

Interactive comment on “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 $\delta^{34}\text{S}_{\text{SO}_4}$ ” by D. Han et al.

Anonymous Referee #1

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In their manuscript 'Identification of anthropogenic and natural inputs of sulfate into a karstic coastal groundwater system in northeast China: Evidence from major ions, $\delta^{13}\text{CDIC}$ and $\delta^{34}\text{SSO}_4$ ', Han et al., describe the results of a hydrogeochemical and stable C and S isotope study carried out in a carbonate karst area under high impact of anthropogenic activity as indicated by enhanced dissolved nitrate loads. In association with two sampling campaigns in 2006 and 2010, the authors combine the concentrations and stable isotope composition of dissolved inorganic carbon (DIC) and sulfate and try to derive an ion balance for different potential sources. In principle the

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study deals with an interesting and environmentally very important topic, the fate and transport of nitrogen and sulfur compounds from the surface through the groundwater finally reaching the mixing zone with seawater. Using a cationic balance the authors try to differentiate possible subterrestrial water-rock-interactions, including congruent and incongruent dissolution of carbonates.

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). Currently, important issues are not considered ore over-simplified in the manuscript: - I am missing an information about the reference of stable isotope measurements to the international scales (standards used etc.). - Deines et al. (1974; GCA) outlined the relevance of the evolution of ground waters under wrt a CO₂ 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 d¹³C-DIC. - I wonder how the 4-endmember-mixing sulfur isotope balance works when the range of d³⁴S values for the potential sources significantly overlaps? - 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?

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.

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