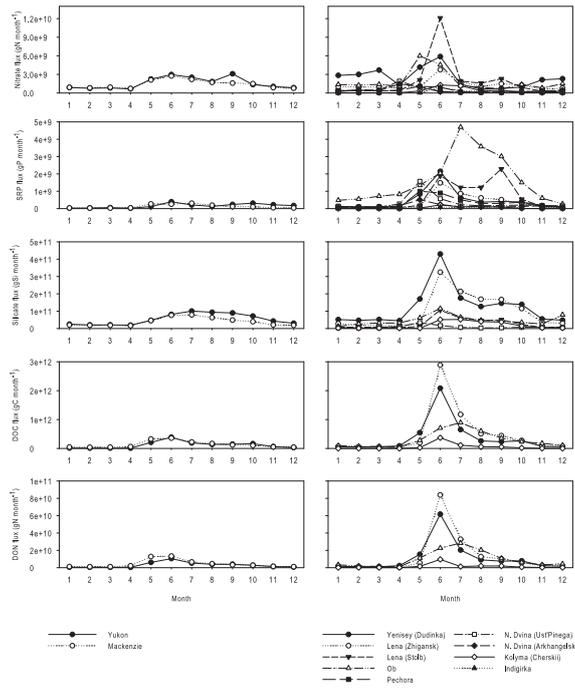
**Fig. 1.** Caption too long. Please refer to the PDF file providing supplementary material.

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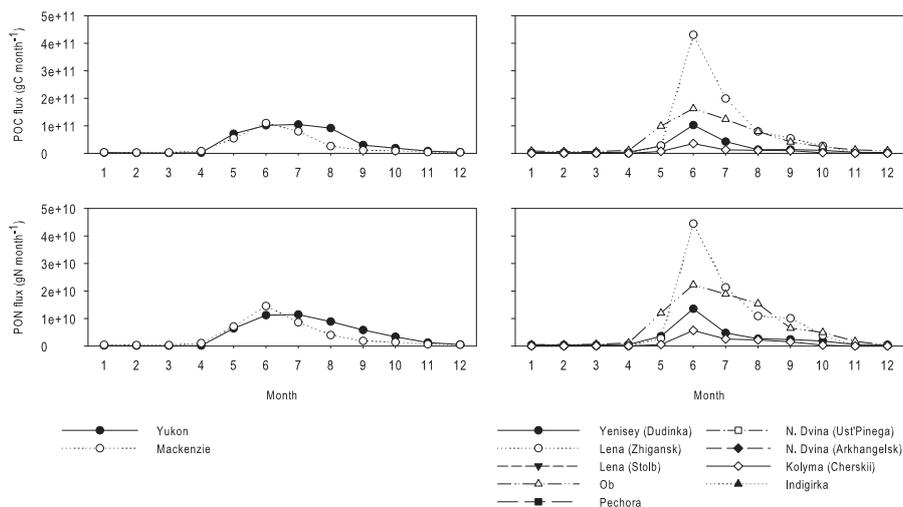
**Fig. 2.** Monthly-binned concentrations of riverine POC and PON for the North-American and Eurasian rivers. Bars with no standard deviations indicate single values. No filled bars indicate no data available.

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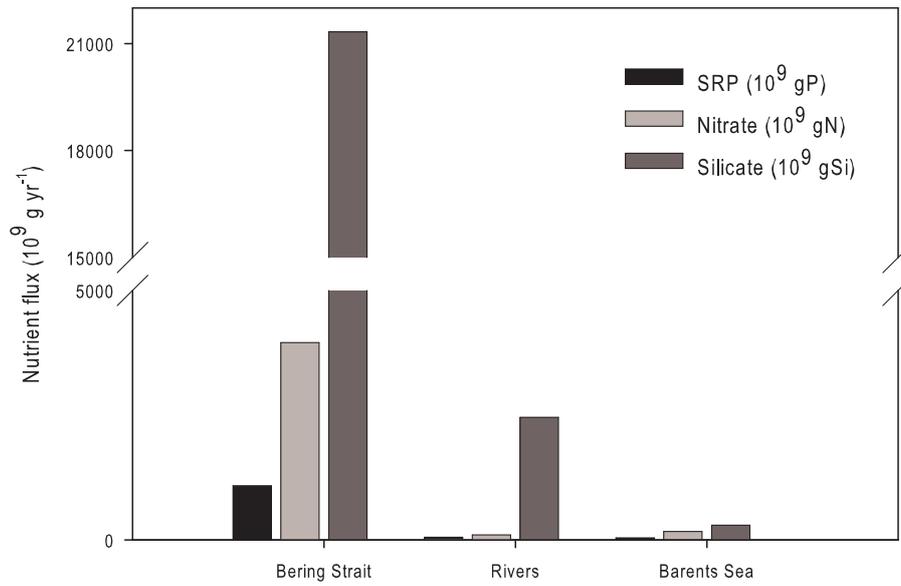
**Fig. 3.** Monthly flux estimates of riverine nitrate, SRP, silicate, DOC and DON for the North-American and Eurasian rivers.

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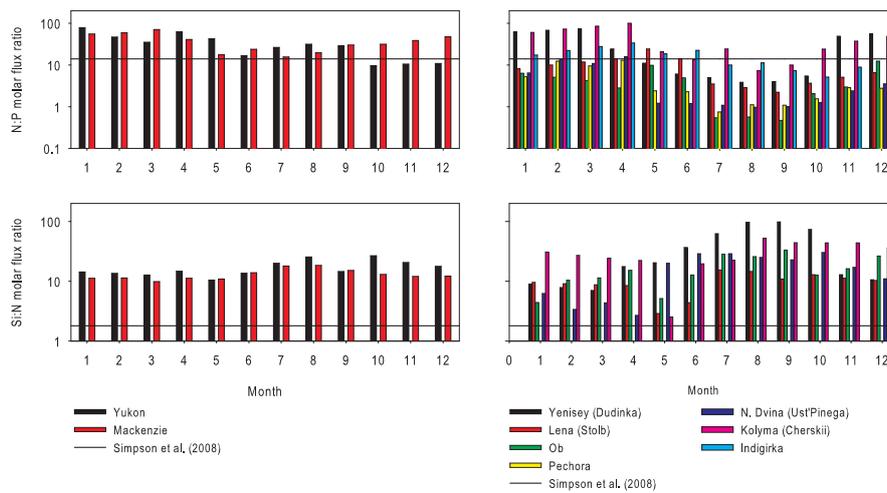
**Fig. 4.** Monthly flux estimates of riverine POC and PON for the North-American and Eurasian rivers.

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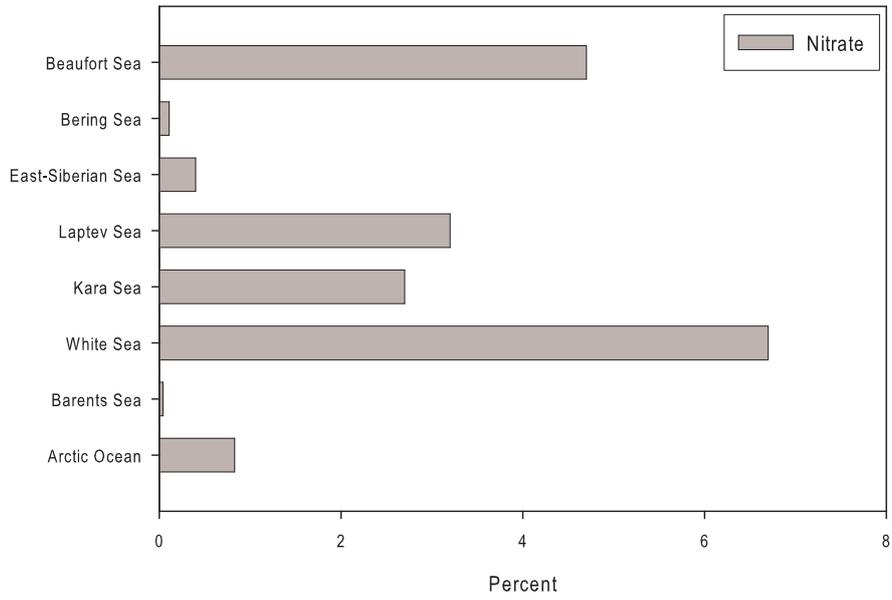
**Fig. 5.** Format issue. Please refer to the PDF file providing supplementary material.

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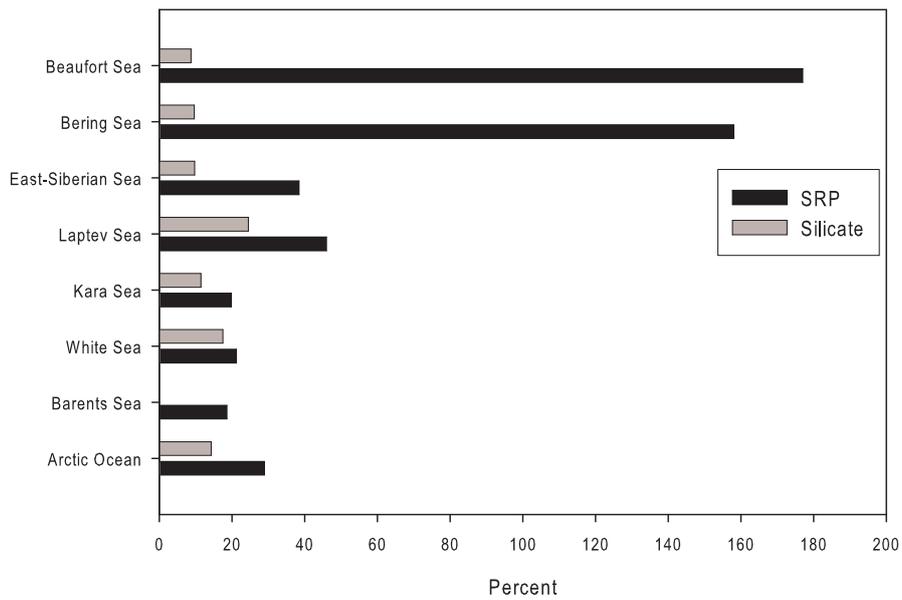
**Fig. 6.** N:P (top panels) and Si:N (bottom panels) molar flux ratios computed from monthly flux estimates for the North-American and Eurasian rivers.

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**Fig. 7.** Contribution of riverine nitrate to new primary production.

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**Fig. 8.** Fraction of riverine SRP and silicate consumed by phytoplankton in case all riverine nitrate is taken up. Note there were no silicate data for the Pechora River (Barents Sea).

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