

Interactive comment on “Sources of Fe-binding organic ligands in surface waters of the western Antarctic Peninsula” by Indah Ardinarsih et al.

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Thank you for your kind words efforts to improve this manuscript. We have answered all the questions with the details listed below.

(1) The relationship between complexation capacity of the ligands and Fe distributions
The authors explained the relationship between complexation capacity of the ligands and Fe distributions in the beginning of section 4.2, but it was about the specific sample. How was the overall trend?

Reply: In general, the complexation capacity ($\log \alpha$) was highest in mCDW, and lower in AASW compared to mCDW and uCDW. We have added text regarding the overall trend of complexation capacity in this study (lines 248 – 249). “The largest \log “K” “Fe”L”

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“cond” and $\log \alpha$ was measured in shelf waters, particularly in mCDW (mean $\log \alpha = 3.4 \pm 0.2$, N=8; Figure 4b). The overall decreasing trend of \log “K” “Fe”L” “cond” and $\log \alpha$ was observed from mCDW, uCDW to AASW.”

(2) The meaning of excess ligands in this study area, [L] was always observed and additional Fe input was expected to be stabilized in the dissolved form. Although particulate Fe was not investigated in this study, it was expected that some portion of Fe might exist as particulate form in the WAP (Seyitmuhammedov, 2020). The co-existence of [L] and particulate Fe sounds like a contradiction. How do the authors think about the contradiction? But I could not access the reference Seyitmuhammedov (2020) via online because it is Doctoral thesis; so I’m not sure whether Seyitmuhammedov (2020) researched the total dissolvable Fe during the same cruise to this study. If so, please explain brief results from Seyitmuhammedov (2020).

Reply: In seawater, we can expect a steady state between dissolved and particulate Fe fractions. Dissolved Fe fractions consist predominantly of organic complexes. The particulate Fe fraction is formed by adsorption and aggregation processes. The particulate Fe fraction should be competing with the organically complexed dissolved Fe fraction, assuming that Fe is reversibly bound. The formation of particulate Fe fraction depends on pH, dissolved oxygen concentration and the concentration of dissolved Fe not bound by organic ligands (Fe’). If the concentration of Fe’ is above a threshold value, the particulate Fe will precipitate. This Fe’ is thus governed by pH, adsorption sites on particles and competing strength of natural Fe-binding ligands. Competing strength of organic ligands is also called complexation capacity (α), which depends on availability of ligand binding sites (concentration of ‘free’ ligands, [L]) and the conditional binding strength of ligands (“K” “Fe”L” “cond”).

In summary, all species co-exist in a steady state, which depends pH, dissolved oxygen, α and adsorption sites on particles. Briefly, the dissolved-Fe concentrations along the transect from shore to open ocean ranged from 0.08 – 4.88 nmol/L (Seyitmuhammedov et al., submitted). Relatively elevated concentrations of DFe (0.31 –

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1.84 nmol/L) were observed in the surface layer at the shelf break and mid-shelf; and near to the seafloor on the shelf.

Minor comments: Page 2, L38. CO₂ "2" should be written in subscript.

Reply: corrected.

Page 3, L72-79. Humic substances (HS) and HS-like substances. . . Complicated notation. Because this study did not investigate the HS and HS-like substances specifically, the authors can unify the terms and explain in this section.

Reply: We have simplified the notation to become "humic and humic-like substances (HS)".

Page 4, L114-115. Low density polyethylene bottle (LDPE, Nalgene). In general, GEOTRACES cookbook recommends fluorinated high density polyethylene bottle (FLPE) or Teflon bottles for the sampling of ligands in order to avoid the absorption to the bottle wall. Did the authors check the influence of the difference on the CLE-AdCSV?

Reply: We have not specifically checked the influence of different bottle types (FLPE and LDPE) on CLE-AdCSV in this study. However, previous studies (Fischer et al., 2006; Gerringa et al., 2015; Jensen et al., 2020) have checked the adsorption of Fe on the bottle walls. Gerringa et al. (2015) reported that the DFe concentration in subsamples taken the ligand samples is about 13% lower compared to the DFe concentration in samples immediately acidified on board. The adsorption of DFe in the bottle wall is not uniform and depends on the material of the bottles, whether they are new or old bottles, on the character of the ligands, on the saturation of the ligands. We conditioned the sample bottles by rinsing five times with the seawater sample before filling it.

Page 6, L137-. Section 2.3 Did the authors apply air purge method? Please add the information about the purging method.

Reply: To improve the sensitivity of voltammetric measurement, air-blanketing and air-purging are recommended by Abualhaja et al. (2014) if samples are not already in

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equilibrium with air. The voltammetric cell in the BASi system (instrument used in this study) is open to the atmosphere, thus, we assumed that the sample in the cell is in equilibrium with air, therefore, we did not purge during the analysis. The sample in the voltammetric cell was stirred, i.e. as done by Buck et al. (2017).

Page 6, L158-159. . . .the product of [L'] and log K,. . . Probably the authors can eliminate "log" from the sentence.

Reply: done.

Page 7, L164-165. The conditional stability constant of. . . Did it mean that different calibration result from the original method (Abualhaja and van den Berg, 2014) was obtained?

Reply: We have a different value than in (Abualhaja and van den Berg, 2014) since we used pH adjusted values of $\log \alpha_{inorg} = 10.4$ for pH = 8.2 (Liu and Millero, 2002). These are slightly different from the commonly used $\log \alpha_{inorg} = 10$. This $\log \alpha_{inorg}$ is used to transform the conditional stability constant of SA ($\log K$) in respect to Fe³⁺, into the one with respect to Fe'. We obtained a conditional stability constant of SA in respect to Fe³⁺ = 16.34 or conditional stability constant of SA in respect to Fe' = 5.94, whereas (Abualhaja and van den Berg, 2014) obtained a conditional stability constant of SA in respect to Fe³⁺ = 16.5 or conditional stability constant of SA in respect to Fe' = 6.5. The results of our calibrations are reported by Gerringa et al. (submitted).

Page 8, Figure 2 (b) and (c). Please add the boundary line between mCDW and uCDW in Figures 2 (b) and (c).

Reply: the approximate boundary line between mCDW and uCDW is added in figure 2b.

Page 9, Figure 3 (a), (b) and (c) Please add the titles for x-axis.

Reply: Done.

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Page 11, Figure 5 (b) and (c). Please add the data points in the Figures 5 (b) and (c), too.

Reply: Done.

Page 12, L249- Section 4.1 Why there was the huge differences in [L'] distributions in deeper water between stations 70 and 72? Both stations are located in the shelf region but separated by a sill. It is very interesting. In the deeper waters at station 72, high Si* and low N/DFe values were observed. Is [L'] likely to have a relationship with Si* or N/DFe?

Reply: We have done correlation tests for the correlations between [L'] and Si*; and between [L'] and N/DFe. There is no significant correlation between [L'] and N/DFe, whereas [L'] positively correlates with Si* ($R^2=0.37$; $F(1,25)=14.85$; $p<0.01$, coef. correlation $r = 0.61$). Since a negative value of Si* indicates Fe limitation, the positive correlation between [L'] and Si* indicates that the high [L'] in deeper water on the shelf was not related to Fe-limited conditions. Furthermore, the ratio of Mn:Fe at this station (Seyitmuhammedov et al., in review) indicates a lithogenic source of Fe at this location, thus it is possible that [L'] at station 72 was a result of sediment resuspension.

Page 13, L285 However, given. . . I think the mixing process influenced on the distribution of phytoplankton as well as on those of Fe, L and nutrients. I think the ligand production rate by phytoplankton is different between species and their physiological status, too.

Reply: We agree with the referee that different phytoplankton species have different rates of organic ligand production, and different species may also produce different type of organic ligands. We modified the existing paragraph with this information (lines 300 – 306). “However, given the consistently low and constant distribution of [L] at the shelf break, it seems that mixing determines the distribution and net concentrations of ligands (Figure 3a) and the microbial species composition. Different microbial species have different rates of organic ligand production, and different microbial species may

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produce different type of organic ligands (Norman et al., 2015). The influence of mixing on ligands and microbial species composition is confirmed by the relatively constant distribution of DFe and macronutrients (i.e. nitrate; Figure 5c) at the same station, indicating that prominent mixing at the shelf break indeed is the major factor governing the distribution of ligands, DFe and nutrients. ”

Page 16, L341-. Section 4.2. Are there any information about the phytoplankton species during this observation? Reply: we did not look at the phytoplankton species in particular, however, another group from the same cruise has examined the community composition in our study area (Joy-Warren et al., 2019). The study conducted by Joy-Warren et al. (2019) showed that Phaeocystis Antarctica dominated this region during our sampling period in Austral spring. We have added this information to the text (lines 366 – 369): “A longer residence time has a positive feedback on the development of local primary productivity upon sea ice melting (Arrigo et al., 2017), supplying DFe to primary producers on the shelf, which were dominated by Phaeocystis Antarctica during our sampling period (Joy-Warren et al., 2019).”

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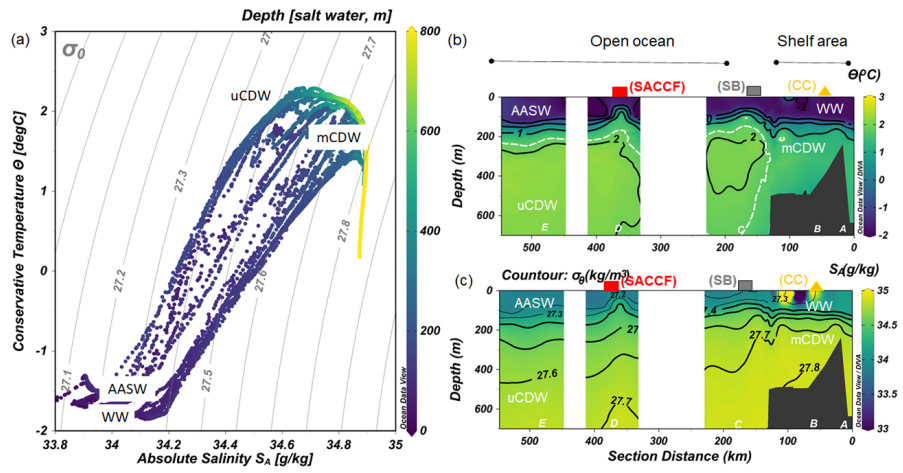


Fig. 1.