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Discussions

Interactive comment on "Sources of Fe-binding organic ligands in surface waters of the western Antarctic Peninsula" *by* Indah Ardiningsih et al.

Indah Ardiningsih et al.

indah.ardiningsih@nioz.nl

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Thank you for the suggestions to improve the manuscript. we have revised the manuscript with details below.

(1) First, the title (Sources of Fe-binding organic ligands in surface waters of the western Antarctic Peninsula) and the introduction of the manuscript give me the impression that this study will use a new method/technique other than CLE-AdCSV to identify the sources of organic ligands in the WAP region. In the Introduction, the authors wrote "The application of AdCSV gives the total concentration ([Lt]) and conditional binding strength of the dissolved organic ligands but does not provide information on the identity of ligands" (line 56-57) then stated that "the sources and identities of Fe-binding

ligands are still largely unknown" (line 58=59). Thus, I was excited to see what (new) methods the authors would use to pinpoint the sources of organic ligands in the WAP region, which is a very important issue to address, and I think, have not been done before. However, at the end of the Introduction, the authors wrote (line 97-100): "In order to probe sources and distributions of Fe-binding ligands along a natural gradient of Fe, the CLE-AdCSV technique was used to quantify the total concentrations and conditional stability constants of Fe-binding ligands". To be honest, I was a bit disappointed and confused at this point. As an ocean biogeochemistry modeler who does not have a strong background on measurement techniques, I do not understand how the authors can probe the sources of ligands by using the CLE-AdCSV technique, which was stated before that cannot be used to provide information on the identity of ligands. It turns out that, if I understood correctly, the authors used CLE-AdCSV to measure the concentration and strength of organic ligands, then they based on other hydrographic and biogeochemical features, as well as previous studies, to hypothesize/argue about the potential origins of the measured ligands. While their arguments are valid, I think it is different from measurements that directly pinpoint to ligands' origin and identity. Thus, I would suggest the authors to modify the title and introduction such that they are not misleading and reflect correctly the problems that the manuscript directly address and the methods that the authors use to achieve this goal. Again, in my mind, this is a study that measures the ligands concentration and binding strength, then suggest their potential sources, not a study that directly identify the sources of ligands.

Reply:

We agree with the referee that this study measures the concentration and binding strength of ligands. And then, the information is used to trace the potential sources of organic ligands. Therefore, we have revised some part of the introduction section, as listed below:

Tittle : The title is changed into "Fe-binding ligands in coastal and frontal regions of the Western Antarctic Peninsula"

Introduction: Lines 53 – 62: we modified the paragraph about the use of the Cle-AdCSV technique to measure the total concentration and conditional stability constant of ligands. We mentioned that the parameters obtained from the CLE-AdCSV analysis together with ancillary data can be used to infer the potential source of organic ligands in seawater.

“Different ligand types exist, with characteristics (i.e binding strength) often being defined by their origin. The characteristics of organic ligands can be measured by the competition against well-characterized artificial ligands with known stability constants. Analysis is done using an electrochemical technique, competitive ligand exchange (CLE) - adsorptive cathodic stripping voltammetry (AdCSV). The application of AdCSV gives the total concentration ([Lt]) and conditional binding strength ("K" _"Fe'L" ˆ"cond") of the dissolved organic ligands but does not provide information on the identity of ligands. Despite that identities of Fe-binding ligands are still largely unknown, [Lt] and "K" _"Fe'L" ˆ"cond" obtained from CLE-AdCSV measurement, together with ancillary data, can be used to infer the potential sources of these organic ligands. The organic ligands in seawater either have a terrestrial or marine source. The terrestrial-sourced ligands supply originate from lithogenic inputs within the boundary region between land and sea (i.e coastal seas and estuaries) (Buck and Bruland, 2007; Batchelli et al., 2010; Kondo et al., 2007; Buck et al., 2007; Bundy et al., 2015; Gerringa et al., 2007; Laglera and van den Berg, 2009). The organic ligands with a marine source come from in situ biological activities, being either actively produced or passively generated through microbial activity.”

Lines 102 – 106: we have revised the sentences to reflect the goals of this manuscript.

“In this study, surface waters were sampled in a region of mixing between shelf-influenced waters and HNLC waters in the Bellingshausen Sea along the WAP. The CLE-AdCSV technique was used to quantify the total concentrations and conditional stability constants of Fe-binding ligands. These parameters were used to examine the distribution and identify the potential sources of organic ligands from ice covered shelf

waters to the open ocean of the Antarctic Zone.”

Second, in section 4.2 of the manuscript, the authors discussed at length on how a high complexation capacity of ligand and ice-melting processes can control the ocean primary productivity in the WAP region. They also discussed on the potential impact of global warming on Fe chemistry and ligand, and stated that (line 387-390): “Overall, the continued sea-ice melt and glacial retreat can be expected to increase the supply of Fe (Lannuzel et al., 2016), other micronutrients (Co, Mn, etc.), and Fe-binding ligands (Lin and Twining, 2012), but the consequences for their complexation capacity and overall bio-availability of Fe remain elusive.” But what about the impact of ligand production from ice-algal exudates, sediments, and phytoplankton bloom? How will these processes change in the future under the impact of global warming? Is the ligand production from ice-algal exudates going to increase or decrease with sea-ice melting? Since these are major processes in producing ligands, I would love to see more discussion on them.

Reply:

Environmental alteration due to global warming influences the dynamics of marine ecosystems (as mentioned in lines 380 – 385), and thus the production of ligands via many different processes (i.e production from ice-algal exudates, sediments, and phytoplankton blooms). We have implicitly mentioned the potential impact of ongoing environmental changes on ligand production associated with phytoplankton blooms (lines 389 - 394). We have added discussion related to the potential release of organic ligands from sediment entrapped with sea-ice (line 397) and organic ligands associated with microbial excretion (lines 398 – 400).

“Changes in planktonic community composition affect net primary production and overall carbon drawdown, which lead to further alteration of the food web and carbon cycling (Alderkamp et al., 2012; Arrigo et al., 1999; Joy-Warren et al., 2019; Schofield et al., 2017). These and other ongoing changes in the food web will also affect production of

dissolved organic carbon (DOC) and thus ligands as they form a fraction of the DOC pool (Gledhill et al., 2012; Whitby et al., 2020). Generally, one expects that increased DOC production would lead to more ligands, but the binding strength depends on which molecules are formed (Gledhill and Buck, 2012; Hassler et al., 2017). Additionally, intensified light exposure alters log "K" _"Fe'L" ˆ"cond" by photo-oxidative processes, possibly reducing the complexation capacity and binding strength for Fe (Barbeau et al., 2001; Mopper et al., 2015; Powell et al., 2003) as well as the bioavailability (Hassler et al., 2020). Furthermore, complexation capacity is affected by pH, implying that ongoing ocean acidification also influences the speciation of Fe (Ye et al., 2020). The melting of black sea-ice entrapped with sediment potentially releases organic ligands (Genovese et al., 2018). Organic ligands from microbial excretions are expected to be abundant on the base of sea ice (Norman et al., 2015), although the fluctuation rate (decrease or increase) under on-going changes cannot be confirmed without further experiment."

Minor comments:

Line 16: Our results indicate that organic ligands in "the" surface water. Reply: Corrected.

Line 17: Organic ligands in "the" deeper shelf water. Reply:Corrected.

Line 41: Should the reference here be Henley et al., 2019? Reply:Corrected.

Line 69-70: covered by sea-ice (remove with) Reply:Done.

Line 85-86: such as glacial meltwater, sediments", and" upwelling. Reply:Corrected.

Line 171: hydrographic features of the WAP "was" described elsewhere. Reply:Corrected.

Line 173: Two distinct horizontal currents exist in the study area: The Coastal Current (CC) and the Antarctic Circumpolar (replace, by:) Reply: Corrected.

Figure 3 caption: remove depth in colors denoting depth the values. Reply: Done.

Line 323-326: Maybe revise this sentence to make it shorter and clearer: "Mopper et al. (2015) suggested that the absorption of solar radiation by chromophoric dissolved organic matter as part of the ligand pool which commonly produced by sea ice algae (Norman et al., 2011), leads to the photochemical transformation of these compounds. Reply: The sentence is divided into two sentences.

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