# Response to Anonymous Referee #1

We thank Referee #1 for the time and effort devoted to the review of our manuscript. Below we reproduce his/her comments and address them point by point. The reviewer's comments are in regular font black with our responses in blue. Text from the manuscript is shown in italics and changes are shown with deletions in strikethrough and additions in bold.

Conrad et al. (2018) conducted a systematic study on the distribution of Fe and its isotopes in different phases to investigate Fe cycling, fate of Fe transport to ocean and biogeochemical processes that control distribution and transport of Fe along the salinity gradient of Lena River plume, Laptev Sea. This study would definitely add to our understanding about the processes/mechanism that control Fe distribution, transport, association with different phases which is indeed important to constrain river input of Fe and $\delta^{56}$Fe (dissolved and particulate both) to the Arctic ocean. The topic of this manuscript is important to fill up the knowledge gap, up-to-date in current literature and very much within the scope of this journal. I appreciate this work and encourage publishing in this journal for the global scientific community. However, some of the conclusions reached here are tenuous and lacking sufficient explanations.

My final recommendation would be to publish this manuscript after major revision.

**General comments:**

I find difficulties in reviewing this manuscript as there is no continuous line number. What do these numbers indicate? Are these line number or paragraph number.

We used the technical instructions for MS Word of Biogeosciences to prepare the manuscript. Under "Manuscript preparation guidelines for authors", we downloaded the Copernicus Publications Word template. The line numbers in this template are set with "Restart at each page".

Number of samples analyzed for dissolved Fe conc. and d56Fe are too less to infer unequivocally about the processes. To discern the trend of loss/gain of Fe in highly transition zone like this, more high frequency samples are required, at least from the lower salinity region where redox sensitive elements show non-conservative behaviour.

We agree that it would be good to have a more detailed profile along the Lena River freshwater plume with more samples separated by ultrafiltration. The Lena River freshwater plume was sampled during the 50-days ISSS-08 field campaign. The number of samples, which can be obtained during sampling such a remote and inaccessible area is limited by logistical constraints, e.g. sampling permissions. Furthermore, the process of cross-flow ultrafiltration is quite time consuming and could not be carried out at all stations. In total, water from 15 stations were filtered with this methodology.

The samples from the Lena River freshwater plume might be limited, but they give insights into the different size fraction for isotopes and the riverine transport of Fe to the open ocean. The distribution of Fe between the three size fractions (particulate, colloidal, and truly dissolved) and their concentration range along the Lena River freshwater plume can be used to identify different estuarine processes, e.g. mixing, transformation, and removal by settling. The Fe isotope composition sheds light on the composition of Fe particles and colloids, which are transported into the Arctic Ocean. We think this information are valuable and potential future sampling regimes, with a more comprehensive sampling along the Lena River freshwater plume, will deepen the knowledge further and confirm our conclusions.

In this study pH and oxygen concentrations are important parameters which should have measured. Fe speciation/species distribution is very much depending on Eh-PH relationship. These are the basic parameters (O2 conc and pH) which are generally measured in any seawater sampling.
We added the pH and $O_2$ data for the stations where they have been measured to table 1. The data can be found on the PANGAEA website for download. The average pH for the water samples was 7.6 ± 0.1(1SD) and the oxygen saturation was 99.4±2.1%. Within the Lena River freshwater plume the pH ranged from 7.5 to 7.9. The methods are described in the supplement.

Sampling protocol for Fe should be as per the GEOTRACES protocol which is now being strictly followed by the oceanographic community. Author should mention in the manuscript whether it was as per the standard protocol.

Yes, the sampling was part of the Arctic GEOTRACES program. We clarified the information that the samples have been taken according to the GEOTRACES protocol and added the according reference.

*"The sampling transect is 600 km long, stretching from off the Lena River mouth across the Laptev Sea, and samples from ten stations were collected **after the GEOTRACES protocol** (Fig. 1, Fig. 2 and Table 1), (Cutter et al., 2010)."*

**Specific comments:**

**Affiliation:**

'3' superscript is missed in front of Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden. Please check.
Thank you for pointing out this mistake. It has been corrected.

*[3]Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden*

**Introduction:**

*"The riverine input of Fe is the most important contribution to the oceanic Fe budget (Raiswell and Canfield, 2012)".*

Authors should provide some information about other major sources of Fe e.g. atmospheric, hydrothermal and how much is supplied by the riverine input to global oceanic budget compared to other sources.
We added the other major sources of Fe to the global ocean (aeolian dust, sediment recycling, subglacial and iceberg meltwaters, hydrothermal fluxes) to the manuscript. Furthermore, we added information on the amount of Fe supplied by rivers.

*The riverine input of Fe **is one of** the most important contribution to the oceanic Fe budget, **as well as aeolian dust, recycled sediment, subglacial and iceberg meltwaters, and hydrothermal fluxes** (Raiswell and Canfield, 2012). **Estimations of filterable***

***Fe ($< 0.45$ µm) fluxes to the Global Ocean reveal that about 140 of a maximum of 4800 Gg yr$^{-1}$ is delivered by rivers (de Baar and de Jong 2001; Tagliabue et al. 2010). Particulate Fe supplied by rivers to the oceans is three orders of magnitude higher than filterable Fe (Martin and Meybeck, 1979).***

*"Different forms and sizes of Fe and OC can be separated using a variety of filtration techniques"*. What authors mean by sizes of Fe and OC. Please modify this sentence.

Changed towards:

*~~Different forms and sizes of Fe~~* ***Iron*** *and OC* ***in water samples*** *can be separated using a variety of filtration techniques.*

"*Carbon-iron cycling is complex, and stable Fe isotope data show that the isotopic compositions might be used to investigate chemical pathways for Fe and OC during weathering and estuarine mixing in the boreal-arctic region*"

Can Fe isotopes trace all the pathways of carbon? This sentence needs to be modified and be more specific.
We specified that we refer to OC, which is bound to Fe.

*Carbon-iron cycling is complex, and stable Fe isotope data show that the isotopic compositions might be used to investigate chemical pathways for Fe* ***and Fe bound*** *to OC during weathering and estuarine mixing in the boreal-arctic region (Dos Santos Pinheiro et al., 2014; Escoube et al., 2015, 2009; Ilina et al., 2013; Ingri et al., 2006; Mulholland et al., 2015; Poitrasson, 2006; Poitrasson et al., 2014).*

Para 20: "*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*".

No mentioned about Fe isotopes in the main objective. Please incorporate Fe isotopes here.

We added the following sentence to the introduction:

***Furthermore Fe-isotope analysis of the colloidal and particulate fraction should help us to gain a better understanding of the composition of Fe particles and colloids transported out in the Arctic Ocean.***

### 2.1 Study Area

"*Larch forests cover 72%..............*"

Is it typo here "Larch"?
No, we are referring to the tree type Larch, which is one of the most common tree species in Siberia.

### 2.2 Sampling and Processing

Table 1: what "dec" means. Is it typo? Please provide degree and minute.

We used decimal degrees in table 1. We changed it to degree and minute as published in the Cruise report of the ISSS-08. Furthermore, we corrected the depths data (as found in the cruise report) and the salinity data. It seems there occurred a mistake in the original table 1. Additionally, pH, oxygen saturation, and organic carbon data are now in table 1.

Why authors did not provide pH data. I don't see pH data here which is very much important in this study.

Added, please see comment above.

Table 1: In estuary, salinity from sea to land or vice versa, is expected to change linearly with distance. But, here I see that is not the case. Salinity is not changing linearly with distance. Is it because the plume system different from normal estuarine system?

We agree that the salinity data in table 1 seem to behave a little bit unconventional. The salinity is affected by flow patterns of the water and the distribution can rapidly change, which might cause non-linear behavior. The high increase from station YS-10 (5.37) to station YS-9 (8.15) followed by a drop at station YS-08 (5.29) indicates a non-linear behavior of salinity from land to sea. We plotted the salinity versus distance (Fig. R1) and found a broad linear relationship between the two parameters. Different others found similar salinity patterns in the Lena River freshwater plume (e.g. Gonçalves-Araujo et al. 2015). Alling et al. (2010) reports the border between the inner and the outer plume at 73°22'N and 129°60', which is between the two above named stations. They were using the same salinity CTD data as we use in this study. Furthermore, organic carbon and nutrients showed elevated concentrations at these locations. We could observe a trench underneath this station, which could be responsible for the upwelling of more saline, nutrient rich bottom water, which entrains into the Lena River freshwater plume.

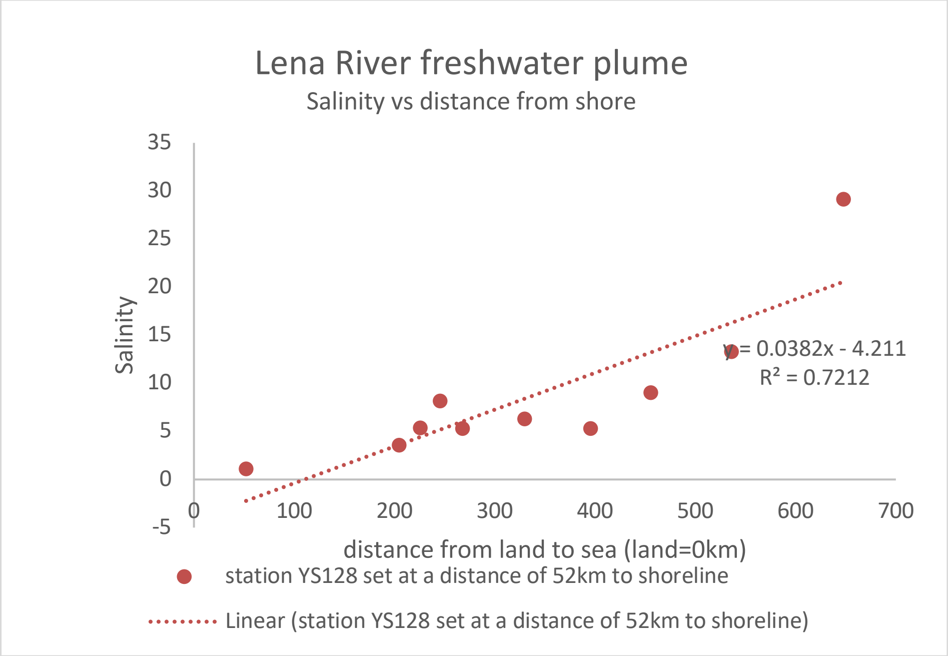


*Figure R1. Salinity versus distance between the stations from land to sea, with land at 0km and open sea at 700km. Series one (red) starts with station Ys-14 at 52 km, whereas series 2 (green) includes a forced 0 psu value at 0km. The red dots are hidden behind the green dots, as they are the same, except for (0psu,0km). The data reveal an acceptable linear relationship with R2 values of 0.72 (red) and 0.73 (green).*

### 2.3 Analytical Methods

A direct measurement of Fe in seawater/estuary water is very tricky. Matrix is big issue for direct measurements using ICP. Author did not provide sufficient proof that there was no matrix effect during the analysis. Any reference water (Sea or estuary) in which Fe conc. is known was measured during the analysis. Else, how do you check accuracy of the measurements? Good precision can be achieved even there is systematic error in the measurements. For example, if there was constant metrics effect in the measurements, you could get good precision but might have large offset from the actual value.

The measurements of Fe concentrations and Fe isotopes were carried out in cooperation with the analytical laboratory ALS Scandinavia AB by Ilia Rodushkin and Emma Engström. Elemental concentration and Fe isotope composition methodologies follow the description of several previous publications (e.g. Bauer et al. 2018; Ingri et al. 2000; 2004; 2006; 2014; 2018; Malinovsky et al., 2003; 2005; Wortberg et al., 2017). In the elemental analysis by ICP-MS methane addition to the plasma was used to decrease formation of oxide-based spectral interferences, improve sensitivity for elements with high first ionization potentials, and to minimize matrix effects. The analytical procedure was validated with different reference materials (SLRS-4 River Water CRM for Trace Metals, SLEW-2 Estuarine Water CRM for Trace Metals and NASS-4 open ocean water (all supplied from National Research Council, Ottawa, Canada) (Rodushkin et al., 2005; Rodushkin et al. 2016).

If I assume that there was no matrix effect as high matrix sample was sufficiently diluted, but there is no discussion on the detection of the instrument. Sample was diluted maximum up to 200 times. Average concentration in water (dFe) is 8 nmol (480 ppt). After dilution, conc level was 480/200 ≈ 2.4 ppt during the analysis. Here, detection limit of the instrument and blank are critical. Author should provide sufficient discussion on these aspects.

For the Fe analysis the samples were diluted 50-fold (p. 6 l. 21). 480/50 = 9.6 ppt.

The detection limit for Fe in seawater (35) at a dilution factor of 50 is 250ppt, but the majority of our samples had lower salinities, which improves the limit of detection. We added the information to the manuscript under 2.3 Analytical methods.

***The limit of detection for Fe in seawater (salinity 35) is 250ppt, the salinity in the analyzed samples were much lower, which decreases the limit of detection.***

Table 3: Why author did not provide concentration data of Fe in table 3.

We added the Fe concentration data to the manuscript. We took Table S3 from the supplements and implemented it as Table 3 to the manuscript. The former Table 3 (Fe isotope data) is now Table 4.

*"Replicated measurements of sample concentrations showed a precision of ±3% (n=5 4)".* Is it same for all three phases (e.g. water, colloids and sediments samples). If not, then author should separately report precision for all three types e.g. dissolved, colloids and particulate.

The precision was determined based on replicates of particulate samples.

In case of Fe isotope measurements, author only provided internal precision of the measurements (reported in table). What about external precision? To resolve natural variations in d56Fe, external precision should be the basis. I don't see any reference materials (e.g. sediments, waters) were analyzed for iron isotopes. This is important to check the quality of the Fe isotope measurements.

The Fe isotope method was validated using two reference materials from the US Geological Survey (A1 and P1) by Malinovsky et al. 2003. Furthermore, to assure the quality of the procedure and measurement the Fe standard IRMM-14 undergoes the entire separation process.

Author should provide slope with uncertainty in the triple isotope plot (Fig. S1.). The slope of the triple isotope should be compared with the theoretical slope to check whether they are same within their uncertainty.

We replaced the linear regression line in the three-isotope plot (Fig. S1) with the theoretical slope of kinetic fractionation. The slope of our data (0.59±0.11, 95%) falls within the theoretical slope of kinetic fractionation.

Total 10 samples were collected along salinity gradient but why only 4-6 samples were analyzed for iron isotopes. Number of samples are too less to infer about any trend of gain/loss in such transition system where chemistry is highly variable. Five data points in 600 km distance, in such transition zone, numbers of data points are not enough. Author should add more data, at least five other samples which they collected for this study but did not analyze.

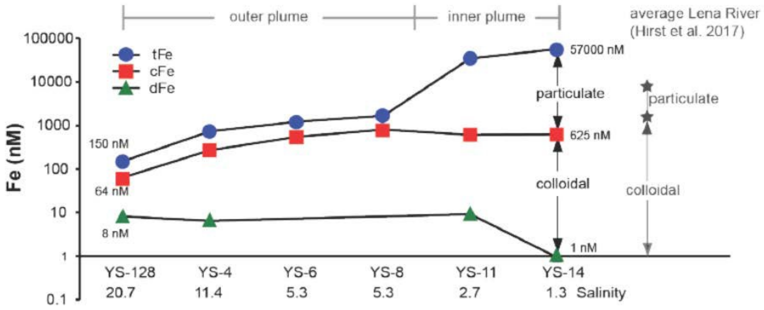
As described above the main focus of this cruise was to study the ESAS not the Lena River freshwater salinity plume. The here presented data set of the Lena River freshwater plume turned out to be very informative in turns of Fe transport to the ocean. We think this manuscript will help to improve the understanding about processes controlling the Fe distribution and transport of different size fractions along a salinity gradient, despite the limited number of samples. Unfortunately, we do not have samples available for further analyses.

### 3.2 Iron concentrations in the Lena River freshwater plume

"*The pFe concentration decreased from 56 to 0.1 µM along the Lena River freshwater plume (Fig. 4). 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 have strong apprehension about the estimation of particulate Fe loss. It should be reflected in its counter phase i.e. dissolved Fe. I don't see any concomitant increase in dissolved Fe. This decrease in pFe could be due to dilution by carbonate which is known in the estuarine system. Second possibility could be the grain size effect. Elemental concentration is highly effected by grain size variation. If Al data are available in these particulate samples, author can normalize pFe by Al and (pFe/Al) and can remove such effect.

Author cannot just interpret that these decrease pFe in terms of loss. Also other possibility should be discussed as I mentioned above.



The loss of Fe (particulate and colloidal) has been widely documented. Iron behaves non-conservatively during the mixing of freshwater and seawater and is removed to sediments (Boyle et al., 1977; Eckert and Sholkovitz, 1976; Gustafsson et al., 2000; Sholkovitz, 1978, 1976) since Fe-rich particles and colloids flocculate and settle in this mixing zone, which has been found in other estuaries before (Sholkovitz et al. 1978; Bale and Morris 1981; Mayer 1982; Forsgren et al. 1996; Zhou et al. 2003). Within the estuaries, Fe colloids and particles flocculate along the salinity gradient (e.g. Sholkovitz 1978). Dissolved Fe often contains a significant amount of Fe colloids (Sholkovitz et al. 1978; Pokrovsky et al. 2012; Conrad et al. under review). The destabilisation of Fe-rich colloids and particles (0.01 to 1 µm) by seawater cations are one of the major factors for the flocculation (Mosley et al. 2003; Gerringa et al. 2007; Escoube et al. 2009). Colloids flocculate into particles and particles will aggregate into larger ones, these flocculates sink to the surface sediment or might be transported out of the estuaries (Daneshvar et al. 2015). The loss of particles by settling seems to be the most obvious explanation, especially if the colloidal fraction does not increase. An increase of that fraction would suggest a dissolution of break-up of the particles.

To clarify the estuarine mixing processed we added references and additional text to the discussion.

*Estuarine processes, including flocculation and sedimentation* ***(e.g. Boyle et al. 1977; Sholkovitz, 1978****), are the primary cause for the sharp decrease of particulate and dissolved Fe concentrations along the transect from the river towards the open Arctic Ocean.* ***Within the estuaries, the destabilization of the Fe-rich colloids and particles by seawater cations causes flocculation along the salinity gradient (Mosley et al. 2003; Gerringa et al. 2007; Escoube et al. 2009) and successively sedimentation of the newly built flocculates (Daneshvar et al., 2015).***

….

*Organic C hinders the coagulation of the particles during riverine transport, but in the estuarine mixing zone the negatively charged* ***iron-bearing*** *particles will react with seawater cations and form larger aggregates (Boyle et al., 1977).* ~~*This results in flocculation and sinking*~~ ***The larger aggregates sink more readily*** *to the sediments in the Lena River – Laptev Sea transect and can thus explain the observed non-conservative behaviour (Martin et al., 1993).*

Aluminum data for the stations are available (Table R1). Similar to the Fe data the Al behaves non-conservative along the Lena River freshwater plume. The increasing Fe/Al ratio and decreasing Al/Ti ratio towards the open ocean suggests the loss of detrital material. The Fe/Ti ratio is enriched compared to the upper continental crust ratio, which indicates that a fraction of Fe is not associated to the Ti, which is concentrated in detrital material and considered to be immobile.
We added this table also to the supplement and added a reference to it to the manuscript.

*Table R1:Elemental concetration for the oarticulate phase (> 0.22 µm), as well as their ratios. Upper continental crust (UCC) composition after McLennan, 2001)*

| Station | Al µM | Ti µM | Fe µM | Fe/Al mol ratio | Fe/Ti Mol ratio | Al/Ti Mol ratio |
|---|---|---|---|---|---|---|
| YS128 | 0.091 | 0.003 | 0.086 | 0.954 | 32.324 | 33.866 |
| YS4 | 0.570 | 0.011 | 0.463 | 0.812 | 43.305 | 53.340 |
| YS6 | 1.106 | 0.020 | 0.670 | 0.605 | 32.894 | 54.332 |
| YS8 | 1.004 | 0.015 | 0.861 | 0.857 | 57.516 | 67.080 |
| YS11 | 96.406 | 0.964 | 33.970 | 0.352 | 35.252 | 100.042 |
| YS14 | 150.622 | 1.586 | 56.177 | 0.373 | 35.425 | 94.981 |
| UCC | 0.298 | 0.009 | 0.063 | 0.210 | 7.317 | 34.789 |

Why dissolved Fe conc are not reported for the sample YS-6 and YS-8 corresponding to other phases. I don't see in the plot.

At the stations YS-6 and YS-8 no ultrafiltration separation was performed. At these stations just normal membrane filtration with a cutoff of 0.22µm was performed.

There is no representative river water endmember here. I see dissolved Fe conc at 1.3 salinity is almost lower than the higher salinity. Is it gain/loss in the dFe profile? This should be discussed rather saying uniform conc.

We added an endmember for the truly dissolved Fe phase from Hirst et al. (2017). We did not include this value in the first version, as they used a different methodology. Hirst et al. (2017) use tubular dialysis membranes with cutoff sized of 1kDa in their study. The average DFe concentration in the Lena River is about 54 nM, which is about 6 times higher than the concentration measured in the freshwater plume. Therefore, we suggest a loss of the DFe concentration from the river to the estuary, where the DFe concentration seems to stabilize around 8 nM (excluding station YS-14). More detailed, the DFe concentration at station YS-14, closest to the coastline, was 1 nM, according to our measurements. This low concentration is surprising, when looking at the DFe in Lena River (about 54 nM, Hirst et al. 2017) and at the stations further out in the Lena River freshwater plume (about 8 nM, this study). Furthermore, earlier studies showed DFe concentrations in a similar range (3 to 10 nM in the upper 20 m in the Laptev Sea (Klunder et al. 2012) and 36 to 44 nM (Ob River) and 9 nM (Yenisey River) with almost constant concentrations along their estuaries (Dai and martin, 1995)). We cannot explain this low concentration at station YS-14, but the overall trend of this study (and earlier studies) is that the truly dissolved Fe concentration decreases from the Lena River to the Lena River freshwater plume and behaves almost constant along the freshwater plume.

We modified the discussion on the truly dissolved Fe phase with regards to the DFe river endmember.

*The DFe (<1kDa) concentrations along the freshwater plume are almost constant around 8nM (**except station YS-14, 1 nM**). **The average DFe concentration in the Lena River is about 54 nM (Hirst et al., 2017). These data suggest a loss of DFe at low salinities (<1.3) before the concentration stabilize around 8 nM in the Lena River freshwater plume**. These observations are in accordance with previous studies in the Laptev Sea where dissolved Fe concentrations of **3 to**10 nM **in the upper 20 m** has been reported (Klunder et al., 2012). It has also been reported that about 74 to 83% of the dissolved Fe is present in the truly dissolved phase in the Arctic Ocean (Thuróczy et al., 2011). Slagter et al. (2017) report dissolved Fe concentration of 2.6 nM in the Transpolar Drift, which is transporting surface water from Siberian great rivers, e.g. Lena River, across the Arctic Ocean into the Atlantic. Available evidence indicates that the Ob River similarly contributes Fe into the open Arctic Ocean. Along the Ob River, the DFe shows relatively constant DFe concentrations of 36–44 nM in the 10kDa fraction (Dai and Martin, 1995), which are somewhat higher than reported here for the Lena possibly due to a larger ultrafiltration cutoff size**. The overall trend of this and earlier studies suggests a loss of DFe from the Lena River to the Lena River freshwater plume and almost constant concentrations along the freshwater plume.***

There is no mention about how the %loss was estimated.

The loss of particulate Fe was calculated as follows (equation 1; Table R1). We added this information to the supplement material.

$$X = 100 - \left(\frac{100}{PFe_{Max}} * PFe_S\right)$$

With $PFe_{Max}$ = PFe station YS14 and $PFe_S$=PFe at each station.

*Table R1: Particulate Fe concentration and loss of Fe in % at each station.*

| **Station** | **Pfe** nM | loss of PFe % |
|---|---|---|
| **YS-128** | 86.47 | 99.84607 |
| **YS-4** | 462.57 | 99.1765732 |
| **YS-5** | - | |
| **YS-6** | 669.59 | 98.8080643 |
| **YS-7** | - | |
| **YS-8** | 860.90 | 98.4675112 |
| **YS-9** | - | |
| **YS-10** | - | |
| **YS-11** | 33970.07 | 39.5297964 |
| **YS-14** | 56176.55 | 0 |

## 4 Discussions

*"In the Laptev Sea close to the river mouth about 18% of the total OC was present as POC…..".*
In figure caption, it is mentioned 20%. Author should be consistent.

Thank you for pointing this out. We changed it to 18% in the figure caption. This number is more accurate.

In Fig. 5, legend is missing.

Thank you. We added the legend for colloidal and particulate Fe.

"*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)".* Put full stop after this sentence. Fig.5 represents pFe vs. salinity plot. I don't see OC data in Fig. 5. Or I am missing something here.

Of course, you are right there is no OC in Figure 5, we meant Figure 3. We changed this accordingly and added the full stop. Thank you.

"*The cFe concentrations are higher close to the coast and decreasing in the outer plume to values that are similar to cFe concentrations reported from further out in the Arctic Ocean."*
Please provide reference here.

We added Thuróczy et al., 2011as reference for Fe cocentrations in the Arctic Ocean.

Removal of dissolved Fe is common and reported in many estuaries. However, author highlighted here about the removal of particulate Fe (up to 98%). Has such removal processes reported in similar setting elsewhere, if any, please provide references.

We do not think that similar numbers have been published elsewhere. We observed a loss of 90% of particulate Fe in two estuaries in the northern Bothnian Bay (unpublished data). Many authors (e.g. Sholkovitz et al. (1978); Escoube et al. (2009)) concentrate on the flocculation and removal of dissolved Fe (> 0.22µM). For the dissolved phase removal of >95% at salinities of 15 have been found (Sholkovitz et al. 1978).

“*The loss of Fe-OC aggregates close to the shoreline might also cause a great loss of phosphorous….”*

This is a speculation.

We agree that this is speculative, but other authors showed that the sediments of lakes and coastal seas contain Fe-oxide bound P and that Fe is essential for the sedimentation of P (Slomp et al. 2013) We added this information to the manuscript, as we think it supports the idea of Fe-OC aggregates as sink for P.

***Slomp et al. (2013) showed that Fe concentrations are likely to affect the sedimentation of organic matter and P in sediments of lakes and coastal seas. Therefore,*** *the loss of Fe-OC aggregates close to the shoreline might also cause a great loss of phosphorous and thus contribute to the suggested “rusty carbon sink” (Lalonde et al., 2012; Salvadõ et al., 2015).*

“The measured $\delta_{56}$Fe compositions in the Lena River plume are broadly similar to those reported in previous studies in other arctic/subarctic regions.”

Please provide references here.

We added the references to this sentence (e.g. Escoube et al. 2009; Staubwasser et al. 2013).

“*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). …………………...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*.”

As I mentioned that pH data is indeed important to explain variation processes of Fe chemistry. But, I don’t see pH data.

We added the pH data of the Lena River freshwater plume. The pH ranges from 7.5 to 7.9. In the studies of Neubauer et al (2013) and Sundman et al. (2013) the chemistry of Fe in much lower pH are discussed. We intended to use these references to describe the origin of the different Fe isotope compositions in the Lena River freshwater plume. Neubauer et al. (2013) and Sundman et al. (2013) showed the importance of pH variations in the source area of rivers. The change of 0.4 ph units in the fully oxidized freshwater plume has most likely no influence on the Fe isotope composition. The change of pH might in fact increase the possibility to form solid-phase ferric iron oxides or hydroxides within the estuaries (e.g. Daneshvar 2015).

**Conclusion:**

"*In the outer part of the plume, the pFe and cFe concentrations are almost equal, as more than 99% of the total Fe is lost. The loss of pFe, most likely in the form of chemically reactive ferrihydrite, results from increasing ionic strength, due to increasing salinities, which promotes flocculation".*

I am not convinced about the loss up to 99% of the total Fe. Secondly, without Eh-pH data, reason for Fe removal provided is not sufficient.

Flocculation of dissolved and particulate Fe has been shown by several authors. Iron behaves non-conservatively during the mixing of freshwater and seawater and is removed to sediments (Boyle et al., 1977; Eckert and Sholkovitz, 1976; Gustafsson et al., 2000; Sholkovitz, 1978, 1976) since Fe-rich particles and colloids flocculate and settle in this mixing zone (Sholkovitz, 1978).

We rephrased some sentences of the discussion and added some text for the better understanding.

*We observed non-conservative mixing of **P**Fe at salinities lower than 5 and conservative mixing at salinities higher than 5 (Fig. 5). Recent studies showed that the majority of PFe (70±15%) coming from the Lena River is in the form of chemically reactive ferrihydrite (Hirst et al., 2017). Organic C hinders the coagulation of the particles during riverine transport, but in the estuarine mixing zone the negatively charged **iron-bearing** particles will react with seawater cations and form larger aggregates (Boyle et al., 1977). ~~This results in flocculation and sinking to~~ **The larger aggregates sink more readily to** the sediments in the Lena River – Laptev Sea transect and can thus explain the observed non-conservative behaviour (Martin et al., 1993). This process is a common feature for Fe that is observed in other estuaries and is responsible for at least 80% loss of "dissolved" riverine Fe (Boyle et al., 1977; Figuères et al., 1978; Guieu et al., 1996; Windom, H. L., Beck, K., Smith, 1971). The large amount of PFe (99%) lost in the inner Lena River freshwater plume is likely due to removal of chemically reactive ferrihydrite, which is the main form of PFe in the Lena River. Furthermore, it has been shown that about 20% of OC in the Eurasian Arctic Shelf is bound to reactive Fe phases (Salvadõ et al., 2015). It has also been shown that part of the ferrihydrite might be transported via surface attachment to POC in a network of organic fibrils (Hirst et al., 2017). The attachment of POC to the ferrihydrite possibly reduces the density of Fe-oxyhydroxides (Passow, 2004), allowing both POC and **P**Fe to be transported into the Arctic Ocean, where they are present at about 2% of their initial concentration in rivers. Concentrations **of PFe at salinities >5 and CFe along the whole salinity gradient show a linear correlation with salinity**, suggesting that these particles and colloids are less affected by changes in ionic strength and therefore might be mainly in the form of Fe-oxyhydroxides. **Gregor et al. (1997) showed that the optimal range for cationic flocculation is a pH between 6 and 7. At higher pH, more cations are needed for achieve the same efficiency of flocculation. Anyhow, Asmala et al. (2014) showed that the pH range is important at salinities below 1-2, but at higher salinities the pH is negligible. Furthermore, they showed that it is likely that high Fe concentrations are a more significant factor and will yield to the same flocculation rates.***

Fe isotope data together with conc, can be used to quantify Fe removal. Author should provide some quantification of isotope fraction based on the isotope mass balance in three phases.

Author also should provide some discussion of the isotope fraction processes e.g. the Rayleigh/batch fractionation. Which processes is dominant here.

The isotope mass balance for the three phases can be done as follows:

$$(PFe * \delta^{56}PFe) + (CFe * \delta^{56}CFe) = (TFe * \delta^{56}TFe)$$

with the truly dissolved being a negligible term. This is a good way to check on the method, if the equation is true. In case it is not true the sample water measured for the total Fe concentration contained more or less particles and colloids than the filtered sample water. We cannot use this equation to check on the methodology as we do not have measured concentrations and / or isotopic compositions of unfiltered water samples.

The isotope difference between the colloidal and particulate phase are not due to fractionation between the colloids and particles, as the total Fe concentration changes along the Lena River freshwater plume. If the concentration would be stable along the plume fractionation between the two phases could be considered. Furthermore, the flocculation of CFe to PFe would not change the Fe isotope composition. The difference in the isotopic composition between the colloids and the particles is based on different sources of the particles and colloids in the Lena River system. The Fe isotope composition in the estuary is inherited from the river. We hope that our improved discussion clarifies these topics.

*"Climate warming is increasing discharge and accompanying OC and Fe from land to the ocean….."*

This conclusion is unsupported.

We deleted this sentence, as it is no conclusion we can justify with our limited data set.

References added to the manuscript and the response to the reviewer:

Andersson, Leif; Jutterstrøm, Sara (2008): Seawater carbonate chemistry and nutrients measured on water bottle samples during the International Siberian Shelf Study 2008 (ISSS-08) in the Laptev, East Siberian and Chukchi Seas. Department of Chemistry, University of Gothenburg, PANGAEA, https://doi.org/10.1594/PANGAEA.715045

Asmala, E., Bowers, D., Autio, R., Kaartokallio, H., Thomas, D.N., 2014. Qualitative changes of riverine dissolved organic matter at low salinities due to flocculation. J. Geophy. Res.: Biogeosci. 119,1919–1933, doi:10.1002/ 2014JG002722.

Cutter, G., Andersson, P., Codispoti, L., Croot, P., Francois, R., Lohan, M., Obata, H., Rutgers, M. (2010). Sampling and sample-handling protocols for GEOTRACES cruises, [Miscellaneous]. 10013/epic.42722

de Baar, H.J.W. and de Jong, J.T.M, 2001. Distributions, sources and sinks of iron in seawater. In Turner D.R., Hunter, K.A. (Eds) Biogeochemistry of Iron in Seawater. Wiley, New York, pp. 123-253.

Dudarev,O., 2008. Cruise report International Siberian Shelf Study 2008 (ISSS-08). Swedish Knut and Alice Wallenberg Foundation, the Far-Eastern Branch of the Russian Academy of Sciences, the Swedish Research Councli, the Russian Foundation for Basic Research, NoAA, and the Swedish Polar Research Secretariat, Bremerhaven, PANGAEA. Hdl:10013/epic32714Gerringa et al. 2007;

Gregor, J. E., C. J. Nokes, and E. Fenton (1997), Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation, Water Res., 31(12), 2949–2958.

Homoky, W.B., Severmann, S., Mills, R.A., Statham, P.J., Fones, G.R., 2009. Proe-fluid Fe isotopes reflect the extent of benthic Fe redoc recycling: Evidence from continental shelf and deep.sea sediments. Geology 37, 751-754. https://doi.org/ 10.1130/G25731A.1

Ingri, J., Conrad, S., Lidman, F., Nordblad. F., Engström. E., Rodushkin. I., Porcelli. D., accepted. Iron pathways in the boreal landscape: role of the riparian zone. Geochim. Cosmochim. Acta

Martin, J.M., and Meybeck, M., 1979. Elemental mass-balance or material carried by major world rivers. Mar. Chem. 7, 173-206.

Mosley, L.M., Hunter, K.A., Ducker, W.A., 2003. Forces between colloid particles in natural waters. Environ. Sci. Technol. 37, 3303-3308. https://doi.org/ 10.1021/es026216d

Radic, A., Laca, F., Murray, J.W., 2011. Iron isotopes in the seawater of the equatorial Pacif Ocean: New constraints for the oceanic iron cycle. Earth Planet. Sci. Lett. 306, 1-10. https://doi.org/ 10.1016/j.epsl.2011.03.015

Rodushkin, I., Engström, E., Baxter, D., 2010. Sources of contamination and remedial strategies in the multi-elemental trace analysis laboratory. Anal. Bioanal. Chem. 396, 365-377. DOI 10.1007/s00216-009-3087-z

Rodushkin, I., Pallavicini, N., Engström, E., Sörlin, D., Öhlander, B., Ingri, J., Baxter, D.C., 2016. Assessment of the natural variability of B, Cd, Cu, Fe, Pb, Sr, Tl, and Zn concentrations and isotopic compositions in leaves, needles, and mushrooms using single sample digestion and two-column matrix separation. J. Anal. At. Spectrom. 31, 220-233. https://doi.org/10.1039/C5JA00274E Severmann, S., McManus, J., Berelson, W.M., Hammond, D.E., 2010. The continental shelf benthic iron flux and its isotope composition. Geochim. Cosmochim. Acta 74, 3984-4004. https://doi.org/ 10.1016/j.gca.2010.04.022

Slomp, C.P., Mort, H.P., Jilbert, T., Reed, D.C., Gustafsson, B.G, Wolthers, M., 2013. Coupled dynamics of iron and phosphorous in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane. PLoS ONE 8(4): e62386. doi:10.1371/journal.pone.0062386

Tagliabue, A., Bopp, L., Dutay, J.-C., Bowie, A.R., Chever, F., Jean-Baptiste, P., Bucciarelli, E., Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., Jeandel, C., 2010. Hydrothermal contribution to the oceanic dissolved iron inventory. Nature Geoscience 3, 252-256. https://doi.org/10.1038/ngeo818