

Review of the manuscript with ref. no. bg-2018-181, titled “**Distribution of Fe isotopes in particles and colloids in the salinity gradient along the Lena River plume, Laptev Sea**” by Conrad et al.

The present study of distribution of iron and its isotopes along the 600 km long Lena River freshwater plume in the Laptev Sea is aimed to understand the iron pathways to the Arctic Ocean. For this purpose authors have studied the Fe concentrations and its isotope distribution in three phases mainly, particulate, colloidal and truly dissolved. The study is important to understand how the riverine Fe is exported to open ocean. Authors have a very limited particulate Fe data (6 stations out of 10) and also colloidal Fe data (4 stations out of 10) presented in this study. Based on this small data set, I believe it is difficult to explain the Fe pathways. Apart from that, the truly dissolved iron isotope composition of any station is not given and explained. But in the objectives and in methodology they have mentioned about the truly dissolved iron isotope composition. It is difficult to understand the iron isotope fractionation during the estuarine mixing without truly dissolved iron isotope composition. There are many other shortcomings in the MS for example, very crucial analytical methodology for iron isotopes was not written clearly, units in the text and figures are different, citing the actual concentrations in the text are not correct etc. So I can't recommend the manuscript in its present form to publish in BGD journal. Please find the comments below as page wise.

Comments: Please find the comments and question in the font in bold.

[Page 1](#)

Line 8: **Number 3 for author affiliation is missing.**

Page 3

Line4-5: **third reference is not cited properly**

Line 18: This study presents Fe concentrations and Fe isotope compositions in the particulate, colloidal, and truly dissolved phase along the Lena River freshwater plume in the Laptev Sea.

I couldn't find the Fe isotope data for the truly dissolved phase.

Line 21: The main objectives were to study the distribution of Fe in the Lena River – Laptev Sea transect and the variations in the partitioning of Fe between the different size fractions, as well as to identify the impact of processes such as mixing, transformation, and removal by settling on the export of Fe to the deeper ocean.

To explain the above mentioned processes and partitioning of Fe between different size fractions truly dissolved phase studies are very important (both concentration and isotope composition). But the concentrations are reported only for 4 samples out of 10 samples and the isotope compositions have not reported for truly dissolved phase.

Page 5

Table 1: **unit for salinity?**

Line 1: **Which acid and what concentration was used for acidification?**

Page 6

Line 19: For element analysis, the water samples were diluted (2-200 fold) with 10 % HNO₃.

What grade acid was used and what are the blank levels?

Line 20: For Fe analysis, the samples were diluted by a factor of 50.

Fe concentrations at such a low level (nano-molar level) require a proper sample handling and pre-processing of samples in clean rooms etc. Authors have not mentioned anything about that and also what standard was used?

Page 7

Line 6-7: For the Fe isotope ratio measurements, water samples and digested filters were evaporated to dryness, and the residue was redissolved in 1 mL 9M HCl.

There is no data shown for the water samples in the whole manuscript, I really do not know how they wrote about water samples. They might have analyzed the water samples for Fe isotope composition but not included in the MS?

Line 7: Iron was separated from the matrix by ion exchange, with a recovery rate above 95%.

Details about the column chemistry is necessary. I wonder how come they haven't cited any paper for their methodology.

Line 14-15: We only discuss the $\delta^{56}\text{Fe}$ in this 15 study, although all Fe isotope data are reported in Table 3 including 2σ (n=4;).

Which standards were analyzed prior to the sample analysis? It is very important to report the standard values along with their precision and accuracy to make sure the presented data is of good quality.

Page 8

Table 3: Fe isotope data for the sediment and the particulate and colloidal phase.

The description in the legend is not followed in the table. The 2σ is high for the samples with highest concentrations.

Page 9

Line 1: **I really do not see the necessity for the supplementary material S2 in which only organic carbon data is given and rest is duplication of Table 1.**

Line 4: **Please cite the S2 after numbers. And change the concentration 300 to 320.**

Line 6-8: It has been shown that DOC is behaving conservatively during mixing between Lena River water and Arctic Ocean water along the sampling profile (Alling et al., 2010; Opsahl et al., 1999; Pugach et al., 2018).

Does sampling profile means the same transect of the present study?

Line 16: The pFe concentration decreased from 56 to 0.1 μM along the Lena River freshwater plume (Fig. 4).

Figure 4 do not have the same units of μM . It is good practice to use the same units in both table and figure for easy understanding.

Line 16-17: Between the inner and the outer plumes (i.e. between YS-10 and YS-9), the pFe concentration dropped to 0.9 μM , a loss of 98% of pFe.

I do not find any data either in table or in figure.

[Page 10](#)

Line 4-5: In the Laptev Sea close to the river mouth about 18% of the total OC was present as POC and this was apparently rapidly lost during mixing (Fig. 5)

Please put full stop after the sentence.

Line 11-12: The pFe concentrations found in the Laptev Sea close to the shore are higher than the average pFe concentration in the Lena River, but similar to the highest river values up to 32 μM (Hirst et al., 2017).

These values are similar to the pFe values of Hirst et al., 2017? Please state which phase it is?

Line 12-13: The cFe and dFe in the Lena River (Hirst et al., 2017) showed higher average concentrations (cFe: 1.5 μM ; dFe: 54 nM) that are similar to concentrations found in the Lena River – Laptev Sea transect.

I do not see any values close to 1.5 μM in the present study. They are only half of the reported values.

Line 24: We observed non-conservative mixing of pFe at salinities lower than 5 and conservative mixing at salinities higher than 5.

Please do cite the figure.

Line 26-28: Organic C hinders the coagulation of the particles during riverine transport, but in the estuarine mixing zone the negatively charged particles will react with seawater cations and form larger aggregates (Boyle et al., 1977).

What are these negatively charged particles?

[Page 11](#)

Line 1: freshwater plume is likely due removal of ...

Freshwater plume is likely due to removal of ...

Line 8: The truly dissolved Fe (<1kDa) concentrations along the freshwater plume are almost constant around 8nM

But the concentration in the river mouth is about 1 nM (S2). Is the value not correct?

Line 8-10: These observations are in accordance with previous studies in the Laptev Sea where dissolved Fe concentrations of >10 nM has been 10 reported (Klunder et al., 2012)

These Fe concentrations are from the surface? Because the concentrations may vary from surface to the bottom.

Line 27-29: In these areas, within the fully oxidized water column, the pFe phase show negative $\delta^{56}\text{Fe}$ values, while the dissolved phase generally shows higher values (Escoube et al., 2015, 2009; Ingri et al., 2006; Staubwasser et al., 2013; Zhang et al., 2015).

What does it mean by higher values? Author means positive $\delta^{56}\text{Fe}$?

Line 27-29: Hirst et al. (in prep.) show a seasonal dependence of the $\delta^{56}\text{Fe}$ composition of the dissolved fraction (colloidal and truly dissolved) in the Lena River, with summer flow $\delta^{56}\text{Fe}$ values higher than those of the continental crust, and spring flood $\delta^{56}\text{Fe}$ values of the dissolved phase lower than those of the continental crust.

Why the $\delta^{56}\text{Fe}$ composition varies with the summer and spring flood? The reason for such variations are not explained.

[Page 12](#)

Line 5: flood discharge, which has much higher DOC concentrations (1170 μM), their samples would plot on a different mixing line (Alling et al., 2010).

Font is smaller than the previous lines. Please make uniform font.

Line 7-9: The variations in the distributions of Fe between the different species in the iron-organic complexes are controlled by pH and OC concentrations (Neubauer et al., 2013; Sundman et al., 2013).

Authors have cited the importance of pH but have not given the pH data of the present study.

Line 12-13: Laboratory experiments of the oxidative precipitation of Fe(II) to Fe(III), which can occur in natural streams, show an overall fractionation factor of 0.9.

Authors have not given the reference for this fractionation factor. It is very important to see under which conditions the laboratory experiments were conducted?

Line 17-18: The Fe isotope variation along the plume and the composition of the surface sediment suggest that the chemically reactive ferrihydrite represent colloids and particles, with a negative $\delta^{56}\text{Fe}$ value, sedimenting close to the shoreline.

Which phase of the Fe isotope variation along the plume?

Line 17-18: The surface sediments in the shelf areas along the Laptev Sea have $\delta^{56}\text{Fe}$ values of -0.2‰ (Figure 6). This value results from the removal of particulate and colloidal Fe(II, III)oxyhydroxides from the water column and burial in the sediment.

Does the sedimentary resuspension and diagenesis do not affect the iron isotope composition of the sediment?

[Page 13](#)

Line 10-12: Climate warming is increasing discharge and accompanying OC and Fe from land to the ocean. Increasing the amount of colloidal and truly dissolved Fe, which is passing the estuarine mixing zone will lead to a higher Fe flux towards the Arctic Ocean.

It is very difficult to say that higher Fe flux towards the Arctic Ocean with this small data set.

[Page 22](#)

Figure 1 Legend: **Please give the full abbreviation of ESAS.**

[Page 23](#)

Figure 2 Legend: **Lena River transect is same as in the Figure 1? If yes please use uniform name.**

[Page 24](#)

Figure 3 Legend: **Please use the same terminology for the Lena River Laptev Sea transect. I do not see the outermost station YS-128 in the graph.**

[Page 25](#)

Figure 4 Legend: Particulate, colloidal and truly dissolved Fe concentrations along the Lena River freshwater plume. Concentrations of pFe 5 and cFe decreased along the salinity gradient, while the concentrations of truly dissolved Fe is almost constant. Note the logarithmic scale and the sharp decrease of pFe between the inner and the outer plume.

I do not see the Particulate Fe in the graph. The labels say that tFe. I'm not sure whether author mean this as particulate Fe. I did not find the stations YS-5, 7, 9 & 10 in the graph. The manuscript is based on this graph and there are only 6 stations particulate and colloidal Fe data and only four truly dissolved Fe data out of 10 stations. The units used in this figure are in nano-moles. But in the text, authors have discussed that data in micro-moles. I also find the difference in citing the exact values.

[Page 26](#)

Figure 5 Legend: **Please give unit for Salinity**

[Page 27](#)

Figure 6 Legend: **What is ESAS? I do not see truly dissolved Fe isotope data in this figure. But in the methodology it was mentioned.**