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 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.

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.

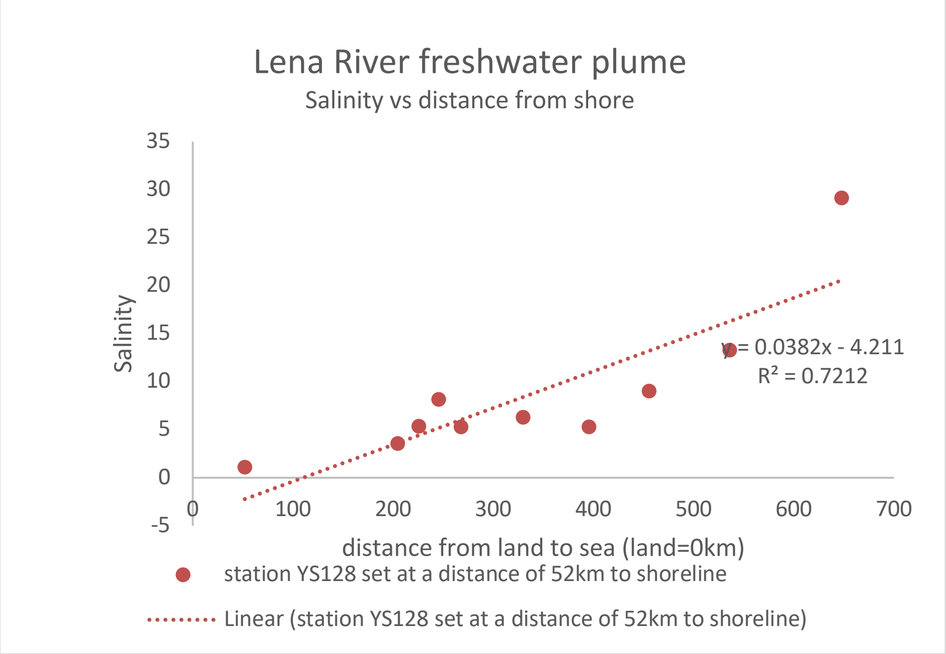


Figure R1. Salinity versus distance between the stations from land to sea, with land at 0km and open sea at 700km. Series one (red) starts with station Ys-14 at 52 km, whereas series 2 (green) includes a forced 0 psu value at 0km. The red dots are hidden behind the green dots, as they are the same, except 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.

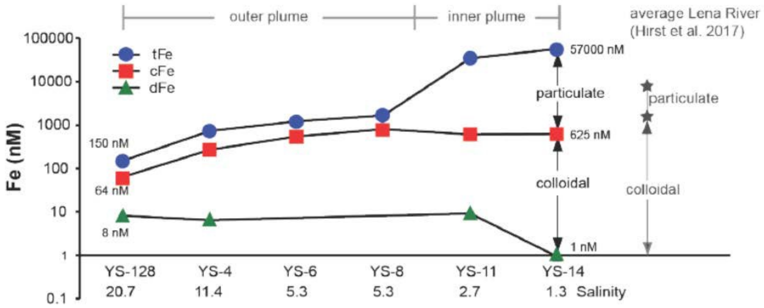
As described above the main focus of this cruise was to study the ESAS not the Lena River freshwater salinity plume. The here presented data set of the Lena River freshwater plume turned out to be very informative in turns of Fe transport to the ocean. We think this manuscript will help to improve the 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 δ56Fe 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

Response to Anonymous Referee #2

We thank Referee #2 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 green. Text from the manuscript is shown in italics and changes are shown with deletions in strikethrough and additions in bold.

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 short comings 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.**

Thank you for pointing out this mistake. It has been corrected.

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

Page 3

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

The reference has been removed, as it just provides measurements from other studies.

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.

That is correct. We do not present Fe isotope data for the truly dissolved phase. We rephrased the sentence. The Fe concentration of the truly dissolved phase is too small to achieve reliable Fe isotope data.

This study presents Fe concentrations and Fe isotope compositions in the particulate ***and*** *colloidal phase along the Lena River freshwater plume in the Laptev Sea,* ***as well as Fe concentrations in 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.

This concern was also raised by reviewer #1.

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.

The reason that there are no Fe isotope values reported is that they have not been measured during this project. The samples have been measured at ALS Scandinavia AB, where we have a cooperation with I. Rodushkin and E. Engström. The minimum amount of Fe concentration in a sample should be 0.1 mg/L to measure reliable Fe isotope concentrations.

Page 5

Table 1: **unit for salinity?**

The salinity is displayed in the practical salinity scale. The International Association for the Physical Science of the Ocean (IAPSO) recommends that the practical salinity is expressed by dimensionless numbers only. We added the information that the salinity is expressed on the Practical Salinity Scale to the table caption.

Salinity is based on the Practical Salinity Scale PSS-78.

Line 10: **Which acid and what concentration was used for acidification?**

We added the missing information. The water samples were acidified with ultrapure HNO_3.

All water samples were stored in acid-cleaned polyethylene (PE) bottles and acidified ***with ultrapure HNO_3 to a pH <2****, and all nitrocellulose filters (0.22µm, Millipore®) were stored at -18°C until further analysis (Ödman et al., 1999).*

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?

We used high purity Suprapure ® acids during the whole sample treatment and the analysis. The information can be found in the second sentence under 2.3 Analytical Methods.

Rodushkin, Engström, and Baxter (2010) summarized the routines at ALS Scandinavia AB and reported concentrations of Fe in Milli_Q water with 1% HNO_3 after several purification steps (3.6 ng/L (SD: 0.7 ng/L).

High purity Suprapure® acids were used throughout sample treatment and analysis.

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?

We added the following information to the text.

All sample manipulations were performed in a clean laboratory (Class 10 000) by personnel wearing clean room gear and following all general precautions to reduce contamination (Rodushkin, Engström, and Baxter, 2010).

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).

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?

When we wrote water samples we were referring to the colloidal fraction (1kDa-0.22µM). We added additional information (under 2.3 Analytical methods) to the elemental analysis, where the colloidal and truly dissolved phase are the water samples and to the Fe isotope analysis, where just the colloidal phase was measured. Please see text below.

For element analysis, the water samples ***(colloidal: 1 kDa to 0.22µm; truly dissolved: <1 kDa)*** *were diluted (2-200 fold) with 10 % HNO_3.*

For the Fe isotope ratio measurements, water ***samples (colloidal: 1 kDa to 0.22µm)*** *and digested filters were evaporated to dryness, and the residue was re-dissolved in 1 mL 9M HCl.*

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.

Thank you for pointing out this flaw. Apparently, we missed to cite the column chemistry. We added some additional text about the column chemistry to the method section. Please see below.

Iron was separated from the matrix elements by using an AG-MP-1M ion-exchange resin (Ingri et al., 2006; Rodushkin and Ruth, 1997). After the sample was loaded, the matrix was washed with 9.6 M HCl, and Cu was eluted with 8 ml 5M Cl. Afterwards, Fe was eluted with 6 ml 2 M HCl and can be used for further steps (Rodushkin et al. 2015). After evaporating to dryness, 50 µL of concentrated HNO_3 was pipetted directly to the residue followed by the addition of 5 mL MQ-water. Samples with high Fe content were diluted with 0.2M HNO_3 to a concentration of 2 mgL^{-1} in the measurement solutions. Low Fe concentration water samples were further diluted to 40-50 μgL^{-1} and measured using high-efficiency desolvation nebulizer (Aridus) in a separate analytical sequence.

Line 14-15: We only discuss the δ56Fe in this 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.

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 as a known sample.

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 2 σ is high for the samples with highest concentrations.

We changed the caption of the figure to make it easier for the reader to follow the manuscript. Furthermore, we would like to make you aware of the fact, that the former table 3 is now table 4. The second reviewer suggested to include a table with the Fe concentration to the manuscript, which can be found in table 3.

Table 4: Fe isotope data for ~~the sediment and~~ the particulate and the colloidal phase, ***as well as Fe isotope data for the surface sediments.***

We cannot see a correlation between high Fe concentrations and high 2σ, which we would expect if there is any systematic error in the measurements. Furthermore, we checked if we could find a relationship between DOC and 2 σ, as it can occur that Fe isotope measurements can be problematic In samples with high organic carbon contents. We could not find a correlation between the two parameters, why we would exclude problems caused by DOC at the Fe isotope measurements.

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.**

We agree and included the organic carbon concentrations into Table 1 of the manuscript. Furthermore, we added pH and oxygen saturation values. The new supplement consists of Fig. S1, which contains the three-isotope plot and Tab. S2, which includes all Fe isotope values.

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

Changed accordingly. We refer to Table 1, as we moved the DOC data to that table.

*The DOC concentrations show a small variation of between 3**2**0 and 440 µM in the surface waters of the inner and outer plume (**Tab. 1**; Fig. 3).*

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?

The references Alling et al. (2010) and Pugach et al. (2018) use samples from the same cruise (ISSS-08) in their studies. So yes, they are from the same transect as data from this study. Opsahl et al. published data from the Arctic Ocean, e.g. in the Laptev Sea. These samples were not taken at the same place as samples from the ISSS-08 cruise.

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.

Thank you for pointing this out. We changed it accordingly throughout the text, tables and figures towards µM. We decided to keep the truly dissolved Fe concentration in nM.

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.

We understand the confusion. Indeed we do not have measurements at station YS-9 or YS-10. In an earlier version of Fig. 4, we included all stations of the profile for a better visualization where each station is located. Then it occurred that the Fe drops between these two stations. We changed the station numbers in the text towards station YS-11 and YS8.

Between the inner and the outer plumes (i.e. between ***YS-11*** *and* ***YS-8****), the PFe concentration dropped to 0.9 µM, a loss of 98% of PFe. The CFe concentration decreased from 0.6 to 0.1 µM along the freshwater plume, a loss of about 85% CFe (Fig 4).*

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.

We added the full stop. Furthermore, we referred to the wrong figure, which we changed.

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. ***3).***

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?

Yes, we were referring to the PFe values in the Lena River, published by Hirst et al. (2017). We added this information.

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 ***PFe*** *river values up to 32 µM (Hirst et al., 2017).*

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.

That is correct, we changed the sentence. We furthermore added some explanation, why the concentration of CFe and DFe is higher in the Lena River than in the Lena River freshwater plume.

The CFe and DFe in the Lena River (Hirst et al., 2017) showed higher average concentrations (CFe: 1.5 µM; DFe: 54 nM) tha~~nt are similar to~~ concentrations found in the Lena River – Laptev Sea transect. ***Most likely some of the CFe and DFe from Lena River already flocculated at salinities below 1, where the first sample of our sampling profile was taken (YS-14).***

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.

We added the reference to Figure 5 here.

We observed non-conservative mixing of PFe at salinities lower than 5 and conservative mixing at salinities higher than 5 ***(Fig. 5)****.*

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?

We added the information.

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).*

Page 11

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

Freshwater plume is likely due *to* removal of …

Added to the text.

The large amount of pFe (98%) lost in the inner Lena River freshwater plume is likely due ***to*** *removal of chemically reactive ferrihydrite, which is the main form of particulate Fe in the Lena River.*

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?

Yes, 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 behaves almost constant along the freshwater plume.

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.

Thank you for pointing this out. You are correct that concentrations > 10 nM were measured in the bottom water samples in the Laptev Sea by Klunder et al (2012). In the upper 20 m they measured values of 3 to 10 nM. We changed this accordingly in the manuscript.

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).*

Line 27-29: In these areas, within the fully oxidized water column, the pFe phase show negative δ56Fe 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 δ56Fe?

By higher values we were referring to δ^{56}Fe values in the DFe phase, which are more enriched in the heavy Fe(III) compared to the δ^{56}Fe of the PFe phase. This does not have to be a positive δ^{56}Fe, e.g. Staubwasser et al. (2013), report negative values for the PFe and less negative (and positive) δ^{56}Fe values for the DFe. Other studies, e.g. Escoube et al. (2009), report negative δ^{56}Fe for the PFe phase and positive d56Fe for the DFe phase.

We rephrased the sentence for the better understanding.

In these areas, within the fully oxidized water column, the PFe phase show negative δ^{56}Fe values, ~~while the dissolved phase generally shows higher values~~ ***while the dissolved phase generally shows values, enriched in Fe(III) compared to the PFe phase*** *(Escoube et al., 2015, 2009; Ingri et al., 2006; Staubwasser et al., 2013; Zhang et al., 2015).*

Line 27-29: Hirst et al. (in prep.) show a seasonal dependence of the δ56Fe composition of the dissolved fraction (colloidal and truly dissolved) in the Lena River, with summer flow δ56 30 Fe values higher than those of the continental crust, and spring flood δ56Fe values of the dissolved phase lower than those of the continental crust.

Why the δ56Fe composition varies with the summer and spring flood? The reason for such variations are not explained.

Hirst et al. (2017, conference contribution) show that the sources of Fe vary throughout the season. This change in sources results in varying Fe isotope compositions. They observed a shift from negative δ^{56}Fe to crustal values from winter to spring. During winter the system is ice-dominated, while during spring the system is fluvial dominated causing a change in δ^{56}Fe. Furthermore, Ingri et al. (accepted at GCA in July) showed that temporal variations of the

δ56Fe can be explained by changing sources of Fe within the soil throughout the year.
We modified the text to clarify the discussion.

~~*Hirst et al. (in prep.) show a seasonal dependence of the δ56Fe composition of the dissolved fraction (colloidal and truly dissolved) in the Lena River, with summer flow δ56Fe values higher than those of the continental crust, and spring flood δ56Fe values of the dissolved phase lower than those of the continental crust. Therefore, the Lena River can be a source of CFe with both negative and positive isotope compositions.*~~ ***It has been shown that the Fe isotope composition is affected by seasonal variations of water flow pathes to the river (Hirst et al., 2017). Ingri et al. (accepted at GCA) showed that the Fe isotope composition is an indiactor for different Fe aggregates and for changing primary Fe sources throughout the season.***

Page 12

Line 5: flood discharge, which has much higher DOC concentrations (1170 µM), their samples would plot on a different mixingline(Allingetal.,2010).

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

Thank you, we changed the font size to fit the other text.

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.

As mentioned above we added the pH and oxygen to table 1. 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. We do not think that the change of 0.4 ph units in the freshwater plume has an influence of 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).

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?

We added the references to the sentence and rewrote it slightly. We did not want to give a fractionation factor for laboratory studies, but for measured natural values.

The fractionation factor of 0.9‰ was measured by Bullen et al. (2001) in spring water of the lower western flank of Mount Ruapehu, a composite volcano in Tongariro National Park, New Zealand. Fe isotope compositions of ferrihydrite and coexisting aqueous Fe samples along the first 600 m of down- stream reached a δ56Fe of ferrihydrite, which is >0.9‰ greater than that of coexisting aqueous Fe.

Laboratory experiments ***showed the existence*** *of oxidative precipitation of Fe(II) to Fe(III)* ***(e.g. Welche et al., 2003),*** *which can occur in natural streams.* ***Bullen et al. (2001) measured an*** *overall fractionation factor of* **about** *0.9* ***in natural streams****.*

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 δ56Fe value, sedimenting close to the shoreline.

Which phase of the Fe isotope variation along the plume?

We were referring to the negative δ^{56}Fe values of the colloidal and particulate phase. We added this information to the sentence.

The Fe isotope ~~variation~~ ***values of CFe and PFe*** *along the plume and the composition of the surface sediment suggest that the chemically reactive ferrihydrite represent colloids and particles, with a negative* δ^{56}Fe *value, sedimenting close to the shoreline.*

Line 17-18: The surface sediments in the shelf areas along the Laptev Sea have δ56Fe 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?

Yes, we think that both processes are possible. The wave base can reach the sediment, but we do not have data on resuspension. We believe that the uppermost sediment is newly sedimented in the form of colloidal and particulate ferrihydrites, with negative δ^{56}Fe values. The data across the ESAS show that the Fe isotope composition of the uppermost sediment is the same.
The resuspension of sediment would favor a non-reductive dissolution of sediment to the seawater (Radic et al., 2011). The word dissolution expresses a flux from the particulate to the dissolved phase (<0.4µm).
The slightly negative δ^{56}Fe of the colloidal and particulate fraction (0.0 to -0.4‰) indicates that iron is not produced by dissimilatory iron reduction and redox cycling (characterized by a very negative δ^{56}Fe; -3.3 to -1.7‰), (Homoky et al. 2009; Severmann et al. 2006; 2010). Furthermore, non-reductive dissolution of sediment particles to the seawater would result in positive δ^{56}Fe of the DFe in the water column (Radic et al., 2011).
We added some lines to the discussion to rule out resuspension and non-reductive dissolution responsible for the Fe isotope composition of the uppermost sediment.

Other processes, as resuspension of sediment and non-reductive dissolution of sediment to the seawater (Radic et al., 2011) would lead to a much more negative (-3.3‰ to -1.7‰) Fe isotope composition of the sediment (Homoky et al., 2009; Severmann et al., 2006; 2010). Therefore, the δ^{56}***Fe of the uppermost sediment reflecting the*** δ^{56}***Fe of the sedimenting colloids and particles from the water column seems reasonable.***

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.

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

Page 22

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

Changed accordingly.

Figure 1: Sampling stations in the Arctic Ocean. Black dots mark the stations in the detailed ***East Siberian Arctic Shelf*** *~~ESAS~~ map. Along the Lena River-Laptev Sea transect membrane filtration and/or ultrafiltration was carried out. The sampling stations of this study follow the Lena River freshwater plume. The green numbers display δ56Fe values, measured in the uppermost sediment.*

Page 23

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

Changed accordingly.

*Figure 2: The salinity gradient along the Lena River****-Laptev Sea*** *transect.* ***Salinity is based on the Practical Salinity Scale PSS-78.*** *The freshwater builds an almost 10 m thick surface layer in the Laptev Sea, and the plume itself extends over an area of about 50 times 600 km. The plume is divided into an inner and outer plume between station YS-8 and YS-11 by a sharp increase of salinity.*

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.**

Unfortunately, there are no DOC and POC data available for station YS-128.

Changed accordingly. Furthermore, we corrected 20 % towards 18% to be more concise.

*Figure 3: Dissolved (< 0.70 µm) and particulate (> 0.70 µm) organic carbon concentrations along the Lena River****-Laptev Sea transect*** *~~freshwater plume in the Laptev Sea~~. Close to the Lena River mouth POC constitutes about* ***18%*** *of the TOC input, while at the outermost station it is only 2% of the TOC.*

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.

This is right we do not show PFe in the graph, indeed we show TFe. Particle Fe is indicated as the difference between TFe and CFe. We changed the figure caption accordingly. We changed the unit in the figure towards µM and we added data for the truly dissolved Fe in the Lena River (Hirst et al., 2017) as reference for the river endmember.
Unfortunately, we do not have PFe, CFe, and DFe concentration for the stations YS-5, YS7, YS-9, and YS-10.

*Figure 4: **Total,** colloidal and truly dissolved Fe concentrations along the Lena River freshwater plume. Concentrations of **P**Fe and **C**Fe decreased along the salinity gradient, while the concentrations of **D**Fe is almost constant. Note the logarithmic scale and the sharp decrease of **P**Fe between the inner and the outer plume. **The reference for the Lena River is an average of all analyzed samples (PFe n=3; CFe and DFe n=5) by Hirst et al. 2017.***

Page 26

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

We changed figure 5 slightly, by adding a legend (please see below). We added information for the salinity to the figure caption.

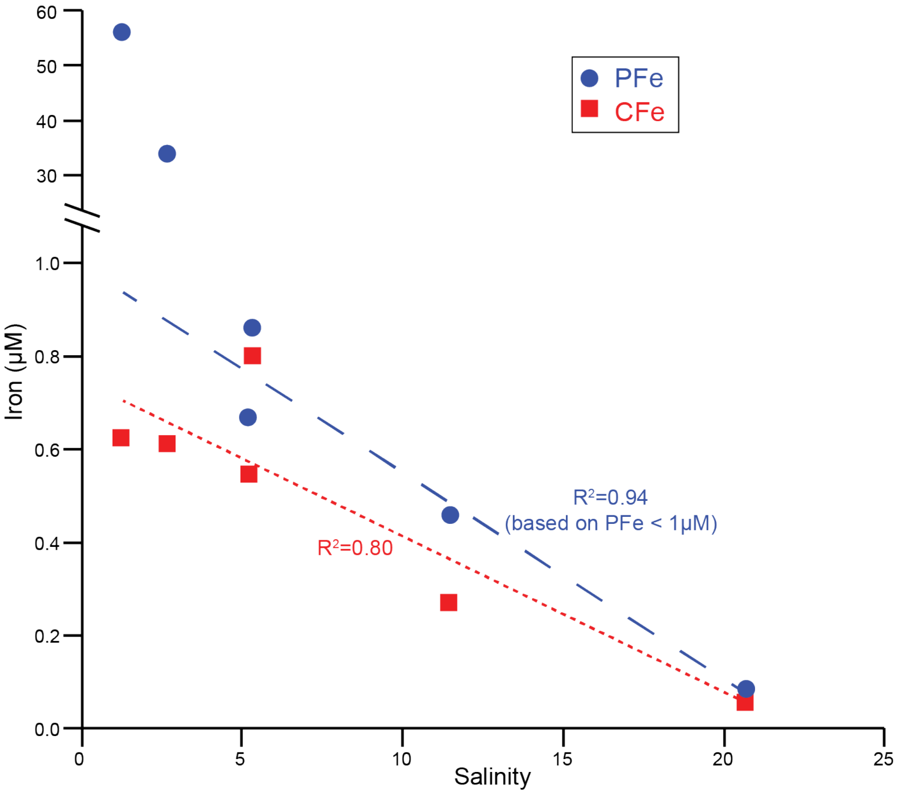


Figure 5: The colloidal and particulate Fe concentrations plotted versus salinity. ***Salinity is based on the Practical Salinity Scale PSS-78.*** *Note the y-axis break due to the high range of PFe in the inner plume. The linear correlation between PFe and salinity is based on the data points below 1µM PFe. In the low salinity environment, the PFe is much higher compared to the CFe, whereas at salinities above 5 the differences are smaller.*

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.**

We added the information to the figure caption. There are no Fe isotope data for the truly dissolved phase. As mentioned earlier, the DFe Fe isotope values were not measured due to the low Fe concentrations in that phase. We changed the description of what we did in the introduction. Please see below.

Figure 6: Iron isotope values along the Lena River freshwater plume and the uppermost sediment of the ***East Siberian Arctic Shelf*** *(ESAS). The error bars represent ±2 σ, in some cases the symbol is larger than the error. The δ^{56}Fe values of PFe are negative at all stations, values close to zero close to the coast and more negative towards the open sea. The δ^{56}Fe values of the CFe are negative in the inner plume and positive in the outer plume. The δ^{56}Fe of the sediment samples were around -0.2 ‰, displaying the overall composition of the entire ESAS area.*

From the introduction:

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

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

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Distribution of Fe isotopes in particles and colloids in the salinity gradient along the Lena River plume, Laptev Sea

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Abstract. Riverine Fe input is the primary Fe source to the ocean. This study is focused on the distribution of Fe along the Lena River freshwater plume in the Laptev Sea using samples from a 600 km long transect in front of the Lena River mouth. Separation of the particulate (>0.22µm), colloidal (0.22µm – 1kDa), and truly dissolved (<1kDa) fractions of Fe was carried out. The total Fe concentrations ranged from 0.~~15~~2 to 57 µM with Fe dominantly as particulate Fe. The loss of > 99% of particulate Fe and about 90% of the colloidal Fe was observed across the shelf, while the truly dissolved phase was almost constant across the Laptev Sea. Thus, the truly dissolved Fe could be an important source of bioavailable Fe for plankton in the central Arctic Ocean, together with the colloidal Fe. Fe-isotope analysis showed that the particulate phase and the sediment below the Lena River freshwater plume had negative δ^{56}Fe values (relative to IRMM-14). The colloidal Fe phase showed negative δ^{56}Fe values close to the river mouth (about -0.20‰) and positive δ^{56}Fe values in the outermost stations (about +0.10‰).

We suggest that the shelf zone acts as a sink for Fe particles and colloids with negative δ^{56}Fe values, representing chemically reactive ferrihydrites. While the positive δ^{56}Fe values of the colloidal phase within the outer Lena River freshwater plume, might represent Fe ~~-~~oxyhydroxides, which remain in the water column, and will be the predominant δ^{56}Fe composition in the Arctic Ocean.

1 Introduction

The cycling of Fe is a key component for understanding water quality and biogeochemical processes. Iron is the 4th most abundant element in the continental crust (Wedepohl, 1995). The concentration in seawater is low compared to riverine input (Martin and Gordon, 1991). 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). 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).

It has been recognised that dissolved Fe is related to dissolved organic carbon (DOC) in freshwater (Perdue et al., 1976) and so to investigate the pathways for organic carbon (OC) in the Arctic, knowledge about Fe cycling and the coupling between the boreal-arctic watershed and the Arctic basin is crucial. ~~Different forms and sizes of Fe~~Iron and OC in water samples can be separated using a variety of filtration techniques. These include both membrane filtration (0.22 to~~–~~ 0.7 µm) and ultrafiltration (1kDa, 10kDa, or 30kDa) and size fractions are thus often operationally defined as particulate matter (larger than 0.22µm or 0.7µm), colloidal (smaller than particles, but do not pass an ultrafilter) and truly dissolved phases (passing through an ultrafilter). Due to the technical complexity with ultrafiltration, including the extensive filtration time, there are few ultrafiltration Fe data available (Guo and Santschi, 1996; Ingri et al., 2000; Pokrovsky et al. 2012). Truly dissolved Fe data are scarce and deliver insights into this part of the Fe pool.

Previous studies showed that there is a relationship between Fe and OC in the dissolved fraction and found two main forms of Fe compounds: Fe-OC and Fe oxyhydroxides (Escoube et al., 2015; Hirst et al., 2017; Ilina et al., 2013; Ingri et al., 2006, 2000; Kritzberg et al., 2014; Pokrovsky et al., 2010, 2006; Pokrovsky and Schott, 2002; Raiswell and Canfield, 2012; Stolpe et al., 2013). It has also been shown that humic substances (HS) are associated with newly formed Fe oxyhydroxides in freshwater (Pédrot et al., 2011; Tipping, 1981). The behaviour of these Fe and OC particles and colloids during estuarine mixing depend on their chemical reactivity, which is defined by their size and speciation (Poulton and Raiswell, 2005; Tagliabue et al., 2017). Hirst et al. (2017) found that about 70% of the total suspended Fe in the Lena River to be in the form of reactive ferrihydrite. These ferrihydrites are independent particles within a network of amorphous particulate OC (POC) and are attached to the surfaces of primary organic matter and clay particles (Hirst et al., 2017).

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). The $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ ratios are defined relative to the international reference material IRMM-14 and are expressed as deviations from the standard in parts per thousand, or δ notation (in per mill ‰), as

$$\boxed{\delta^{56}Fe \;=\left[\frac{\left(^{56}Fe/^{54}Fe\right)\;\; _{sample}}{\left(^{56}Fe/^{54}Fe\right)\;\; _{IRMM-14}}-1\right]*10^{3}}, \tag{1}$$

$$\boxed{\delta^{57}Fe \;=\left[\frac{\left(^{57}Fe/^{54}Fe\right)\;\; _{sample}}{\left(^{57}Fe/^{54}Fe\right)\;\; _{IRMM-14}}-1\right]*10^{3}}, \tag{2}$$

Using this definition, the continental crust has a $\delta^{56}Fe$ value of 0.07±0.02‰. In low-temperature environments the $\delta^{56}Fe$ can vary by about 5‰ (Anbar, 2004; Beard et al., 2003;~~ Dauphas and Rouxel, 2006;~~ Fantle and DePaolo, 2004; Rouxel~~, A.~~ Bekker, ~~K.J.~~ Edwards, 2005). The variations in $\delta^{56}Fe$ can be used to trace different Fe phases in rivers (Dos Santos Pinheiro et al., 2014; Ilina et al., 2013; Ingri et al., 2006; Poitrasson et al., 2014) and to map the origin of Fe (Conway and John, 2014). Isotope fractionation processes result in a $\delta^{56}Fe$ value that can be higher or lower compared to continental crust. The Fe isotopic composition is impacted by redox reactions (Wiederhold et al., 2006), complexation with organic ligands, and inorganic speciation of Fe, as well as the immobilization of Fe by precipitation and adsorption (Beard et al., 2003, 1999; Beard and Johnson, 2004; Brantley et al., 2001; Bullen et al., 2001; Icopini et al., 2004; Poitrasson and Freydier, 2005; Skulan et al., 2002; Welch et al., 2003). These processes can yield either negative or positive $\delta^{56}Fe$ values, depending on the initial Fe isotopic composition and the fractionation factor. Recent studies showed that subarctic and temperate rivers, with high Fe and OC concentrations, have low $\delta^{56}Fe$ values in the particulate phase, while the dissolved phase has high $\delta^{56}Fe$ (Escoube et al., 2015, 2009; Ilina et al., 2013; Ingri et al., 2006; Rouxel et al., 2008; Severmann et al., 2006). Also, high $\delta^{56}Fe$ values have been reported in the Low Molecular Weight (LMW) fraction (< 10kDa), while colloids and particles showed high $\delta^{56}Fe$ values (Ilina et al., 2013). Furthermore, seasonal variations in the Fe isotopic composition and Fe speciation have been reported (Allard et al., 2004; Escoube et al., 2015; Ingri et al., 2006).

This study presents Fe concentrations and Fe isotope compositions in the particulate and~~,~~ colloidal~~, and truly dissolved~~ phase along the Lena River freshwater plume in the Laptev Sea, as well as Fe concentrations in the truly dissolved phase. ~~-~~The Lena River – Laptev Sea transect is stratified, with a freshwater layer that is on top of more saline and dense, deep waters and plays an important role in the transport of Fe and the distribution of Fe isotopes in the Arctic Ocean. 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. 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 Sampling Site and Analytical Methods

2.1 Study Area

The Lena River is 4,387 km long and has the 8th largest discharge in the world. It is the 2nd largest river draining into the Arctic Ocean and flows into the Laptev Sea (Fig. 1). The Lena watershed covers an area of 2.46 x 10^6 km^2 (Rachold et al., 1996) and is bound by the Verkhoyansk Mountain Ridge in the northeast and the central Siberian uplands in the west. Larch forests cover 72% of the watershed area and shrublands about 12% (Wagner, 1997; Walter and Breckle, 2002). Permafrost underlays 78–93% of the watershed (Zhang et al., 1999) and extends to depths of up to 1,500 m (Anisimov and Reneva, 2009). The annual discharge to the Arctic Ocean is 581 km^3 (Yang et al., 2002). During spring flood, late May to June, 31–45% of the annual runoff occurs (Amon et al., 2012). The Lena River delivers 5.6–5.8 Tg of DOC into the Arctic Ocean annually (Holmes et al., 2012; Raymond et al., 2007), along with about 0.4 Tg of particulate OC (Semiletov et al., 2011). More than 50% of the total OC (TOC) is delivered during a two-month period in summer, with 6.6 Tg $year^{-1}$ in June (Le Fouest et al., 2013) and 3.5 Tg $year^{-1}$ in July (Kutscher et al., 2017). The run-off from the Lena River accounts for more of 70% of the overall river inflow to the Laptev Sea (Antonov, 1967). The freshwater plume in the Laptev Sea is a mixing zone of about 600 km length and 50 km wide (Fig. 2). A low salinity freshwater plume overlies denser highly saline Arctic seawater (Alling et al., 2010). The Lena River plume can be divided into an inner and an outer plume based on a sharp increase in salinity, with salinities up to 5 in the inner plume and up to 15 in the outer plume (Alling et al., 2010). Both parts of the plume are separated by a strong halocline at about 10 m depth from the underlying dense Arctic sea water that has salinities up to 35 (Alling et al., 2010; Chester, 2003; Martin et al., 1993).

2.2 Sampling and Processing

The samples were collected in August 2008 during the International Siberian Shelf Study (ISSS-08) from the RV Yacob Smirnitskyi. The ISSS-08 was part of the International Polar Year (IPY) and the Arctic GEOTRACES programs. 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). Additionally, surface sediment (upper 2 cm) samples were taken from the Kara, Laptev and East Siberian Seas (Fig. 1). Samples from this region collected during this cruise have also been studied for DOC (Alling et al., 2010; Bröder et al., 2016; Karlsson et al., 2016; Salvadó et al., 2017), dissolved inorganic carbon (Alling et al., 2012), POC (Karlsson et al. 2016; Sánchez-García et al., 2011), nutrients and alkalinity (Anderson et al., 2009; Pipko et al., 2017), and stable O isotopes (Rosén et al., 2015).

Table 1: Sampling stations in the Laptev Sea of the ISSS-08 research cruise. Temperature, salinity, pH and Oxygen data for the Lena River freshwater plume are obtained from waters at a depth of 4 m, whereas the data for the shelf sediment sample locations are obtained from the overlying bottom waters. The measurements were done with a CTD Seabird 19+. Salinity is based on the Practical Salinity Scale PSS-78.

	Station	**Lat. (N)**	**Long. (E)**	**Date**	**Water depth**	**Salinity**+	**Temp.**	**pH**	**Oxygen**	**POC**	**DOC**	**TOC**
		degrees (°) minutes (')	degrees (°) minutes (')		**m**		**°C**		**%**	μM	μM	μM
Lena River freshwater plume	**YS-128**	76°59.220	130°21.340	08/09/2017	51	29.13	-1.43	7.9	99.6	-	-	-
	YS-4*	75°59.220'	129°59.050'	08/08/2023	52	13.3	-1.54	7.7	99.4	8	320	-
	YS-5	75°15.590'	130°0.990'	08/08/2024	44	9.03	-1.56	7.6	99.5	12	434	503
	YS-6	74°43.440'	130°0.980'	08/08/2024	34	5.29	-1.61	7.6	100.5	13	440	543
	YS-7	74°7.920'	129°59.980'	08/08/2024	17	6.31	-1.26	7.6	100.6	11	432	454
	YS-8	73°33.940'	130°0.470'	08/08/2024	13	5.29	-0.78	7.6	99.4	15	391	-
	YS-9	73°21.980'	129°59.820'	08/08/2025	25	8.15	-1.13	7.6	101.7	11	397	437
	YS-10	73°11.040'	129°59.740'	08/08/2025	21	5.37	-0.89	7.6		36	414	441
	YS-11	73°1.110'	129°59.350'	08/08/2025	12	3.54	-0.32	7.5	94.6	53	435	468
	YS-14*	71°37.820'	130°2.970'	08/08/2027	8	1.08	11.14	-		89	442	476
Shelf sediment sample locations	**YS-2**	73°24.300'	72°59.710	08/08/2019	30	31.53	-1.09	7.5	67.9	20	544	-
	YS-3	73°29.520'	79°53.090'	08/08/2019	38	32.27	-1.06	7.6	70.5	-	-	-
	YS-13	71°58.080'	131°42.080'	08/08/2026	22	27.82	-1.03	-	-	10	453	-
	YS-26	72°27.590'	150°35.740'	08/08/1931	17	27.13	-0.72	7.3	62.3	5	185	-
	YS-28	72°39.050'	154°11.120'	08/09/2001	29	31.05	-0.86	7.2	42.9	4	94	-
	YS-30	71°21.460'	152°9.160'	08/09/2001	10	22.94	1.19	7.5	90.4	13	198	-
	YS-39	71°13.150'	169°22.370'	08/09/2004	46	32.41	-1.64	7.4	64.3	5	46	-

* station was also sampled for surface sediment 0

\+ salinity. pH. And oxygen saturation for shelf sediment samples are measured in bottom water

^ measured with a Hydrosonde M5

~~**Table 1: Sampling stations in the Laptev Sea of the ISSS-08 research cruise. Temperature and salinity data for the shelf sediment sample locations are obtained from the overlying bottom waters.**~~

	~~**Station**~~	~~**Lat.**~~ ~~**dec.**~~	~~**Long.**~~ ~~**dec.**~~	~~**Date**~~	~~**Water depth**~~ ~~**m**~~	~~**Salinity**~~	~~**Temp.**~~ ~~**°C**~~	~~**pH**~~
~~Lena River freshwater plume~~	~~**YS-128**~~	~~76.987~~	~~130.356~~	~~17/09/08~~	~~51~~	~~20.66~~	~~-1.43~~	
	~~**YS-4***~~	~~75.987~~	~~129.984~~	~~23/08/08~~	~~44~~	~~11.45~~	~~-1.54~~	
	~~**YS-5**~~	~~75.266~~	~~130.017~~	~~24/08/08~~	~~42~~	~~7.03~~	~~-1.56~~	
	~~**YS-6**~~	~~74.724~~	~~130.016~~	~~24/08/08~~	~~32~~	~~5.23~~	~~-1.61~~	
	~~**YS-7**~~	~~74.132~~	~~130.000~~	~~24/08/08~~	~~16~~	~~6.32~~	~~-1.26~~	
	~~**YS-8**~~	~~73.566~~	~~130.008~~	~~24/08/08~~	~~13~~	~~5.34~~	~~-0.78~~	
	~~**YS-9**~~	~~73.366~~	~~129.997~~	~~25/08/08~~	~~23~~	~~8.47~~	~~-1.13~~	
	~~**YS-10**~~	~~73.184~~	~~129.996~~	~~25/08/08~~	~~20~~	~~3.78~~	~~-0.89~~	
	~~**YS-11**~~	~~73.019~~	~~129.989~~	~~25/08/08~~	~~11~~	~~2.67~~	~~-0.32~~	
	~~**YS-14***~~	~~71.630~~	~~130.050~~	~~27/08/08~~	~~8~~	~~1.28~~	~~11.14~~	
~~Shelf sediment sample locations~~	~~**YS-2**~~	~~73.405~~	~~72.995~~	~~19/08/08~~	~~30~~	~~7.85~~	~~-1.09~~	
	~~**YS-3**~~	~~73.492~~	~~79.885~~	~~19/08/08~~	~~35~~	~~5.54~~	~~-1.06~~	
	~~**YS-13**~~	~~71.968~~	~~131.701~~	~~26/08/08~~	~~21~~	~~3.79~~	~~-1.03~~	
	~~**YS-26**~~	~~72.460~~	~~150.596~~	~~31/08/08~~	~~16~~	~~19.18~~	~~-0.72~~	
	~~**YS-28**~~	~~72.651~~	~~154.185~~	~~01/09/08~~	~~28~~	~~19.73~~	~~-0.86~~	
	~~**YS-30**~~	~~71.358~~	~~152.153~~	~~01/09/08~~	~~9~~	~~19.31~~	~~1.19~~	
	~~**YS-39**~~	~~71.217~~	~~169.347~~	~~04/09/08~~	~~44~~	~~27.56~~	~~-1.64~~	

~~* also sampled for sediment~~ *

All water samples, besides YS-14, were collected between 2.5 m and 5.0 m depth using a peristaltic pump and acid-cleaned, silicon tubing. The tubing was attached to a flagpole, which was mounted to the bow of the ship. To avoid contamination from the ship, the flagpole was extended about 10 m in front of the ship. The samples were pumped into a 25 L container, which was rinsed with MQ water between each station. Station YS-14 was sampled at 4.0 m depth using a 60 L Go-Flo® water sampler. All equipment in contact with the samples were cleaned with 5% HNO_3, rinsed with MQ water, and dried in a HEPA-filtered clean air hood. Membrane filtration was carried out within 12 hours of sampling. All water samples were stored in acid-cleaned polyethylene (PE) bottles and acidified with ultrapure HNO_3 to a pH <2, and all nitrocellulose filters (0.22µm, Millipore®) were stored at -18°C until further analysis (Ödman et al., 1999). Samples for particulate organic carbon were filtered with 0.7 µm GF/F glassfiber filters (Whatman®). The filters were pre-combusted for four hours at 450°C to limit the C blank.

Sediment samples were taken with a GEMAX gravity corer and a Van Veen grab sampler as described earlier (Vonk et al., 2012).

During cross-flow ultrafiltration the sample water (< 0.22µm) flows across a membrane surface at a constant pressure. This process prevents clogging, since while particles smaller than the membrane cut-off can pass, larger suspended particles remain circulating in the sample water. The sample water progressively decreases in volume as the permeate crosses the filter, and the larger colloids and particles remain in the retentate, which therefore are progressively concentrated. The cross-flow ratio (CFR=Q_R/Q_P, where Q_R and Q_P are the flow rates of the retentate and permeate, respectively) (Forsberg et al., 2006; Ingri et al., 2000; Larsson et al., 2002) was kept between 60 and 100 to achieve an overall concentration factor larger than 10 (Conc. Fact.= $(V_P+V_R)/V_R$, where V_P and V_R are the final volumes of the permeate and retentate, respectively). For the concentration factors and cross-flow ratios, see Table 2. In this study, the water used for ultrafiltration was pre-filtered through a membrane (<0.22µm) prior to introduction into the MilliPore® Prep/Scale ultrafiltration system, which had a cutoff of 1 kDa. Thus, the permeate is < 1 kDa, while the retentate includes colloids between < 0.22 µm and 1kDa.

Table 2: Cross-flow ultrafiltration details

Sample	Retentate (V_R) litre	Permeate (V_P) litre	Conc. Factor	Retentate Q_R (ml/min)	Permeate Q_P (ml/min)	Cross-flow ratio (CFR)
YS-128	0.97	16.4	18	>3,000	30-50	60-100
YS-4	1.14	11.8	11	3,000	30	100
YS-11	1.10	10.5	11	>3,000	30-50	60-100
YS-14	0.61	12.2	21	>3,000	30-50	60-100

2.3 Analytical Methods

Iron concentrations and isotopic compositions were measured at ALS Scandinavia AB. All sample manipulations were performed in a clean laboratory (Class 10 000) by personnel wearing clean room gear and following all general precautions to reduce contamination (Rodushkin, Engström, and Baxter, 2010). High purity Suprapure® acids were used throughout sample treatment and analysis. Organic carbon analyses were carried out at Stockholm University (for analytical details, see Alling et al., 2010; Sánchez-García et al., 2011).

For element analysis, the water samples (colloidal: 1 kDa to 0.22µm; truly dissolved: <1 kDa) were diluted (2-200 fold) with 10 % HNO_3. The degree of dilution was dependent on the salinity of the sample. At least two dilutions of each sample were carried out; one high dilution for determination of major elements and one low dilution for minor and trace elements. For Fe analysis, the samples were diluted by a factor of 50. In order to analyze the particles on the filters, the filters were treated with a 1,000:1 mixture of HNO_3/HF overnight, followed by closed-vessel microwave-assisted digestion. Prior to analysis, the digests were further diluted in 10% HNO_3.

Multi-elemental analysis of the water and filter samples was performed on an Inductively Coupled Plasma Sector Field Mass Spectrometer (ICP-SFMS, ELEMENT2 Thermo Scientific) at ALS Scandinavia AB. The measurement procedure combines internal standardization and external calibration. For internal standardization, indium was added to all the solutions (Rodushkin et al., 2005; Rodushkin and Ruth, 1997). 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; 2016).

The blanks of digested filters (0.22µm) for Fe were 2.79 µg/L, which is about 0.25% of the average Fe concentration in the samples for the Lena River sampling transect. Replicated measurements of sample concentrations showed a precision of ±3% (n=4). 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. Fe concentrations for the particulate, colloidal and truly dissolved phase are reported in Table 3. Aluminum and titan concentrations can be found in the supplement.

For the Fe isotope ratio measurements, water samples (colloidal: 1 kDa to 0.22µm) and digested filters were evaporated to dryness, and the residue was re-dissolved in 1 mL 9M HCl. Iron was separated from the matrix elements by using an AG-MP-1M ion-exchange resin (Ingri et al., 2006; Roduhskin and Ruth, 1997). After the sample was loaded, the matrix was washed with 9.6 M HCl, and Cu was eluted with 8 ml 5M Cl. Afterwards, Fe was eluted with 6 ml 2 M HCl and can be used for further steps (Rodushkin et al. 2016). After evaporating to dryness, 50 µL of concentrated HNO_3 was pipetted directly to the residue followed by the addition of 5 mL MQ-water. Samples with high Fe content were diluted with 0.2M HNO_3 to a concentration of 2 mgL^{-1} in the measurement solutions. Low Fe concentration water samples were further diluted to 40-50 µgL^{-1} and measured using high-efficiency desolvation nebulizer (Aridus) in a separate analytical sequence. Iron was separated from the matrix by ion exchange, with a recovery rate above 95%. The Fe isotope compositions in separated fractions from filters and water samples were measured using a Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS, NEPTUNE PLUS®, Thermo Scientific) equipped with micro-concentric nebulizer and tandem cyclonic/Scott double pass spray chamber. Instrumental mass biases were corrected by sample-standard bracketing using IRMM-14 CRM, while an internal standard (Ni) was added to all samples and used to correct for instrumental drift. Each sample was measured twice with the sample-standard bracketing method. Detailed information on the correction procedures can be found in Baxter et al. (2006). During the Fe isotope analysis, δ^{56}Fe and δ^{57}Fe were measured. In the three isotopes plot of δ^{56}Fe and δ^{57}Fe all samples plot on a single mass fractionation line (Fig. S1). We only discuss the δ^{56}Fe in this study, although all Fe isotope data are reported in Table ~~3~~4 including 2σ (n=4;).

Table 3: Iron concentrations of the different fractions for the Lena River freshwater plume.

Station	**Location**	**Particulate**	**Colloidal**	**Truly dissolved**	**Total**	**pFe/cFe**
-	-	µM	µM	nM	µM	mol ratio
YS-128	Lena transect; Laptev Sea	0.1	0.1	8	0.2	1
YS-4	Lena transect	0.5	0.3	7	0.8	2
YS-5	Lena transect	-	-	-	-	-
YS-6	Lena transect	0.7	0.6	-	1.3	1
YS-7	Lena transect	-	-	-	-	-
YS-8	Lena transect	0.9	0.8	-	1.7	1
YS-9	Lena transect	-	-	-	-	-
YS-10	Lena transect	-	-	-	-	-
YS-11	Lena transect	34.0	0.6	9	35.0	56
YS-14	Lena transect; Mohtaba Island	56.0	0.6	1	57.0	90

Total Fe is calculated as a sum of particulate, colloidal, and truly dissolved Fe

Table ~~3~~4: Fe isotope data for the ~~sediment and the~~ particulate ~~and~~and the colloidal phase, as well as Fe isotope data for the surface sediments.

Particulate >0.22µm				
Station	**$\delta^{56/54}$Fe**	**2σ**	**$\delta^{57/54}$Fe**	**2σ**
	‰	‰	‰	‰
YS-128	-0.289	0.050	-0.487	0.024
YS-4	-0.406	0.126	-0.735	0.114
YS-6	-0.360	0.014	-0.644	0.082
YS-8	-0.130	0.008	-0.266	0.136

YS-11	-0.067	0.040	-0.106	0.008
YS-14	-0.048	0.106	-0.097	0.114

Colloidal 1kDa-0.22µm

Station	$\delta^{56/54}$Fe ‰	2σ ‰	$\delta^{57/54}$Fe ‰	2σ ‰
YS-128	0.112	0.069	0.233	0.050
YS-4	0.102	0.079	0.277	0.038
YS-11	-0.227	0.089	-0.312	0.298
YS-14	-0.171	0.015	-0.267	0.030

Surface Sediment

Station	$\delta^{56/54}$Fe ‰	2σ ‰	$\delta^{57/54}$Fe ‰	2σ ‰
YS-13	-0.233	0.070	-0.324	0.006
YS-4	-0.220	0.040	-0.355	0.028
YS-26	-0.209	0.002	-0.298	0.116
YS-14	-0.250	0.110	-0.404	0.100
YS-2	-0.351	0.150	-0.439	0.102
YS-3	-0.230	0.024	-0.396	0.106
YS-11	-0.083	0.022	-0.209	0.094
YS-28	-0.131	0.074	-0.220	0.118
YS-30	-0.102	0.028	-0.185	0.088
YS-39	-0.241	0.086	-0.403	0.124

3 Results

The average pH for the water samples was 7.6 ± 0.1(1SD) and the oxygen saturation was 99.4±2.1% (Tab. 1), (Andersson and Jutterstrøm, 2008). Within the Lena River freshwater plume the pH ranged from 7.5 to 7.9. The methodology for pH and oxygen is described in the supplement (after Dudarev, 2008).

~~All concentration results are reported in the supplement (Tab. S2 and Tab. S3).~~

3.1 Organic Carbon distributions in the Lena River plume

The DOC concentrations show a small variation of between 3~~0~~20 and 44~~0~~2 μM in the surface waters of the inner and outer plume (Tab. 1; Fig. 3). The average DOC concentration of 410 μM in the surface water of the Lena River freshwater plume has been reported by Alling et al. (2010) and is similar to previous studies (Cauwet and Sidorov, (1996): 300–600μM). 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). The POC concentrations decrease from high values (89 μM) close to the coast to low values (8 μM) in the outer plume (Fig. 3~~; S2~~). In the inner plume (YS-14 to YS-10) the POC concentrations are high, between 89 μM and 36 μM, whereas in the outer plume the POC concentrations were almost constant, with an average value of about 12 μM. The overall average POC concentration of about 28 μM has been earlier reported by Sánchez-García et al. (2011).

3.2 Iron concentrations in the Lena River freshwater plume

Three size fractions were analyzed for Fe: particulate Fe (P~~p~~Fe, > 0.22 μm), colloidal Fe (~~c~~CFe, 1kDa-0.22 μm), and truly dissolved Fe (~~d~~DFe, < 1 kDa). The total Fe (T~~t~~Fe) concentration was calculated as the sum of P~~p~~Fe, ~~c~~CFe, and ~~dFe~~ DFe (Tab. 3~~S3~~).

The ~~pFe~~ 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-1~~0~~1 and YS-~~9~~8), the P~~p~~Fe concentration dropped to 0.9 μM, a loss of > 99~~8~~% of ~~p~~PFe. The loss of Fe was estimated as fraction of the maximum Fe concentration of each size fraction (details can be found in the supplement). The ~~cFe~~ CFe concentration decreased from 0.6 to 0.1 μM along the freshwater plume, a loss of about 90~~85~~% ~~c~~CFe (Fig 4). The concentration of ~~d~~DFe was low, at around 8 nM, and relatively constant along the plume (Fig. 4). In total, a loss of >99% T~~t~~Fe was observed between the first station (YS-14) and the last station (YS-128).

We observed non-conservative behaviour of ~~p~~PFe during mixing between Lena River water and Arctic Ocean water, while ~~c~~CFe showed generally conservative behaviour, with an almost linear correlation with salinity (Fig. 5). The P~~p~~Fe concentrations below 1 μM also showed an almost linear correlation at salinities above 5 in the outer plume. In the inner plume, at salinities below 5, the P~~p~~Fe showed non-conservative behaviour.

3.3 Iron isotopes in the Lena River freshwater plume

The Fe isotope compositions in the particulate and the colloidal phases, as well as in the surface sediments, are reported in Fig. 6. The δ^{56}Fe values in the particles varied between -0.05 ± 0.11‰ (YS-14) in the inner plume and -0.41 ± 0.12‰ (YS-4) in the outer plume (Fig. 6), with the δ^{56}Fe values in the outer plume all lower compared to the inner plume. The ~~c~~CFe show negative δ^{56}Fe values (average -0.20 ± 0.06‰) in the inner plume and positive δ^{56}Fe values (average 0.11 ± 0.08‰) in the outer plume. The surface sediments from the Laptev Sea all had negative δ^{56}Fe values (-0.23 ± 0.08‰ and -0.25 ± 0.12‰). Surface sediments obtained from 10 samples in other parts of the East Siberian Arctic Schelf (~~-~~ESAS) showed only small variations (Fig 1 and Fig. 6; Tab. ~~3~~4; Tab. S2~~4~~).

4 Discussion

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~~3). In the outer plume only about 2% of the total OC was present as POC. It has been suggested that POC in the Lena River freshwater plume is transported in different forms, including large particles, which can sink, and almost neutrally buoyant flocculates of humic substances (Gustafsson and Gschwend, 1997; Gustafsson et al., 2000; Sánchez-García et al., 2011). The POC, which is associated with larger particles (> 0.7µm), will settle close to land, whereas the humic substance flocculates will travel further out (Vonk et al., 2010).

4.1 Iron behaviour in the Lena River freshwater plume

The P~~p~~Fe concentrations found in the Laptev Sea close to the shore are higher than the average P~~p~~Fe concentration in the Lena River, but similar to the highest PFe river values up to 32 µM (Hirst et al., 2017). The ~~c~~CFe and ~~dFe~~ DFe in the Lena River (Hirst et al., 2017) showed higher average concentrations (C~~c~~Fe: 1.5 µM; ~~dFe~~DFe: 54 nM) than~~t are similar to~~ concentrations found in the Lena River – Laptev Sea transect. Most likely some of the CFe and DFe from Lena River already flocculated at salinities below 1, where the first sample of our sampling profile was taken (YS-14). Within the Arctic Ocean, dissolved Fe (~~cFe~~ CFe + ~~dFe~~DFe) concentrations vary between 0.2 and 63 nM and the concentrations depend on distance to the shore and depths of sampling, with generally higher values in surface waters as well as close to the bottom sediment, which might be related to resuspension, sinking of brines, or resuspension from the sediment of Fe (Klunder et al., 2012; Thuróczy et al., 2011). The ~~cFe~~ CFe concentrations are higher close to the coast and decreasing in the outer plume to values that are similar to ~~cFe~~ CFe concentrations reported from further out in the Arctic Ocean (e.g. Thuróczy et al., 2011). 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 (Escoube et al. 2009; Gerringa et al. 2007; Mosley, Hunter, and Ducker 2003) and successively sedimentation of the newly built flocculates (Daneshvar, 2015). ~~-~~The distribution of Fe between the different phases show that ~~pFe~~ PFe is the dominant Fe-phase in the inner plume system (with a ~~p~~PFe/~~cFe~~ CFe ratio of about 90). However, most of the ~~pFe~~ PFe is lost in the inner plume close to the shore and the ratio P~~p~~Fe/C~~c~~Fe decreases towards a ratio of about 1 in the outer plume.

We observed non-conservative mixing of P~~p~~Fe at salinities lower than 5 and conservative mixing at salinities higher than 5 (Fig. 5).~~-~~ Recent studies showed that the majority of ~~particulate~~ 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). The larger aggregates ~~is results in flocculation~~sink more readily to the~~ and sinking to~~ 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, Martin, and Meybbeck~~ et al.~~, 1978; Guieu et al., 1996; Windom~~, H. L.~~, Beck, and~~K.,~~ Smith, 1971). The large amount of P~~p~~Fe (9~~8~~9%) lost in the inner Lena River freshwater plume is likely due to removal of chemically reactive ferrihydrite, which is the main form of ~~particulate~~ 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~~p~~Fe to be transported into the Arctic Ocean, where they are present at about 2% of their initial concentration in rivers. Concentrations of P~~p~~Fe at salinities >5 and ~~cFe~~ CFe along the whole salinity gradient ~~in the form of Fe oxyhydroxides~~ show a linear correlation with salinity~~ at salinities >5~~, 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. The ~~truly dissolved~~D Fe (<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 to10 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 ~~d~~DFe shows relatively constant ~~d~~DFe concentrations of 36~~–~~ to 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. The conservative behaviour of ~~d~~DFe concentrations along a salinity gradient has been examined in estuarine mixing experiments, and it has been shown that freshwater Fe oxyhydroxide colloids aggregate into much larger particles in contact with seawater, whereas the truly dissolved phase was virtually unaffected (Gustafsson et al., 2000; Stolpe and Hassellöv, 2007). The observation that the truly dissolved phase is less affected by the increase in salinity suggests that this phase can be transported through estuaries and further out into the open ocean (Laglera and Van Den Berg, 2009).

River water is the most important source of Fe for the central Arctic Ocean (Klunder et al., 2012) and estuarine processes significantly modify the amount and distribution of Fe between different fractions, and therefore also the bioavailability of the river-derived Fe. 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).

4.2 Iron isotopes in the Lena River freshwater plume

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 (e.g. Escoube et al. 2009; Staubwasser et al. 2013). In these areas, within the fully oxidized water column, the ~~p~~PFe phase show negative δ^{56}Fe values, while the dissolved phase generally shows values, enriched in Fe(III) compared to the PFe phase ~~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). ~~Hirst et al. (in prep.) show a seasonal dependence of the δ^{56}Fe composition of the dissolved fraction (colloidal and truly dissolved) in the Lena River, with summer flow δ^{56}Fe values higher than those of the continental crust, and spring flood δ^{56}Fe values of the dissolved phase lower than those of the continental crust. Therefore, the Lena River can be a source of colloidal Fe with both negative and positive isotope compositions.~~It has been shown that the Fe isotope composition is affected by seasonal variations of water flow pathes to the river (Hirst et al., 2017). Ingri et al. (accepted at GCA) showed that the Fe isotope composition is an indiactor for different Fe aggregates and for changing primary Fe sources throughout the season. Along the freshwater plume the ~~colloidal~~ CFe phase has two different Fe isotope compositions, positive and negative δ^{56}Fe values, therefore it might also represent water masses from different seasons. This would suggest that the water masses in the inner plume represent spring flood discharge, whereas the water masses in the outer plume represent summer flow discharge. In contrast, Alling et al. (2010), claim that the age of the entire freshwater plume is approximately two months. All measured DOC samples (400-420 µM) from their study plot on a mixing line of Lena River water measured in August and Arctic Deep water. If the water would represent spring flood discharge, which has much higher DOC concentrations (1170 µM), their samples would plot on a different mixing line (Alling et al., 2010).

Sundman et al., (2014) measured the speciation of Fe in stream water samples with X-ray absorption spectroscopy and found iron-organic complexes with mixed speciation states of Fe as Fe(II, III)-OC and Fe(III)oxyhydroxides associated to OC. 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). The Fe speciation~~s~~ of these complexes regulate the Fe isotopic composition. When Fe(II) is oxidized to Fe(III), the heavy ^{56}Fe is enriched in the Fe(III) phase whereas Fe(II) becomes depleted in the ^{56}Fe isotope (Bullen et al., 2001; Homoky et al., 2012; Rouxel et al., 2008; Severmann et al., 2006; Welch et al., 2003; Wu et al., 2011). Laboratory experiments showed the existence of ~~the~~ oxidative precipitation of Fe(II) to Fe(III) (e.g. Welch et al. 2003), which can occur in natural streams.~~,~~ Bullen et al. (2001) measured ~~show~~ an overall fractionation factor of about 0.9 in natural streams. Hence, Fe(III)oxyhydroxides should show a enrichment of ^{56}Fe in oxidized river water, while Fe(II, III)-OC complexes should show a depletion of ^{56}Fe. The differences of the Fe isotope composition in the PFe and CFe fraction clearly indicates different sources for the two phases, as flocculation of CFe into PFe would result in PFe with the same isotopic composition (e.g. Escoube et al. 2009). The existence of two different Fe colloid pools, composed of organic-rich and Fe rich particles, was shown by Pokrovsky and Schott (2002) in small boreal rivers. Fe-isotope data from this study show the existence of two colloidal Fe phases with different δ^{56}Fe within the Lena River – Laptev Sea transect. The Fe isotope values ~~variation~~of CFe and PFe along the plume and the composition of the surface sediment suggest that the chemically reactive ferrihydrite represent colloids and particles, with a negative δ^{56}Fe value, sedimenting close to the shoreline. The Fe~~-~~ oxyhydroxides that remain in the water column could then be responsible for the positive δ^{56}Fe values in the colloidal phase in the outer plume. Therefore, in this case the Lena River is an important source of positive δ^{56}Fe values to the Arctic Ocean, along with small OC-rich arctic and subarctic rivers (Ilina et al., 2013; Pokrovsky et al., 2014).

The surface sediments in the shelf areas along the Laptev Sea have δ^{56}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. As seen in earlier studies, flocculation during estuarine mixing did not fractionate the Fe isotopic composition of the colloids and particles (Bergquist and Boyle, 2006; Escoube et al., 2009; Fantle and DePaolo, 2004; Poitrasson et al., 2014). Other processes, as resuspension of sediment and non-reductive dissolution of sediment to the seawater (Radic et al., 2011) would lead to a much more negative (-3.3‰ to -1.7‰) Fe isotope composition of the sediment (Homoky et al., 2009; Severmann et al., 2006; 2010). Therefore, the δ^{56}Fe of the uppermost sediment reflecting the δ^{56}Fe of the sedimenting colloids and particles from the water column seems reasonable.

5. Conclusions

Close to the coast and within the inner part of the river plume, the concentration of ~~p~~PFe dominates the total Fe budgets. In the outer part of the plume, the ~~p~~PFe and ~~cFe~~ CFe concentrations are almost equal, as more than 99% of the total Fe is lost. The loss of P~~p~~Fe, most likely in the form of chemically reactive ferrihydrite, results from increasing ionic strength, due to increasing salinities, which promotes flocculation. The coagulation and removal appear at the beginning of the mixing zone at low salinities (0-5). Colloidal Fe concentrations are almost constant along the inner plume and the decrease along the outer plume due to conservative mixing. The truly dissolved Fe shows little variation along the Lena River freshwater plume. Therefore, the river-derived truly dissolved fraction could be an important source of bioavailable Fe, along with colloidal Fe, which may affect the primary production in the central Arctic Ocean.

The Fe isotope compositions in the Lena River freshwater plume provide clear indications of which forms of Fe reach the deep ocean basin. There are significant differences between the particulate and colloidal phases. The negative δ^{56}Fe values, found in the colloidal and particulate phases, are lost during estuarine mixing and buried in the sediment. These negative δ^{56}Fe values seem to represent chemically reactive ferrihydrite. Within the colloidal phase, we measured positive δ^{56}Fe values further out in the plume, which likely represent Fe-oxyhydroxide, which remain buoyant in the water column, transported along the Lena River freshwater plume into the Arctic Ocean.

~~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.~~

Competing interests

The authors declare that they have no conflict of interest.

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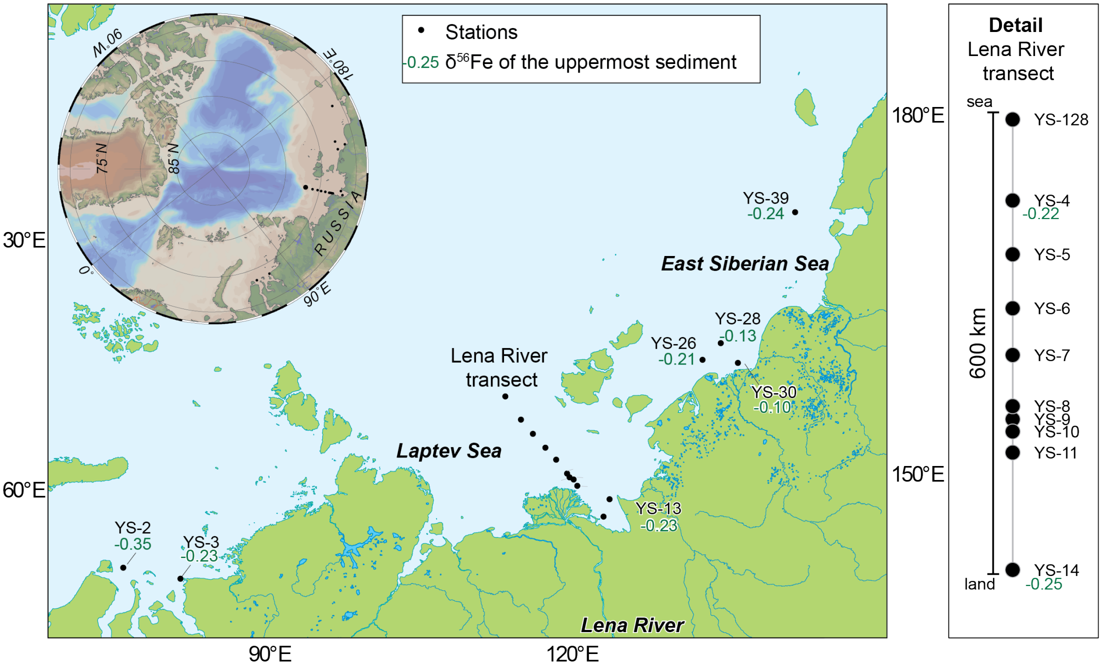


Figure 1: Sampling stations in the Arctic Ocean. Black dots mark the stations in the detailed East Siberian Arctic Shelf ~~ESAS~~ map. Along the Lena River-Laptev Sea transect membrane filtration and/or ultrafiltration was carried out. The sampling stations of this study follow the Lena River freshwater plume. The green numbers display δ56Fe values, measured in the uppermost sediment.

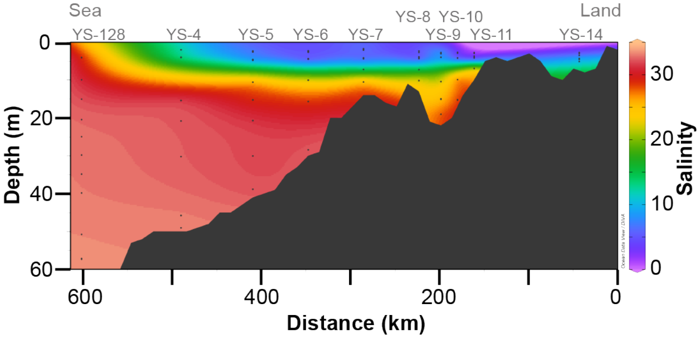


Figure 2: The salinity gradient along the Lena River-Laptev Sea transect. Salinity is based on the Practical Salinity Scale PSS-78. The freshwater builds an almost 10 m thick surface layer in the Laptev Sea, and the plume itself extends over an area of about 50 times 600 km. The plume is divided into an inner and outer plume between station YS-8 and YS-11 by a sharp increase of salinity.

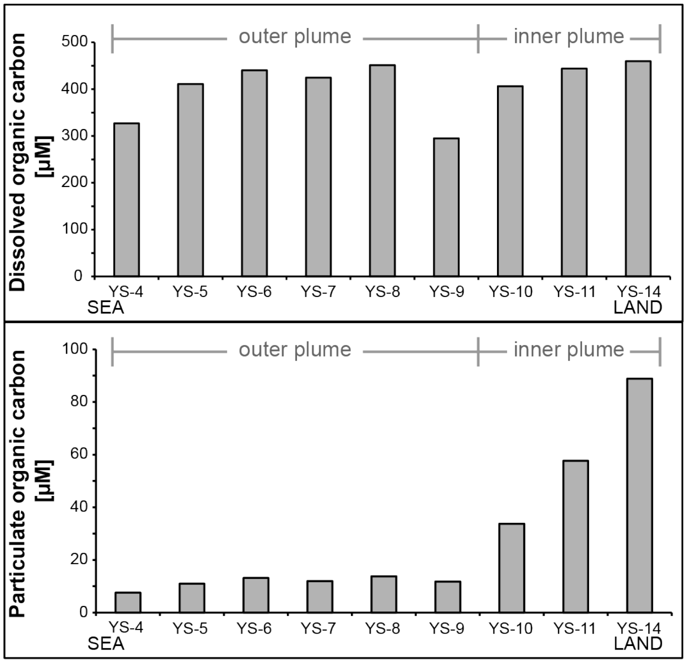


Figure 3: Dissolved (< 0.70 µm) and particulate (> 0.70 µm) organic carbon concentrations along the Lena River-Laptev Sea transect ~~freshwater plume in the Laptev Sea~~. Close to the Lena River mouth POC constitutes about ~~2~~18~~0~~% of the TOC input, while at the outermost station it is only 2% of the TOC.

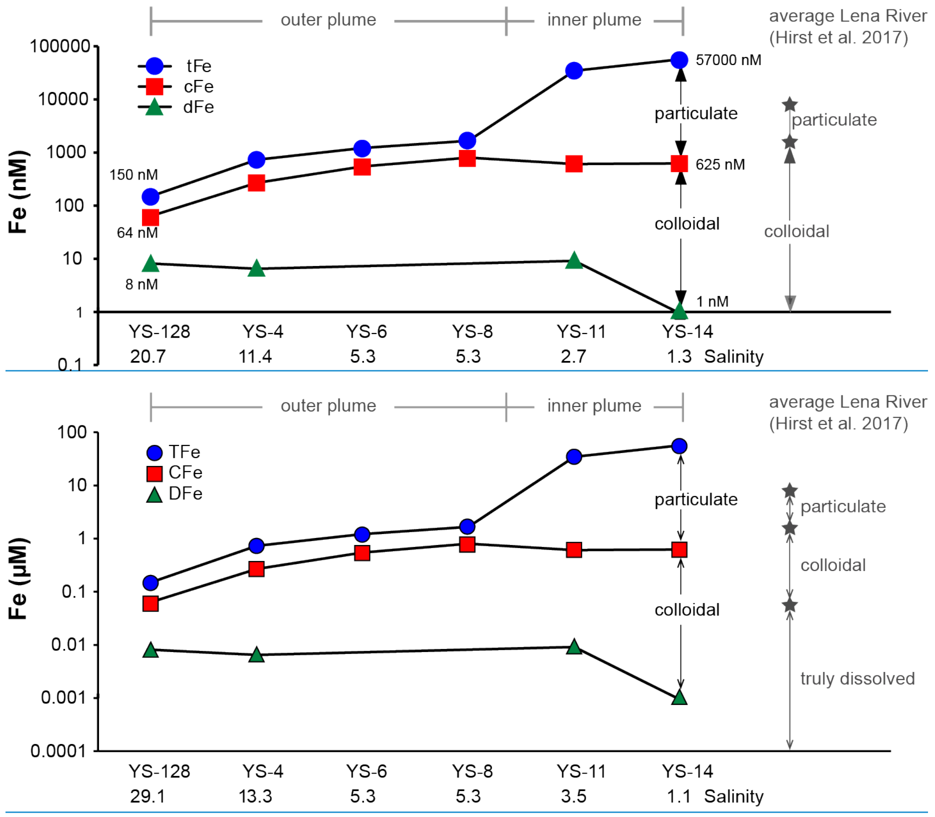
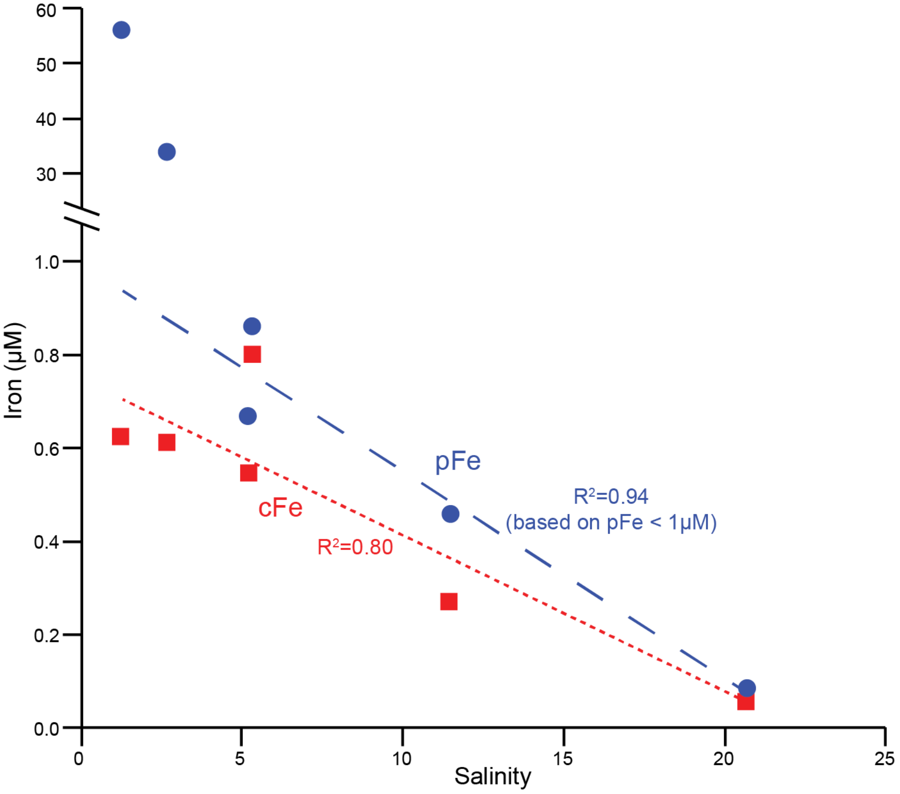


Figure 4: ~~Particulate~~Total, colloidal and truly dissolved Fe concentrations along the Lena River freshwater plume. Concentrations of ~~p~~PFe and ~~c~~CFe decreased along the salinity gradient, while the concentrations of ~~truly dissolved~~ DFe is almost constant. Note the logarithmic scale and the sharp decrease of P~~p~~Fe between the inner and the outer plume. The reference for the Lena River is an average of all analysed samples (PFe n=3; CFe and DFe n=5) by Hirst et al. 2017.


Iron (µM)
60
50
40
30
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
Salinity
pFe
R²=0.94
(based on pFe < 1µM)
cFe
R²=0.80

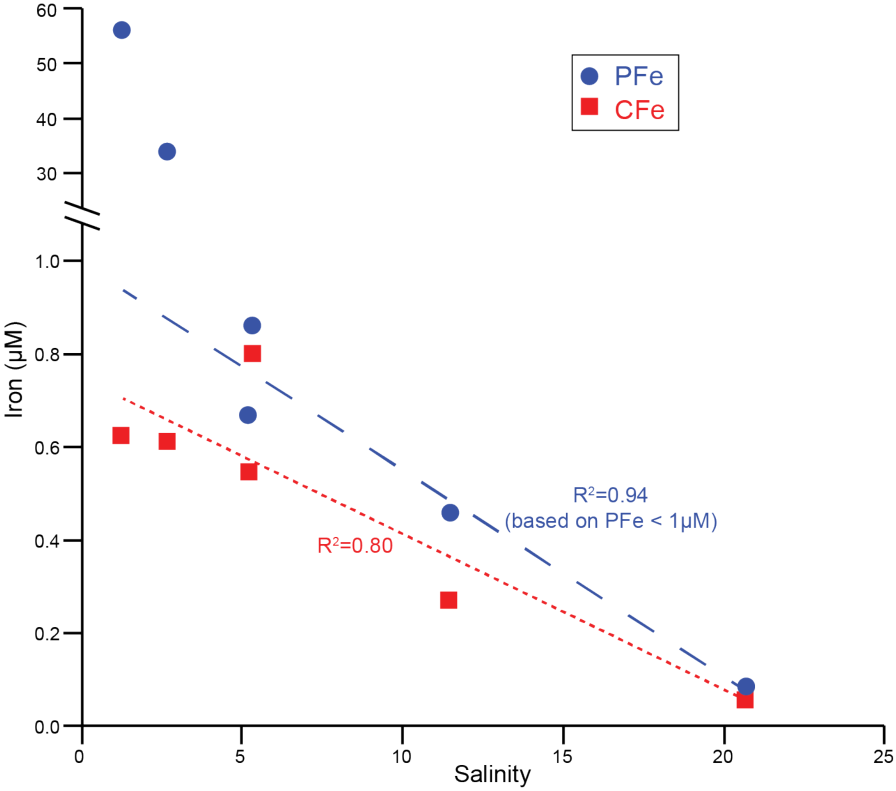


Figure 5: The colloidal and particulate Fe concentrations plotted versus salinity. Salinity is based on the Practical Salinity Scale PSS-78. Note the y-axis break due to the high range of ~~p~~PFe in the inner plume. The linear correlation between ~~p~~PFe and salinity is based on the data points below 1µM ~~p~~PFe. In the low salinity environment, the P~~p~~Fe is much higher compared to the C~~c~~Fe, whereas at salinities above 5 the differences are smaller.

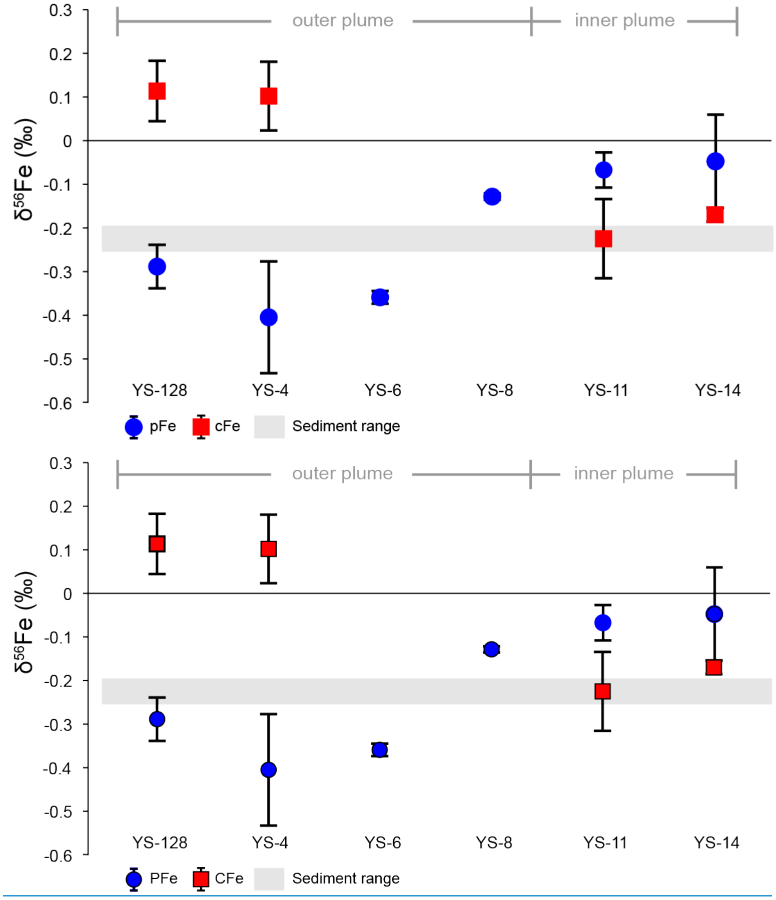


Figure 6: Iron isotope values along the Lena River freshwater plume and the uppermost sediment of the East Siberian Arctic Shelf~~SAS~~ (ESAS). The error bars represent ±2 σ, in some cases the symbol is larger than the error. The δ^{56}Fe values of ~~p~~PFe are negative at all stations, values close to zero close to the coast and more negative towards the open sea. The δ^{56}Fe values of the C~~c~~Fe are negative in the inner plume and positive in the outer plume. The δ^{56}Fe of the sediment samples were around -0.2 ‰, displaying the overall composition of the entire ESAS area.