Responses to Editor and Reviewers

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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, $\delta^{13}C_{DIC}$ and $\delta^{34}S_{SO4}$" (HESSD-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 is included in the revised version of the manuscript as a new figure (Figure 8), and referred to in the updated text (Lines 475-489).By comparing Sr content and Cl/TDS ratios and showing end-members for seawater and possible anthropogenic inputs, this data further refines the analysis of salinity sources in groundwater.

We did not measure the oxygen isotope composition of sulfate in our samples (in addition to the δ^{34}S, which we did report). Measurement of $\delta^{18}O_{SO4}$ 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 δ^{34}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. δ^{15}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 isotope data will therefore likely not add greatly to our understanding of the sources.

(2) Currently, important issues are not considered ore 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. -δ^{13}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 δ^{13}C analysis are expressed in conventional delta (δ) notation, defined as $\delta = (R_{sample} - R_{standard})/R_{standard} \times 1000$, where R is the ratio of ^{13}C/^{12}C. The δ^{13}C values of dissolved inorganic carbon (DIC) are expressed relative to the standard Vienna Peedee Belemnite (VPDB), with an analytical precision of ±0.2‰. (Lines 163 to 170)

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 Geographysics, CAS. The method of Halas and Szaran (1999) was used for converting precipitated $BaSO_4$ to SO_2. The international standard against which δ^{34}S values are referenced is the troilite (FeS) phase of the Cañon Diablo meteorite (CDT), which

has a $^{34}S/^{32}S$ abundance ratio of 0.0450 and are reported as δ (‰) difference from the standard with an analytical precision of better than or about ±0.4‰. (Please see Lines 170 to 178)

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_{CO2} and $\delta^{13}C_r$. The solution reacts with carbonate of a given isotopic composition ($\delta^{13}C_{rock}$) 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.
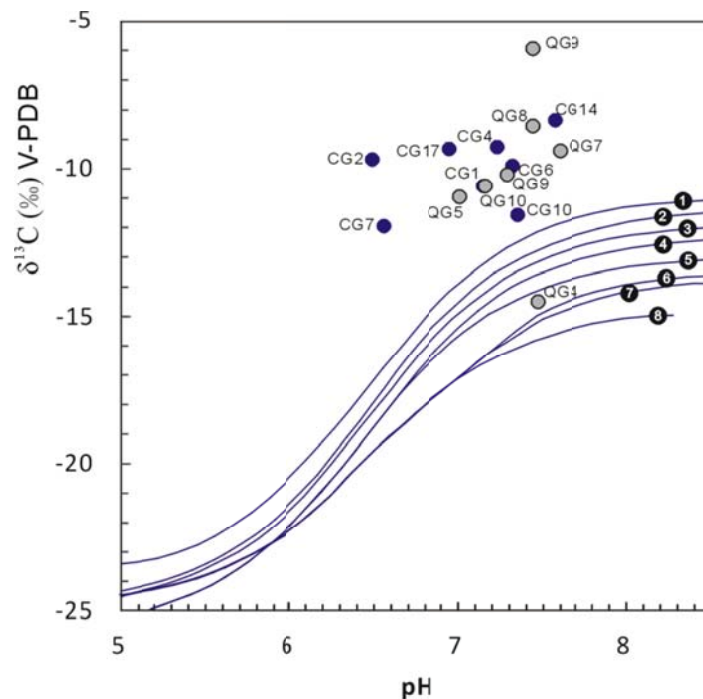

Fig. R1 The relationship between $\delta^{13}C$ and pH values for closed and open system models.
Models' background is from Deines et al.(1974). Closed system solution curves: ① $\delta^{13}C_r$ = -23‰, $\delta^{13}C_{rock}$=+2‰, pH=5; ② $\delta^{13}C_r$ = -24‰, $\delta^{13}C_{rock}$=+2‰, pH=5; ③ $\delta^{13}C_r$ = -24‰, $\delta^{13}C_{rock}$=+1‰, pH=5; ④ $\delta^{13}C_r$ = -24‰, $\delta^{13}C_{rock}$=+1‰, pH=6; ⑤ $\delta^{13}C_r$ = -25‰, $\delta^{13}C_{rock}$=0‰, pH=5; ⑥ $\delta^{13}C_r$ = -24‰, $\delta^{13}C_{rock}$=+2‰, pH=7; ⑦ $\delta^{13}C_r$ = -24‰, $\delta^{13}C_{rock}$=+1‰, pH=7; Open system solution curve: ⑧ $\delta^{13}C_r$ = -24‰.

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:

$$Ca^{2+} + 2HCO_3^- = CaCO_3\downarrow + CO_2(g)\uparrow + H_2O$$

At isotopic equilibrium CO_2 is enriched in ^{12}C and $CaCO_3$ in ^{13}C with respect to HCO_3^- (Deines et al., 1974). Since for each mole of CO_2 exsolved one mole of $CaCO_3$ is precipitated, the kinetic isotope effects is removal of ^{12}C enriched carbon from the solution, which concentrates ^{13}C in the remaining HCO_3^-. In the study area, the enrichment of $\delta^{13}C_{DIC}$ along flow paths in the carbonate aquifer may therefore be inferred to be indeed caused by $^{12}CO_2$ loss during exsolution (leading to ^{13}C enrichment in the residual solution). The pH and $\delta^{13}C$ 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 CO_2 or minor carbonates under open system conditions (∼-18 to -25‰)

The lower $\delta^{13}C$ 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 manuscript has been updated to reflect this additional understanding of the carbonate chemistry (lines 439 - 468)

(4) - I wonder how the 4-endmember-mixing sulfur isotope balance works when the range of $\delta^{34}S$ 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 SO_4^{2-} 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 SO_4^{2-} concentrations in groundwater (Hong et al, 1994; Clark and Fritz, 1997; Li et al., 2006). 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 is taken into account by way of a sensitivity analysis, which tested a variety of different end-member compositions in the mass balance (the estimates presented in the revised manuscript: "We analyzed the sensitivity of the mass balance by changing ±10% of the end-member sulfur isotope compositions of fertilizer and evaporate, respectively. We found the change on $\delta^{34}S_{fer}$ varied the contributions from fertilizer and evaporate by ± 0.1% and ± 0.2% respectively. The ±10% change in $\delta^{34}S_{evp}$ leads to changes in the contributions from fertilizer and evaporate by ± 0.4% and ± 2%, respectively. This suggests that the results are more sensitive to $\delta^{34}S_{evp}$ values in the mass balance." Line 525-530). 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 $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ 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. During our field investigations the (ephemeral) Daweijia River was dry each time, and therefore we could not collect and measure water samples from River. The lack of flow in the river during each field campaign indicates that flow is only periodic, during high rainfall events, and thus its contribution to the aquifer is limited. 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 ($BaSO_4$) 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 on the $BaSO_4$ or precipitated nitrogen salts ($\delta^{15}N$) 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 as was the original objective.

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. We have undertaken 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 (e.g. removed Lines 317-319; Lines 344 to 358; Lines 395 to 413; Lines 494 to 498 in the Marked Revision)

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

Reply: We agree.   In a revised manuscript, we have made a greater effort to situate the study within a global context, such that others are in a position to learn from the findings. The literature review has been updated with new references (Lines 53 to 60) and the global implications of the work highlighted in the introduction (Lines 85 to 91) and a new paragraph at the end of the conclusions section (Line 671 to 680):

"Coastal carbonate aquifers, a prolific groundwater source worldwide, are characterized by rapid groundwater circulation and recharge and are therefore highly vulnerable to anthropogenic contamination. Human activities in heavily populated areas such as the current study are now potentially the key driver in the hydrology and hydrochemical evolution of some of these coastal aquifers, as demonstrated here. Only by strictly controlling anthropogenic land-use and water use activities can the pollution and degradation of these aquifers be prevented. Future studies could focus on the seasonal variation of sulfur and nitrogen isotopes of dissolved SO_4^{2-} and NO_3^-, respectively, and more detailed analysis of these stable isotopes in soil profiles. This could provide more insight into the dynamics of contamination of this and other similar aquifers"

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

Reply: We agree. These sections have been re-organized (e.g. Lines 141 to 153 and Lines 164 to 169 in the Marked Revision have been removed and replaced with a more concise paragraph – lines 129-141) with a view to making the paper more concise and focused on the main topic. The results are now presented in a more logical structure such that the reader clearly understands which data type is useful in understanding particular aspects of the evolution of water quality (e.g. sections 4.1 to 4.3).

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), Najib et al., 2016 (Journal of African Earth Sciences 115:17-31) and Kumar et al., 2015 (Asian Journal of Earth Sciences 111: 936-947) and have inserted these into a revised version of the manuscript (lines 50 to 61).

(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 have been addressed in the revised version of the manuscript. Line 117 to 130 gives a concise history of water management strategies in the region through time:

"Seawater intrusion was first discovered in the Dalian area in 1964. This study focuses on the

coastal aquifers around Daweijia well field (Fig. 1), which was established in 1969 and formerly provided major water supply for Dalian City as the pumping rates of 12 ~ 24×10^3 m^3/d in 1970 (Lü et al., 1981). With the increase of pumping rate till 1983 (up to 4.8~6.2×10^3 m^3/d in 1977), the average chloride concentration of groundwater from eight fixed monitoring wells increased from 380 mg/L in 1968 to 1137 mg/L in 1982 (Song, 2013), indicating the serious seawater intrusion occurred. The groundwater withdrawal of the Daweijia well field was changed from a perennial pattern to a seasonal regime with a decrease by two-thirds of the pumped volume. The abstraction increased after 1991 but was reduced again from 20 ×10^3 m^3/d in 1995 to 4×10^3 m^3/d in 2000 (Li et al., 2006). Alternatively, in order to reduce the threat of seawater intrusion to the aquifer, with the establishment of surface water supply projects, water supply for Dalian City from the well field has ceased since 2001, with seasonal pumping for local agricultural irrigation (Song, 2013)."

(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. See response to points (4) & (5), we have revised this section and consolidated the information into one part of the introduction.

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

Reply: 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. This has been added in the relevant part of the text (Lines 111-113).

(8) Pg. 11335 line 9. Define m.a.s.l on first usage.
Reply: We agree, and have updated accordingly (Line 102).

(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 have included figures 1 and 2 (cross section) together when describing the study area.

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

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Reply: We agree. Further detail on the precise changes occurring in these different areas (e.g. comparison between the recent data and previous data) has been included (e.g., Lines 290 to 298)

Methods:

Reply: We agree. Additional detail on the analysis methods for carbon and sulfur isotopes have been added (Lines 163 to 178). See also response to the comment from Reviewer #1 (comment 2).

Reply: We agree. 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 does show some depletion compared to seawater (Figure R2, shown below).
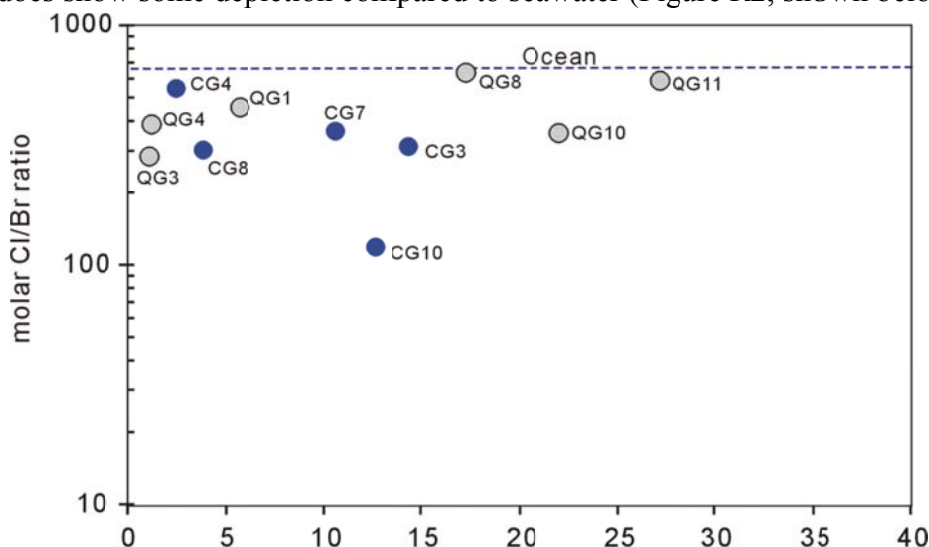

Fig. R2. Molar Cl/Br ratios vs. Cl concentrations in groundwater from the Quaternary aquifer (grey) and carbonate aquifer (dark). Data are from Yang (2011).

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 is noted and discussed in the revised manuscript (lines 281 to 288).

"The molar Cl/Br ratios (based on values from this study and Yang et al, 2011) range from 118.3 to 633.1 (n=11, mean value 394.3), which is generally below the oceanic ratio of ~650 (Drever, 1997). As halite is Br-depleted from its mineral structure, halite precipitation may lead to depletion of the ratios, however it is unlikely that saturation with respect to halite could be reached in the groundwater (e.g., McCaffrey et al., 1987; Edmunds, 1996; Cartwright et al., 2004). Minor contamination, e.g., with pesticides such as ethyl dibromine, methyl bromide and/or preferential Cl adsorption on organic material may explain the lower than usual ratios. Overall the ratios do not indicate significant sources of additional Cl."

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 have tightened up the descriptions in the results section, so that interpretations are removed and instead included in the discussion section (e.g. Line 249-250; Lines 254-257; Lines 289-392 in the Marked Revision).

Discussion:

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

Reply: We agree. The relevant sections have been moved here (Lines 330 to 344 in the Marked Revision).

(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. The paragraph is removed and replaced with a statement regarding overall TDS changes (as distinct from other ions like sulfate) over time (Lines 330 – 340 in the Marked Revision)

(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 agree and have endeavored to keep section 5 as concise as possible, even though additional detail was needed in some places to address reviewer comments. The number of sub-sections in the discussion section has been reduced from five to four, to focus more on the key topics.

(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 and believe the revised version is more concise and focused on this topic.

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 detail about the broader implications have been added in a new paragraph at the end of the conclusions section (Lines 580-589). See response to comment 2 also.

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 referenced in the text have been added to the 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, a stronger contrasting color scheme is adopted in the revised version of these 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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