

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.

Anonymous Referee #2

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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.

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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 to be different.

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.

Similarly, I do not understand the reasoning presented on page 10 line 6–10. The paper says that the $\delta^{13}\text{C}$ value of DOC should get lighter due to microbial processing, and that yes, in fact the groundwater DOC $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ -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. 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 $\delta^{13}\text{C}$ 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

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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. 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 section—I find it a little confusing cause important discussion material is listed here, but then there is a separate discussion section

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.

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 groundwater—perhaps 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 4.1.). Especially in the results, it would be useful to see the values from the Huber et al 2011 study and

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this study to show how they compare. Technical Corrections:

Page 4 line 9: “may be” not “maybe”

Page 4 line 17: “Dissolved” not “Dissolve”

Page 9 line 5: Organic should not be capitalized

Figure 3: “the polygon” is unclear—perhaps call it the “dashed rectangle” Figure 6: “Siberian Sea” not “Siberiansea”

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2018-627>, 2019.

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