

## Response to Anonymous Referee #2 comments (RC2)

This research investigates the concentrations and distributions of dissolved iron (dFe) and manganese (dMn) in the surface waters of the Laptev and East Siberian Seas (LESS) during the late summer of 2021. The study concludes that the concentrations of dFe and dMn in the LESS are primarily controlled by river discharge and shelf sediment inputs rather than by sea ice melt. The manuscript contributes important data to the relatively understudied area of trace metal dynamics in the Arctic. The descriptions of sampling and analyzing methods are solid. While this manuscript leans more toward descriptive analysis, it still offers valuable insights into the region's biogeochemical processes. I have several comments on this manuscript:

We sincerely appreciate the reviewer for helping to improve our manuscript. We thoroughly revised it following the reviewer's comments.

### Major comments

1) RC2 Revise the Abstract: The abstract lacks clarity and does not efficiently summarize the entire article. The wording is awkward in places, such as in the phrase "Nutrient-rich Pacific-sourced water exists....," which does not clearly convey that this water mass is dominant in the region. The conclusion section is clearer and does a better job of summarizing the findings. Please rewrite or revise the abstract for better clarity and conciseness.

Following the reviewer's comments, we revised the abstract for clarity and conciseness as follows:

**Abstract.** The Arctic's Laptev and East Siberian Seas (LESS) are areas with high biogeochemical activity. Nutrient inputs associated with river runoff and shelf sediment-water exchange processes are vital for supporting primary production in the LESS. Relative to macronutrients, data on dissolved iron (dFe) and manganese (dMn), essential micronutrients for primary producers, have been historically sparse in the LESS. Some dFe and dMn are reportedly carried in the Central Arctic by the Transpolar Drift, a major current that directly transports Eurasian shelf water, river waters, and sea ice from the LESS continental margins. However, dFe and dMn supply to the surface waters of the LESS and subsequent biogeochemical processes are not well constrained. In the summer of 2021, we investigated the questions: *what are the sources of dFe and dMn to the surface layer and what factors control their concentrations and distributions on the LESS continental margins?* We demonstrated strong regional controls in dFe and dMn distribution based on distinct hydrographic regimes between the eastern side of the LESS (the East Siberian Sea and the Chukchi Abyssal Plain) and the western side (the Makarov and Amundsen Basins). Specifically, the East Siberian Sea and Chukchi Abyssal plain were governed by Pacific-sourced water and the Makarov and Amundsen Basins were influenced by Atlantic-sourced water. Pacific-sourced waters contained higher levels of dMn released from the continental shelf sediments than Atlantic-sourced water. In contrast, elevated dFe signals were not observed; which is likely because sedimentary dFe was more rapidly removed from the water column through oxidation or scavenging than dMn.

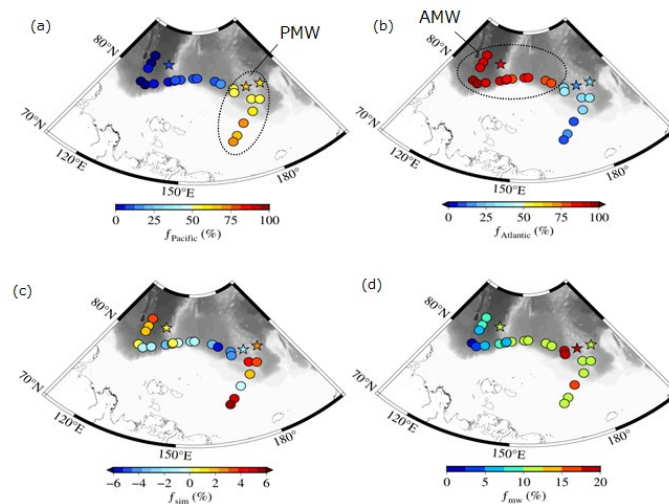
The impact of river water discharge on the dFe distributions of Pacific- and Atlantic-sourced water is significant. A positive correlation between the fraction of meteoric water (river water and precipitation), dFe, and humic-like colored dissolved organic matter (CDOM) in these waters confirmed a common freshwater source for dFe and CDOM. Terrigenous organic ligands likely stabilized Fe in the dissolved phase, which was not the case for Mn. Sea ice melting/formation was not a significant source during our observation period. We conclude that the major sources controlling dFe and dMn distributions in the LESS continental margins are river discharge and the input of shelf sediment. “

2) RC2 Reorganize the structure. The method for calculating water mass fractions, described in lines 181–210, should be moved to Section 2 (Methods)

Following the reviewer’s suggestion, we created a new subsection 2.5 in the Method section and moved the calculation for water mass fractions there.

3) RC2 Lines 211–220 do not present the mass fraction of Atlantic water. This information should be included. And its also not shown in Figure 3.

As the reviewer indicated, we included the mass fraction of Atlantic water ( $f_{\text{Atlantic}}$ ) in the figure. We made a new figure regarding the results of mass fraction analysis because the previous Figure 3 contained much information. The conclusion of the text has not been changed by this revision. The revised figure is as follows:



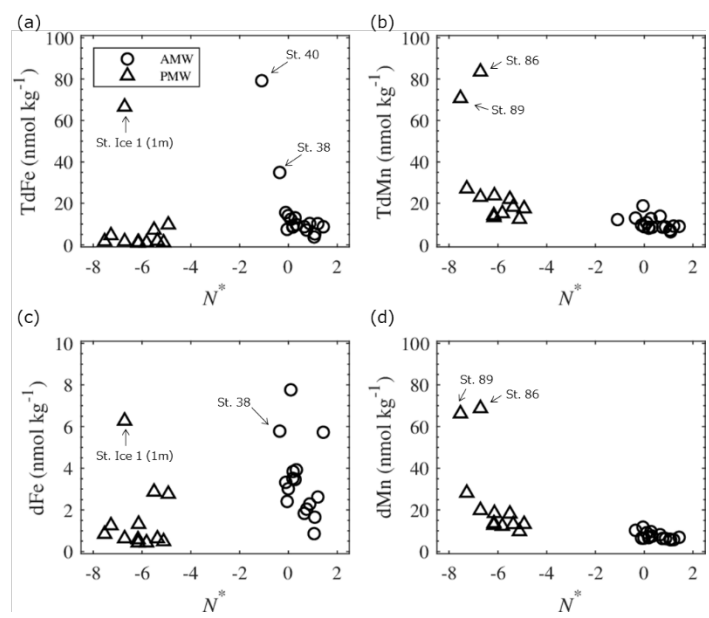
“**Figure 4** Spatial distributions of fractional (a) Pacific Water ( $f_{\text{Pacific}}$ ), (b) Atlantic Water ( $f_{\text{Atlantic}}$ ), (c) sea ice meltwater ( $f_{\text{sim}}$ ), and (d) meteoric water ( $f_{\text{mw}}$ ) in the surface of the Arctic’s Laptev and East Siberian Seas. Abbreviations in (a) and (b): Surface Polar Mixed Water (PMW) and Surface Atlantic Mixed Water (AMW). “

4) RC2 Section 4.2.1: The sedimentary contribution to dFe and dMn is not adequately discussed.

In response to the reviewer’s comment, we plotted dissolved fractions of the metals with  $N^*$  as well. We also added a discussion to the text regarding the sedimentary contribution to dFe and dMn. The revised manuscript is as follows:

Section 4.2.1

“Our results showed that the  $N^*$  value in PMW was much lower ( $< -5$ ) than that in AMW (Fig. 7). Although Fe and Mn are thought to be released in the dissolved phase from reductive sediments over the Chukchi Shelf, these metals are gradually removed from the water column as the particulate phase (Jensen et al., 2020). The TdMn and dMn concentrations tended to be high in low- $N^*$  PMW, suggesting a reductive sedimentary flux that released Mn from the Chukchi Shelf (Fig. 7b and d). Mn was more elevated at shallow shelf stations 86 and 89, which were the most influenced by shelf inputs. Given that the dMn to TdMn ratio in PMW is as high as  $85.2 \pm 10.2\%$ , Mn was primarily in the dissolved phase. On the contrary, the TdFe and dFe concentrations in PMW were relatively low (Fig. 7a and c) compared to those typically observed in the continental margin of the Arctic Ocean (Aguilar-Islas et al., 2013; Cid et al., 2011, 2012; Jensen et al., 2020; Klunder et al., 2012; Kondo et al., 2016; Nakayama et al., 2011; Nishimura et al., 2012). This is likely because Fe was much more rapidly removed in the Chukchi Shelf water column than Mn via oxidation and re-precipitation (Jansen et al., 2020; Vieira et al., 2019; Millero et al., 1987). Indeed, we observed a lower dFe to TdFe ratio ( $43.6 \pm 23.8\%$ ) in PMW, such that Fe was primarily in the particulate phase. The relatively high Fe concentrations at stations Ice-1, 38, and 40 are likely attributable to riverine flux because these stations show relatively high fractional  $f_{mw}$  (see discussion below). “



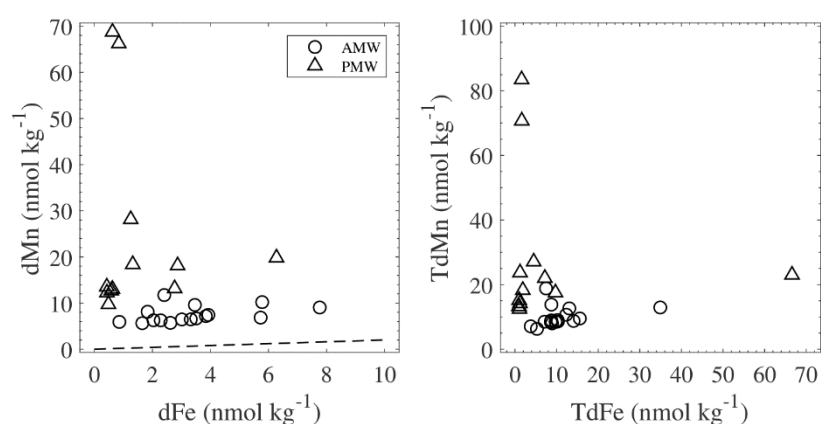
“Figure 7 Plots of (a) TdFe, (b) TdMn, (c) dFe, and (d) dMn in Surface Atlantic Mixed Water (AMW) and Surface Polar Mixed Water (PMW) against  $N^*$  values.”

5) RC2 Line 334–335: This section is unclear. Although sedimentary inputs to dFe and dMn were discussed in Section 4.2.1, the correlations between TdFe, TdMn, dFe, and dMn should be more clearly explained.

In response to the reviewer's comment, we plotted the correlations between TdFe, TdMn, dFe, and dMn in the supplement figure S6. We also explained the correlations between them in the Section 4.2. The revised text is as follows:

Section 4.2.

“A significant correlation between dFe and dMn has been observed in the deeper waters (>3000 m) of the Amundsen and Makarov Basins because scavenging removal is the dominant process in the deep water masses (Klunder et al., 2012). In the surface water of the LESS, Fe was not correlated with Mn in the unfiltered and filtered fractions (Fig. S6). More factors, such as external input, influence the dFe and dMn distribution in the surface waters, leading to a disappearance of the Fe-Mn relationship. Moreover, enrichment in dMn compared to dFe (Fig. S6a) was observed in all sampled surface water, suggesting the importance of input fluxes of dMn or the preferential scavenging of dFe relative to dMn.”



“Figure S6 (a) Plot of dMn in Surface Atlantic Mixed Water (AMW) and Surface Polar Mixed Water (PMW) against dFe. (b) Plot of TdMn against TdFe. The dashed line in (a) presents the relation of both metals found in the deeper waters (>3000 m) of the Amundsen and Makarov Basins, with a correlation:  $[dMn] = (0.15 \times [dFe]) / 0.75$  (Klunder et al., 2012).”

6) RC2 Figure 6 and Line 297: What are the possible explanations for the outliers with high TdFe and TdMn? Are these stations heavily influenced by sedimentary inputs? Please address these points.

We highlighted the outliers in the figure. The outliers with high TdMn were obtained at two shallow southernmost stations on the shelf of the East Siberian Sea, and therefore the outliers were likely influenced by sedimentary inputs. For the TdFe, the sampled water seems to be influenced by the inputs of river runoff because these stations show relatively high fractional  $f_{mw}$ . We addressed the points as follows:

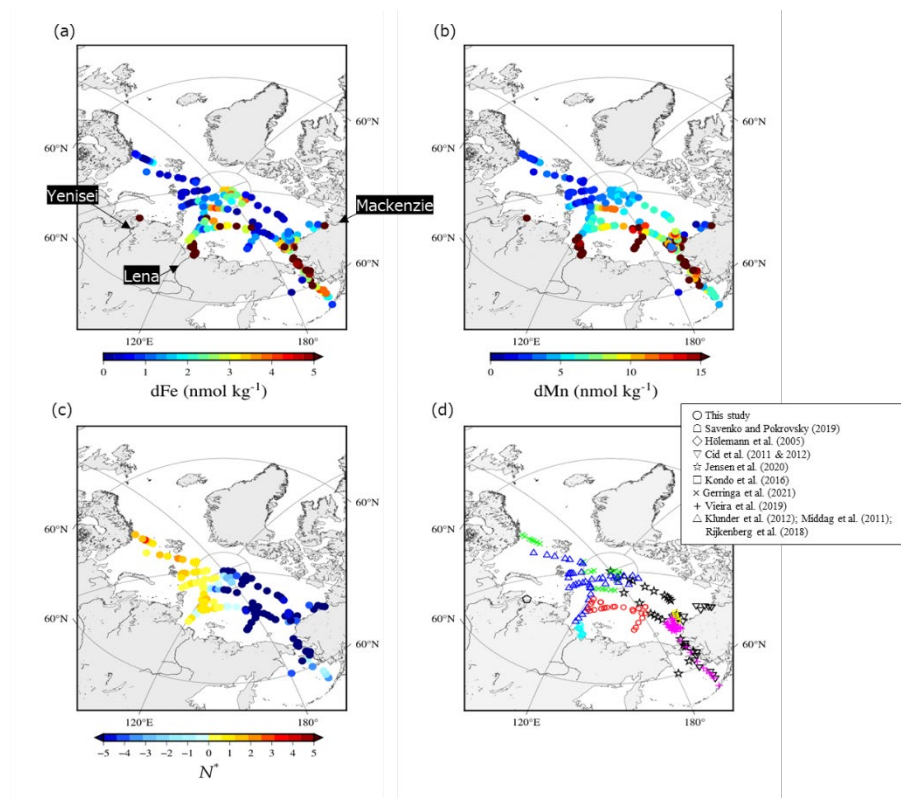
Line 297:

“Although Fe and Mn are thought to be released in the dissolved phase from reductive sediments over the Chukchi Shelf, these metals are gradually removed from the water column as the particulate phase (Jensen et al., 2020). The TdMn and dMn concentrations tended to be high in low- $N^*$  PMW, suggesting a reductive sedimentary flux that released Mn from the Chukchi Shelf (Fig. 7b and d). Mn was more elevated at shallow shelf stations 86 and 89, which were the most influenced by shelf inputs. Given that

the dMn to TdMn ratio in PMW is as high as  $85.2 \pm 10.2\%$ , Mn was primarily in the dissolved phase. On the contrary, ... The relatively high Fe concentrations at stations Ice-1, 38, and 40 are likely attributable to riverine flux because these stations show relatively high fractional  $f_{mw}$  (see discussion below). “

7) RC2 Section 4.4 and Figure 11: The comparison with other studies is valuable, but Figure 11 caption is not informative enough and needs to be modified. Please properly cite data sources in the figure captions. Use different symbols for different data sources instead of the same symbols, and highlight the data from this study using distinct symbols. Additionally, I suggest adding a summary figure by region to show how the data from this study compares with or complements the range of data reported in previous research.

When we use different symbols on the figure with a color ramp, the figure looks hard to see. Instead, we revised the figure with proper symbols and citations as follows:



"Figure 12 Spatial distributions in (a) dFe, (b) dMn, and (c)  $N^*$  in surface water (< 25 m depth) in the Arctic Ocean. (d) Location of stations on dFe, dMn, and  $N^*$  reported by this study and the previous studies."

It should be noted that we plotted additional data on Vieira et al (2019) in Figure 12 because that data is also worthwhile in this comparison.

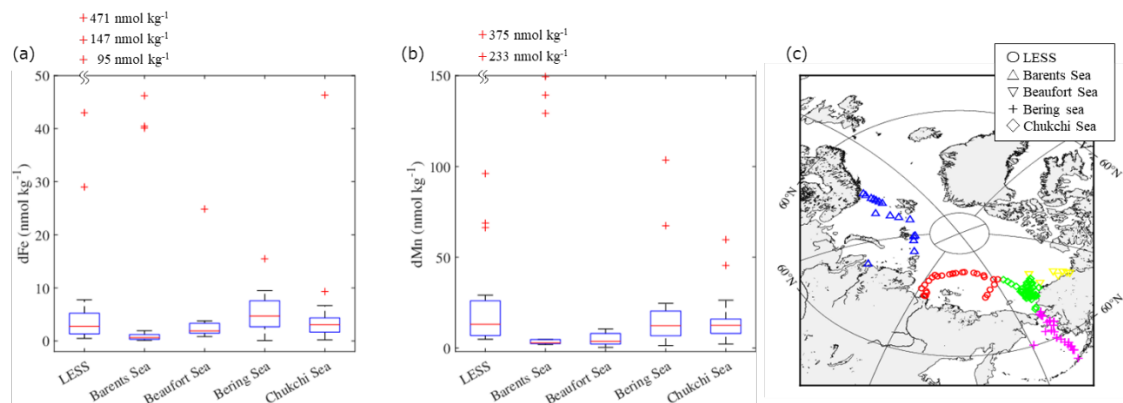
We also added a summary figure in section 4.4. to explain how the data from this study compares with the previous study. The revised text and figure are follows:

#### Section 4.4.

“To investigate the distribution patterns of dFe and dMn in surface waters, we combined our dataset with available data reported for the Arctic Ocean (Cid et al., 2011, 2012; Gerringa et al., 2021; Hölemann et al., 2005; Jensen et al., 2020; Klunder et al., 2012; Kondo et al., 2016; Middag et al., 2011; Rijkenberg et al., 2018; Savenko and Pokrovsky, 2019; GEOTRACES Intermediate Data Product Group, 2023). The dFe concentrations are relatively low (up to 2 nmol kg<sup>-1</sup>) in the Atlantic sectors of the Arctic Ocean (Fig. 12a). In the surface of the Nansen Basin and Barents Sea, Fe is expected to be the first nutrient to be depleted by primary producers (Rijkenberg et al., 2018), and phytoplankton consumption could be an important sink for Fe. In the LESS continental margins, however, surface dFe concentrations are significant (>5 nmol kg<sup>-1</sup>) and even persist in the late summer of 2021 (Fig. 12a). Figure 13a shows a boxplot of the surface dFe concentration combined our dataset with available data reported for each region in the Arctic Ocean (Fig. 13 a and c). All sampled water in Figure 13 has salinity larger than 25. The result shows that the median value is the highest in Bering Sea (4.7 nmol kg<sup>-1</sup>) followed by Chukchi Sea (3.1 nmol kg<sup>-1</sup>) and by LESS (2.8 nmol kg<sup>-1</sup>). We deduce that sedimentary Fe originating from reductive Bering Shelf is gradually removed in Chukchi Sea after entering it from the Bering Strait (Jansen et al., 2020), and then penetrate East Siberian Sea. The dFe concentrations also increased toward the estuaries of the Lena, Yenisei, and Mackenzie Rivers (Fig. 12a). Other studies determined that dFe concentration in the estuary water (salinity < 25) of the Lena River was as high as 9,000 nmol kg<sup>-1</sup>, as well as in the estuary waters of the Yenisei and Mackenzie Rivers. Fe-binding organic ligands in the form of humic substances originating from Lena River strongly affect the dFe concentration here, as discussed in the previous section. The natural humic substances Fe ligands of the surface Arctic Ocean have known to belong to the group of strong ligands ubiquitous in surface ocean waters (Laglera et al., 2019). The strongly complexed Fe may be less biologically available to the phytoplankton community than the weakly complexed Fe released from grazing and bacterial remineralization of organic matter (Gledhill and Buck, 2012). The river-influenced water from the LESS continental margins is the source water of the Trans Polar Drift, which enriches in dFe in the central Arctic Ocean (Fig. 12a) (Charette et al., 2020; Gerringa et al., 2021; Klunder et al., 2012).

High dMn found in the central Arctic Ocean (Fig. 12b) is also related to the presence of Trans Polar Drift (Charette et al., 2020; Gerringa et al., 2021). In addition to the riverine inputs, sediment-water column exchange over the shelves leads to relatively dMn-rich water in the Pacific sectors of the Arctic Ocean. The dMn concentrations increased toward the broad shelves of the East Siberian Sea (~68 nmol kg<sup>-1</sup>), Chukchi Sea (~45 nmol kg<sup>-1</sup>), and Bering Sea (~103 nmol kg<sup>-1</sup>), whereas the concentration was relatively low (~8 nmol kg<sup>-1</sup>) over a narrow shelf of Beaufort Sea (Fig. 12b). Boxplot of the surface dMn concentration in Figure 13b shows that the difference of median value is relatively small among LESS (13.0 nmol kg<sup>-1</sup>), Chukchi Sea (12.4 nmol kg<sup>-1</sup>), and Bering Sea (12.2 nmol kg<sup>-1</sup>). As previously discussed, the shelf sediment-water exchange processes over the Chukchi Shelf largely influence the Fe and Mn distributions in the East Siberian Sea. Vieira et al. (2019) provided the first estimate of the benthic flux of the radium isotope (Ra<sup>228</sup>) in the Chukchi Sea as tracers of benthic trace metal inputs,

which was among the highest rates reported globally. The low- $N^*$  water spreads over regions where nitrate is already depleted relative to phosphate, mainly due to the oxidation of organic matter by bacteria in the reductive shelf sediment (Fig. 12c). The East Siberian Sea, as well as Chukchi Sea, are likely hotspots of sediment-sourced dMn via the reductive dissolution of Mn oxide in the sediment. A multi-step removal process of dMn has been suggested in the Arctic (Jansen et al., 2020): dMn is rapidly removed to the particulate phase within 150 km of the shelf break, but some dMn remains conserved through the next 1000 km away from the shelf. The dMn originating from the LESS continental margins appears to be exported by the Trans Polar Drift to the central Arctic Ocean effectively (Fig. 12b), even though stabilization by organic complexation is unlikely for Mn during offshore transport. “

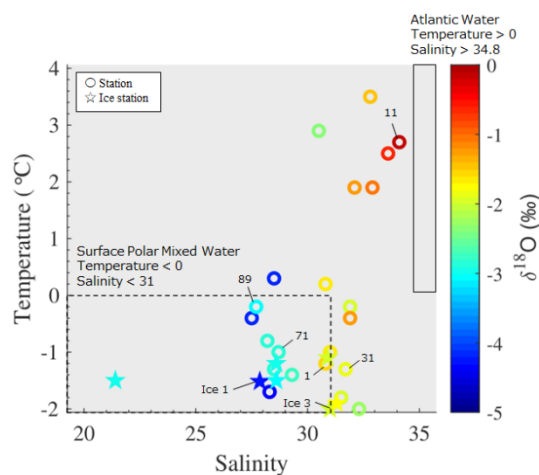


“**Figure 13** Boxplots of (a) dFe and (b) dMn concentrations in surface water (< 25 m depth) in each region of the Arctic Ocean. (c) Location of stations used in this boxplot. The bottom and top of the box in (a)–(b) indicate the 25th and 75th percentiles, respectively, and the line inside the box indicates the median. The bottom and top error bar in (a)–(b) show minimum and maximum values, respectively, and the outliers are plotted individually using the '+' marker symbol. Some outliers are plotted the outside of figures to better show differences between regions. “

#### Minor comments

8) RC2 Considering color figure 2 by the  $\delta^{18}O$  values and using different symbols to distinguish the different ice stations.

As the reviewer suggested, we made a color figure by the  $\delta^{18}O$  values. Data on ice stations were presented by different symbols. The previous Figure 2 was moved to a supplementary figure. The revised figure and its caption are as follows:



“**Figure 2** Temperature versus salinity diagram on the surface with stations sampled in the Arctic’s Laptev and East Siberian Seas. The color scale shows the  $\delta^{18}\text{O}$  values in each water sample. The temperature and salinity ranges of Surface Polar Mixed Water and Atlantic Water are indicated by the area surrounded by dashed and solid lines, respectively. “

9) RC2 The differences between total dissolved iron (TdFe) and total dissolved manganese (TdMn) should be clearly defined in the methods section. A detailed explanation is not provided until line 184. It should be clarified that total dissolved Fe includes both dissolved and particulate Fe in the water column.

As the reviewer suggested, we defined it in the method section of 2.1. The revised text is as follows:

Section 2.1.

"Seawater was collected from the side of the ship at a depth of approximately 10 m using a peristaltic pump (Geopump, Geotech Environmental Equipment, USA) and a Tygon tube. Filtered and unfiltered samples of Fe and Mn were obtained in this study to assess the labile particulate fractions of these metals. Samples of the dissolved fractions of Fe and Mn (dFe and dMn) were collected into LDPE bottles after filtration through Acropak filters connected to a Tygon tube. The samples for total dissolvable Fe and Mn (TdFe and TdMn) were collected without filtration into LDPE bottles. The pH for Fe and Mn samples was adjusted to  $< 1.8$  by adding ultrapure grade 6 M hydrochloric acid (Tama pure AA-100, Tama Chemicals, Japan), and they were stored for a year before the analysis. The concentration differences between the unfiltered (i.e., TdFe and TdMn) and filtered samples (i.e., dFe and dMn) were therefore attributed to the acid-labile particulate fraction. "

10) RC2 Line 257–260: The phrase "deviated towards" is confusing in this context. The surface water is not close to the meteoric  $\delta^{18}\text{O}$  values, although the salinity is close. It seems you might mean "deviated from" instead. Please revise this sentence for clarity.

As the reviewer pointed out, we revised the text as "deviated from".

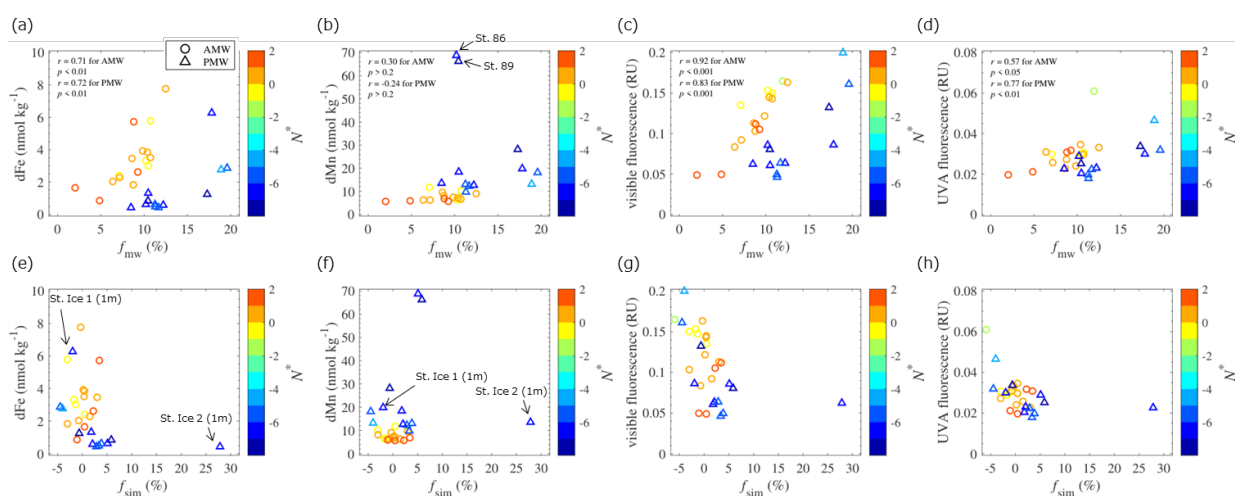


11) RC2 Definition of  $f_{mw}$ : On line 306, clarify that  $f_{mw}$  includes river runoff and local precipitation in the calculation of water mass fractions. (Please refer to Major Comment 3)

Following the reviewer's indication, we included the definition of  $f_{mw}$  in the section on the calculation of water mass fractions.

12) RC2 Figure 7b and Line 319: I am curious about the  $r$  and  $p$  values for AMW and PMW separately. Please include these in the figure, as you have done in Figure 7a, even if they are not statistically significant.

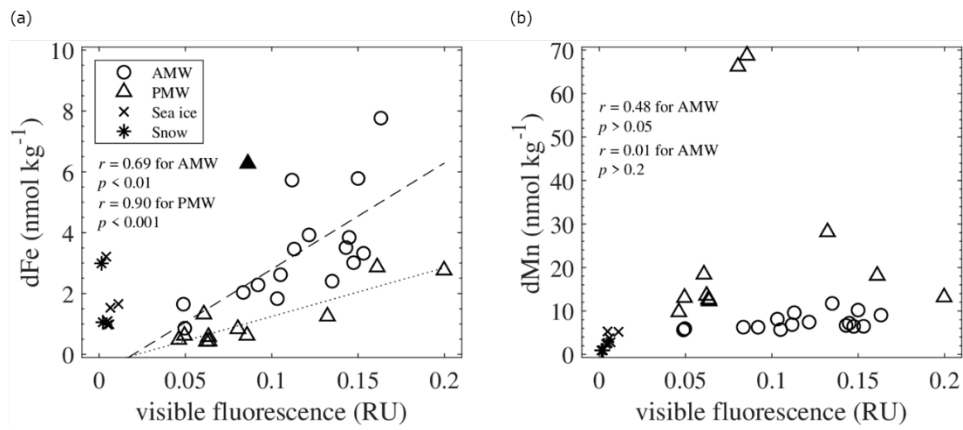
As the reviewer suggested, we included the  $r$  and  $p$  values in the figure as follows:



"Figure 8 Plots of dFe, dMn, visible fluorescence, and UVA fluorescence in Surface Atlantic Mixed Water (AMW) and Surface Polar Mixed Water (PMW) against fractional meteoric water ( $f_{mw}$ ) in (a)–(d) and sea ice meltwater ( $f_{sim}$ ) in (e)–(h). The color scale shows the  $N^*$  values of each water sample. Linear relationships were evaluated based on Pearson correlation coefficients ( $r$ ). The liner fits of the visible fluorescence- $f_{mw}$  relationships in the AMW and PMW are shown by dashed and dotted lines in (c), respectively."

13) RC2 Figure 10b: Please report the  $r$  and  $p$  values in Figure 10b, as you did in Figure 10a, even though the correlations are not statistically significant.

As the reviewer suggested, we included the  $r$  and  $p$  values in the figure as follows:



**Figure 11** Relationships of visible fluorescence with (a) dFe and (b) dMn in Surface Atlantic Mixed Water (AMW), Surface Polar Mixed Water (PMW), sea ice, and snow. Linear relationships were evaluated based on Pearson correlation coefficients ( $r$ ), except for an outlier ( $\blacktriangle$ ) in (a). The linear fits of the relationships in the AMW and PMW are shown by dashed and dotted lines in (a), respectively."