Review of the manuscript bg-2018-181 “*Distribution of Fe isotopes in particles and colloids in the salinity gradient along the Lena River plume, Laptev Sea*” Conrad et al. (2018).

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 δ^{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.

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 higlighly 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.

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.

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.

Specific comments:

Affiliation:

‘3’ superscript is missed in front of Department of Geosciences, Swedish Museum of Natural History, Stockholm, Sweden. Please check.

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.

“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.

“*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.

Para 20: “*The main objectives were to study the distribution of Fe in the Lena River – Laptev Seatransect 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.

2.1 Study Area

“*Larch forests cover 72%.............”*

Is it typo here “Larch”?

2.2 Sampling and Processing

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

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

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?

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.

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 analaysis. Here, detection limit of the instrument and blank are critical. Author should provide sufficient discussion on these aspects.

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

"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.

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.

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.

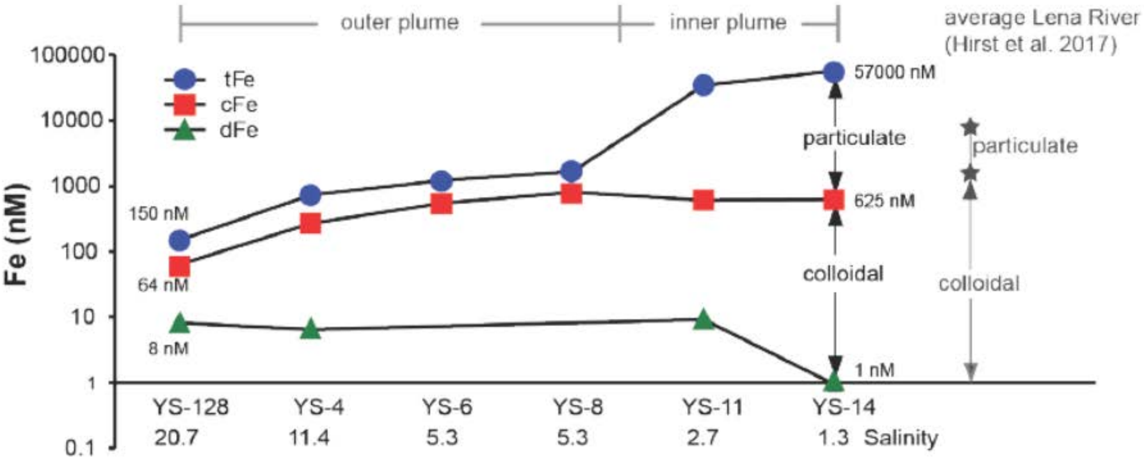
Total 10 samples were collected along salinity gradient but why only 4-6 samples were analyzed for iron isotopes. Number of samples are too less to infer about any trend of gain/loss in such transition system where chemistry is highly variable. Five data points in 600 km distance, in such transition 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.

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.



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.

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.

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

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.

In Fig. 5, legend is missing.

“*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.

“*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.

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

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

“The measured δ_{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.

“*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.

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 30 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 upto 99% of the total Fe. Secondly, without Eh-pH data, reason for Fe removal provided is not suffiecient.

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.

“Climate warming is increasing discharge and accompanying OC and Fe from land to the ocean…..”
This conclusion is unsupported.