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Interactive comment on "Groundwater and nutrient discharge through karstic coastal springs (Castelló, Spain)" *by* E. Garcia-Solsona et al.

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This paper deals with a timely topic that is clearly suitable for BG. The authors report an interesting dataset for a groundwater dominated coastal system. I have no issues with their sampling strategy and analytical approaches, but I feel that their discussion can be significantly improved and their calculations have to be revised (or clarified) before publication. Below, I describe my major concerns and later I list some minor points:

1) My main problem with many recent SGD papers is that the assumptions are not discussed, validated, or checked. For example, on page 640 (line 26) and page 641, the authors justify an important assumption (constant groundwater endmember concen-

tration) by simply saying that this is a "...a common assumption...". Recent papers by Matt Charette's group show that radium isotopes in groundwaters can be highly variable. The authors have performed seasonal groundwater samples and it seems that they might be able to use a temporally-variable groundwater endmember in their calculations.

R1) We appreciate the comment and we concur with the reviewer in that the groundwater endmember is not constant in many instances, presenting spatial and temporal variability that depends on natural and anthropogenic forcing factors (Charette et al., 2003). In our study, we considered that the main endmember is constituted by the karstic coastal springs visibly discharging at the water edge, which were also identified by TIR images.

In this work we considered the time range during which coastal waters are integrating the SGD signal (hours-to few days). Therefore, we think that the best strategy is to use the groundwater endmember collected almost simultaneously to coastal waters inspection. This is why, rather than temporally averaged groundwater samples over several months, we have applied the springs' concentration measured in each coastal sampling period. Thereby, we do not use a constant groundwater endmember. In fact, one of the objectives of the manuscript was to compare two different temporal periods: June and October. The text has been revised to clarify this point.

2) What about the assumptions about coastal water residence times? After examining the data in detail, I find difficult to agree that equation 5 can be useful in the system under investigation. As acknowledged by the authors on page 642, the residence time equation relies on the more rapid decay of radium-224 relative to the other isotopes. The authors estimate a residence time of about 2 days – if this is correct, one should be able to see a curvature in the scatter plots between radium-224 and the conservative variables. However, the scatter plots in the paper show perfectly linear relationships between radium-224 and all the other variables (salinity, radium-228, radium-223, silicate). These linear correlations imply that mixing is much faster than radium-224 decay.

In other words, no detectable radium-224 decay occurs within the plume under investigation, which would prevent equation 5 from being applied. The use of an equation that relies on decay in a system where radium-224 does not seem to decay has to be reconciled.

R2) We agree with the reviewer that is not easy to appreciate the decay of 224Ra from the Figures showed in the manuscript because it is probably masked by mixing. However, the equation 5 is conceptually correct and we consider it can be applied to calculate maxima estimates of plume water residence times. Probably, a larger set of coastal water samples would have allowed further modeling. However, the application of maxima residence times brings us to determine conservative, lower-limit, SGD fluxes in our study area. The text has been modified to specify that we are estimating maxima residence times and, therefore, minima SGD fluxes.

3) Still related to the comment above, Equation 5 was used only for Ra-224: Ra-223 ratios. What would happen when applying the equation to Ra-224 : Ra-228 and Ra-224 : Ra-226 ratios? The analytical uncertainties in the measurements of radium-223 are much higher than the uncertainties associated with measuring the long-lived radium isotopes, so I do not understand why the authors chose to use only 224:223 ratios. Is that why a >2-day residence time was estimated? From the linear trends in the data, I suspect that residence times would approach zero if using ratios between radium-224 and the long lived isotopes.

R3) Water residence times would actually come near 0 if using Ra-224: Ra-226 or Ra-228. However, since long-lived radium isotopes may integrate processes occurring at longer time scales (e.g., upper ocean mixing, vertical mixing, seasonal riverine input etc.) than the rapid SGD movement, we think it is more appropriate to use the two short-lived isotopes as indicative of the SGD signal. For example, seawater collected out of the fresher plume in the October 2006 sampling has a 224Ra/228Ra activity ratio (AR) of 2.2 while spring groundwater endmember presents an AR of 1.2. The mixture of these endmembers brings coastal waters to slightly higher AR's than the groundwater

source, thus precluding the use of the 224Ra/228Ra AR method to estimate water apparent ages.

4) I also believe that the authors could have explored more the recent SGD literature. For example, they are dealing with a site dominated by point groundwater sources, while most of the recent literature is based on sites dominated by diffuse groundwater sources. How point and diffuse groundwater sources determine the relative contribution of fresh and saline SGD? What about conservative versus non-conservative nutrient behaviour? And radium sources? Matt Charette's (I am not part of his group!) recent papers showed that radium is originated primarily from saline SGD, while the authors found a strong radium signal in a system dominated by fresh SGD. I found that remarkable. Bill Burnett's FSU group also has some recent papers on fresh versus saline SGD and non-conservative nutrient behaviour in systems dominated by diffuse groundwater sources. These papers have to be explored.

R4) Point SGD areas in karst formations are not commonly affected by diffusion but considerably influenced by advective flows through conduits or channels produced by dissolution of the CaCO3, which are generally driven by water table gradients. Thus, these areas are predominantly dominated by fresh-to-brackish SGD, as demonstrated by the low salinity in the springs (from 5 to 13), though it is sufficient to cause significant Ra enrichment. This salt content is presumably driven by Venturi effect and/or density differences between fresh and saline waters. Also, our study area is barely affected by tides (steep Mediterranean costs are under a microtidal influence of few cm), limiting the potential seawater recirculation through coastal sediments. On the other hand, diffuse SGD movements allow for a higher proportion of recirculated seawater through sediments, especially in areas with an important tidal range and a wide distribution of sandy sediments (Kim et al., 2005).

We agree with the reviewer in that most published SGD studies deal with diffuse groundwater sources. Indeed, point SGD fluxes mostly occur in coastal regions dominated by karst (or lava) formations. Due to the different nature of the processes, point and diffuse groundwater inputs entail different approaches to be considered and this makes hard any direct comparison. We refer to several works in Mediterranean coastal regions in the revised version of the manuscript to put our estimated fluxes in context. We also refer to Peterson et al., (2009) as an example of a point-SGD dominated area (Hawaii). Although these authors did not found Ra enrichment in their groundwater source so that they used Rn to estimate the SGD fluxes, the reference has been introduced in the manuscript for SGD comparison purposes.

As pointed out by the reviewer, both nutrients and radium isotopes may experience non-conservative processes in the subterranean estuary (Gonneea et al., 2008). However, our groundwater endmember was sampled at the location were it discharges into coastal waters; thus, we consider the composition of the actual endmember, regardless of any non-conservative behavior inside the subterranean estuary.

Minor comments:

1) I suggest using "saline" rather than "salty" throughout the paper.

R1) The term "salty" has been replaced with "saline", as suggested by the reviewer.

2) Page 633, line 21: "hydrological modification: : :". I found this statement confusing. What is meant by hydrological modification and how nutrients can interfere with local hydrology?

R2) We appreciate the comment. There was a mistake in the sentence: the text should read "ecological modification" (such as habitat loss) instead of "hydrological modifications". The correction has been made in the new version.

3) Page 634, line 8: "important reverse" – please clarify or rewrite.

R3) Thanks for the comment. We've clarified the sentence and it now reads: "Then, the contamination of its aquifers, and especially the karstic ones, could represent an important concern to be addressed in water resource management".

4) Page 634, line 11: "subterranean aquifers". Redundant. All aquifers are subterranean.

R4) We concur and we have eliminated the redundancy.

5) Page 634, line 25: ": : :can be only: : :". I understand what the authors want to say here, but there are a number of other ways to estimate residence times (models, tidal prism, etc). Please revise. Radium is probably one of the most unconventional (though powerful!) ways of estimating residence times.

R5) We've modified the text to clarify the sentence. The paragraph now reads: "...The approach is based on the groundwater enrichment in radium and the detection of the excess radium in coastal waters (Moore, 1996). In addition, coastal waters residence times can also be derived from radium isotopes owing to their different half-lives (from 3.7 days to 1,600 years). On the other hand, other elements may be enough enriched or diluted in groundwater (e.g. dissolved inorganic silicate-Hwang et al., 2005a- and seawater major elements, respectively) that enable us to estimate the groundwater fraction in coastal waters."

6) Page 637, last paragraph: the authors compare a range in groundwater concentrations to an average in surface waters. Please be consistent (show both averages) so that the reader can have a better feeling about the real radium enrichment in groundwater.

R6) We agree with the reviewer and we have included both averages (spring groundwater and surface waters) for the same sampling periods to make the comparison clearer for the reader.

7) Page 638; line 7: Delete "but also"

R7) The unnecessary terms have been eliminated as suggested.

8) Page 638: The authors make some comparisons to other sites. While this is useful information, this probably belongs to the discussion section.

R8) We think it is better to keep the mentioned comparisons in the "Results" section because they are useful to understand whether nutrient concentrations are elevated or not. The "discussion" section is focused on the evaluation of the SGD-associated input of nutrients.

9) Page 639, line 19: there is no "bad" or "good" correlation. Use "not significant" or "significant" correlation.

R9) The manuscript has been revised according to the reviewer's comment.

10) Equation 3, 4 and throughout the paper: Why use the subscript "std" to refer to coastal waters? Probably better to use a more obvious abbreviation such as "cw".

R10) We concur and the subscripts of the equations have been checked and modified as recommended by the reviewer.

11) Page 640, line 24: here the authors use average concentrations; later, in order to calculate residence times, they use equation slopes rather than averages. Please be consistent or justify why making different choices.

R11) The authors think that it is better to use slopes (rather than averages) whenever possible because they minimize the potential bias of a somewhat heterogeneous sampling. This is why we decided to apply slopes in the 224Ra/223Ra method to estimate water apparent ages. However, this approach cannot be used in the mixing model to calculate endmember fractions because these terms are already included in the activity ratios. The text has been revised to introduce this clarification.

12) Page 641, first paragraph: Hard to follow. Are you using a constant groundwater endmember or not? This comment is related to my first major comment.

R12) We are not using a constant groundwater endmember and the text has been revised to clarify this point. Please, see also response to major comment 1.

13) Equation 5: The authors cite Moore, 2006b, but the equation does not appear in

this paper. I feel they refer to Moore, W. S. 2000. Ages of continental shelf waters determined from 223Ra and 224Ra. Journal of Geophysical Research 105: 117-122.

R13) We were actually refering to Moore 2006a (and we have corrected the reference in the text) where Moore applied the same equation in a coastal karstic Mediterranean site in Sicily. We have also added Moore (2000) as a reference.

14) Section 5.3: This section (and the SGD rates derived from here) needs to be revised as the equation results do not seem to be internally consistent with the diagrams (see major comment above).

R14) We have addressed this comment above (see response to major comment #2).

15) Section 5.4: This section could be explored further using the literature (see major comment 4 above). I believe that just reporting numbers without discussing uncertainties and putting the results into perspective has limited usefulness.

R15) Section 5.4. has been extended according to the reviewer suggestion.

16) Page 643 shows a very interesting analysis.

R16) We appreciate the comment

17) Page 644, line 8: reads a little confusing, perhaps because the sentence is too long. Please revise.

R17) We concur and the sentence has been shortened.

18) Page 644, line 13: ": : :strictly correct: : :". Their approach will be valid if nutrients are conservative, not necessarily because samples were "located close to the water edge".

R18) According to the reviewer, the text has been revised to clarify the confusing sentence.

19) Page 644, line 16: "new + recirculated" . Isn't the paper dealing only with springs?

If so, all nutrients should be new. If recirculated seawater is a source of nutrients, one would not expect to observe clear linear mixing trends. Or am I misunderstanding the flow of information?

R19) Since the sampled springs are not completely fresh (average salinities of 5.5 and 11.2 for Jun 07 and Oct 06), these fluxes may include both new and recirculated nutrients. Although expected to be low, a certain load of recirculated nutrients may enter the fractured coastal aquifer with the portion of intruding seawater and mix with new nutrients before flowing back to the coastal sea through the springs. This explanation has been introduced in the revised manuscript.

This fresh + seawater mixing of nutrients that occurs at the end of the subterranean estuary (before the springs' sampling) is not in contradiction with the linear mixing trends obtained in coastal plume waters. As explained in the manuscript, these linear or non-linear mixing patterns would be basically the result of biogeochemical processes occurring in the water column.

20) Page 645, line 8: Denitrification in groundwater or seawater? This passage may have to be revised. The linear relationships imply no nitrogen transformations (such as denitrification) along the transport pathway.

R20) We refer to denitrification "in coastal waters" (now specified in the text) that could take place in the October '06 sampling, when no linear relations between radium and nitrogen were detected (see Fig 13).

21) Language: in general fine (compliments to the authors), but some typos and inaccuracies can be revised and the text can be polished. Some paragraphs are very long and can be shortened.

R21) We appreciate the comment and the text has been revised.
