

Responses to Editor and Reviewers

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Beijing, 9 February, 2015

To:
Prof. Christine Stumpp
Editor
Hydrology and Earth System Sciences

Dear Prof. Christine Stumpp,

We are submitting the revised manuscript titled "Identification of anthropogenic and natural inputs of sulfate into a karstic coastal groundwater system in northeast China: evidence from major ions, $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ " (HESD-12, 11331-11370, 2015) to *Hydrology and Earth System Sciences*. Following the constructive comments from the Editor and two reviewers, the authors have completed the required revisions on the previous manuscript. We gratefully acknowledge their generous help.

Some explanations for the important points are as follows.

Reply to the anonymous Referee #1:

Dear Reviewer,

We would like to thank you for the valuable comments on our manuscript. These comments will be very helpful to improve the quality of the manuscript. Here, we will give our point-by-point reply to reviewer's comments.

(1) Although a lot of information is tried to derive from the hydrochemical and stable isotope data set in the present study, I have the impression that the study area is strongly under-sampled and the ion balance would require more parameters, like the oxygen isotope composition of sulfate, the stable isotope composition of nitrate and possibly selected rock-relevant trace elements (e.g., Sr).

Reply: While we agree that further data could potentially add to a greater understanding of processes and/or contribute to more precise mass balances, this could also prove not to be the case. We believe

that overall the data collected to date is sufficient to meet the objectives of the paper – e.g. separating the likely natural and anthropogenic inputs to groundwater dissolved ion load. Strontium data from the study area was in fact collected and this data could be included in a revised version of the manuscript as a new figure (e.g. by comparing Sr content and Cl/TDS ratios and showing end-members for seawater and possible anthropogenic inputs). This data could further refine the analysis of salinity sources in groundwater.

We did not measure the oxygen isotope composition of sulfate in our samples (in addition to the $\delta^{34}\text{S}$, which we did report). Measurement of $\delta^{18}\text{O}_{\text{SO}_4}$ in groundwater is typically of benefit when examining the effect of secondary processes on the sulfate pool, such as aerobic oxidation of sulfides, reduction of sulfate or exchange with oxygen in water at higher temperatures. These processes are likely to be of relatively minor importance in the study area – as was shown in the analysis of $\delta^{34}\text{S}$ and SO_4/Cl ratios (Figure 4). We believe that the sulfur stable isotopes in themselves, along with ionic ratios, are sufficient to define sources of sulfate and other inputs, which is the ultimate aim.

We agree to some extent that nitrate isotope analysis (e.g. $\delta^{15}\text{N}$) may also be of some benefit to further confirm sources of nitrate in groundwater, although in this case it is clear that the majority of nitrate in groundwater has an anthropogenic source (e.g. fertilizers and/or sewage). The nitrate isotopes may be able to distinguish between the different possible sources, however we believe that the use of sulfate /sulfur isotope composition and nitrate concentration is adequate to define these inputs, or at least to clearly show the natural versus anthropogenic nitrate load (figure 8), which was the main objective. The contribution of nitrate concentrations from seawater can be estimated by the chloride mass balance method, without requiring the use of the nitrogen isotopes, while the NO_3^- contributed from rainwater is well constrained (e.g. CGS, 2007). We further suspect that as in many cases where there is significant nitrate pollution, the pollution sources will show significant overlap between different isotopic signatures, particularly as in this case the inputs are diffuse over a large agricultural region (rather than representing distinct point sources). The additional data will therefore likely not add greatly to our understanding of the sources.

(2) Currently, important issues are not considered or over-simplified in the manuscript: - I am missing information about the reference of stable isotope measurements to the international scales (standards used etc.).

Reply: We agree. Additional details on the stable isotope analysis could be easily added to the text – for example noting the following points:

1. - $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) were measured using continuous flow on a Finnigan MAT 252 mass spectrometer, with the automated headspace analysis of the preparation device, in the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry (Guiyang), CAS. The results of $\delta^{13}\text{C}$ analysis are expressed in conventional delta (δ) notation, defined as $\delta = (\text{R}_{\text{sample}} - \text{R}_{\text{standard}})/\text{R}_{\text{standard}} \times 1000$, where R is the ratio of $^{13}\text{C}/^{12}\text{C}$. The $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) are expressed relative to the standard Vienna Pee Dee Belemnite (VPDB), with an analytical precision of $\pm 0.2\text{‰}$.
2. - Samples for ^{34}S in dissolved sulfate were measured by a Finnigan Delta-S gas mass spectrometer after on-line pyrolysis with an EA (Elemental Analyzer) in the Laboratory for Stable Isotope Geochemistry, Institute of Geology and Geophysics, CAS. The method of Halas and Szaran (1999) was used for converting precipitated BaSO_4 to SO_2 . The international standard against which $\delta^{34}\text{S}$ values are referenced is the troilite (FeS) phase of the Cañon Diablo meteorite (CDT), which has a $^{34}\text{S}/^{32}\text{S}$ abundance ratio of 0.0450 and are reported as δ (‰) difference from the standard with an

analytical precision of better than or about $\pm 0.4\text{‰}$.

(3) - Deines et al. (1974; GCA) outlined the relevance of the evolution of ground waters under wrt a CO_2 gas phase open or closed conditions that could be relevant for the shallow and deeper carbonate ground waters. This is not considered here in the discussion of the data, but may be relevant for the relations between both DIC and Ca to $\delta^{13}\text{C}$ -DIC.

Reply: We agree, this is an important point and we thank the reviewer for raising it. Changes in water chemistry during dissolution and precipitation of carbonates are accompanied by changes in the ^{13}C content of the total dissolved carbonate of the ground water. The previous study by Deines et al.(1974) showed that there are significant differences in the relationships between carbon isotopic composition and chemical variables for open and closed system conditions. Based on their approach, due to the similar initial conditions with this study, the model results can be used to estimate the chemical and isotopic composition of groundwater at a given pH in equilibrium with a reservoir of a given P_{CO_2} and $\delta^{13}\text{C}_r$. The solution reacts with carbonate of a given isotopic composition ($\delta^{13}\text{C}_{\text{rock}}$) under open or closed system conditions. We evaluated our measured results based on this scheme (Fig. R1). Given that pH values of most groundwater samples range from 7.0 to 8.5, the major C species is dissolved HCO_3^- , indicating that using HCO_3^- rather than total DIC will not influence the results.

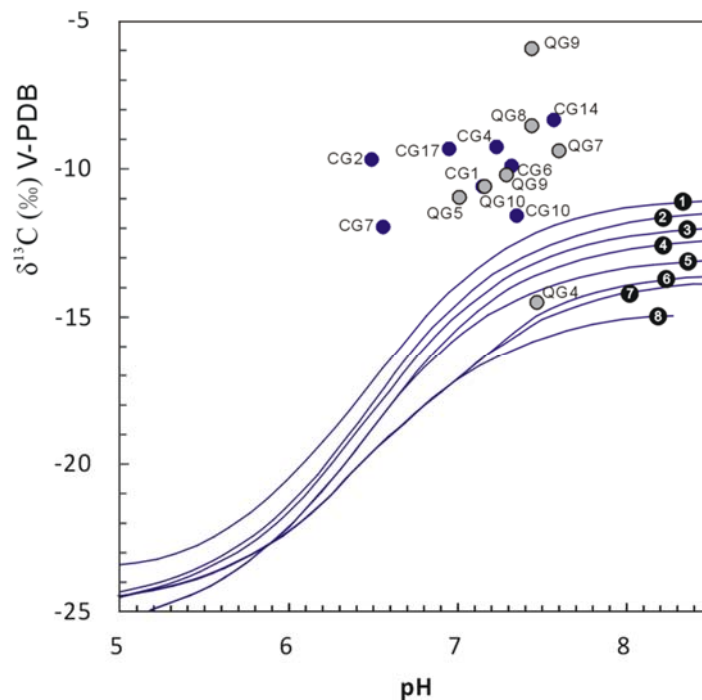


Fig. R1 The relationship between $\delta^{13}\text{C}$ and pH values for closed and open system models.

Models' background is from Deines et al.(1974). Closed system solution curves: ① $\delta^{13}\text{C}_r = -23\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = +2\text{‰}$, pH=5; ② $\delta^{13}\text{C}_r = -24\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = +2\text{‰}$, pH=5; ③ $\delta^{13}\text{C}_r = -24\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = +1\text{‰}$, pH=5; ④ $\delta^{13}\text{C}_r = -24\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = +1\text{‰}$, pH=6; ⑤ $\delta^{13}\text{C}_r = -25\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = 0\text{‰}$, pH=5; ⑥ $\delta^{13}\text{C}_r = -24\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = +2\text{‰}$, pH=7; ⑦ $\delta^{13}\text{C}_r = -24\text{‰}$, $\delta^{13}\text{C}_{\text{rock}} = +1\text{‰}$, pH=7; Open system solution curve: ⑧ $\delta^{13}\text{C}_r = -24\text{‰}$.

Most groundwater in the study area is supersaturated with respect to calcite and dolomite (Han et al., 2015). The hydrochemical composition of groundwater is influenced by CO_2 exsolution and CaCO_3 precipitation, which can be described by the reaction:



At isotopic equilibrium CO₂ is enriched in ¹²C and CaCO₃ in ¹³C with respect to HCO₃⁻ (Deines et al., 1974). Since for each mole of CO₂ exsolved one mole of CaCO₃ is precipitated, the kinetic isotope effects is removal of ¹²C enriched carbon from the solution, which concentrates ¹³C in the remaining HCO₃⁻. In the study area, the enrichment of δ¹³C_{DIC} along flow paths in the carbonate aquifer may therefore be inferred to be indeed caused by ¹²CO₂ loss during exsolution (leading to ¹³C enrichment in the residual solution). The pH and δ¹³C values of the investigated groundwater (plotted above in figure R1) are largely consistent with this model, and suggest evolution in a predominantly closed system (rather than mixed open and closed system evolution as would follow curves 1 to 8), as the values are enriched well above those expected in meteoric waters interacting with soil gas CO₂ or minor carbonates under open system conditions (~-18 to -25‰)

The lower δ¹³C value (-14.5‰) of shallow groundwater (QG4) in the recharge area is more consistent with predominantly open system dissolution, with the slightly higher value than typical due to irrigation with water from the deeper carbonate aquifer leading to some minor mixing between the shallow groundwater and the deep water.

The results of this further analysis according to the Deines et al. (1974), model could be added to a revised version of the manuscript.

(4) - I wonder how the 4-endmember-mixing sulfur isotope balance works when the range of δ³⁴S values for the potential sources significantly overlaps?

Reply: We agree that this is a reasonable point to raise, but believe it is something we can address. The four sources of sulphate in the dissolved SO₄²⁻ of groundwater were assumed to be from precipitation, seawater, fertilizer and evaporate dissolution. For seawater and precipitation, the isotope composition can be confirmed as this is well known. For fertilizer and evaporate dissolution, we used average stable isotope compositions of these sources from the literature to estimate the potential contribution of the dissolved SO₄²⁻ concentrations in groundwater. While we acknowledge that the overlap between the possible isotopic ranges in these sources increases the uncertainty of the mass balance results, we still think it is important to attempt quantification to get approximate estimates. The uncertainty can be taken into account by way of a sensitivity analysis, which tests a variety of different end-member compositions in the mass balance (which could be included in a revised manuscript). The calculated results show a real contribution from different sources notwithstanding the overlap, which is confirmed by other lines of evidence, such as the nitrate and other ionic ratios. Future research could focus on further determination of δ³⁴S_{SO4} and δ¹⁸O_{SO4} composition of fertilizers and carbonate minerals from the study area which could help constrain the mass balance further, however this is considered to be beyond the current scope of our study.

(5) - The area seems to be under impact of the Daweijia river, that may loose water to underground drainage. Why has the hydrochemical and stable isotope composition of river water (as a function of season and discharge) not been measured and considered in the discussion of the ground water results?

Reply: We agree that river leakage is a possible influence that is not accounted for in our study, however, we believe the importance is minor. Unfortunately, during our field investigations the (ephemeral) Daweijia river was dry each time, and therefore we could not collect and measure water samples from River. According to the report from the water supply managers in Dalian City (Geological survey institute of Liaoning Province), river leakage in the Jinzhou area occupied only 8% of total infiltration into the shallowest aquifer in 2005, and as such we did not consider the impact

of river leakage to be a major impact on the chemical mass balance of the groundwater system.

(6) Summarizing, to my impression, the authors target an important issue, but should continue in carrying out new measurements both on old samples (BaSO₄) but also now try to look into the isotope composition of nitrate and selected trace elements, and finally reset the mass balance approach considering further parameters and model boundary conditions.

Reply: We don't agree that further sampling and isotope analysis from the existing sample set is required in order to meet the objectives of the paper. Due to issues over holding time (most samples were collected in 2010), we cannot carry out new measurements the BaSO₄ or precipitated nitrogen salts ($\delta^{15}\text{N}$) of these particular groundwater samples. We believe that the dataset we have collected in itself is of value, and does provide a solid basis for separating anthropogenic from natural inputs to the groundwater system in the study area.

Reply to Ian. Cartwright (Referee):

We are very grateful for the constructive comments and generous help from Prof. Ian Cartwright. We are trying to give our careful response to your comments for improving our paper quality.

Our responses to the points raised by the reviewer are listed below:

(1) a) A rethink about what material is strictly necessary in Section 5 and/or better guidance to how the information addresses the main points of the paper. This is probably the major concern.

Reply: We agree that better structuring of sections 4 and 5 would lead to a better manuscript. This point could be addressed by means of a careful review of section 5, removing extraneous information and discussion, and focusing on the topic of the paper- determining the natural as distinct from anthropogenic inputs to the dissolved ion load (particularly sulfate) in groundwater.

(2) b) More consideration as to how this study can inform others elsewhere in the world.

Reply: We agree. In a revised manuscript, we would make a greater effort to situate the study within a global context, such that others are in a position to learn from the findings. This would involve a more complete literature review of the state of knowledge regarding the techniques adopted, and a review of similar case studies worldwide.

(3) c) Some reorganisation of the introduction and results section.

Reply: We agree. These sections could be re-organised with a view to making the paper more concise and focused on the main topic, and more logical in structure such that the reader clearly understands which data type is useful in understanding particular aspects of the evolution of water quality.

INTRODUCTION:

(4) The introduction provides good background to the study and places it in an international context. Some of the referencing appears to be getting a little dated (mostly before 2012), and I'd suggest that the authors consider whether there are any important more recent papers that they can cite.

Reply: We agree. We have since identified newer references relevant to the topic – such as de Louw et al., 2013 (Journal of Hydrology, 501: 133-145) and Kumar et al., 2015 (Asian Journal of Earth Sciences 111: 936-947) and would insert these into a revised version of the manuscript.

(5) The first paragraph on pg. 11334 could use a few more details. Specifically, it is not clear what is meant by “more serious” and “a range of strategies” etc. Without a detailed knowledge of the area it is difficult to assess exactly the extent of the problem or what has been done to address it. If you provide a few more details, the context will be clearer.

Reply: We agree. These points would be addressed in any revised version of the manuscript. For example, compared with the degree of seawater intrusion in 1982, the lower fraction (less than 4.8%) of seawater reveals that the areal extent of seawater intrusion has been controlled and now has a reduced contribution to modifying the groundwater salinity (which we would clarify). This is due to ceasing the water supply from the well field to the Dalian City in 2001. The language would be improved so that ambiguities are removed.

(6) There is also some repetition of ideas in this section. The statements regarding the need to distinguish seawater intrusion from anthropogenic activity and the use of tracers appear both in the last paragraph on pg.11333 and the final paragraph in this section. I think the flow of the paper would be improved if the paragraph on seawater intrusion in the Dalian area (top pg. 11334) was merged into Section 2 (as it is really a detail about the study area) and have the introduction focus on the broader issues; the statement of aims at the end of the introduction provided sufficient information about the specifics of the study.

Reply: We agree. In a revised version of the paper, we would address this comment and adopt the suggestions of the reviewer in order to make the paper more concise and avoid repetition.

Study Area:

(7) The statement regarding the natural flow in the area (top of pg.11335) should be referenced.

Reply: We agree. The reference relevant to the statement is: Fan, 1984, Seawater intrusion and calculation of groundwater exploitation in the karst area of the west JinXian, Dalian. Hydrogeology & Engineering Geology (in Chinese with English abstract). 1:3-6.

(8) Pg. 11335 line 9. Define m.a.s.l on first usage.

Reply: We agree. This point is straightforward to address (meters above sea level).

(9) The description of the geological framework on pg. 11335 would be much easier to follow with a cross-section. I'd suggest adding a stratigraphic cross-section to Fig. 1 or if that information is on Fig. 9 to move that figure to earlier in the paper and use it to also illustrate the geology.

Reply: We agree. In a revised version of the paper, we would include a cross section (such as that shown in Fig 9) to the section showing the geological framework (section 2; Study area).

(10) The last paragraph (pg. 11336) just compares averages, which may or may not be

informative. For example, if one area increased in salinity by say 10 fold but the rest of the areas remained similar, the average salinity has increased but the pattern is skewed by a small subset of data. Try to put more details around this as it is the main rationale for doing this study, so consider the ranges as well as the averages. If the data comes from the same suite of bores then you can apply t-tests or Z scores (or something similar) to assess this; at the very least report the ranges.

Reply:

We agree. Further detail on the precise changes occurring in these different areas (e.g. comparison between the recent data and previous data) would be included by making the text more specific. In some cases the number of samples required to conduct a valid t-test or Z score is too low, however we would attempt this where possible.

Methods:

(11) Section 3.1. Most of the methods are appropriately described, a few additional details on the C-13 analysis (specifically the preparation device, I assume automated headspace analysis using continuous flow) and the S-34 analysis (probably combustion in an EA) would be good.

Reply: We agree. This point would be addressed in any revised version of the manuscript. See response to the comment from Reviewer #1 above on further details about the analytical methods (2).

(12) Section 3.2. The assumption of Cl being conservative (pg. 11137, line 25) should be better justified. In addition to halite from the aquifer matrix, there is the possibility that contaminant sources introduce Cl. Did you analyse Br, in which case the Cl/Br ratios can be used. Otherwise, you need to be more definitive in ruling out addition of Cl from other sources.

Reply: We agree and could address this issue substantively using data found from literature in the area. Although we could not measure the Br concentration in groundwater, we were able to find Br concentrations in a study which used the same suite of monitoring bores in a previous study (Yang, 2011); Yang (2011) carried out the groundwater investigation in this area in August 2008. The molar Cl/Br ratios in their study ranged from 118.3 to 633.1 (n=11, mean value 394.3, Fig. R2), which is generally below the oceanic ratio of ~650 (Drever, 1997), hence, the groundwater show depletion compared to seawater (Figure R2, shown below).

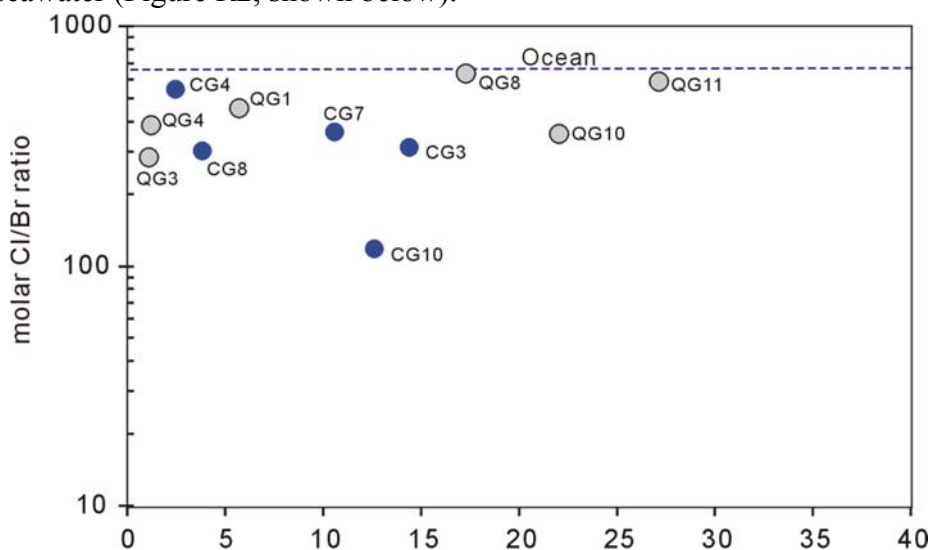


Fig. R2. Molar Cl/Br ratios vs. Cl concentrations in groundwater from the Quaternary aquifer (grey) and carbonate aquifer (dark). Data are from Yang (2011).

A range of natural and anthropogenic processes may modify Cl/Br ratios, although processes causing a decrease (e.g. enrichment in bromide) are relatively poorly known. We suspect either possible anthropogenic source (e.g., pesticides ethyl dibromine and methyl bromide), which may reduce Cl/Br ratios (Davis et al., 1998) and/or preferential adsorption of Br (e.g. on organic material) (Gerritse and George, 1988). Overall the ratios do not indicate that a major modification to mass balances of the ion load would be needed, however the issue would be noted and discussed in any revised manuscript in accordance with this observation.

Results:

(13) The results section is comprehensive and the data is well described. There is a tendency, however to mix observations and interpretations, for example:

Pg. 11339, line 6 – calculated seawater fractions

Pg. 11139, line 13 – inference of anthropogenic inputs

Pg. 11140, line 12 – interpretation of the C-13 data

This interpretations would be better in Section 5 where you interpret the data.

Reply: Thanks for these suggestions.

We agree and would address this issue in a revised version of the manuscript, making sure results and discussion are not mixed in section 5. This would be achieved by removing the discussion points and re-locating them into section 5, keeping the results free of commentary.

Discussion:

(14) Section 5.1. The start of this section is where the discussion of seawater mixing from Section 4 belongs.

Reply: We agree and would follow the reviewer's advice

(15) Page 11341 last paragraph. I struggled to understand the argument here. Surely this approach is just dealing with the details of the chemistry and whether or not major salinization is occurring should be apparent from TDS or Cl changes. I'm not sure that this adds much and it could be replaced with a statement just reiterating the changes to TDS over time (which is in Section 2).

Reply: We agree. We would remove the paragraph in a revised version and replace with a brief statement regarding overall TDS changes (as distinct from other ions like sulfate) over time.

(16) Overall, Section 5 is too long and tries to describe too many things. The thrust of this paper is to distinguish between anthropogenic inputs and seawater intrusion and you should try to keep this as the main focus of the paper. You do get to this at the end of Section 5 but there is a lot of other material in this section that looks to be in there in order to provide a full geochemical interpretation. While that is OK, it does detract from the main message. I'm not convinced that the carbon story is central to answering your main questions and that section probably could be omitted or shortened substantially. If you can keep this section focused, you can make a more convincing case as to the importance of anthropogenic inputs.

It may be that you need to discuss processes such as ion exchange or mineral dissolution in order to fully understand mixing, in which case you need to guide the reader through the

process better. For example, Section 5.2 discusses the interaction with carbonate minerals and while it represents a comprehensive analysis, it is not immediately clear how understanding this helps us with the question of mixing vs. anthropogenic inputs.

Reply: We fully agree. In order to avoid providing a full geochemical interpretation of all of the data, we would make section 5 shorter so that the discussion focusses on the main topic, as correctly identified. While some of the discussion of other aspects of the geochemistry is necessary in order to make interpretations as to the sources of dissolved ion load (natural vs anthropogenic) some sections could be cut and/or reduced in length.

(17) Try to assess critically how each piece of information informs your key hypotheses and then omit or shorten sections that might be just interesting but peripheral but explain more fully how the others relate to the key issues. The main question that you are answering seems to be that while the salinity is decreasing following a cessation of pumping, the sulfate and nitrate are behaving differently and it is important to know whether that is due to contamination – so try to keep everything focussed on that.

Reply: As per the response to the previous comment, we agree with this statement and would seek to make the revised version more concise and focused on this topic. As correctly noted, after the cessation of groundwater pumping in the Daweijia well field, the TDS concentration showed increases, yet the Cl⁻ concentration did not significantly elevate. At the same time, SO₄²⁻ and NO₃⁻ concentrations increased several times compared to parameters measured in 1981. This would be made clear in the introduction and in the discussion sections so that the main points of the paper are clearer.

Conclusions:

(18) This section just summarises the main findings of the project. In this section explain in more detail how your project helps us to understand processes in these environments more broadly; the paper will have more impact if researchers from elsewhere in the world can see relevance to their studies and a paper in a major international journal such as HESS needs to have broad appeal.

Reply: We agree. Further details about the broader implications would be added to a revised version of the manuscript, with particular reference to the way our study helps to understand hydrochemical evolution in areas recovering from saltwater intrusion, and where surface inputs from agriculture begin to manifest as the dominant control on water quality.

Figures

(19) Fig. 1. Make sure that the localities that you discuss in the text are on this Figure (or the inset) and add latitude and longitudes as you also use these in the text.

Reply: We agree. Localities can be updated and shown on all figures.

(20) Figures 2-4 & 6-8. I really struggled with the difference in colours (light blue vs. grey), either make these more contrasting (e.g. dark colour vs grey) or use different symbols

Reply: We agree, and would use a stronger contrasting colour scheme in any revised version of the figures.

If you have any further questions regarding our manuscript, please contact us as soon

as possible.

Thank you very much for your kind consideration.

Sincerely Yours,

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