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Discussions

Interactive comment on "Isotopic and chromatographic fingerprinting of the sources of dissolved organic carbon in a shallow coastal aquifer" *by* Karina T. Meredith et al.

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RC2 - Anonymous Referee #2 Received and published: 20 December 2019 General Comments: In this paper, Meredith et al. describe the age of groundwater and composition of DOM in a coastal anoxic aquifer in coastal New South Wales. They propose several DOM sources present within the aquifer, and suggest that anoxic aquifers can contain substantially more DOC than other aquifers and that further research is needed to understand the stabilization of and potential fates of the DOM contained in anoxic aquifers globally. The paper is short and easy to read, and provides important data on anoxic coastal aquifer chemistry to the scientific literature. Overall, the similarity of DOM composition in the aquifer to the DOM in the wetland seems to need more addressing, particularly given the claim the paper makes that the wetland is not the source of DOM for the aquifer. It would strengthen the paper to further discuss possible reasons (including the possible lack of compositional resolution when using only LC-OCD to assess DOM composition) why the DOM composition is the same, yet the paper claims the sources are be different. Author's response: The limits to the compositional resolution of LC-OCD could explain the small changes in chromatographic character. High resolution mass spectrometric techniques such as FT-ICR-MS have been used in this study site to further probe changes in groundwater DOC character along the transect. Recent research has demonstrated its utility in identifying groundwater DOC compositional changes after recharge at the site (McDonough et al 2020). The isotopic differences and the newly added PCA analysis clearly show that the sources of DOC in the aquifer are different. These new lines of evidence will be discussed in the final MS. A paper by (McDonough et al 2020) accepted in GCA also shows that the DOM has different ages shallow 100 pmc and deeper source 80 pmc. Reference to these recent papers will be made within the final MS discussion. These papers are newly published and were worked completed while this submission was under review with HESS.

The following analysis will be added to the results section. "Principal component analysis (Fig. 6) using water quality, isotopes and DOC variables including LC-OCD fractions (%), ðİŻ£13CDOC (‰, ðİŻ£13CDIC (‰, 3H, pH, Na, pCO2, NO3, Cl, Ca, Sr, DO, SO4, NH4, Ca and DOC concentration (mg C / L) confirms the presence of different groundwater sources." The variables contributing to PC1 (in order of importance) are pH, Na, pCO2, NO3, Cl, Ca, DOC, 3H, Sr and humics. The variables contributing to PC2 in order of importance are ðİŻ£13CDOC, DO, biopolymers, ðİŻ£13CDIC, HS aromaticity, HS mol weight, DOC, Cl and 3H. PC1 mainly explains the variations we see with sample depth. Samples S1_D, S2_S, S2_D and S3_S are the samples most strongly influencing PC1. The deep samples that are likely to have originated from a deeper regional source of water (S1_D and S2_D) are influencing the right hand side of the PCA with high pCO2, NO3, humics, Na, and Cl. These samples are also characterised by low Ca, 3H, Sr and pH. The shallow samples (S2_S and S3_S) are influencing the left hand side of the PCA with low pCO2, NO3, humics, Na and Cl, and have high Ca, 3H, Sr and pH suggestive of rainfall recharge waters. This analysis further highlights the distinct wetland sample that is not related to the other samples (Fig 6) and is heavily influencing PC2 with low ðİŻ£13CDOC values, high DO, high biopolymers, low HS aromaticity, low HS molecular weight and high DOC concentration." The reference to the new work completed: McDonough, L.K., O'Carroll, D.M., Meredith, K., Andersen, M.S., Brügger, C., Huang, H., Rutlidge, H., Behnke, M.I., Spencer, R.G.M., McKenna, A., Marjo, C.E., Oudone, P. and Baker, A. (2020) Changes in groundwater dissolved organic matter character in a coastal sand aquifer due to rainfall recharge. Water Research 169, 115201.

Specific Comments: My main scientific concern about the paper is the claim that DOM is not being processed in these systems. On page 7 line 24-page 8 line 1, a claim is made that DOM would be expected to decrease in DOM aromaticity if it were being biodegraded. I'm not sure this statement holds true for all DOM systems. If DOM were being biodegraded, it could likely become more aromatic along a flowpath due to preferential microbial consumption of more aliphatic, biolabile molecules. I think this statement needs to be backed up by some citations or expanded to explain the degradation pathways being discussed, since higher aromaticity to me suggests preferential microbial processing of biolabile aliphatic fractions is occurring as the DOM moves through the groundwater. Author's response: Agreed. This sentence will be changed to read: "DOC would be expected to have changed in aromaticity and molecular weight along a flow line, the opposite to what is observed here if the samples formed a degradation pathway". Page 8 lines 10-12

The MS has been reviewed extensively and all reference to the DOM character being constant is removed from the MS. It was not the aim of the MS to suggest the DOM is constant. The DOM character varies in the aquifer, but does not vary along hypothesised or expected flowpaths. This just further highlights that there are distinctive

sources of DOM in the aquifer and not one wetland source recharging the aquifer and biodegrading along a 500 m transect.

To address the comment that microbial degradation might be expected to break down the aliphatic fraction. We will reference the importance of sorption and biodegradation in the corrected MS. We could cite Chapelle et al (Hydrogeol. J) as this paper shows changes in optical clarity along a flowpath that are substantial. We also add the experimental work of Oudone et al., 2019, which confirms that sorption predominantly affects the aromatic, HS fraction). For biodegradation, we cite Shen, Chappelle et al 2014 which shows that only a small proportion of groundwater DOC is bioavailable. The new reference of Oudone, P., Rutlidge, H., Andersen, M.S., O'Carroll, D., Cheong, S., Meredith, K., McDonough, L., Marjo, C. and Baker, A. (2019) Characterisation and controls on mineral-sorbed organic matter from a variety of groundwater environments. EarthArXiv https://eartharxiv.org/ue86w/.

We have rewritten the following sentence to highlight . . .. "from S3, S4 and S5_S also had higher humic substances aromaticity and humic substances molecular weight than sites 1 and 2." Page 8 line 10

Page 8, ln 20 was added to read "Furthermore, despite observed differences in DOM characteristics (e.g. higher humic substances aromaticity and molecular weight in S3, S4 and S5S), DOM character does not change significantly along the groundwater flow path, contrary to what was found in other studies where biodegradation, sorption, desorption and biosynthesis controlled DOM (Chappelle et al., 2012; Shen et al., 2015)."

Similarly, I do not understand the reasoning presented on page 10 line 6-10. The paper says that the d13C value of DOC should get lighter due to microbial processing, and that yes, in fact the groundwater DOC d13C values are 1 ppm lighter than those in the wetland, yet the paper seems to be saying that this goes against the idea of microbial fractionation. Doesn't that show that yes, the d13C-DOC values are becoming lighter than the original C3 vegetation wetland source, which would support biological processing as a mechanism at work here? I may have missed a piece of logic, but it would strengthen the point of the paper if this were clarified. Author's response: The groundwater 13CDOC are heavier than the wetland source. The wetland source at the surface is likely to have undergone fractionation due to microbes. Reference to this are made clearer in the MS.

Page 10, ln 23-25 will be added "This suggests that if the wetland was the source of OM then the carbon isotopes were fractionated after recharge and become heavier than the wetland OM". "Alternatively, the difference in isotopic values can be explained by suggesting the DOM in the groundwater system has a different source to the wetland and there is limited interaction of the surface and groundwater."

Further, I do not follow the line of reasoning that claims the modern wetland is not a major source of DOM for these groundwaters on page 10 line 15-16. It appears that DOM composition and d13C are consistent with a wetland source. If the water chemistry is different, it is probable that the DOM source and water source are decoupled, which is interesting. But I do not think the claim that the modern wetland is not the source of DOM to the groundwater is justified based on the explanation of the data provided. Perhaps a more detailed explanation of why the isotopes lead the authors to this conclusion would strengthen the argument. Author's response: The isotopes do not suggest consistent sources of DOM. Water sources have become decoupled from the different to the DOM sources. Further studies completed by McDonough et al., 2020 will be included in the discussion with FT-ICR-MS evidence. We have also found in further time-series studies of the site that desorption of SOM after recharge is occurring. These new findings will be incorporated into the final discussion to strengthen the discussion on sources of DOM. It must be noted these studies have been completed while this MS has been under review.

Other specific comments: Section 4 is a Results and Discussion section, not a pure Results section, and should be labeled accordingly or take some of the discussion out and put it later in the discussion sectionâËŸAËĞ TI find it a little confusing cause

important discussion material is listed here, but then there is a separate discussion section Author's response: Agreed. This section has been removed from page 7 lines 1-7 because it is discussed in detail later in the discussion section. This point was also addressed by R1. The following sentence was added to page 6 ln 20 to describe the results rather than provide discussion "The DIC values also showed various sources and processes influencing inorganic carbon."

Page 7 line 22-24: Was the intention to say that groundwater from sites 3-5 had higher aromaticity than other groundwater/shallower groundwater samples, or higher aromaticity than other surface water samples in other studies? If the former (which is how I initially read this), this seems to contradict the statement in the discussion that the groundwater DOM composition is constant in this study. Author's response: It was not the intention of this study to suggest the DOM is constant as mentioned above, the DOM does not vary along hypothesised or expected flowpaths.

Page 11 lines 19-22: It might strengthen the claim that this carbon may be important for the regional carbon budget to explicitly relate this anoxic, preserved DOM to freshly produced DOM, and to explicitly state how it may impact the regional carbon budget. The claim is made in the conclusion and the abstract that anoxic coastal groundwater systems have the potential to export up to ten times more unreacted carbon than thought, but the calculation or logic to support this is never shown. It would strengthen the claim to demonstrate why that claim is being made, and how the math adds up if the carbon concentrations in the groundwater are only five times higher than those in other aquifers. In general LC-OCD may give too low a resolution to reveal DOM compositional differences between sources and groundwaterâËŸA ËĞ Tperhaps a discussion of other areas where LC-OCD on its own has been able to tease out compositional differences could strengthen the expectation that if there were compositional differences here, LC-OCD could assess them. Twice it's mentioned that the aromaticity for the humic substances is higher than for lakes or rivers (once in 5.1.2, once in 41.). Especially in the results, it would be useful to see the values from the Huber et al 2011 study and this study to show how they compare. Author's response: The groundwater results are shown with respect to Huber's study please refer to Fig 7. More emphasis on this figure will be added to the final MS.

The new addition from Oudone et al., (2019) experimental work, clearly shows how LC-OCD can elucidate sorption processes. Rutlidge et al (2015) GCA shows how it could elucidate DOM sources and transformation during recharge using an artificial rainfall event. McDonough use LC-OCD and FT-ICRMS to understand changes in DOM character after rainfall recharge. A summary of these works will be included in the final discussion.

Technical Corrections: Page 4 line 9: "may be" not "maybe" Author's response: corrected Page 4 line 17: "Dissolved" not "Dissolve" Author's response: corrected Page 9 line 5: Organic should not be capitalized Author's response: corrected Figure 3: "the polygon" is unclearâĖŸAĖĞ Tperhaps call it the "dashed rectangle" Author's response: corrected Figure 6:"Siberian Sea" not "Siberiansea" Author's response: corrected

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