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Discussions
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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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RC1 - Hannelore Waska (Referee) hannelore.waska@uol.de Received and published: 16 October 2019

Overall: Please proof-read the MS carefully, there seem to be a few small typos/ grammatical errors. Author's response: The MS has been proof read. Small typos, etc have been found throughout and adjusted. The MS has been corrected to read in the past tense.

Data analysis: The dataset is well-suited for a multivariate data analysis to decipher

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GW sources (see RDA as example in cited Coutourier et al. 2016). I recommend the inclusion of a multivariate analysis (RDA or PCA). Author's response: The authors agree and have included a PCA. This analysis will be included in the final MS. The methods for PCA were added to page 6 line 5 – "Principal Component Analysis (PCA) was performed in base R. The data was centred to the mean of the variable and then scaled using the variable standard deviations in R using the prcomp function: https://stat.ethz.ch/R-manual/R-devel/library/stats/html/prcomp.html." The following will be added to the results section page 7 ln 21- "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."

New Fig 6 added to text Methods, p4, l15 "Dissolved". Author's response: Corrected

Also, I think the company name is Waterra. Author's response: Corrected p5, l10 ff: Why was GW age (years) not calculated? What is the merit of using TU? Author's

response: The raw 3H measurement value was used as a guide for recent recharge. Rainfall for the regions is expected to be 1.7TU as stated page 6, line 16. If the sample contained values close to rainfall then it can be interpreted that the groundwater contains recent rainfall. The groundwater age was not calculated because there was no rainfall or time-series analysis collected for the system. Groundwater age calculations are non-unique if calculated on a single sample event. Generally when calculating a groundwater age using 3H it is advised to use a lumped parameter model such as what we did in our time-series study of Rottnest island lens using 3H as an age tracer of groundwater age (Bryan et al., 2019). Therefore the authors use 3H as a tracer of rainfall recharge and do not calculate a groundwater age. The following sentence will be added to the final MS "Tritium activities were used as an indication of groundwater recharge occurrence by rainfall and groundwater ages were not calculated due to a lack of time series data collected for this study. Bryan et a. (2019) shows the importance of collecting 3H data and then calculating a groundwater age using a lumped parameter model in a shallow unconfined aquifer."

All methods: Please include details for 14C analysis. Why was 14C of DOC not measured? Author's response: Please note all reference to 14CDIC will be removed from the paper. This tracer indicates that the groundwaters are all modern similar to 3H and 14CDIC is not useful in such a young groundwater environment. The 14C of DOC was measured in a later study by McDonough et al., 2020 accepted in Geochimica et Cosmochimica Acta. Reference to this paper will be made in the discussion section. The 14CDOC results for sites 1 and 2 were:

S1_M S1_D S2_D 14CDOC (pMC) 100.86 88.69 87.94 These results suggest an older peat source at depth compared to the shallow samples. Please note that the results for these samples were processed and submitted in mid-2019, well after this MS was submitted for review in Dec 2018 to HESS.

The reason 14CDOC was not analysed for this study is that it was conducted in 2010, this radioactive isotope was not available for measurement at ANSTOs AMS facility

during this time. We later underwent methods development to add this isotope to our methods development.

Results, p5, l25: Would the authors expect seawater infiltration, due on tidal inundation and/or storm floods, at S5? Or is the GW pressure so high that it immediately dilutes any seawater influence? Author's response: The water chemistry and hydraulic head data suggests S5 is fresh water. The following sentence was added to page 6 ln 5 to clarify this point "and there was no evidence of seawater infiltration after storm events based on the hydrochemical data."

All results and following discussions: Please use either present or past tense continuously throughout. Author's response: The MS has been checked for tense and corrected to past tense.

Results contain interpretations (e.g. indications of marine carbonate dissolution: : :ion exchange processes...methanogenesis: : :) which may better fit in the 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. 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."

p7, l1: "The average DOC concentration (: : :) is high" compared to what? It is not high considering the conditions (anoxic, advective flow, peat hydrolysis in the aquifer). Author's response: The following sentence has been added "compared to the ~1 mg L-1 for the global median DOC concentration in groundwater (McDonough et al., 2019)."

Section 4.1., first two paragraphs: Please refrain from switching between past and present tenses. Author's response: Agreed. This has been corrected throughout the MS.

Discussion, p9, l5-8: Please provide additional literature which supports your claim of a global occurrence. I have added some examples to the reference list below. Author's

response: McDonough et al. (2019) presents the largest global dataset of 7,849 published and unpublished groundwater DOC concentrations. They calculate the global median DOC concentration for groundwater based on this dataset. The papers provided have been reviewed by the authors and considered for the corrections.

McDonough, L., Santos, I., Andersen, M., O'Carroll, D., Rutlidge, H., Meredith, K. and Oudone, P.: "Changes in Global Groundwater Organic Carbon Driven by Climate Change and Urbanization." EarthArXiv. November 21. doi:10.31223/osf.io/vmaku, 2018.

Overall Discussion: It seems that 14C-DIC is not included in the discussion of the results. Why? How can it help in interpreting GW sources? Author's response: The 14CDIC has been removed from this MS. The results all show a modern source of DIC, similar to the 3H results. Please see the description above for a detailed response.

Conclusion, p12, l1ff: Please explain how the estimate of an "order of magnitude higher" is achieved. Author's response: The concentrations found in this coastal system contain up to 10 mg/L of DOC whereas the global medium is 1 mg/L, hence the description of an order or magnitude. The following has been added to the text to describe this further Page 13, ln 20 "The average groundwater DOC concentration for this study was five times higher (5 mg L-1) than the global median DOC concentration for groundwaters. The concentration of DOC doubled with depth, reaching 10 mg L-1 but the DOM chromatographic character did not change significantly with depth or along the groundwater flow path but the carbon isotopic composition did change."

p13, l1: Please explain how the estimate of an "export up to ten times" is achieved. Author's response: The concentrations found in this coastal system contain up to 10 mg/L of DOC whereas the global medium is 1 mg/L, see above comment.

Figure 2: Perhaps there is a way to improve the quality of the figure (some features appear to be blurred). What do the blue, pink, and red arrows mean in contrast to the black ones? Agreed. The Figure has been updated and the various coloured arrows

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have not been removed for clarity.

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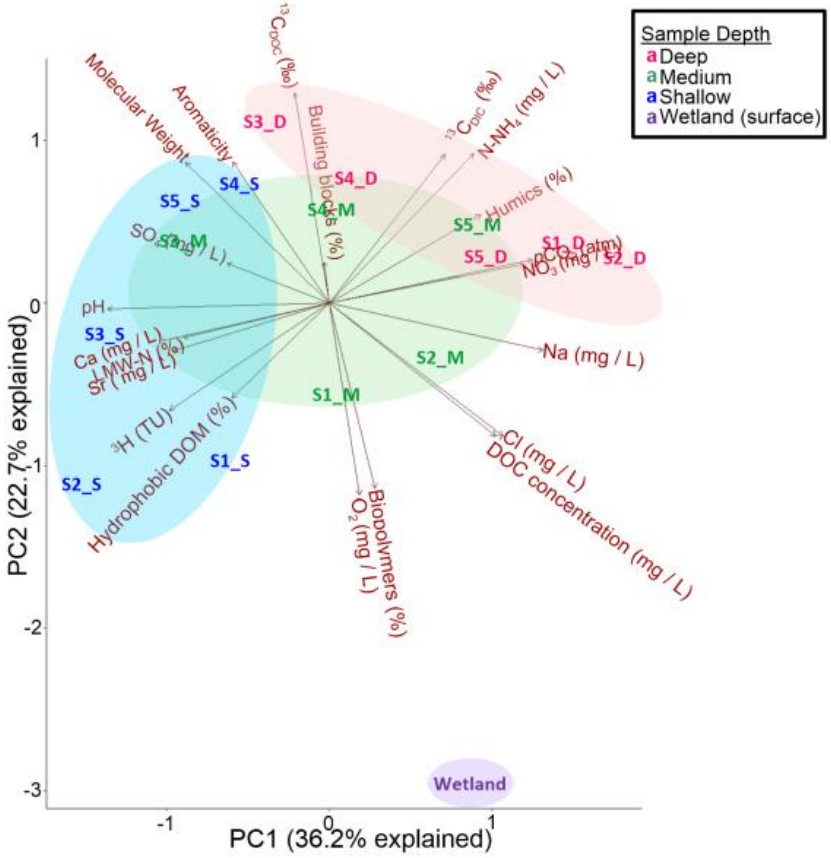

Fig. 1. Fig 6

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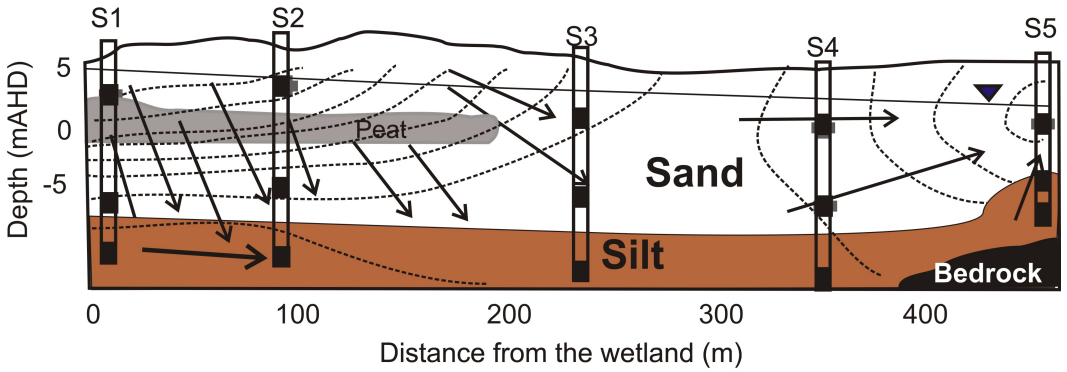

Fig. 2. Fig 2 new

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