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 $\delta^{34}S$, 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 $\delta^{34}S$ 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. $\delta^{15}N$) 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 wasthe 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 ore over-simplified in the manuscript: - I am missing information about the reference of stable isotope measurements to the

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

1. - $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ values of dissolved inorganic carbon (DIC) are expressed relative to the standard Vienna Peedee Belemnite (VPDB), with an analytical precision of ±0.2‰.

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, Institure 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 $\delta^{34}S$ 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‰.

(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 $\delta^{13}C$-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_{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.

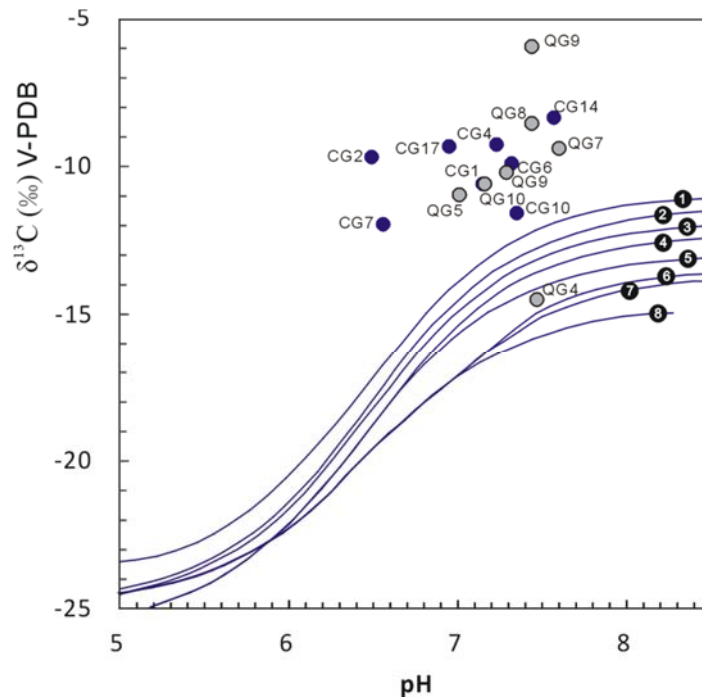Fig. R1 The relationship between $\delta^{13}C$ and pH values for closed and open system models.

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 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 $\delta^{34}S$ 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. 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 $\delta^{34}S_{SO4}$ 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. 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 ($\delta^{15}N$) 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.