RC1 -
Hannelore Waska (Referee)
hannelore.waska@uol.de

5

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 were found throughout and adjusted.
The MS has been corrected to read in the past tense.

10

Data analysis: The dataset is well-suited for a multivariate data analysis to decipher
GW sources (see RDA as example in cited Coutourier et al. 2016). I recommend the
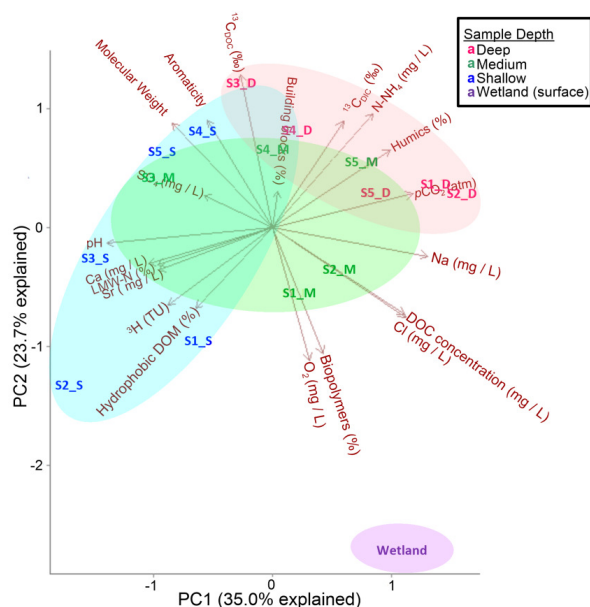inclusion of a multivariate analysis (RDA or PCA).
Author's response: The authors agree and have included a PCA analysis.

15

The methods for PCA is added to page 6 line 1 –
"Principal Component Analysis (PCA) was performed in base R. Parameters which were consistently above their limit of
detection were investigated by PCA. 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."

20 The following will be added to the results section page 7 starting line 8 -
"Principal component analysis (Fig. 6) using water quality parameters, isotopes and DOC variables
including LC-OCD fractions (%), $\delta^{13}C_{DOC}$ (‰), $\delta^{13}C_{DIC}$ (‰), ^3H, pH, Na, pCO_2, Cl, Ca, Sr, DO, SO_4,
NH_4, Ca and DOC concentration confirmed the presence of different groundwater sources. The
variables contributing to PC1 (in order of importance) were pH, Na, pCO_2, Cl, DOC, Ca, humics,

25 LMW-N, Sr and ^3H. The variables contributing to PC2 in order of importance are $\delta^{13}C_{DOC}$, DO,
biopolymers, HS aromaticity, $\delta^{13}C_{DIC}$, HS molecular weight, Cl, DOC and hydrophobic DOM. PC1
mainly explained the variations with sample depth in the aquifer. Samples S1_D, S2_S, S2_D and S3_S
were the samples that most strongly influenced PC1. The deep samples likely to have originated from a
deeper regional source of water (S1_D and S2_D) were influencing the right hand side of the PCA with

30 high pCO_2, humics substances, Na and Cl. These samples were also characterised by low Ca, ^3H and Sr.
The shallow samples (S1_S, S2_S and S3_S) were influencing the left hand side of the PCA with low
pCO_2, humics, Na and Cl, and have high Ca, ^3H, and Sr suggestive of rainfall recharge waters. This
analysis further highlights the wetland sample that is not related to the other samples (Fig 6) and is
heavily influencing PC2 with low $\delta^{13}C_{DOC}$ values, high DO, high biopolymers, low HS aromaticity, low

35 HS molecular weight and high DOC concentration."

Sample Depth
a Deep
a Medium
a Shallow
a Wetland (surface)

PC2 (23.7% explained)

PC1 (35.0% explained)

$^{13}C_{DOC}$ (‰)
Molecular Weight
Aromaticity
S3_D
Building Biomass (%)
$^{13}C_{DIC}$ (‰)
N-NH$_4$ (mg / L)
S4_D
S4_S
S5_S
S3_M
S4_M
S5_M
Humics (%)
S$_4$ (mg / L)
S5_D
pCO$_2$ (atm)
S2_D
pH
Na (mg / L)
S3_S
Ca (mg / L)
LMW-N (%)
Sr (mg / L)
S2_M
^{3}H (TU)
S1_M
Hydrophobic DOM (%)
S1_S
DOC concentration (mg / L)
S2_S
O$_2$ (mg / L)
Biopolymers (%)
Cl (mg / L)
Wetland

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 was used as a guide for recent recharge. Rainfall for the regions is expected to be 1.7 TU as stated in 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., 2020). Therefore the authors use 3H as a tracer of rainfall recharge and do not calculate a groundwater age.
The following sentence was added to page 5 line 14
"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

2

a. (2020) shows the importance of collecting ^{3}H time-series 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 $^{14}C_{DIC}$ was removed from the paper. This tracer indicated the groundwaters are modern and 14CDIC is not useful for calculating groundwater residence times in such a young groundwater environment. The 14C of DOC was measured in a later study by McDonough et al., (2020), on a different dataset. Reference to this paper is made in the discussion section. Page 10, line 11. The 14CDOC results for sites 1 and 2 were:

	S1_M	S1_D	S2_D
$^{14}C_{DOC}$ (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 to a different journal, well after this MS was submitted for review in Dec 2018 to HESS.

The reason 14CDOC was not analysed for this study is that the field samples were collected and analysed in 2014, this method was not available for measurement at ANSTOs AMS facility at that time.

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 data suggests at S5, the most seaward monitoring bore, is fresh water. The following sentence was added to page 6, line 7 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 was 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 was removed from page 7 lines 1-7 because it is discussed in detail later in the discussion section.

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 was added page 6 line 20

"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.

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 was removed from this MS. The results show a modern source of DIC, similar to the 3H. 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 clarify:
page 13, line 3-4 "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?

4

Agreed. The Figure has been updated and the various coloured arrows have been removed for clarity.
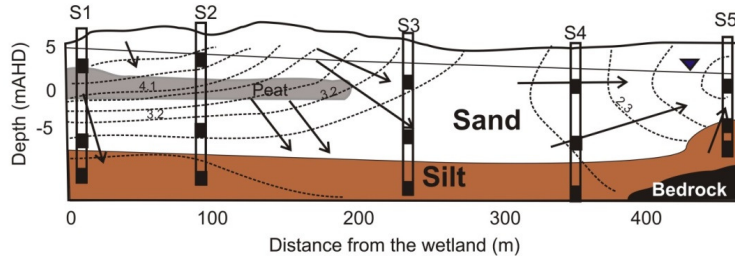
RC2 -

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 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 are discussed in the final MS. A paper by McDonough et al., (2020b) presenting a different dataset from the site, also shows that the DOM has different ages, with the shallow source close to the wetland reflecting $^{14}C_{DOC}$ ages of ~100 pMC and the deeper samples, or samples further from the wetland, reflecting $^{14}C_{DOC}$ age of ~80 pMC. This is indicative of separate DOM sources in the vicinity of the wetland and for samples further from the wetland or in the deeper groundwater system.

The limits to the compositional resolution of LC-OCD could explain the limited changes observed in the chromatographic character of DOM at the site. High resolution mass spectrometric techniques such as FT-ICR-MS have been used in conjunction with LC-OCD in a paper by McDonough et al., (2020a) at the same study site on a different dataset to further probe changes in groundwater DOC character along the transect. Recent research has demonstrated the utility in identifying groundwater DOC

5

compositional changes after recharge at the site using LC-OCD and FT-ICR MS (McDonough et al., 2020a).

The two papers by McDonough et al., (2020a and 2020b) are newly published and the work was completed while the current submission was under review with HESS (for over 13 months).

5

The following analysis will be added to the results section.

page 7 starting line 8

"Principal component analysis (Fig. 6) using water quality parameters, isotopes and DOC variables including LC-OCD fractions (%), $\delta^{13}C_{DOC}$ (‰), $\delta^{13}C_{DIC}$ (‰), ^3H, pH, Na, pCO_2, Cl, Ca, Sr, DO, SO_4, NH_4, Ca and DOC concentration
10 confirmed the presence of different groundwater sources. The variables contributing to PC1 (in order of importance) were pH, Na, pCO_2, Cl, DOC, Ca, humics, LMW-N, Sr and ^3H. The variables contributing to PC2 in order of importance are $\delta^{13}C_{DOC}$, DO, biopolymers, HS aromaticity, $\delta^{13}C_{DIC}$, HS molecular weight, Cl, DOC and hydrophobic DOM. PC1 mainly explained the variations with sample depth in the aquifer. Samples S1_D, S2_S, S2_D and S3_S were the samples that most strongly influenced PC1. The deep samples likely to have originated from a deeper regional source of water (S1_D and
15 S2_D) were influencing the right hand side of the PCA with high pCO_2, humics substances, Na and Cl. These samples were also characterised by low Ca, ^3H and Sr. The shallow samples (S1_S, S2_S and S3_S) were influencing the left hand side of the PCA with low pCO_2, humics, Na and Cl, and have high Ca, ^3H, and Sr suggestive of rainfall recharge waters. This analysis further highlights the wetland sample that is not related to the other samples (Fig 6) and is heavily influencing PC2 with low $\delta^{13}C_{DOC}$ values, high DO, high biopolymers, low HS aromaticity, low HS molecular weight and high DOC
20 concentration."

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
25 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
30 aliphatic fractions is occurring as the DOM moves through the groundwater.

Author's response:

Agreed. This sentence was changed to read:

Page 8, lines 10-12

"The DOC did not show significant or consistent trends in aromaticity or molecular weight, nor did it
35 show a trend of declining DOC concentration with depth or along the flow path".

The MS has been reviewed extensively and all reference to the DOM character being constant has been removed from the MS. It was not the aim of the MS to suggest the DOM is constant. The DOM character varied in the aquifer, but does not along any clear trends hypothesised or expected flowpaths.
40 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 reference the importance of sorption and biodegradation. We also cite Chapelle et al 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.

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), percentages of LC-OCD fractions did not show any consistent trend 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).

page 8 starting line 22

"The experimental work of Oudone et al. (2019) also confirmed that sorption predominantly affects the humic substances fraction, especially that with high aromaticity. If biodegradation were occurring, we would expect to see a decline in the LMW-N and BP fractions (Catalán et al., 2017) however we do not make a clear observation of this in our data. In contrast Fig. 6 shows that the shallow samples located further from the wetland (S4_S and S5_S) have higher humic substances aromaticity and molecular weight which supports the conclusion that sorption is not the dominant process determining DOM character from the wetland to the coastline."

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:

Agreed. The following sentence has been added to clarify that the 13C values would be expected to become more enriched with microbial processing. As we only see a 1 ‰ variation in the $^{13}C_{DOC}$ values, we suggest that microbial processing is minimal:

Page 11, line 4-9:

"The carbon isotope value in the wetland was 1 ‰ lighter compared to the shallowest groundwater sample located near the wetland. This suggests a small amount of microbial processing may have occurred, or that unprocessed DOM inputs are very high at this site."

Ln 5, pg 11 "If biological processing was influencing the wetland DOM during transport into the groundwater, it would be expected that the $\delta^{13}C_{DOC}$ values would become heavier than the original C_3

vegetation source where the bacteria metabolize the isotopic light organics because the ^{12}C-H bonds are easier to break leaving the resultant OM more enriched than the original source (Clark and Fritz, 1997)."

We also note:

Page 9, line 19-22: "A possible explanation for the similar constant character of the DOM with the evolved inorganic redox chemistry is that the rates of biodegradation are far lower than the rate of DOM leaching into the groundwater. Furthermore, if there are additional sources of DOM along the flowpath, we would expect to see the inconsistent variations in LC-OCD fractions along the flow path that we observe in our data, rather than a consistent decline in any DOM fraction or DOC concentration."

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 aquifer contains several buried peat units that are also the source of DOC for groundwater. We agree the water sources have decoupled from the different to the DOM sources. The new PCA analysis of DOC, isotopes and water chemistry variables now provides the extra reasoning necessary to show that the wetland water is different to the groundwater (Fig 6). In addition, a paper by McDonough et al., (2020b) also shows that the DOM has different ages shallow 100 pmc and deeper source 80 pmc. Page 10, lines 11-14. This paper is newly published and the work was completed while this submission was under review with HESS (for over 13 months). Reference to this recent paper will be made within the final MS discussion.

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 sectionăˇAˇ 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.

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:

This refers to higher aromaticity and molecular weight at sites 3-5 compared to sites 1 and 2, rather than compared to samples from other studies. We have also changed the statement in the discussion which implied that the groundwater DOM composition is constant in this study. We note that it was not the intention of this study to suggest the DOM is constant. We intend to show that the LC-OCD fractions do not show trends along hypothesised or expected flowpaths. As noted in response to the previous comments, we would expect reduced LMW-N and BP associated with microbial degradation, and a decline in aromaticity and molecular weight associated with sorption, however we do not observe these changes.

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 groundwaterâ˘A˘ 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 concentrations found in this coastal system contain up to 10 mg/L of DOC whereas the global medium is 1 mg/L, hence the emphasise of an order of magnitude difference. The following has been added to the text to clarify:

Page 13, ln 14 "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 fractions did not change significantly with depth or along the groundwater flow path. We note that the carbon isotopic composition did however vary slightly."

The groundwater results were originally shown with respect to Huber's study in the old Figure 6 and now in the updated Fig 7. The samples have a higher aromaticity than surface water previously studied. The new work completed by Oudone et al., (2019) including experimental work, clearly shows how LC-OCD can elucidate sorption processes. McDonough et al., 2020a use LC-OCD and FT-ICRMS to understand changes in DOM character associated with adsorption and desorption before and after rainfall recharge. This research shows that changes in DOM fractions due to processing are able to be observed through LC-OCD data. A summary of these works will be included in the final discussion.

9

Technical Corrections:
Page 4 line 9: "may be" not "maybe"
Author's response: corrected

5 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 unclearâ˘Aˇ Tperhaps call it the "dashed rectangle"

10 Author's response: corrected
Figure 6:"Siberian Sea" not "Siberiansea"
Author's response: corrected, the names of the system have been removed on the amended Figure 7.
This is because the systems are not described in detail in the text.

15 Below is the marked-up manuscript version

20

25

30

35

Isotopic and chromatographic fingerprinting of the sources of dissolved organic carbon in a shallow coastal aquifer

Karina T. Meredith[1,2], Andy Baker[2,~~3~~4], Martin S. Andersen[2,~~4~~3], Denis M. O'Carroll[2,~~4~~3], Helen Rutlidge[2,~~4~~3], Liza K. McDonough[2,~~3~~4], Phetdala Oudone[2,~~3~~4], Eliza Bryan[5], Nur Syahiza Zainuddin[6].

[1]Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW, 2234, Australia.
[2]Connected Waters Initiative Research Centre, UNSW Sydney, Australia.
[3]School of Biological, Earth and Environmental Sciences, UNSW Sydney
[~~4~~3]School of Civil and Environmental Engineering, UNSW Sydney, Australia.
[4]~~School of Biological, Earth and Environmental Sciences, UNSW Sydney~~
[5]Golder Associates, Sydney, NSW, Australia. 124 Pacific Highway, St. Leonards, New South Wales 2065, Australia.
[6]Faculty of Civil Engineering, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia.

Correspondence to: Karina T. Meredith[1] (kmj@ansto.gov.au)

Abstract. The terrestrial sub-surface is the largest source of freshwater globally. The organic carbon contained within it and processes controlling its concentration remain largely unknown. The global median concentration of dissolved organic carbon (DOC) in groundwater is low compared to surface waters suggesting significant processing in the subsurface. Yet the processes that remove this ~~dissolved organic carbon (~~DOC~~)~~ in groundwater are not fully understood. The purpose of this study was to investigate the different sources and processes influencing DOC in a shallow anoxic coastal aquifer. Uniquely, this study combines liquid chromatography organic carbon detection with ~~inorganic ($\delta^{13}C_{DIC}$) and~~ organic ($\delta^{13}C_{DOC}$) carbon isotope geochemical analyses, to fingerprint the various DOC sources that influence the concentration, carbon isotopic composition and character with distance from surface water sources, depth below surface and inferred groundwater residence time (using ^3H activities) in groundwater. It was found that the average groundwater DOC concentration was five times higher (5 mg L^{-1}) than the global median concentration and the concentration ~~it~~ doubled with depth at our site, but the chromatographic character did not change significantly. The anoxic saturated conditions of the aquifer ~~have~~ limited the rate of organic matter processing leading to enhanced preservation and storage of the DOC sources ~~from~~such as peats and palaeosols contained within the aquifer. All groundwater samples were~~are~~ more aromatic for their molecular weight in comparison to other lakes, ~~and~~ rivers and surface marine samples studied. The destabilisation or changes in hydrology, whether by anthropogenic or natural processes could lead to the flux of up to ten times more unreacted organic carbon from this coastal aquifer than compared to deeper inland aquifers.

1 Introduction

Organic matter (OM) in aquatic systems forms a fundamental part of the global carbon cycle. The soil and unsaturated zone has the potential to store at least three times more organic carbon than in the atmosphere or in living plants (Schmidt et al., 2011, Fontaine et al., 2007) and represents the largest source of carbon within terrestrial ecosystems (Keiluweit, et al., 2017).

The below-ground environment forms the largest source of freshwater and the organic carbon within these systems remains largely unaccounted for in the global carbon budget. Groundwater replenishment can occurs as either diffuse recharge through the OM-rich soil zone and/or as direct recharge originating from streams and wetlands that have the potential to contain high concentrations of OM. Despite the many sources of OM, groundwater DOC concentrations are typically low (~1 mg L^{-1} for the global median DOC concentration; McDonough et al., (2019)), suggesting that significant processing has occurred in the subsurface.

Very few studies have investigated why low concentrations of DOC in groundwater are low occur. Recent research has provided evidence of the attenuation of chromophoric dissolved organic matter (DOM) at a scale of tens of meteres along a flow path through with measurements of increased optical clarity of groundwater (Chapelle et al., 2016). This attenuation was proposed to be due to the combined effects of biodegradation and sorption. Chapelle et al. (20162) also showed that the presence of a hyperbolic relationship between DOC concentrations and dissolved oxygen provideds indirect evidence for groundwater DOC that is bioavailable to microbes. Direct monitoring of groundwater DOC within a fractured rock aquifer in South Carolina, USA, includeding measurements of both bioavailable and chromophoric DOM were performed by Shen et al., (2015). They demonstrated a decrease in lignin-derived phenols in groundwater compared to surface inputs, and prevalent amino acids in groundwater. At this site, it was proposed that a small fraction (8±4%) of groundwater DOC was bioavailable and that a substantial fraction of groundwater DOC was of bacterial origin (15-34%). Shen et al. (2015) suggested that DOM mobility couldan be described by a 'Regional Chromatography Model' (Hedges et al., 1986, 1994) as it moveds through the soil column to the groundwater. It wasis shown that the molecular size, polarity, charge and bioavailability determined the observed decrease in hydrophobicity of DOM along the flow path due to their controls on sorption, desorption, biodegradation and biosynthesis (Shen et al., 2015).

Carbon isotope ratios were first used in the 1960s to distinguish sources of OM in the coastal zone to identify the difference between saltmarsh sediments and freshwater peats (Emery et al., 1967). The use of carbon isotopes as tracers has been instrumental in providing greater understandings of the sources of carbon in coastal, terrestrial and marine environments

12

(Bennerrner et al., 19847, Lamb et al., 2006). Very few studies that used DOM chromatographic techniques have also employed isotopic techniques to understand the source of OM in groundwater, and vice versa. The uUse of multiple DOM characterisation techniques to improve our understanding of the role of different OM sources in contributing to the concentration, character, and its subsequent processing along groundwater flow paths is therefore in its early stages of

5   research.

Further work is clearly warranted to improve our understanding of the role of different OM sources and the physicochemical properties of the aquifers on groundwater DOM. To thisat end, we present groundwater DOC concentration, stable carbon isotopic signatures (δ^{13}C) and organic matter character data from a shallow (less than 20 in depth) anoxic coastal aquifer.

10   Within this hydrogeologically well characterised system, it is anticipated that multiple sources of OM exist including wetland, soil, peat and palaeosols. To better understand and test thea regional chromatography model, we utilise a chromatographic technique (liquid chromatography organic carbon detection- LC-OCD; Huber et al. (2011)). Uniquely, this study combines the chromatographic technique with inorganic and organic isotope geochemical analyses, to fingerprint the various DOC sources that influence the concentration, carbon isotopic composition (δ^{13}C$_{DOC}$) and character with distance,

15   depth and inferred groundwater residence time (using ^{3}H activities). This wasis done to identify controls on groundwater DOC sources and processing in a coastal groundwater system.

2 Environmental Setting

The coastal environment of Samurai Beach is located north-east of Anna Bay, New South Wales, Australia (Fig. 1). The Holocene sand dunes at the site rise 30 m above sea level and extend up to 800 m inland. A freshwater wetland and forest lie

20   in the northwest corner of the sand dunes near Site 1 (i.e., S1) and the aquifer is part of the Tomaree Groundwater Source supplying towns in the Hunter Valley with portable water. The local geology of the field site was investigated during borehole construction and using hydraulic profiling tools to produce the lithology cross-section depicted in Fig. 2 (Maric, 2013 and Howley, 2014). The lithological cross-section is parallel with the main groundwater flow direction from the wetland to the coast.

13

The upper 15 m of the aquifer containeds a combination of barrier and back barrier sand deposits, capped by aeolian dune deposits. Site 1 (S1) wasis located in the northwest corner, closest to the freshwater wetland, while Site 5 (S5) wasis closest to the Pacific Ocean. The lithology of the aquifer differs with distance along the transect, with a peat layer identified at ~5 m below ground level at Sites 1 and 2, and a clay unit at Site 5 (Fig 2). A shallower organic-rich layer was also identified at about 1 m bgl (below ground level) at Site 1S1.

Five sites were drilled and wells installed to three different depths; shallow (S_3.4 to 5.0 m bgl), medium (M_9.8 to 12.5 m) and deep (D_12.7 to 17.5 m), which formeding a ~500 m long transect. The boreholes were drilled by hollow stem auger using a Geoprobe rig and wells were constructed out of 50 mm diameter PVC with screened intervals of 1 m located at the bottom.

Three different sources of groundwater were identified based on hydrochemistry and the evaluation of groundwater flow direction (Maric, 2013 and Howley, 2014). These groundwater sources included; (1) direct rainfall recharge through the dunes, (2) indirect wetland infiltration, and (3) deeper regional groundwater (Fig. 2). Multiple sources of OM may be present at the site such as from (1) surface vegetation (2) transported particulate organic matter (POM) and/or (3) in-situ sedimentary sources such as peat, palaeosol or finely disseminated POM.

3 Methods

From 17th to 22nd of February 2014, fifteen groundwater samples were collected from the five nested sites (Fig. 12). Surface water samples were also collected from the adjacent wetland. Waters were measured for major ion chemistry, carbon isotopes ($\delta^{13}C_{DIC}$ and, $\delta^{13}C_{DOC}$ and $^{14}C_{DIC}$), tritium (^{3}H) and DOM character.

Groundwater samples were generally collected using a submersible centrifugal pump (Monsoon). A HACH multimeter (HQ40d) and probes were used for Dissolved Oxygen (LDO probe) and pH measurements in an inline flow-cell (WaterraWattera) isolated from the atmosphere. Sub-samples for laboratory analysis were collected through an in-line, 0.45 μm filter (bypassing the flow-cell), with $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ samples further filtered through 0.22 μm. Total alkalinity was determined in the field by Gran-titration (Stumm and Morgan, 1996) using a HACH Digital Titrator (Model 16900) and 0.16 N H_2SO_4. Samples for anions were collected in 50 mL pPolyethylene centrifuge vials bottles, with no further treatment, but

14

stored cool (~5 °C) and dark. Samples for cations were collected in 20 mL high density polyethylene HDPE acid-washed bottles and acidified with 1% of concentrated nitric acid (HNO_3). The $\delta^{13}C_{DIC}$ samples were collected in pre-combusted 12 mL glass vials (Exetainers) with no head space. The DOC and $\delta^{13}C_{DOC}$ were collected in acid washed 60 mL HDPE bottles and frozen within 12 hours of collection. Samples for ^{14}C and ^3H analysis were collected in 1 L Nalgene HDPE bottles and

5   were sealed with tape to eliminate atmospheric exchange during storage. Major and minor cations were determined using a Perkin Elmer NexION300D ICP-MS and Perkin Elmer Optima 7300 ICP-OES. Anions (for Cl and SO_4) were analysed using Dionex IC1000 Ion Chromatography System. Cations and anions were assessed for accuracy by evaluating the charge balance error percentage (CBE%; Table 2). Samples fell within the acceptable ±5% range.

The $\delta^{13}C_{DIC}$ isotopic ratios of waters were analysed by Isotope Ratio Mass Spectrometer and results were reported as ‰

10   deviation from the international carbonate standard, NBS19 with a precision of ±0.1‰ according to methods reported in Meredith et al., (2016). The DOC concentration and $\delta^{13}C_{DOC}$ were analysed using a total organic carbon analyser interfaced to a PDZ Europa20-20 IRMS utilising a GD-100 gas trap interface. Results were reported as per mil (‰) deviation from the NIST standard reference material with an analytical precision of ±0.6‰. The ^3H activities were expressed in tritium units (TU) with an uncertainty of ±0.1 TU and quantification limit of 0.3 TU. Samples were analysed by liquid scintillation

15   counting. Extended methods for ^3H activities can be found in Meredith et al., (2012). 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. (2020) shows the importance of collecting ^3H data and then calculating a groundwater age using a lumped parameter model in a shallow unconfined aquifer.

The dissolved organic matter (DOM) character was determined using optical spectroscopy and liquid chromatography (LC-

20   OCD). The LC-OCD technique is a size-exclusion chromatographic technique that allows for the characterisation of DOC, based on molecular weight, into six fractions. The fractions obtained are biopolymers (> 20 kDa), humic substances (~1000 Da), building blocks (300-500 Da), low molecular weight acids (< 350 Da), and low molecular weight neutrals (< 350 Da) and a hydrophobic fraction (fraction of DOC that remains in the column and determined by the difference between total DOC and the total of the other fractions), for full details see Huber et al., (2011). The humic substances fraction is further

25   characterised for its molecular weight (based on retention time of the humic substances peak) and aromaticity (the specific

UV absorption at 254_nm of the humic substances peak). Calibration is based on the chromatograms of the International Humic Substances Society (IHSS) Suwanee River humic and fulvic acid standards. 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

4 Results

Although common at coastal sites, a fresh-saline water interface was not identified in the wells, even though Site 5 is located ~100 m from the ocean and there was no evidence of seawater infiltration after storm events based on the hydrochemical data. Groundwater had low salinities with Cl concentrations ranging from 0.5-1.2 mmol L^{-1}. The highest Cl concentration occurred in the deeper groundwater at Sites 1 and 2 (Table 1 and Fig. 3a). Water level data suggested that under most conditions groundwater followeds a west to east direction towards the coastline (Fig. 2). Notably, groundwaters wereare anoxic with dissolved oxygen below 0.2 mg L^{-1} (Table 1). Water level patterns suggested that a buried-peat layer identified at Sites 1 and 2 wasis restricting the vertical flow of rainfall derived recharge into the deeper sections of the aquifer at these two sites.

The presence of detectable ^{3}H in all samples (>0.7 TU) indicated groundwater has a component of water that has been in contact with the atmosphere during the past decade. Variations in ^{3}H contents were seen with depth and distance from the wetland suggesting groundwaters have varied water residence times (Fig. 3b). The wetland had the highest ^{3}H content (1.7 TU) and represented a rainfall value for the region (Tadros et al., 2014). All wells located between 3.4 to 12.5 m bgl hadve high ^{3}H contents greater than 1.2 TU. Groundwaters from Site 3 hadve consistent values around 1.5 TU, suggesting a similar source of water and that the aquifer is hydraulically connected at this site. Deeper groundwaters (other than Site 3) hadve lower ^{3}H values (less than 1 T.U.), indicating slightly older groundwater at depth (Table 2).

The δ^{13}C$_{DIC}$ values ranged from -14.8 (S3_S) to -2.6 ‰ (S2_D) with an average of -9.7 ‰ (n = 15). The wetland had a significantly lower δ^{13}C$_{DIC}$ value (-23.6 ‰).The higher δ^{13}C$_{DIC}$ values found in the deeper system at Sites 1 and 2 (-4.1 to -2.6 ‰) could indicate marine carbonate dissolution with the groundwater isotopic signature moving closer towards 0 ‰. But

16

The average DOC concentration in groundwater for this site ~~is~~ was high (5.0 mg L^{-1}; n = 15) compared to the ~1 mg L^{-1} for the global median DOC concentration in groundwater (McDonough et al., 2019). The carbon isotopic signature of the groundwater DOC represent~~s~~ed a C$_3$ vegetation signature (average $\delta^{13}C_{DOC}$ value of -27.4 ‰; n = 15). Significant variation in DOC concentration and $\delta^{13}C_{DOC}$ values occur~~r~~ed within the aquifer (Fig. 4). The increase in DOC concentration in deeper groundwaters compared to shallow (except Site 4) suggest~~s~~ed a source(s) of DOC within the aquifer, which is generally not seen in groundwater environments and will be discussed below.

The LC-OCD results did not show significant differences in DOM character in the groundwater (Fig. 5). The humic substances fraction was generally between 40-60% of the total DOC (Fig. 5a). Minor exceptions existed in the shallow samples at Sites 2 and 3 for humic substances and at Sites 2, 3 and 5 for the Low Molecular Weight-Neutrals (LMW-Ns). The LMW-Ns were low representing approximately 10% of the total DOM and they did not change significantly along the groundwater flow path (i.e. with distance from the wetland) (Fig. 5b).

Principal component analysis (Fig. 6) using water quality parameters, isotopes and DOC variables included LC-OCD fractions (%), $\delta^{13}C_{DOC}$ (‰), $\delta^{13}C_{DIC}$ (‰), ^{3}H, pH, Na, pCO$_2$, Cl, Ca, Sr, DO, SO$_4$, NH$_4$, Ca and DOC concentration confirmed the presence of different groundwater sources. The variables contributing to PC1 (in order of importance) were pH, Na, pCO$_2$, Cl, DOC, Ca, humics, LMW-N, Sr and ^{3}H. The variables contributing to PC2 in order of importance were $\delta^{13}C_{DOC}$, DO, biopolymers, HS aromaticity, $\delta^{13}C_{DIC}$, HS molecular weight, Cl, DOC and hydrophobic DOM. PC1 mainly

explained the variations with sample depth in the aquifer. Samples S1_D, S2_S, S2_D and S3_S were the samples that most strongly influenced PC1. The deep samples likely to have originated from a deeper regional source of water (S1_D and S2_D) influenced the right hand side of the PCA with high pCO$_2$, humics substances, Na and Cl. These samples were also characterised by low Ca, ^{3}H and Sr. The shallow samples (S1_S, S2_S and S3_S) influenced the left hand side of the PCA with low pCO$_2$, humics, Na and Cl, and have high Ca, ^{3}H, and Sr suggestive of rainfall recharge waters. This analysis further highlighted the wetland sample that is not related to the other samples (Fig 6) and heavily influenced PC2 with low δ^{13}C$_{DOC}$ values, high DO, high biopolymers, low HS aromaticity, low HS molecular weight and high DOC concentration.

4.1 DOC variation in groundwater

The wetland had the highest DOC (18 mg L^{-1}) concentration and the lowest carbon isotope value (δ^{13}C$_{DOC}$ = -30.3 ‰) for the site. It also had a similar LC-OCD character to groundwater. The closest groundwater sample to the wetland located less than 5 metres downgradient at 3.5 m depth (S1_S) had a significantly lower DOC concentration (5 mg L^{-1}) and 1 ‰ higher carbon isotopes value (δ^{13}C$_{DOC}$ = -29.3 ‰). Interestingly this decrease in DOC was~~is~~ not reflected in the change~~s~~ in the mass fraction of the LC-OCD results.

The deeper samples (>17.0 m) at Sites 1 and 2 had~~ve~~ the highest DOC concentrations (10 ± 0.5 mg L^{-1}) for groundwaters at the site. The δ^{13}C$_{DOC}$ values were~~are~~ higher in the deeper groundwaters (-27.6 ± 0.2 ‰) compared to the shallow samples (-29.0 ± 0.2 ‰). The humic substances aromaticity and molecular weight showed~~s~~ there were~~are~~ two distinct groups of DOM (Fig 7~~6~~). Samples that generally had~~ve~~ lower values were~~are~~ from Sites 1, 2 and the wetland. All samples were~~are~~ more aromatic for their molecular weight in comparison to surface lakes, ~~and~~ rivers and marine samples (Huber et al., 2011).

Groundwaters from Sites 3 to 5 had lower DOC concentrations (<6 ppm) and a 1 ‰ higher average δ^{13}C$_{DOC}$ value (-26.6 ‰) than shallow and medium groundwater samples from Sites 1 and 2. Samples from S3, S4 and S5_S also had higher humic substances aromaticity and humic substances molecular weight than sites 1 and 2 (Fig. 7~~6~~). ~~Importantly,~~The DOC did not ~~would be expected to have decreased~~ show significant or consistent trends in aromaticity or ~~and~~ molecular weight, nor did it show a trend of declining DOC concentration with depth or along a flow path~~line~~. ~~, the opposite to what is observed here if the samples formed a degradation pathway.~~ This suggests that the OM source in this section of the aquifer differs from Sites

18

1 and 2. Sample S5_S is the exception where it has the highest δ¹³C_DOC value, which falls within the marine OM range (Fig. 4b).

5 Discussion

Our results showed that groundwater DOC varied in concentration and isotopic character along a 500 m groundwater flow path. The average groundwater DOC concentration found in this coastal site was five times higher (5 mg L⁻¹) than the global median DOC concentration for groundwaters (McDonough et al., 2019). Interestingly, we also see that The concentration of groundwater DOC doubled with depth, but we did not see any consistent trends of changing in the DOM chromatographic character related to depth (Fig. 5). These results were in contrast to results those from a deeper fractured rock aquifer (Shen et al., 2015), where DOC decreased with depth. Furthermore, despite observed differences in DOM characteristics (e.g. higher humic substances aromaticity and molecular weight in S3, S4 and S5_S), percentages of LC-OCD fractions the DOM character did oes not show any consistent trend 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., 2016²; Shen et al., 2015). The experimental work of Oudone et al. (2019) also confirmed that sorption predominantly affects the humic substances fraction, especially with high aromaticity. If biodegradation were occurring, we would expect to see a decline in the biopolymer and low molecular weight neutral fractions (Catalán et al., 2017) however we do not make a clear observation of this in our data. In contrast, Fig. 6 shows that the shallow samples located further from the wetland (S4_S and S5_S) have higher humic substances aromaticity and molecular weight which supports the conclusion that sorption is not the dominant process determining DOM character from the wetland to the coastline.

It is well known that OOrganic matterM is more readily preserved under anoxic conditions (Bertrand and Lallier-Verges, 1993), particularly in saturated environments. In such systems, remineralisation can be low, leading to enhanced preservation and storage of OM (Schefuß et al., 2016). In fact, Mmarine sediments, wetlands or peatlands have been suggested to have between 60-95% reduced mineralisation rates (Keiluweit, et al., 2017). The OM itself is thermodynamically unstable but

19

Schmidt et al., (2011) suggesteds it can persist because of the physicochemical and potentially biological influences of the surrounding environment that reduces the rate of decomposition.

Our hydrochemical data showeds there is strong evidence to suggest OM degradation has may have occurred. Dissolved oxygen wasis less than 0.2 mg L^{-1} for all groundwaters, which we inferinferred to be due to the respiration of microbes that haveare adapted to access OM in relatively anoxic conditions. Additional evidence for microbial activity includeds the presence of significant concentrations of reduced redox-sensitive species such as ammonium (up to 0.9 mg L^{-1}) and ferrous iron (up to 3.3 mg L^{-1}) together with very low nitrate concentration (<0.3 mg L^{-1}), the absence of sulphate in the deeper groundwaters (Table 1) and detection of H$_2$S odour. This fits with what was observed iIn anoxic subsurface environments were microbes utilise nitrate, Fe-oxides and sulphate as electron acceptors in the absence of oxygen increasing the ammonia, ferrous iron and sulphide concentrations (Berner, 1981; Appelo and Postma, 2005). A possible explanation for the similar constant character of the DOM with the evolved inorganic redox chemistry is that the rates of biodegradation are far lower than the rate of DOM leaching into the groundwater. Furthermore, if there are additional sources of DOM along the flowpath, we would expect to the see inconsistent variations in LC-OCD fractions along the flow path that we observe in our data, rather than a consistent decline in any DOM fraction or DOC concentration. all DOM fractions are being released from the OM sources at constant rates, combined with a slightly slower decomposition of all dissolved fractions.

5.1 Sources of OM

DOC in groundwater may originate from various sources. The most abundant source is generally from decomposing OM in the soil zone and sedimentary OM from buried peat or palaeosols can also be a source. The wetland oOrganic-rich sediments such as organic muds and silts associated with freshwater depressions are characteristic of coastal dune-slack systems which have formed since the maximum Holocene sea-level transgression and have a global occurrence, including along the southeastern coast of Australia (MacPhail, 1973). These units have the potential to form peat. In suitable environments, the decay of OM under anaerobic conditions is much slower (Bennrner et al., 1984a), allowing a greater accumulation of refractory OM, which may lead to peat accumulation (Lamb et al., 2006). Three 'peat' horizons were identified in a similar coastal environment to Anna Bay (Finga Bay, Central Coast, NSW) and ranged in age from 3.0 to 6.5 ka (MacPhail, 1973). The peat formation was suggested to be very rapid, with metres of sediment accumulating over the past few thousand years.

20

The sand dunes at Anna Bay were are likely to have formed around 7 ka (Sloss et al., 2007; Jones, 1990; MacPhail, 1973) and the OM-rich layers contained within them would have formed over this time. Organic matterM can be characterised by very long turnover times that increase with depth from 1 to 10 ka depending on the system (Schmidt et al., 2011). The radiocarbon age of DOC for the deeper groundwaters at S1_D and S2_D was measured by McDonough et al., (2020b) for the Anna Bay site. The results showed that DOC was ~1 ka (88.3±0.4 pMC) in the deeper groundwater samples while the shallow water was modern (>100 pMC), suggesting an older OM source at depth. The destabilisation of these older OM-rich units whether by anthropogenic or natural processes could result in an increase in the flux of older carbon into the surface water environment as observed by (Moore et al., (20163). Furthermore and the transport of this carbon has been shown to be dependent on the hydrological response in coastal systems (Webb et al., 2018).

5.1.1 Wetland OM

Initially, it was thought that the wetland was the major source of OM for the groundwater system because it contained elevated DOC concentrations (18 mg L^{-1}) and it appeared to be hydraulically connected to the aquifer. Based on these assumptions, it would mean that approximately 70% of the OM from the wetland would be is removed after groundwater recharge (i.e. 10 metres downgradient at sample S1_S at 3.5 m depth). This estimate seems reasonable when considering Shen et al., (2015) found that about 90% of surface-derived DOC was removed prior to reaching the saturated zone.

Our data showeds that the chromatographic character of the DOM in the wetland wasis similar to the groundwater, suggesting if the wetland was a significant source of OM, the chemical composition and bioavailability of the wetland derived DOM remaineds relatively unchanged during transport through the aquifer. The higher relative contribution of DOC and evidence for the limited transformation of the wetland OM compared to groundwater at this site could also be explained by the limited sorption capacity of the predominantly quartz sand aquifer.

If biological processing was influencing the wetland DOM during transport into the groundwater, it would be expected that the $\delta^{13}C_{DOC}$ values would become heavier lighter than the original C$_3$ vegetation source where the bacteria metabolize the isotopic light organics because the ^{12}C-H bonds are easier to break leaving the resultant OM more enriched than the original source (Benner et al., 1987Clark and Fritz, 1997). However, Tthe carbon isotope value ($\delta^{13}C_{DOC}$) of the OM in the wetland is was 1 ‰ lighterower compared to the shallowest groundwater sample located near the wetland. This suggests that if the

21

~~wetland was the source of OM then the carbon isotopes were fractionated after recharge.~~ a small amount of microbial processing may have occurred, or that unprocessed DOM inputs are very high at this site.

Alternatively, because we do not observe clear decreases in DOC concentration or major changes in the LC-OCD fractions, the difference in isotopic values could be explained by the ~~-~~DOM in the groundwater system having~~s~~ a different source to the wetland and limited interaction of the surface and groundwater at this site. The lack of interaction ~~A different source of OM~~ would also explain the distinctly different water chemistry of the wetland sample compared to the groundwater (Table 1 and Fig. 6). The wetland contained~~s~~ elevated ~~levels~~ concentrations of DOC but it is likely that the OM is being mobilised and deposited into the hyporheic zone of the wetland (i.e. 1-2 metres) by either sorption or abiotic transformation (Kerner et al., 2003). This hypothesis is being investigated with further detailed water-sediment investigations at this location. ~~Significantly this study does show that the modern wetland is not a major source of DOM for these groundwaters.~~

5.1.2 In-situ OM sources

Organic-rich sediments were~~are~~ present in the unconsolidated aquifer units and ~~it is clear that~~ the physicochemical properties of the aquifer are governing the persistence of the OM within the aquifer. We see ~~there are~~ several *in-situ* DOM sources based on the carbon isotopes and the humic substances aromaticity and molecular weight data (Fig. 7~~6~~). Two major groundwater groups were identified at Sites 1-2 and Sites 3-5. The aromaticity of the humic substances in both groups was~~is~~ higher than those previously reported for rivers and~~,~~ lakes for the corresponding molecular weight, especially for Sites 3-5. Furthermore, we see groupings for the deeper samples from Sites 1 and 2 that corresponded~~s~~ with carbon isotopes that are 1 ‰ higher (-27.6 ± 0.2 ‰) than other groundwater at Site 1 and 2. These groundwaters contained less tritium suggesting they were ~~are~~ older (<0.8 T.U.) and the OM is likely to have originated from ~~a~~ the deeper older palaeosol unit(s) contained within the coastal sediments (Fig. 8~~7~~). The shallow groundwaters had~~ve~~ lower DOC concentrations and lower carbon isotope values (-29.0 ± 0.2 ‰) suggesting the OM originating from these sources are also different from the deeper palaeosol. The overlying peat units most likely formed in a similar environment to the palaeosol located at depth but contained younger OM with lower source $\delta^{13}C_{DOC}$ values.

Groundwater from Sites 3-5 had~~ve~~ lower DOC concentrations (<6 mg L^{-1}) and higher humic substances aromaticity and humic substances molecular weight~~s~~ (Fig. 7~~6~~) together with higher consistent $\delta^{13}C_{DOC}$ values (average $\delta^{13}C_{DOC}$; -26.6 ‰).

22

The exception ~~is~~was the shallow sample at Site 5, which ha~~s~~d the highest $\delta^{13}C_{DOC}$ value (-25.0‰) and trend~~s~~ed towards a marine OM value (Lamb et al., 2006) with a DOC concentration (2.1 mg L^{-1}) well below the average for this site ~~(2.1 mg L^{-1}) further~~ which suggest~~ing~~ a localised source of OM that may be derived from marine sources due to its close proximity to the ocean. ~~The stability and similarity in the overall chromatographic and isotopic character suggests that these groundwaters contain OM from within the aquifer that has not undergone significant processing.~~

5.2 Implications

Most studies investigate the character or carbon isotope signatures ~~for~~of DOC in groundwater but rarely use both techniques. Our findings show~~ed~~ that there are several sources of OM within this coastal aquifer ranging from buried peat units to palaeosols, and if ~~without utilising~~ both techniques were not used these sources would not have been identified. ~~This~~It is important to understand the sources for estimating the contribution of sub-surface carbon to the global carbon cycle. The combination of the low sorption capacity of the coastal aquifer sediments, the presence of various sources of OM, together with associated anoxic aquifer conditions, appears to have limited the sorption and/or biodegradation that might be observed elsewhere in groundwater. Therefore this study further demonstrated that the persistence of OM ~~is~~was found to be due to complex interactions between the OM and its environment ~~as suggested by~~ (Schmidt et al.,~~(~~2011).

The groundwater that discharges from ~~the~~ young unconsolidated coastal environments such as th~~is~~ese have much higher DOC concentrations than groundwater from older deeper aquifers that have undergone a greater degree of OM processing (McDonough et al., 2020b). The degradative processes that act on freshly produced DOM can produce greenhouse gases and produce less reactive DOM that is exported (Davidson and Janssens, 2006; Zhou, et al., 2018). This means that the DOM transported from this coastal system has the potential to impact the carbon budget. Moreover, sandy coastal aquifers containing palaeosol horizons are globally widespread as they formed during Holocene sea-level changes. These systems are sensitive to sea level changes and climate change drivers ~~and~~that are likely to impact ~~affect~~ DOC export from coastal systems because of ~~the~~ changes in either the hydrology or ecosystem dynamics. The OM sources found in this system are currently saturated and anoxic. If the physicochemical conditions of the aquifer were altered, these coastal groundwater systems would then have the potential to export an order of magnitude higher volume of unreacted carbon to the surface than previously realised based on the current global median DOC concentration of 1 mg L^{-1} for groundwaters (McDonough et al.,

23

2019). These coastal groundwater systems form a significant ~~OM~~ source that is ~~largely~~ unaccounted for in the global carbon budget. The magnitude and timing of the soil C reservoir changes as a result of climate and land-use changes is difficult to quantify and is a large source of uncertainty in global C cycle models (Kendall and McDonnell, 1998). Therefore studies like this that identify the sources of OM in aquifers will contribute to refining calculations in the future.

5 **6 Conclusion**

The purpose of this study was to investigate the role of different OM sources and the influence ~~of~~ the physicochemical properties of an aquifer ~~has~~ on groundwater DOM. This was done to identify the major controls on groundwater DOC sources and processing in a coastal groundwater system. Our results showed that groundwater DOC varied in concentration and isotopic character along a 500 m groundwater flow path. The average groundwater DOC concentration for this study

10 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~~ fractions did not change significantly with depth or along the groundwater flow path. We note that the carbon isotopic composition did however vary slightly.

Multiple sources of organic matter were identified ~~by measuring the concentration, carbon isotopic composition ($\delta^{13}C_{DOC}$) and character (by LC-OCD) of groundwater DOC. These sources have~~including those formed ~~during~~since the maximum

15 Holocene sea-level transgression ~~and include~~such as wetland, soil, peat and palaeosols. It was found that ~~there was not enough OM processing in the subsurface to significantly change the DOC character. t~~The DOC character at this site ~~therefore~~ did not follow the regional chromatography model due to OM processing with depth and along a groundwater flow path. All samples ~~were~~ are more aromatic for their molecular weight in comparison to surface lakes, ~~and~~ rivers and marine samples. It was also found that the physicochemical properties of the aquifer and in this case the anoxic, saturated conditions

20 limited OM processes leading to enhanced preservation and storage of OM. The contradiction in DOM trends when compared to the redox chemistry of the groundwater for this study, challenge~~d~~s our current understanding of groundwater DOC mobilisation and degradation in coastal aquifers. A possible explanation for ~~not~~the observ~~ing a decrease and change in~~ ~~ed constant character of the~~ DOM character with evolved inorganic redox chemistry is that ~~all~~ DOM ~~fractions are~~is being released from the OM sources at a higher rate than biodegradation is occurring~~constant rates~~.

24

In-situ sources such as peats and palaeosols are the main contributor of OM to the groundwater DOC in this coastal system. ~~However~~ ~~T~~the destabilisation or changes in hydrology, whether by anthropogenic or natural processes could result in increased fluxes of <u>unreacted old</u> carbon from deep within the peat column. Significantly, the results of this study show that understudied anoxic coastal groundwater systems have the potential to export up to ten times more unreacted carbon to the surface than previously realised <u>when considering the global median DOC concentration is 1 mg L^{-1} for groundwaters</u>. These coastal groundwater sources are ~~still~~ <u>largely</u> unaccounted for in the global carbon budget and are likely to play more of a role in carbon transport in the future.

7 Acknowledgements

References

Appelo C.A.J. and Postma D.:Geochemistry, Groundwater, and Pollution, second ed. A.A. Balkema, Rotterdam, 649 pp, 2005.

<u>Benner, R., Newell, S.Y., Maccubbin, A.E., Hodson, R.E., 1984 Relative contributions of bacteria and fungi to rates of degradation of lignocellulosic detritus in salt-marsh sediments. Applied and Environmental Microbiology 48, 36–40.</u>

~~Benner, R., Fogel, M.L., Sprague, E.K. and Hodson, R.E.: Depletion of 13C in lignin and its implications for stable carbon isotope studies. Nature 329, 708, 1987.~~

Berner R.A.: A new geochemical ~~classificaion~~<u>classification</u> of sedimentary environments. Journals of Sedimentary Research, 51(2), 359-365, 1981.

Bertrand, P. and Lallier-Vergès, E.: Past sedimentary organic matter accumulation and degradation controlled by productivity. Nature 364, 786, 1993.

<u>Bryan, E., Meredith, K.T., Baker, A., Andersen, M.S., Post, V.E.A. and Treble, P.C. (2020) How water isotopes (18O, 2H, 3H) within an island freshwater lens respond to changes in rainfall. Water Research 170, 115301.</u>

<u>Catalán, N., Casas-Ruiz, J. P., von Schiller, D., Proia, L., Obrador, B., Zwirnmann, E., & Marcé, R.: Biodegradation kinetics of dissolved organic matter chromatographic fractions in an intermittent river. Journal of Geophysical Research: Biogeosciences, 122(1):131-144, 2017.</u>

Chapelle, F.H., Shen, Y., Strom, E.W. and Benner, R.: The removal kinetics of dissolved organic matter and the optical clarity of groundwater. Hydrogeology Journal 24, 1413-1422, 2016.

<u>Clark, I.D. and Fritz, P.:Environmental Isotopes in Hydrogeology. Taylor & Francis. 1997.</u>

Davidson, E.A. and Janssens, I.A.:Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 440, 165, 2006.

Emery, K.O., Wigley, R.L., Bartlett, A.S., Rubin, M. and Barghoorn, E.S.: Freshwater Peat on the Continental Shelf. Science 158, 1301-1307, 1967.

5   Fontaine, S., Barot, S., Barré, P., Bdioui, N., Mary, B. and Rumpel, C.: Stability of organic carbon in deep soil layers controlled by fresh carbon supply. Nature 450, 277, 2007.

Hashimoto T.R and Troedson A.L.: Nelson Bay 1:100 000 and 1:25 000, Coastal Quaternary Geology Map Series. Geological Survey of New South Wales, Maitland, 2008. https://www.resourcesandgeoscience.nsw.gov.au/miners-and-explorers/geoscience-information/products-and-data/maps/coastal-quaternary-maps/CQGNB

10   Hedges, J.I., Ertel, J.R., Quay, P.D., Grootes, P.M., Richey, J.E., Devol, A.H., Farwell, G.W., Schmidt, F.W. and Salati E.: Organic carbon-14 in the Amazon River system. Science 231(4742):1129–1131, 1986.

Hedges, J.I., Cowie, G.L., Richey, J.E., Quay, P.D., Benner, R., Strom, M. and Forsberg, B.R.: Origins and processing of organic-matter in the Amazon River as indicated by carbohydrates and amino-acid. Limnol Oceanogr 39(4):743–761, 1994.

15   Howley, E.: Lignin in a coastal groundwater aquifer: a useful tracer?. Bachelor of Engineering (Hons) Thesis. School of Civil and Environmental Engineering UNSW, Sydney, 2014.

Huber, S.A., Balz, A., Abert, M. and Pronk, W.: Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND). Water Research 45, 879-885, 2011.

20   Jardine, P.M., McCarthy, J.F. and Weber, N.L.: Mechanisms of Dissolved Organic Carbon Adsorption on Soil. Soil Science Society of America Journal 53(5):1378-1385, 1989.

Jones, R.L.: Late Holocene vegetational changes on the Illawarra coastal plain, New South Wales, Australia. Review of Palaeobotany and Palynology 65, 37-46, 1990.

Kaiser, K. and Zech, W.: Competitive Sorption of Dissolved Organic Matter Fractions to Soils and Related Mineral Phases. 25   Soil Science Society of America Journal 61(1):64-69, 1997.

Kendall, C. and McDonnell, J.J.: Isotope Tracers in Catchment Hydrology. Elsevier Science. 1998

Keiluweit, M., Wanzek, T., Kleber, M., Nico, P. and Fendorf, S.: Anaerobic microsites have an unaccounted role in soil carbon stabilization. Nature Communications 8, 1771, 2017.

Kerner, M., Hohenberg, H., Ertl, S., Reckermann, M. and Spitzy, A.: Self-organization of dissolved organic matter to 30   micelle-like microparticles in river water. Nature 422, 150, 2003.

Lamb, A.L., Wilson, G.P. and Leng, M.J.: A review of coastal palaeoclimate and relative sea-level reconstructions using δ13C and C/N ratios in organic material. Earth-Science Reviews 75, 29-57, 2006.

Lehmann, J. and Kleber, M.: The contentious nature of soil organic matter. Nature 528, 60, 2015.

McDonough, L., Santos, I, Andersen, M., O'Carroll, D., Rutlidge, H., Meredith, K. and Oudone, P.: "Changes in Global 35   Groundwater Organic Carbon Driven by Climate Change and Urbanization." EarthArXiv. November 21. doi:10.31223/osf.io/vmaku, 2018.

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.: Changes in groundwater dissolved organic matter character in a coastal sand aquifer due to rainfall recharge. Water Research 169, 115201, 2020a.

40   McDonough, L.K., Rutlidge, H., O'Carroll, D.M., Andersen, M.S., Meredith, K., Behnke, M.I., Spencer, R.G.M., McKenna, A.M., Marjo, C.E., Oudone, P. and Baker, A.:Characterisation of shallow groundwater dissolved organic matter in aeolian, alluvial and fractured rock aquifers. Geochimica et Cosmochimica Acta, in press. 2020b.

Macphail, M.: Pollen analysis of a buried organic deposit on the backshore at Fingal Bay, Port Stephens, New South Wales. Proceedings of the Linnean Society of New South Wales, 98, 222-233, 1974.

45   Maric, I.: Groundwater quality changes in a coastal aquifer due to groundwater abstraction:A case study. Bachelor of Engineering (Hons) Thesis. School of Civil and Environmental Engineering UNSW, Sydney, 2013.

Meredith, K., Cendón, D.I., Pigois, J.-P., Hollins, S. and Jacobsen, G.: Using 14C and 3H to delineate a recharge 'window' into the Perth Basin aquifers, North Gnangara groundwater system, Western Australia. Science of The Total Environment 414, 456-469, 2012.

Meredith, K.T., Han, L.F., Hollins, S.E., Cendón, D.I., Jacobsen, G.E. and Baker, A.: Evolution of chemical and isotopic composition of inorganic carbon in a complex semi-arid zone environment: Consequences for groundwater dating using radiocarbon. Geochimica et Cosmochimica Acta 188, 352-367, 2016.

Moore, S., Evans, C.D., Page, S.E., Garnett, M.H., Jones, T.G., Freeman, C., Hooijer, A., Wiltshire, A.J., Limin, S.H. and Gauci, V.: Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes. Nature 493, 660, 2013.

Schefuß, E., Eglinton, T.I., Spencer-Jones, C.L., Rullkötter, J., De Pol-Holz, R., Talbot, H.M., Grootes, P.M. and Schneider, R.R.: Hydrologic control of carbon cycling and aged carbon discharge in the Congo River basin. Nature Geoscience 9, 687, 2016.

Oudone, P., Rutlidge, H., Andersen, M.S., O'Carroll, D., Cheong, S., Meredith, K., McDonough, L., Marjo, C. and Baker, A.: Characterisation and controls on mineral-sorbed organic matter from a variety of groundwater environments. EarthArXiv https://eartharxiv.org/ue86w/ 2019.

Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S. and Trumbore, S.E.: Persistence of soil organic matter as an ecosystem property. Nature 478, 49, 2011.

Shen, Y., Chapelle, F.H., Strom, E.W. and Benner, R.: Origins and bioavailability of dissolved organic matter in groundwater. Biogeochemistry 122, 61-78, 2015.

Sloss, C.R., Murray-Wallace, C.V. and Jones, B.G., Holocene sea-level change on the southeast coast of Australia: a review. The Holocene 17, 999-1014, 2007.

Stumm, W., and J. J. Morgan.: Aquatic chemistry. 3rd edition. Wiley and Sons, New York, 1996.

Tadros, C.V., Hughes, C.E., Crawford, J., Hollins, S.E. and Chisari, R.: Tritium in Australian precipitation: A 50 year record. Journal of Hydrology 513, 262-273, 2014.

Webb, J.R., Santos, I.R., Maher, D.T., Tait, D.R., Cyronak, T., Sadat-Noori, M., Macklin, P. and Jeffrey, L.C.: Groundwater as a source of dissolved organic matter to coastal waters: Insights from radon and CDOM observations in 12 shallow coastal systems. Limnology and Oceanography, doi: 10.1002/lno.11028, 2018.

Zhou, Y., Davidson, T.A., Yao, X., Zhang, Y., Jeppesen, E., de Souza, J.G., Wu, H., Shi, K. and Qin, B.: How autochthonous dissolved organic matter responds to eutrophication and climate warming: Evidence from a cross-continental data analysis and experiments. Earth-Science Reviews 185, 928-937, 2018.
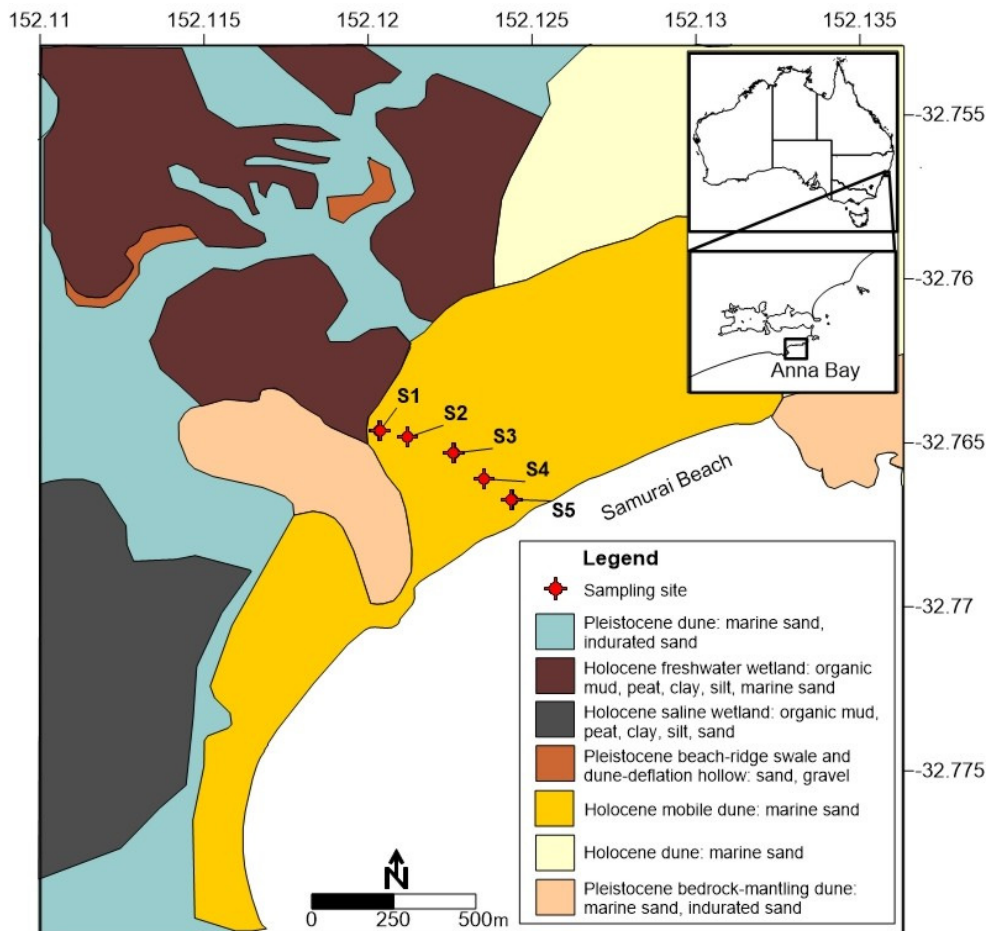
Figure 1: Location of the study area and groundwater monitoring wells in relation to Coastal Quaternary Geology (Adapted from Hashimoto and Toedson, 2008).
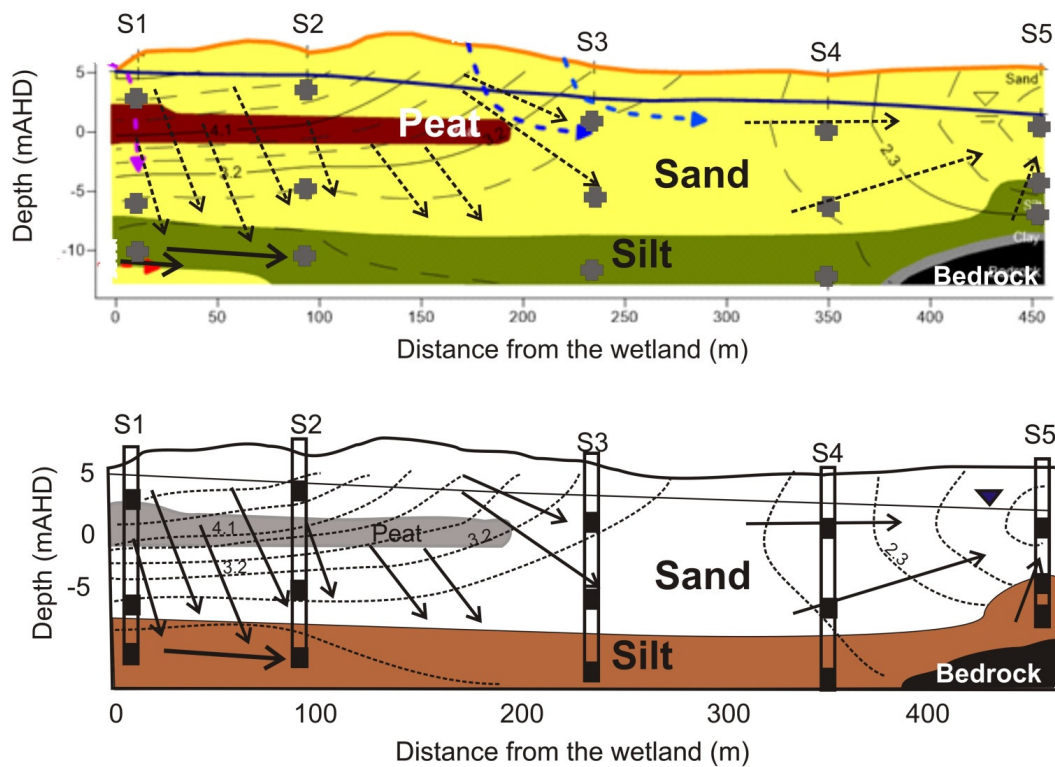
Figure 2: Lithology and potentiometric contours (in metres) in the aquifer in February 2014 (adapted from Maric, 2013 and Howley, 2014). Black open rectangles represent groundwater wells and filled rectangles are the location of the well screen (Grey crosses are the location of screened intervals within the aquifer and arrows indicate groundwater flow direction.
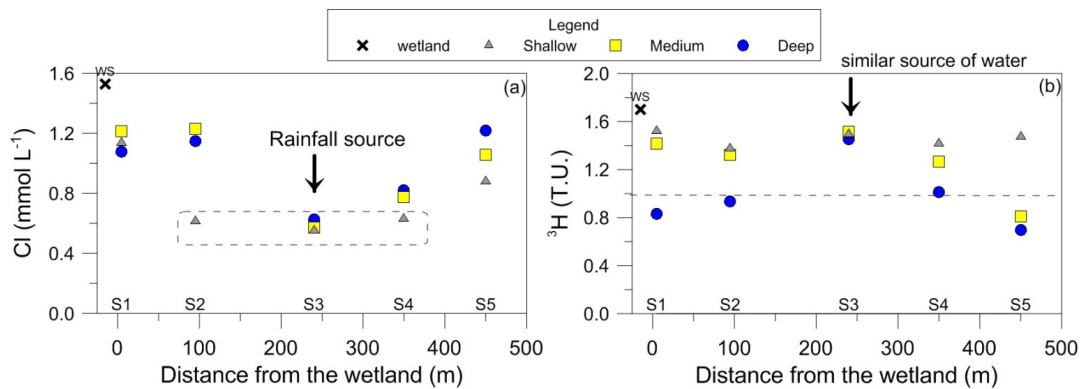
Figure 3: The relationship between (a) chloride concentration (mmol L⁻¹) ~~with and~~ the ~~dashed rectangle~~polygon represent~~ings~~ rainfall values and (b) tritium (TU) content with distance from the wetland ~~with and~~ the dotted line represent~~ings~~ recently recharged groundwaters (i.e. between 1 to ~~-~~5 years old).
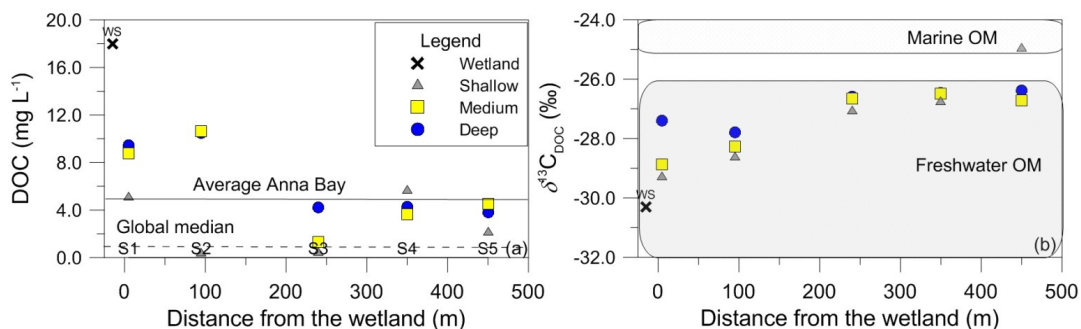

Figure 4: The relationship between (a) DOC concentration compared to average DOC for Anna Bay (solid black line) and global median DOC concentration for groundwater (dotted line; McDonough et al., 2019) and (b) $\delta^{13}C_{DOC}$ values for groundwaters from Anna Bay with distance from the wetland and compared to the terrestrial and marine OM ranges from Lamb et al., (2006).

5
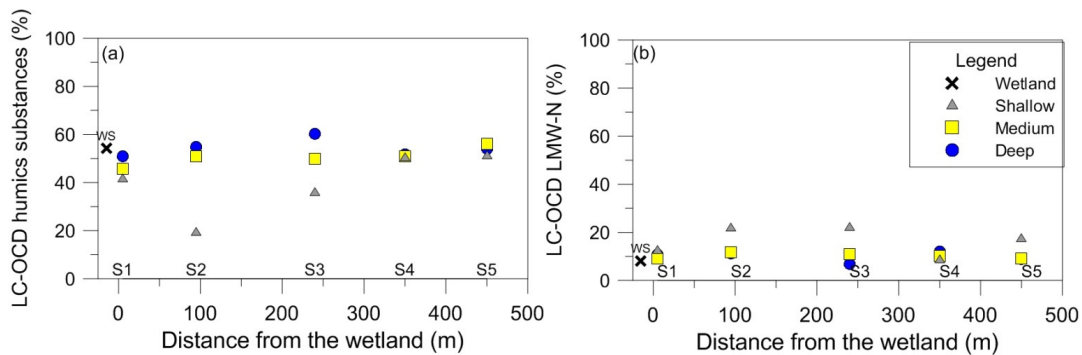
Figure 5: The relationship between (a) LC-OCD results with the total percentage of humic substances and (b) LC-OCD total percentage of light molecular weight neutral with distance from the wetland.

Fig. 2 Principle Component Analysis for Anna Bay waters. The blue oval represents the shallow waters, the green oval medium and the red oval represents the deeper waters. The wetland sample plots at the bottom of the graph with a distinct chemistry compared to the groundwater samples.

Figure 76: The relationship between humic substances molecular weight (M$_n$) and humic substances aromaticity (SAC/OC = Spectral Absorption Coefficient/Organic Carbon)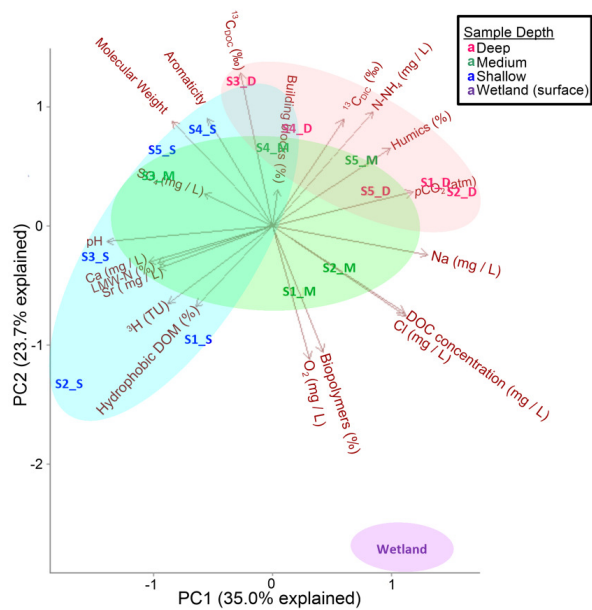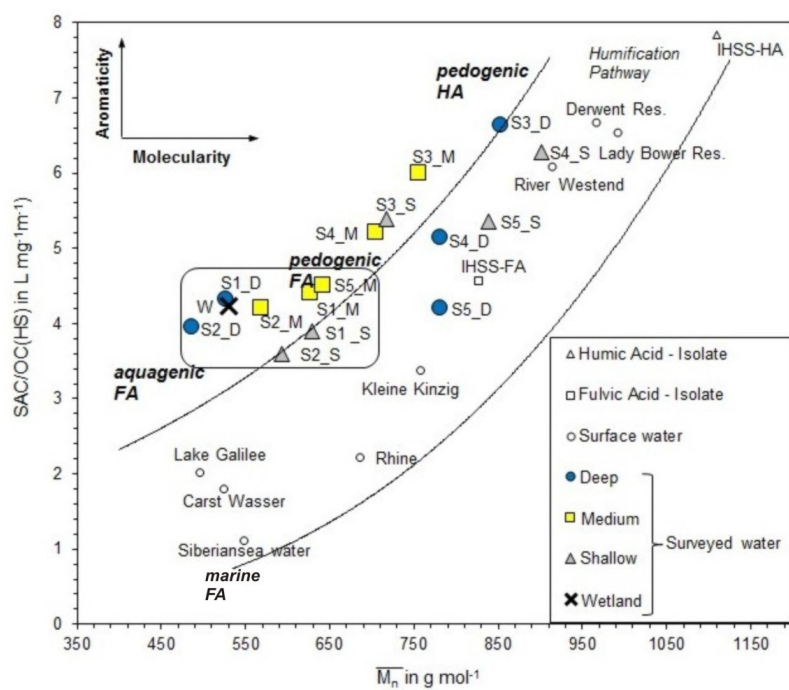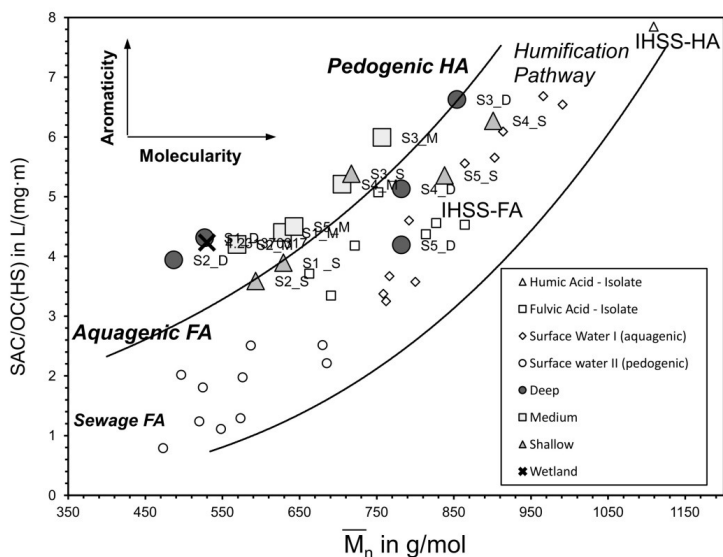. ~~The polygon shows samples from Sites 1 and 2 plus the wetland sample, which have lower values than those from Sites 3-5.~~ The curved lines show the area that samples would plot if the humic substances of aromaticity and molecular weight are derived from the humic substances standard and water samples from Huber et al., 2011. The figure also indicates the origin of humic substances samples plotting at the top interpreted as pedogenic in origin and the fulvic acids at the bottom are aquagenic origin. Note: humic acid (HA) and fulvic acid (FA) ~~is~~ are isolated from humic substances standard of the IHSS from Suwannee River (Huber et al., 2011). Surface water samples with humic substances-aquagenic origin and humic substances-pedogenic origin are also indicated.
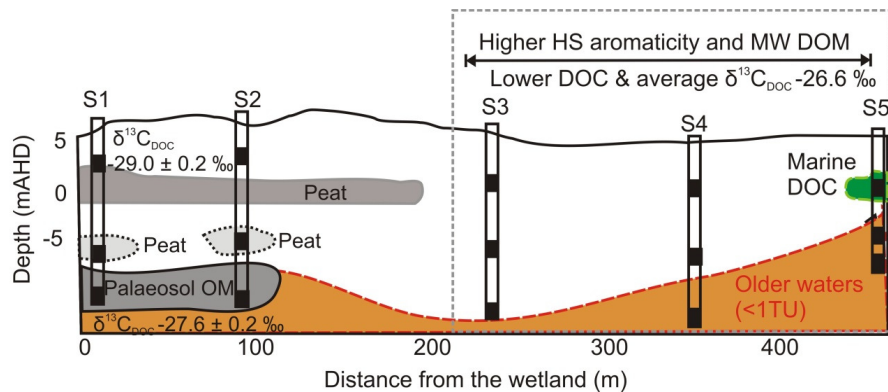

Figure 87: Schematic of OM sources and processes influencing DOC within the coastal aquifer at Anna Bay based on concentration, character (isotopic and chromatographic), tritium and hydrochemical data (Table 1 and 2). ~~Black open rectangles~~

33

~~represent groundwater wells and filled rectangles are the location of the well screen (■).~~ **Marine and freshwater DOM characterisation from Lamb et al. (2006).**

Table 1: Water chemistry data for the site. Elevation of mid-point of the screen (m AHD), EC = electrical conductivity (µS cm^{-1}), DO = dissolved oxygen (mg L^{-1}) T = temperature (°C), Eh = redox potential (mV), and cations and anions (mg L^{-1}), n.a = not detected.

ID	Elevation	Field pH	EC	DO	T	Eh	Ca	Fe	K	Mg	Mn	Na	Si	Sr	Cl	SO$_4$	NO$_3$	N-NH$_4$
S1 _S	2.9	7.19	495	0.06	22.1	-97.2	81.20	3.27	0.81	4.12	0.08	23.11	2.56	0.70	40.21	n.a.	n.a.	0.22
S1_M	-6.1	6.1	337	0.04	19.6	-14.5	38.60	1.40	0.97	7.96	0.02	24.05	2.11	0.35	43.03	n.a.	n.a.	0.14
S1_D	-10.4	5.36	215	0.04	20.4	7.8	7.91	0.58	1.15	3.65	0.01	32.00	5.27	0.08	38.19	n.a.	0.18	0.80
S2_S	3.4	8.2	293	0.12	22.8	-59.2	45.80	0.07	0.49	4.46	0.01	10.98	2.23	0.36	21.75	1.07	n.a.	0.00
S2_M	-5.3	6.03	408	0.06	21.2	-42.9	45.31	0.17	1.66	14.54	0.01	24.65	2.04	0.35	43.69	n.a.	0.16	0.40
S2_D	-10.5	5.32	231	0.06	20.8	-6.7	8.19	0.41	1.20	6.75	0.01	30.49	5.80	0.08	40.69	n.a.	0.28	0.90
S3_S	1.0	7.24	306	0.17	24.1	-42.9	45.95	0.23	0.54	4.58	0.01	12.36	2.67	0.36	19.48	4.45	n.a.	0.03
S3_M	-5.7	6.98	282	0.04	21.4	-47.8	43.93	0.05	0.63	4.24	0.02	13.19	2.63	0.33	20.34	5.20	n.a.	0.08
S3_D	-11.9	6.5	245	0.05	21.9	-40.6	10.67	0.25	1.00	18.56	0.01	13.68	1.49	0.06	22.24	11.61	n.a.	0.81
S4_S	0.1	6.59	323	0.1	21.9	-28.1	47.49	0.03	1.09	5.81	0.01	14.02	1.88	0.37	22.40	0.67	n.a.	0.57
S4_M	-6.3	6.26	268	0.03	22	-49	24.71	0.21	1.33	10.35	0.01	17.26	1.65	0.18	27.44	0.10	n.a.	0.84
S4_D	-12.8	6.24	319	0.04	22.4	5.5	7.44	0.22	1.38	27.28	0.03	18.44	2.57	0.04	29.06	n.a.	n.a.	0.51
S5_S	0.1	6.69	365	0.06	21.8	-62.5	51.22	0.71	1.10	5.96	0.00	19.13	2.43	0.42	31.16	10.18	n.a.	0.16
S5_M	-4.6	6.1	316	0.04	22.1	-46.5	7.89	0.31	2.25	21.38	0.03	26.61	3.39	0.06	37.46	n.a.	0.14	0.69
S5_D	-7.4	6.16	348	0.1	21	-58.4	8.10	0.59	2.89	22.39	0.04	34.13	3.72	0.07	43.15	n.a.	0.17	0.43
WS	5.3	5.48	200	1.01	21.7	87.1	8.00	0.43	2.18	2.74	0.01	28.01	1.23	0.07	54.23	3.93	n.a.	0.03

Table 2: Environmental isotope data for the site. DOC = Dissolved organic carbon, uncert = tritium uncertainty, QL = tritium quantification limit, CBE = charge balance error, SI$_{cc}$ = saturation index for calcite, P$_{CO2}$ = partial pressure of carbon dioxide.

ID	date	$\delta^{13}C_{DIC}$	DOC	$\delta^{13}C_{DOC}$	^3H	^3H uncert	QL	CBE	DIC	SI$_{cc}$	P$_{CO2}$
		(‰)	ppm	(‰)	TU	TU	TU	%	mmol/L		atm
S1 _S	18/02/2014	-11.8	5.0	-29.3	1.52	0.07	0.15	0.10	4.97	0.03	0.016
S1_M	18/02/2014	-10.5	8.8	-28.9	1.41	0.07	0.15	1.25	6.64	-1.64	0.107
S1_D	18/02/2014	-4.1	9.5	-27.4	0.83	0.05	0.16	1.69	11.31	-3.37	0.265
S2_S	19/02/2014	-14.0	0.3	-28.6	1.37	0.07	0.15	-0.54	2.53	0.59	0.001
S2_M	18/02/2014	-4.2	10.6	-28.3	1.32	0.06	0.15	0.74	9.91	-1.50	0.175
S2_D	18/02/2014	-2.6	10.5	-27.8	0.94	0.05	0.16	0.62	14.23	-3.33	0.340

S3_S	19/02/2014	-14.8	0.4	-27.1	1.49	0.08	0.16	0.87	2.88	-0.33	0.009
S3_M	19/02/2014	-12.3	1.3	-26.7	1.51	0.08	0.16	0.94	2.99	-0.66	0.015
S3_D	19/02/2014	-12.3	4.2	-26.6	1.45	0.07	0.16	2.54	3.14	-1.86	0.034
S4_S	20/02/2014	-9.0	5.6	-26.8	1.42	0.07	0.15	-0.07	4.48	-0.95	0.043
S4_M	20/02/2014	-11.0	3.6	-26.5	1.27	0.07	0.16	0.14	4.71	-1.67	0.069
S4_D	20/02/2014	-7.2	4.3	-26.5	1.01	0.06	0.15	0.90	5.83	-2.13	0.088
S5_S	21/02/2014	-12.9	2.1	-25.0	1.47	0.07	0.16	0.89	4.13	-0.83	0.034
S5_M	21/02/2014	-9.1	4.5	-26.7	0.81	0.05	0.16	-0.34	6.49	-2.28	0.111
S5_D	21/02/2014	-9.4	3.8	-26.4	0.69	0.04	0.16	-0.47	6.66	-2.19	0.105
WS	20/02/2014	-23.6	18.0	-30.3	1.70	0.08	0.15	4.40	1.56	-3.96	0.037