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Interactive comment on "Subaqueous speleothems (Hells Bells) formed by the interplay of pelagic redoxcline biogeochemistry and specific hydraulic conditions in the El Zapote sinkhole, Yucatán Peninsula, Mexico" *by* Simon Michael Ritter et al.

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First, the authors are very grateful for the constructive comments and suggestions by anonymous referee #1 and fully appreciate the time and effort taken for reviewing the manuscript. We addressed all issues raised by the referee in a point by point response below.

Referee′s major comments:

Referee: First, I think the authors could expand the introduction beyond speleothems to draw in a wider readership. Hells Bells have been widely speculated about informally by karst researchers for several years, but I think that there is broader biogeochemical story that would be of interest to critical zone and coastal aquifer scientists. The authors don't have to take my suggestion in order for me to recommend publication, but I do think it would help broaden the appeal of the work.

Response: We agree with the referee that there is a wider biogeochemical story to the formation of Hells Bells, but suggest to wait for more data which are not yet available. We have taken additional samples for genome analysis of water and the surface of Hells Bells which are currently under evaluation and we are hopeful that these results will lead to a wider field of interpretation.

Referee: The second comment is a bit more substantive. I was not convinced that Hurricane activity would be likely to be responsible for sustained upward migration of the mixing zone necessary for Hells Bells to precipitate in areas above the modern redoxcline. The authors might explore droughts, which are well-documented in the Holocene (see Hodell et al., 2001, reference included in comments below), as an alternative process. Droughts would thin the freshwater lens and elevate the mixing zone for prolonged periods of time needed for the slow precipitation of calcite mentioned in the paper to form large Hells Bells features.

Response: We agree that the well documented droughts for the Yucatán Peninsula and a subsequently thinner fresh water layer brought up the halocline and certainly had its effect on Hells Bells formation. We added this point in the MS on page 24 lines 16–18.

We are currently working on the Hells Bells from different angles and produced an amount of data that cannot be shown in one manuscript only. The hypothesis of a recharge-driven upward migration of the halocline was developed integrating all information available, including some that is not shown here. Manuscripts presenting this data are currently in preparation.

The main argument why we did not consider droughts as a mechanism of halocline elevation is U/TH age-dating on Hells Bells specimens of different water depths (MS currently in preparation) show approximately identical young ages (∼150 a) at the lowermost crystal tips (1-2 mm) of the Bells. There is even a weak trend of the youngest samples found in the lowest water depths and the oldest samples found in greater water depths. This makes droughts or prolonged periods of time with an elevated halocline as the sole mechanism for the elevation of the halocline unlikely because this should be reflected in an age-zonation of the Hells Bells.

We are aware of the fact that the described behavior of the halocline in response to recharge is counter-intuitive and that the cited reference (Escolero et al., 2007) does not explain sufficiently why the halocline should be elevated as a response to recharge events. Yet, such a behavior is well documented by their results and additionally we discovered an online available thesis investigating dynamics of the coastal Karst aquifer around Merida that reports a similar halocline elevation in response to recharge events (Heise, 2013). In general, however, there is a scarcity of studies addressing aquifer responses to recharge events in the area and there is only one other that we know of, which is Kovacs et al., (2017) and this study does not have information about the halocline elevation as it only captured data from the fresh water layer.

We try to fill this gap of data and knowledge as we are currently gathering continuous data on the halocline elevation at El Zapote cenote. Preliminary results of one year of measurement are very interesting and reveal a complex hydraulic behavior. Generally, the halocline elevation follows the elevation of the fresh water lens which seems to be controlled by the mean tidal sea level throughout the year which leads to a variation of ∼0.5 m of the halocline elevation. Furthermore, in general, if the freshwater lens gets thinner (water level of the fresh water drops), the halocline rises (determined by increasing conductivity of the data logger in the halocline) and vice versa. However, we detected several short-termed events (∼ 1 day) of an abrupt elevation of the fresh water accompanied by an elevation of the halocline as a response to precipitation/recharge

(Fig .1). Subsequently, the halocline slowly drops as expected from an increase of the fresh water lens due to precipitation. So far, there has not been a major precipitation event (hurricane) within the recorded available data (from Dec 2017- Dec 2018), but the observed effect of an initial halocline rise in response to recharge should increase in scale and time with an increase of the precipitation/recharge event.

Caption to Fig. 1: Preliminary results of data loggers from El Zapote cenote showing two examples of halocline elevation events. Water level was measured in the fresh water layer in 15 min intervals with a temperature and depth Logger (TD-Logger) in ∼6 m water depth. In the halocline conductivity, temperature and depth was measured in ∼38 m water depth also in 15 min intervals (CTD-Logger). The plots show the deviation of the respective elevation with respect to the start of measurement in December 2017.The halocline elevation is calculated from the conductivity values through a linear regression of the electrical conductivity within the interval of 37–40 m water depth. Note the periodic data noise in the halocline elevation, which always occur between 10–16h almost every day. This is most likely caused by diving and or by jumping activities into the cenote. Both cause small turbulences in the stratified water column.

Referee′s minor comments:

Referee: Abstract Line 20: Given that this is a sinkhole, I'm uncomfortable with the author's description of this chamber as lightless in the absence of measurements of light intensity over annual timescales. While it may appear dark to divers, there may be some "light" that still makes it to the chamber during some portions of the year.

Response: You are right, we cannot rule out that there might be some portions of light at some time of the year. We even tried to measure the amount of light with water depth at the cenote around noon in December 2017. We found no measurable light below ∼16 m water depth (<11 Lux). However, we cannot exclude that small portions of light may penetrate deeper into the water body for some daytime and season.

To meet the referee′s comment we replaced "lightless" with "dark" in Abstract Line 20.

Referee: Abstract Line 32: It would be nice if the authors could include information about why Hell's Bells are not more widely distributed in coastal aquifers in general (and the Yucatan more specifically) in the abstract. Improved information and word economy in the preceding sections should create space for this insertion.

Response: To meet the referee′s suggestion we restructured the sentences and added some Information about the prerequisites for Hells Bells forrmation.

Additionally, we are addressing that issue in a MS (in prep.) in which we compare several cenotes with Hells Bells and cenote Angelita. One of the aspects of this study will be the spatial distribution of cenotes with Hells Bells

Referee: Page 2 Line 1: I've been working on karst research problems for almost 20 years and have never heard the term "pending speleothems." That doesn't mean the term does not exist, but it probably means it is not common.

Response: "Pending" was used to refer to the group of pendant speleothemes in this context, however we followed the referee′s concerns and deleted "Pending" and changed the according sentence into "Speleothems, such as stalactites or dripstones, result from physicochemical. . .".

Referee: Page 3 lines 18-19: I don't understand why a recharge event would elevate the freshwater lens. It should depress it, as recharge would increase the thickness of the lens:. The manuscript that was cited wasn't much help in explaining the process either.

Response: We try to be more cautious around the halocline dynamics throughout the MS and therefore change the lines 18-19 on Page 3 to "Although Moore et al. (1992) and Stoessell et al. (1993) report that the thickness of the freshwater lens does not vary significantly between seasons or on a yearly basis, local and short-termed variations are possible and were reported by Escolero et al. (2007), who documented a significant halocline elevation of up to 17.5 m in between two measurements in the years 2000

and 2003."

Referee: Page 10, Line 3: I suggest "oxygenated" or "aerobic" as an alternative to "oxygenized"

Response: Changed to "oxygenated".

Referee: Page 11, Figure 3: The symbols change in panel C but there is no corresponding legend. I'm guessing that the circles are still winch collected and the squares are diver collected, but it would be helpful if the symbols remained constant across each panel.

Response: We agree that this the symbols are misguiding. In panel c the squares and circles stand for different parameters and it is not distinguished between samples taken by divers and those taken with the Niskin bottle. We will address this issued in the final revision once we received all referee comments.

Referee: Page 17 line 9: In this context, "though" is being used to contrast ideas and should not begin a sentence. I suggest restructuring this sentence and the previous one.

Response: Both sentences were restructured as suggested.

Referee: Page 18 line 9: Bells should be plural.

Response: Corrected as suggested.

Referee: Page 18 lines 13-15: I can agree that sulfide oxidation drives calcite precipitation but I'm still clear on why these features are only found here and not in any of the other sulfidic halocline caves in the Yucatan (or elsewhere), but hopefully this is discussed later in the text: : :..

Response: It is discussed later in the MS.

Referee: Page 19 lines 23-24: I find these sentences super confusing. Can you please rephrase them?

Response: The passage was rephrased as recommended.

Referee: Page 19 line 28: change to "debris mound"

Response: Changed as recommended to debris mound throughout the text and also in the legend of Fig. 3.

Referee: Page 20 lines 6-8: I think the authors might want to make this section more clear by saying that methanogenesis in the presence of sulfate isn't expected, but that the methanogenesis could be occurring in the sediments where sulfate is reasonably expected to be depleted. I would then recommend they cite a manuscript or two from the marine sediment pore water research community to demonstrate this depletion is common. The authors' interpretation is also supported by the concentration profile, a point which should be emphasized in the discussion.

Response: We added "...and methanogenesis is not expected in the presence of sulfate, ..." in order to be more clear in this section. Also we followed the referee′s advice and cited supporting literature of pore water profiles.

It is not clear for the authors what the referee meant with "The authors' interpretation is also supported by the concentration profile, a point which should be emphasized in the discussion". We do not think that the concentration profile in the water column reflects the concentration profile in the sediments, if that′s what was meant by the referee. Instead, the concentration profile of the species that are released from organic matter decay are a consequence of the 2 sinks of the system, which are the redoxcline above and an advective depletion through a hydraulic connection somewhere below the cenote (<60 m water depth).

Referee: Page 20, line 13: It might be more clear to say that Fe is only present in low concentrations in limestone and there are limited/no sources of siliciclastic materials that could contribute iron in this part of the Yucatan. Fe-oxides are common in many

karst areas where the Fe is derived from weathering of siliciclastics.

Response: This part was changed as recommended.

Referee: Page 24, Section 4.3.1 (entire section) – I find the role of Hurricanes in elevating the halocline to be a highly implausible explanation for the vertical zonation of the Hells Bells features. Hurricanes are infrequent and the "piston induced oscillation" effect described by the authors would be short lived. I find it hard to believe that any potential upward displacement by this mechanism would be of sufficient duration to allow for the precipitation of large masses of carbonate photographed above the modern redoxcline. I suggest that a more plausible scenario is that periods of drought (which are well-documented over the Holocence) lowered the water table and increased the elevation of the redoxcline for sustained periods of time (see Hodell, D.A., Brenner, M., Curtis, J.H. and Guilderson, T., 2001. Solar forcing of drought frequency in the Maya lowlands. Science, 292(5520), pp.1367-1370.)

Response: We already referred to this comment in detail above.

Referee: Page 28: Section 4.4 prerequisites for formation of Hells Bells. Many cenotes in the Yucatan meet these criteria yet lack Hells Bells. I wonder if one of the more unique aspects of El Zapote is the relatively thick mixing zone, which the authors highlight in their discussion. Many of the haloclines are much thinner, typically due to high flux of fresh or saline water (though I was surprised by how thin the halocline at Cenote Angelita was in the supporting literature – I wouldn't have guessed there was much flow in that location). I suppose many of the haloclines with high fluxes of organic material also have much greater light penetration (such as El Pit and Cenote Angelita), so the location of the mixing zone in a dark cenote (I still hesitate to say that this is completely dark) is also likely important.

Response: Yes, we are also convinced that the thickness of the halocline is an important factor as a thick halocline results from highly stagnant conditions. These have to be met in order to create an oxygen deficient redoxcline where anaerobic protonconsuming sulfide oxidation can occur. We investigated 3 cenotes with Hells Bells and found that all show a very thick halocline, some even thicker than that at El Zapote, and found that the characteristics of the redoxcline are very different to those of cenotes with a thinner halocline, which matches most of the studied cenotes at the Yucatán Peninsula (MS in preparation).

It seems however, that light intensity is not an important factor because Hells Bells occurrence ranges from close to absolute dark cenotes (i.e. cenote Holbox, which has only one tiny opening and is occupied by bats, that probably provide the organic material) to potentially "bright" cenotes (Cenote Tortugas, which has an opening of approximately the same size as cenote Angelita).

Referee: Page 27, line 19-20: I still wonder if the general orientation of all of the speleothems towards the center of the cenote indicates some phototaxic behavior. It would certainly be the simplest explanation and I would encourage the authors to measure light intensity over an annual cycle to see if perhaps small amounts of light are penetrating (not having visited this particular site, I'm unsure how likely this is, but the Cenote profile included in Fig 3, coupled with the fact that the cenote is sufficiently large in diameter to permit cavern tours, suggests that the entrance may be sufficiently large to allow some small amounts of light during some parts of the day/year).

Response: Yes, we cannot rule out that some phototaxic behavior influences Hells Bells formation because small amounts of light may penetrate the cenote. We agree that this would be the simplest explanation. However, we tried to find an explanation for the observed orientation of the speleothems that is consistent with our results and the hypothesis on the biologically-induced mechanism for calcite precipitation. The chemolithoautotrophy within the redoxcline/turbid layer (which is another barrier for light penetration) is the driving agent for Hells Bells formation, thus we concluded that Hells Bells orientate accordingly to the availability of the "food" of those chemolithoautotrophic organisms. To measure the amount of light over time within the cenote would be a good approach though, in order to clarify this particular problem.

References: Escolero, O., Marin, L. E., Domínguez-Mariani, E. and Torres-Onofre, S.: Dynamic of the freshwater – saltwater interface in a karstic aquifer under extraordinary recharge actionâĂŕ: the Merida Yucatan case study, Environ. Geol., 51, 719–723, doi:10.1007/s00254-006-0383-1, 2007. Heise, L.: Dynamics of the coastal Karst aquifer in northern Yucatán Peninsula. [online] Available from: http://ninive.uaslp.mx/jspui/handle/i/3692, 2013. Kovacs, S. E., Reinhardt, E. G., Stastna, M., Coutino, A., Werner, C., Collins, S. V., Devos, F. and Le Maillot, C.: Hurricane Ingrid and Tropical Storm Hanna's effects on the salinity of the coastal aquifer, Quintana Roo, Mexico, J. Hydrol., 551, 703–714, doi:10.1016/j.jhydrol.2017.02.024, 2017. Moore, Y. H., Stoessell, R. K. and Easley, D. H.: Fresh-Water/Sea-Water relationship within a Ground-Water flow system northeastern coast of the yucatan, Ground Water, 30(3), 343–350, 1992. Stoessell, R. K., Moore, Y. H. and Coke, J. G.: The Occurrence and Effect of Sulfate Reduction and Sulfide Oxidation on Coastal Limestone Dissolution in Yucatan Cenotes, Ground Water, 31(4), 566–575, 1993.

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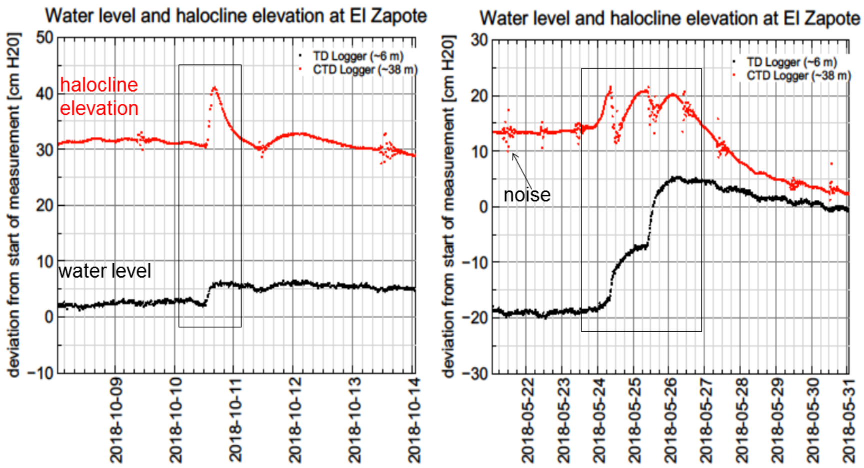

Fig. 1. Preliminary results of data loggers from El Zapote cenote showing two examples of halocline elevation events. (Full caption is given on page C4)