Author's Response

Assessing land-ocean connectivity via Submarine Groundwater Discharge (SGD) in the Ria Formosa Lagoon (Portugal): combining radon measurements and stable isotope hydrology

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1. ***List of major changes to original manuscript***

- **New section** on inter-comparability of isotopic data added under heading 3.2 'Stable isotope hydrology';
- Amendments to **Table 1:** Winter (2009) radon mass balance data illustrating the similarity with the summer radon mass balance (2010) has been added to the original Table 1;
- **New Table 2:** An entirely new additional table, providing an overview of the sampling campaigns (parameters, dates) and associated precipitation data has been added to ensure clarity on the inter-comparability of results across the years;
- **Changed Figure 1** (original redrawn to incorporate new features): Now incorporates two panels, in order to provide a more complete geographical context to the study. Figure 1 now includes a) the location of all the six inlets mentioned in the text, as well as the river Gilão (panel a), and b) additional information pertinent for clarifying pore-water sampling locations for the periods 2007 and 2010 to 2011, other location references as well as a clear cut definition of the western and eastern sectors of the lagoon area focused upon in the study;
- **Changed Figure 4** (amended to incorporate new features): The redrawn Figure 4 now includes a fourth panel (d) illustrating the daily precipitation record over the region (2006-2013), taken from public databases, on which we have superimposed the periods of sampling that are relevant to the study to provide a temporal context on the precipitation regime over the region;
- **Amended Introduction.** Last two paragraphs re-written for objectivity and clarity of purpose;
- **New literature references** (4)

1. Gilfedder B.S., Frei S., Hofmann H., Cartwright I., 2015. Groundwater discharge to wetlands driven by storm and flood events: Quantification using continuous Radon-222 and electrical conductivity measurements and dynamic mass-balance modeling. Geochimica et Cosmochimica Acta 165: 161-177. DOI: 10.1016/j.gca.2015.05.037

2. Kwon, E. Y., G. Kim, Primeau F., Moore W. S., Cho H. M., DeVries T., Sarmiento J. L., Charette M. A., and Cho Y. K., 2014. Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model, Geophysical Research Letters, 41(23), 8438-8444. DOI: 10.1002/2014GL061574

3. Michael H.A., Lubetsky J.S., Harvey C.F., 2003. Characterizing submarine groundwater discharge: A seepage meter study in Waquoit Bay, Massachusetts. Geophysical research Letters 30 (6): 1297, DOI: 10.1029/2002GL016000

4. Taniguchi M., Burnett W.C., Smith C.F., Paulsen R.J., O'Rourke D., Krupa S.L., Christoff J.L., 2003. Spatial and temporal distributions of Submarine Groundwater Discharge rates obtained from various types of seepage meters at a site in the Northeastern Gulf of Mexico. Biogeochemistry 66: 35-53. DOI: 10.1023/B:BIOG.0000006090.25949.8d

2. ***Summary of responses to reviewer comments***

See also response to comments uploaded on HESS-Discussions-net for more detail.

2.1. Response to comment #C5845 (reviewer 1)

This reviewer made a substantial number of comments, divided into specific and technical according to their nature. To facilitate cross-referencing, we have transcribed them into the response online and numbered them according to the original order and type: #1-#20 for the specific comments and #T1-#T16 for the technical ones. The response online addressed these individually (see response to C5845-online).

- Responses to review comments are provided in italic bold font

#1. P12436 L9 After *Indeed, [...]* please add *'on a global scale an estimated 6%...'* as the anticipated percentile SGD contribution is different for oceans/ continents etc. as you certainly know.

R: This was done (see note on edited manuscript).

#2. P12436 L14-19 I suggest rewriting this passage as:
1. I am sure hydrogeologists or any other expert do see SGD, if they are familiar with that term, as any fluid flow regardless of fluid composition or driving as defined by Burnett et al. 2003.
2. In this context, I suggest to simply state the given or any other definition and adapt the following lines accordingly.

R: This was done (see note on edited manuscript).

#3. P12437 L 10 The authors may think about exchanging Lee 1977 with one or two of the rather new and partly very interesting publications concerning direct flux measurements.

R: References to Taniguchi et al 2003 and Michael et al 2003 added at this point, both of which address the issue of small spatial coverage of direct flux measurements and their up-scaling potential.

#4. P12437 L 16 *'fail to include seawater recirculation'* this is not quite correct see e.g. Li, Hu, B., Burnett, W., Santos, I., Chanton, J. (2009) Submarine Ground Water Discharge Driven by Tidal Pumping in a Heterogeneous Aquifer. Groundwater. 47(4): 558-568. Please change.

R: Sentence changed to: 'Frequently however, they incorporate assumptions of a steady state inventory and homogeneity of hydraulic conductivity over large scale-lengths and fail to include seawater recirculation.'

#5. P12441 L12-23 I am not sure why the authors include nitrate contamination at that point. Undoubtedly, it is an important topic, but it does come out of the dark at that point since it is not mentioned in the title nor does anything points at its importance. Since neither 14N nor 15N is used to explain sources later on, do the authors intend to use the contamination aspect for a final assessment as pointed at in the title? If so, it should be better introduced to make the point clear.

R: We have now altered the last two paragraphs of the introduction, in order to hopefully improve on this aspect of clarity of purpose.

#6. P12442 L4-19 From how I perceive it, so measured ^{222}Rn values do reflect an integral of ebb and tide status and is not corrected/normalized to its specific tide level? Is this correct?

R: Radon activities were measured in-situ, under way (as explained in P12442 L16-19). Following processing, they do ultimately reflect integrals of ebb and flood status as represented in Figure 2. Briefly, a total of 124 data waypoints were obtained for each individual survey, covering all the main channel areas. These were divided according to tidal stage at which they were measured into two groups. Salinity and location as well as depth where recorded in parallel with the radon, under way. As explained subsequently (P12442 L19-22), these were then used to calculate the local inventory (one inventory data point for each measurement). The inventories were normalized to mean tidal height for each location (P12442 L21-25). For mass balance purposes, only the normalized values where used, and those are the ones represented in Figure 2.

#7. P12444 L7 *'Samples'* - Could the authors add some words on how the samples were obtained, from which depth, whether they were stored or directly analysed etc. to provide a comprehensible and reproducible sampling strategy?

R: This was done (see note on edited manuscript).

#8. P12444 L24f *'which in combination with its location implied very low [...] so we neglected the* - I cannot follow the reasoning of neglecting surface water inputs. Rather intuitive would be to provide a salinity time series at this location that, if there is no surface water contribution, should be rather constant over time. Plus, did the authors check whether or not any floods occurred prior to the campaigns that might have changed the ^{222}Rn signal, if not at the outlet than possibly within the lagoon?

R: We should clarify that we are not neglecting surface water inputs as our statement (P12444 L19-23) indicated: 'Usually, an additional term accounting for the radon influx via river flow is added if the water and particulate flux associated with river discharge is significant. However, the only perennial river in the Ria Formosa is the Gilão, located in the eastern limit of the lagoon'. We then explain why we don't think the input is significant.

Firstly, we clearly stated (Section 2.2. Hydrogeological setting, P 12440) that the average salinity found throughout the year within the lagoon (35) was high – due to low effective precipitation on the catchment, a statement supported in the literature which the reviewer requested be removed (#T3). We nevertheless measured surface salinity (Table S1) during our isotope sampling campaign - it was very high during both tidal stages over the whole lagoon, with the exception of the areas influenced by discharge of the WWTP, where it was slightly above 33 (table S1). Hence surface freshwater inputs, other than the WWTP where generally negligible, something that is consistent with previous studies reported in the literature. In addition, we note that we also compared the annual effective precipitation over the whole catchment with the tidal exchange flux – it makes it clear that the mean volumetric tidal flux is 8 times higher than the annual average effective precipitation – thus compounding the argument above in that surface water inputs are negligible in this lagoon.

Secondly, Newton and Mudge (2003), cited in Mudge et al 2008, find that any freshwater influences caused by the Gilão river (in winter, where the potential to do so would be maximized) are localized to the vicinity of its estuary. Even so, we measured salinity (Table S1) at the Gilão estuary mouth in December 2010 (same month, same tidal conditions as in Dec 2009, same meteorological conditions when the isotope data was collected, see new Figure 4 panel d), just to make sure - and it was very high (>29) – this is very common occurrence – the saline influence extends far inland into the river. Freshwater discharge into the sea is negligible except under flooding, which did not occur at any time during sampling or beforehand.

To reiterate the importance of the distance factor, we also clearly stated that the location of the estuary is important as is its intermittency of discharge (P12440, L16-18) – it is more than 20 km to the east of the eastern border of the area of study represented in the original Fig 1, as the redrafted figure (top panel) now shows clearly. Combined with a perennial eastward alongshore drift on this coast, the lifetime of radon in surface waters subject to degassing, and the overwhelming contribution of seawater (low Rn) to the discharging mixture at the estuary mouth, the facts are strongly in favour of our contention that the Rn inputs eventually brought into the area of interest by the discharge of the river Gilão are not significant, and certainly, just in terms of freshwater contribution, not even comparable to the WWTP if we go as far in detail as we can and look at our salinity data for the isotopic samples, so we simplified the equation to remove the contribution.

We also verified whether there was any intense precipitation prior to the sampling campaigns that could have led to flooding – see additions to section 3.2, the new Fig 4, panel d, Table 2, and response to comment #9.

#9. P12446 L3 'I am not sure in how far the comparability between samples of different campaigns is given. Please add, at a suitable point in the manuscript, a short passage on the comparability of samples as specifically during the isotope section the authors themselves point out that a variance of up to 50% exist between sampling dates. This questions many interpretations of the presented manuscript and needs to be clarified. Plus, use consistent dates/periods for the isotopic data. Sometimes, the author's use 2007, 2009-2010, sometimes it is 2007 and 2013, sometimes it is 2007 and 2009-2011. This is very confusing and raises questions.'

R: This is a fair comment. We had thought carefully about this issue, albeit tensioned against space constraints since the length of the paper was an important consideration. We originally opted to save some space by providing Table S1 as a way in which the reader could have access to the sampling dates and all the data

plotted, but (see also response to #T6, below), the reviewer seemed to be lacking the S1 Table that available as supplementary material at this point. In addition to the sampling dates in table S1, the sampling periods for groundwater source functions where described in Section 4.2.1 (P 12450 L5-7), where we also drew attention to the temporal similarity in stable isotope signatures of the groundwater end-member (L 7-11).

While revising, we also found some typos – one location (Rio Seco, 08/12/2010, table S1) was mistakenly attributed to the Eastern sector and 2013 is an error.

We have corrected these, tightened up the designations, and provided the discussion as suggested in an update to section 3.2, which as a result was comprehensively revised. We complemented this with a new table (Table 2), where we provide a summary of the precipitation during all the sampling campaigns compared to the historical record average, as well as a new panel, added to Figure 4, comprising the daily precipitation record for 2006-2013 in order to provide a wider temporal context to the stable isotope data plotted there and in subsequent figures.

#10. P12447 L19-22 If both, activity range and spatial distribution of ^{222}Rn, are similar I do not understand the neglecting of the winter campaign. I suggest including it, as it may even provide more insights into temporal dynamics despite the associated uncertainties.

R: While this might be a fair comment in other circumstances, we respectfully disagree here. We opted originally to exclude the data and just mention it in the current context for two main reasons:

Firstly, the relative uncertainty associated with the advective radon input to the lagoon derived from the winter data is ~120% of the estimated discharge (7.97±9.62 Bq m^{-2} day^{-1}). Given the variable extremes observed in wind conditions during the survey (see additions to Table 1) and resulting choppy seas (we call attention to the precipitation data on the new Table 2 and the new panel d in Figure 4, where it is very clear that stormy conditions where fast developing and we where actually very fortunate to have carried out the work in the first place), we accepted the fact that both the uncertainty associated with the evasion term and that linked to in-way radon activity measurements (see additions to Table 1) where indeed too great and not representative of usual conditions in the region – the resulting SGD estimate, while similar to that obtained in June 2010, would then be severely affected as we point out, and now make explicit in the additions to Table 1, for completeness. We then took the option of repeating the radon survey the following summer. Even so, as the reviewer points out in the following comment (#11), 'the representativeness of the given SGD mean value is rather low and associated with a lot of uncertainty. (…)'. This is of course a well-known fact in SGD radon tracer studies and is well documented in the literature – it is associated with the assumptions needed to close whole basin mass balances of radon, and within these, in particular to the limitations associated with fluxes estimated with a parameterisation of gas exchange (k) with the atmosphere, as shown by Gilfedder et al (2015). If data that we present and discuss, obtained under the best possible circumstances and attention to detail in order to minimize uncertainty give rise to this commentary, discussing the extra data in addition would increase the space used (it is already a rather long paper) and probably give rise to many more comments of the same nature, while failing to add anything of note, as:

Secondly, we had actually stated that the data was similar as to activity range and distribution, and explained why we chose not to showcase the extra data – it would be redundant as the derived SGD discharge magnitude and the Rn activity range

and distribution was similar (this is now obvious, Table 1). It didn't and still doesn't add anything to our point in the context of the paper. Nevertheless, our calculations, as presented before for the summer (2010), and now on their entirety with the additions made to Table 1, are reinforced by a complete error propagation analysis (hence the high associated uncertainty, since it is accumulated) so that the reader can judge on the merits of our reasoning.

#11. P12449 L11-12 Here and also during the following lines, one SD is almost similar in value as the given mean value. In turn, i.e. the representativeness of the given SGD mean value is rather low and associated with a lot of uncertainty. This even leads to the fact that the resulting advective radon input to the lagoon of 1.36 (±1.28) x106m3day-1 may results in an filtering of the entire tidal-averaged volume of the lagoon (140x106 m3) through its sandy beaches within 100 days, as given by the authors but, with an almost similar probability, it may also be only 74 or 2450 days if we include the SD.

R: See Response to comment #10. Uncertainty is part of the scientific quantification of magnitudes of natural processes. We recall that the error is propagated throughout the entire mass balance calculation process.

#12. P12451 L17f How is the strategy influencing the range, specifically the delta18O range?

R: If we had not taken a sufficiently large and representative dataset (see response to comment #9), the question could be raised, and certainly within such a large pool of data and a lengthy discussion, this point might be lost to the casual reader. Questions could be raised, as we thought under this perspective, essentially because one potential reason for the observed difference would be that we didn't take into account natural variability of the end-member isotopic composition, and we would therefore have a diminished confidence in attribution of source functions for the water in the lagoon. So we provided the possibility and discussed it, even briefly, in spite of the confidence we had on the inter-comparability of results.

#13. P12455 L17 I would encourage the authors to double-check the percent-values. Corresponding to my calculation it would be 3.16, 0.97 and 0.04 (based on the mean value and the mean daily flood prism of $140x10^6m^3$).

R: Indeed – many thanks for pointing this out, we mistakenly wrote 1.04×10^8 m^3 (Line 18 in the same page) rather than 1.40×10^8 m^3, leading to the confusion. This is now corrected.

#14. P12451 L1f This comment is similar as one I have given before, but should underline the importance. On the given line, I started getting very confused. Despite stating in the text that isotope samples were taken 2007 and apparently at least twice between 2009 and 2011 (otherwise the authors would have given only one year) Fig. 5 states sampling years 2009-2010 and the supplement even 2012. I strongly encourage the authors, and this does account for all parameter and samplings to give a clear overview, which samples have been taken at what date and to discuss the comparability between parameter (Rn, 18O, 2H) in the context of the intended aims the authors follow within the presented manuscript.

R: We recall that our strategy was to sample for end-member stable isotope compositions under maximum predicted flow conditions (i.e., winter, as explained now in the redrafted section 3.2. – see also response to comment #9), and also accounting for annual and tidal variability – hence the multiple sampling runs (2009, 2010, 2011). The complete isotope data set is presented in table S1 available

as a supplement to the discussion paper and it doesn't include 2012 (that might be a typo), but it seems the reviewer didn't have access to this for some reason at this stage of the review (see also response to comment #9). In any case, we have tightened the descriptions up, opting for specifying the years whenever deemed necessary, rather than mentioning the periods, and adding clarifying material – Table 2, for example, now includes all the sampling periods summarized against the backdrop of precipitation regime.

#15. P12458 L11f I assume the authors mean the WWTP. If so please state so, for clarification aspects.

R: This was done (see note on edited manuscript).

#16. P12463 L16-18 I cannot follow. I agree, rainwater plots at d-excess of ~25‰, but how do the authors derive the point that water for public consumption was mainly withdrawn from a meteoric source? On the other hand, isn't that somewhat logical? I assume this arid region to use shallow GW to large extents, which should have a meteoric origin.

R: Indeed, all freshwater sources are ultimately meteoric. However, we specifically mention a direct meteoric source, to distinguish it from groundwater captions – the d-excess/δ¹⁸O line P4 (Fig. 7b) rules out groundwater captions as the source of the measured isotopic signature in the lagoon in this particular context (see also response to comment #17 below). Surface reservoirs (Odeleite: 37°20'15"N 7°33'1"W, <u>http://wikimapia.org/13820374/pt/Albufeira-da-Barragem-de-Odeleite</u> and Beliche: 37°17'1"N 7°31'49"W, <u>http://wikimapia.org/13820331/pt/Albufeira-da-Barragem-de-Beliche</u>) are used under the multi-municipal water supply system active since 2000 to cater for public water supply in the eastern region of the Algarve, including the city of Faro, with groundwater captions only used in emergency situations (i.e., when the reserve levels in these two are low), as explained in P12464 L10-19 and in more detail within the cited literature references (Monteiro & Costa Manuel, 2004; Stigter & Monteiro, 2008). Given their location Northeast of the region of interest, important sources of precipitation for recharge are originated in Southern France and the eastern Mediterranean with occasional influences from the Magreb, and these have d-excess signatures that are quite high, as explained in Frot et al, 2007 cited in P12451, L2). In addition – we checked, using the GES DISC (NASA) tool (not shown) – the source of this rain collected in winter 2009 was the centre/south of France and the rain clouds travelled southwest over the mentioned reservoirs. This explains why, in this regional context, local rainwater and groundwater water may have origins in different meteoric water sources and thus have distinct stable isotopic signatures.

#17. P12463 L20 Do the authors mean the mixing line P4? If so, the reasoning is not clear to me as I do not understand the distribution of the surface water and porewater samples? How can surface water plot above the porewater samples? Or, are these the sample points, the authors discuss earlier when mentioning the influence of the WWTP?

R: Yes, we do. Mixing line P4 connects surface water in the Ramalhete channel (Fig 1) that is influenced by water coming out of the WWTP with high d-excess and seawater with low d-excess. This line ultimately extends to a high d-excess signature (~25‰), and this is why we state that it originates in surface reservoirs (see also response to comment #16 above). Mixing of a comparatively small volume of WWTP water with a larger volume of surface water, including seawater, greatly depletes this channel's overall signature in d-excess along its course from the WWTP.

Porewater has an intermediate isotopic signature and lays in between the two endmembers: this is possible for a number of reasons: one, because surface water infiltrates the unsaturated zone of the beaches, located at the outer limits of the system (and hence at the end point of the water path towards the inlets), and while travelling through the pores in the beach toward the seepage face, becomes initially even more depleted in δ^2H and $\delta^{18}O$ because of the distillation effect within the unsaturated zone, as described in Barnes & Allison 1983 and 1989 (cited in P 12458 L 5-9); two, because its mixing ratio with seawater and more depleted surface water (in d-excess) is necessarily small.

#18. P 12463 L23f Again the question of comparability? Was the tidal status the same during both samplings? Or could it be that during 2007 it was a low tide during which all the porewater was sampled plus a wet period just before the sampling campaign? Both in combination might also explain the differences to the 2009-2011 data that might reflect a rather dry period before. Additionally, S1 shows the different porewater samples but there is no information whether they show different depths, or different close by locations with a constant depth, nor how they were retrieved. Please clarify and state some words to the comparability.

R: The issue of comparability has hopefully been addressed at this stage (see response to comment #10). Briefly, January 2007 and 2011 are directly comparable (see new Table 2) – the month was relatively dry, but came on the back of three really wet months. This is why additional sampling was done in 2011 – to make the pore water dataset available under comparable hydrometric conditions in its entirety. Pore water in January 2007 was sampled right along the Ancão peninsula (see redrawn Figure 1), while all subsequent (2010, 2011) porewater samples were taken at a single site through a fixed piezometer profile, but at various depths as explained more carefully in section 3.2 now, as well as catering for different tidal stages. Winters in 2009 and 2010 where directly comparable in terms of hydrometrics (Table 2). The most likely explanation therefore for the stable isotope hydrology of the catchment is the one we put forward – it is anchored on a careful, field-adaptive sampling strategy, and is for extra care compared with historical data (table S1, Fig 4 a, b and c).

#19. P12464 L13-16 '*the activity of the SGD subterranean pathway into the Ria becomes dependent on whether groundwater levels in M12 are sufficient to establish a hydraulic gradient driving the flow as was apparently the case in 2007 (Fig. 7a).* ' I agree, but could the authors underpin this aspect with recorded precipitation amounts in the period before the campaigns?

R: This was done – see added table 2, discussion in section 3.2 on inter-comparability, and new panel on Figure 4 showing the daily precipitation during the period 2006-2013 with the sampling periods overlain to provide a historical context.

#20. P12465 L12-27 Instead of referring to N, I would suggest to briefly list the direct findings of the study and to assess the connectivity as the title suggests. From my perspective, this last paragraph, if intended as assessment, is not at all suitable as such as none of the direct results of the manuscript are used except (possibly) a measurement for N in 2006 but here it is unsure whether it is an own measurement or by Leote et al. (2008).

R: Leote et al 2008 was produced by an earlier project carried out by the same team and directed by the same PI, and in many way laid out the groundwork for the project under which this paper was produced. From the authors' point of view, it is

thus important to underline the importance of the present findings relating them to direct local productive activities and water management. This is of special relevance if we look at the consequences of not having a supported case for attribution of nitrogen loads to the different SGD modes we distinguish using our approach, as we mention in the introduction and discuss further in the conclusion.

<u>Technical Comments:</u>

#T1. P12435 L21-25 It is a very long sentence that is hard to follow. I suggest to shorten or to rewrite it.

R: This was done (see note on edited manuscript).

#T2. P123439 L25 *'six tidal inlets'* – Fig 1 shows only 3 inlets. I assume the other three are east of the region Fig. 1 shows. And this is one point I would encourage the authors to change. Throughout the text, several times locations, rivers, stream (ephemeral and perennial) and inlets are mentioned and not shown on the map. Please include them to provide a comprehensive and complete picture of the area. Plus, please add all sampling sites and possibly indicate the time they were taken (e.g. colour coded).

R: We have redone Figure 1, which now incorporates two panels. We thought this to be the best solution, catering for the reviewer's request for additional information to be inserted while still maintaining the illustration free of clutter.

#T3. P12440 L12-15 Please change from *'The surrounding watershed covers 740 km. and receives effective precipitation of 152mmyr^{-1} (Salles, 2001). This corresponds to a potential annual rainfall of 1.2 106 m3, very small compared to the tidal exchange flux – hence the high average salinity of 35 found throughout the year in the lagoon (Mudge et al., 2008).'*

To *'The surrounding watershed covers 740 km2 and receives effective precipitation of 152 mm yr-1 (Salles, 2001) corresponding to an annual rainfall amount of 1.2 106 m3.'*

R: This was done (see note on edited manuscript).

#T4. P12441 L5 *'The two units'*- It is unclear which two units are meant here. Aforementioned is the M12 as multi-layered aquifer only but no specific units. Please clarify.

R: The two units refer to the superficial Pleistocene aquifer and the underlying Miocene aquifer. To make it clearer, we changed the sentence: see note on edited manuscript.

#T5. P12443 L3 '*Faro Channel Fig.1*' - Where exactly are the two fixed stations located, is it station 3 and 4? Please clarify.

R: In Figure 1 provided with the manuscript, the two stations are identified by a symbol depicting a buoy and a flag. These symbols are captioned in the figure as "Tidal stations", with the northwestern-most one named as 'Quatro-Aguas', in accordance to Figure 1 and the Rn mass balance approach, and the other at the entry of the main inlet, Faro-Olhão (or Barra Nova). We therefore don't quite understand the request, but nevertheless, in the expanded Figure 1 we attempt to make them more visible.

#T6. P12444 L23 There is no Table S1, neither at the end of this document nor in MS manuscript overview of HESSD. Please add it as at least from my perspective it is crucial for the understanding of certain processes and samplings and its evaluation.

R: We agree that it is crucial, but are afraid that this statement is incorrect. The S1 (from Supplementary-1) Table, comprising the entire stable isotope dataset, with locations (coordinates), dates of sampling, number of samples taken, and associated uncertainties, as used in the manuscript does exist. It is 4 pages long, and is available for download as supplementary material online at the site of the discussion paper due to size constraints. This table also addresses some of the other comments made with regards to locations.

#T7. P12445 L11 Please explain 'T'

R: This was done (see note on edited manuscript). For enhanced clarity, we opted to edit the sentence and add the 'T' between parenthesis after the second mention of the word 'period', and it now reads: 'If we then take the mean tide level (MTL) as a reference, it follows that the Rn_{adv} term may be calculated for different periods: the period (T) at which the tidal height in the lagoon is below MTL (Rn_{adv} (T<MTL), i.e., the trough of the tidal wave or low tide, and the one when it is above MTL (Rn_{adv} (T>MTL), corresponding to the peak of the wave, or high tide.'

#T8. P12445 Eq4a/4b Although possibly being pedantic, please move the Rnnet to the end of the equation to match Eq. 3

R: This was done (see note on edited manuscript).

#T9. P12446 L13f '*western sector*' – the 'western sector' is explained later on and may lead to confusion here. Either the author's add the locations in Fig.1 (what I suggest) or they explain the western sector at that point.

R: This was done (see note on edited manuscript). Changes to Figure 1 have been made.

#T10. P12446 L 13f *'Barra Nova'* –this term is not shown on the map but used several times in the text. Please add it to Fig. 1 in order to allow a clear understanding of the spatial context

R: This was done (see note on edited manuscript). There is a now a list of all the inlets, their English and their Portuguese names associated with the new panel in Figure 1.

#T11. P12448 L1-4 The spatial distribution is explained at the example of Rn activity but Fig. 2 shows inventories. To make it easier to follow I suggest to use either inventory or activity, but to use the same for the verbal explanation and Figure 2.

R: We respectively disagree here. While in the text the activity values where shown to make them easily comparable for example with the tidal data shown in Figure 3, the most correct way of showing data on a geographical scale that is directly inter-comparable in spite of the different depths due to the bathymetry and to the tide stage is to show inventories referenced to MTL on the map.

#T12. P12450 L22 *'for the Great Barrier Reef'*–_is this relevant? If not, I would suggest to delete it.

R: It is relevant inasmuch as it provides the location of the study referred to in the citation – contextually, it is also important given the importance of freshwater sources to the marine environment there. The study focuses on the input of freshwater into a marine environment and therefore ties in with ours.

#T13. Equations - Is it relevant to show them in the text, especially the coefficient of determination r2 and later the p-value? I would suggest putting them in the plots as it disturbs the text quite a bit.

R: We understand that it might disturb reading flow a bit. However, it would also clutter the figures quite a bit as well. We intend to show the r2 and p values of mixing lines and meteoric lines because it makes them more immediately comparable to the hydrological literature on the first instance and on the second adds strength to the formulations. Torn between cluttering the text or the figures, we opted for the text as a compromise, in order to maintain the figures as clear as possible in spite of the plethora of data they show.

#T14. P12451 L27 'proper' – I assume the word is wrong here. Please delete.

R: This was done (see note on edited manuscript).

#T15. P12460 L20-25 Very long sentence that I would suggest to split or rewrite.

R: We agree – we have split the original sentence and it now reads as two: (see note on edited manuscript)

P12476 Fig1 Please,
1. add all names, places, sampling locations etc. the authors mention throughout the manuscript and extend the figure to the east,
2. add a colour legend,
3. add a colour to M10-M12 to be able to differentiate it from water
4. add a coordinate system to be able to locate sampling locations from the supplement

R: This was done (see note on edited manuscript) and new Figure 1.

#T16. P12477 Fig2 Is ebb and tide (a and b) erroneously exchanged, as more data points to the west are available for the ebb subset (a) which I would assume for the flood with more water in shallow reaches? Please provide some names in Figure 2 that the authors use during the description of the spatial distribution and, if the authors have it, a bathymetric chart would add some value.

R: No, they have not been confused. The ebb subset contains more points to the west on purpose, as when surveying, we made a point of following the outflow of water westward from the WWTP.

2.2. Response to comment #C6187 (reviewer 2)

This reviewer makes a substantial number of comments, divided into "concerns" and "specific" according to their nature. In the interest of clarity and to facilitate cross-referencing, we have transcribed them into the response and have numbered them according to the original order and type: #1-#2 for the "concerns" and S#1-S#23 for the specific ones. The response online addressed these individually (see response to C6187-online).

-Responses in italic bold font

Main concerns:

#1. "My major concern with the study is the seemingly ad hoc sampling design. The authors state for example that "Samples for stable isotope analysis of water were collected in triplicate from all possible water sources to the lagoon on various occasions between 2007 and 2013." (P12446 L1); and "Quasi-synoptic distributions of 18O and 2H in water at different tidal stages were obtained for the lagoon in the winter of 2009."(P12446 L15). With so much temporal variation in all of the tracers, drawing conclusions from multiple sampling campaigns under differing conditions can be problematic to say the least. This is of particular concern with the natural tracers used as concentrations and fluxes of the tracers would very much be affected by rainfall, tide heights etc. While comparing the results of different campaigns can be done, to do so, it would be necessary to demonstrate that the system was operating under similar hydrological conditions during each of the campaigns. To do this, reporting differences in rainfall (both long and short term), temperature, groundwater water levels, groundwater concentrations/signatures and tide heights would be necessary."

R: This is a fair comment, and raised again in specific comments S13 and S16. A new additional table, providing an overview of the sampling campaigns and associated precipitation data (Table 2) has been added to the original manuscript. Furthermore, winter radon mass balance data (2009) illustrating the similarity we had mentioned existed with the summer radon mass balance (2010) and addressed in S#16 has been added to Table 1; and two of the original figures (Fig 1 and 4) where updated to help clarify this concern and queries related to comments S#9, S#12-S#16 and S#22. In addition, the new section on inter-comparability of isotopic data under heading 3.2 and the additional data provided in Tables 1 & 2 might contribute to clarify the issue.

#2. Another concern is with the selection of an endmember for seawater recirculation. The authors concluded that most of the SGD is comprised of recirculated seawater, but does the beach groundwater endmember represent fully equilibrated recirculated seawater or new seawater with a very low residence time that has yet to fully equilibrate. The authors assume it is fully equilibrated, but it needs to be discussed why they believe this is so.

R: See also response to S#23 below reading the recirculation mechanism and its impact on radon budgeting.

If we assume that the water (from the lagoon, only partly open seawater) infiltrates the unsaturated zone of the beach during flood and is flushed through the permeable zone of the beach driven by tidal pumping, then as part of this endmember, we get radon produced from the sediments during the residence time of the water in the beach plus the radon which was already in the water before recycling through the beach sediments. This recirculation pump is constant, i.e. the residence time of the water in the beach is constant over time, so the added fraction of radon from sediments may be seen as constant. Therefore, we don't require or assume that it is fully equilibrated.

Under the assumptions above, and those pertinent to the calculation of the contribution of re-circulated water to the SGD in the lagoon (lifetime of radon), we always get the same amount of radon from this production in the sediments as long as the recirculation time scales are seen to be constant. So we have an endmember which is probably partly equilibrated (because the residence time within the beach is probably too short for full equilibration to occur) but which is constant; and this endmember was measured, several times (Table 1).

Specific comments

S#1: P12435 L1. I find the first and second sentences contain too many distinct points and both can be written more clearly with shorter sentences.

R: This was done (see note on edited manuscript): We split the sentences that were too long in order to hopefully make the section clearer.

S#2: P12435 L19. This is confusing, I suggest something like "SGD can be separated into fresh groundwater inputs and recirculate lagoon waters" to make it a bit clearer.

R: We rewrote the section as suggested to try and avoid confusion (see note on edited manuscript), but kept the net water input/no net water transfer designations in, as they are important because of the putative association with autochthonous and allochthonous nutrient inputs if a nutrient mass balance is desired. The section is hopefully made clearer.

S#3: P12435 L21. I believe "permanent" is the wrong word here as it implies long, multi temporal sampling. Perhaps "dominant" is a better word.

R: Agreed. We have changed accordingly (see note on edited manuscript)

S#4: P12435 L26 Remove "so more difficult to predict".

R: Done (see note on edited manuscript).

S#5: P12436 L9. Suggest including a more recent estimate such as: Kwon, E. Y., G. Kim, F. Primeau, W. S. Moore, H. M. Cho, T. DeVries, J. L. Sarmiento, M. A. Charette, and Y. K. Cho (2014), Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model, Geophysical Research Letters, 41(23), 8438-8444.

R: This is an important point. We modified the paragraph and added the reference to the literature cited (see note on edited manuscript)

S#6: P12437 Radium is normally absent in "fresh" groundwater.

R: Good point. Sentence was amended (see note on edited manuscript).

S#7: P12438 L9 Sentence is unclear.

R: Yes, we can see this – it has been a point where we have become somewhat stuck for a while. We have attempted to re-write it in order to make it clearer (see note on edited manuscript).

S#8: P12438 L13 Remove "so far to progress beyond our ability".

R: Done (see note on edited manuscript).

S#9: P12438 L13. I believe this can be expanded upon. The endmember is usually the greatest uncertainty in any tracer mass balance. With most studies using a range of endmembers across the catchment/aquifer/study site, determining the endmember concentration in the area of the likely source of groundwater would very much lead to much less uncertainty in SGD estimates.

R: This is a well-made point and a very useful synopsis of the logical thread, and we followed by incorporating the suggestion (see note on edited manuscript).

S#10: P12438 L19. I believe a separate paragraph (of which some of the information occurs in the last paragraph of the introduction) on how O18 and 2H can be used and where they have been used to quantify SGD sources.

R: Considering also comment S#11 below, and the common points made by reviewer 1, we opted to re-write the last two paragraphs of the introduction in order to accommodate what we felt where very valuable contributions (see note on edited manuscript).

S#11: P12438 L15. There quantification of N inputs into the lagoon has not been set up in the introduction but is mentioned in the abstract, methods etc.

R: See response to comment S#10.

S#12: P12444 L22. Unclear why this input is not included. Is it are large potential source, small one, what is the discharge? Rivers of course can be large sources of tracer and nutrient inputs particularly in times of flood. This should be acknowledged, shown on figure 1 & 2 and addressed as a limitation if no data is available.

R: This is an issue raised by reviewer 1 as well. We should clarify that we are not neglecting surface water inputs as our statement (P12444 L19-23) indicates: 'Usually, an additional term accounting for the radon influx via river flow is added if the water and particulate flux associated with river discharge is significant. However, the only perennial river in the Ria Formosa is the Gilão, located in the eastern limit of the lagoon'. We then explain why we don't think the input is significant. See response to #8, reviewer 1 and additions to section 3.2, the new Fig 4, panel d, and new Table 2.

S#13: P12446 L1 As discussed above in the general comments, you need to provide specific information on when the sample collection took place and how comparable the different campaigns are. To do this, a minimum of reporting differences in rainfall (both long and short term), groundwater water levels, temperature, groundwater concentrations/signatures and tide heights would be necessary.

R: This is a fair comment and has now been addressed by adding the information requested. We clarify that we had thought carefully about this issue, albeit tensioned against space constraints since the length of the paper was an important consideration. We originally opted to save some space by providing Table S1 (Supplementary materials) as a way in which the reader could have access to the sampling dates and all the data plotted. In addition to the sampling dates in table S1, the sampling periods for groundwater source functions where described in Section 4.2.1 (P 12450 L5-7), where we also drew attention to the temporal similarity in stable isotope signatures of the groundwater end-member (L 7-11).

While revising, we also found some typos – one location (Rio Seco, 08/12/2010, table S1) was mistakenly attributed to the Eastern sector and 2013 is an error.

We have corrected these, tightened up the designations, and provided a discussion of inter-comparability of all the campaigns as suggested in an update to section 3.2, which as a result was comprehensively revised. We complemented this with a new table (Table 2), where we provide a summary of the precipitation during all the sampling campaigns compared to the historical record average, as well as a new panel, added to Figure 4, comprising the daily precipitation record for 2006-2013 in order to provide a wider temporal context to the stable isotope data plotted there and in subsequent figures.

S#14: P12447 L19. A better explanation of the exclusion of winter data should be given. If higher evasion rates were likely during winter than why were Rn concentrations and distribution similar. This points to very different drivers of SGD temporally and as the comments above suggest, that comparing tracer concentrations over multiple campaigns in problematic.

R: This is also an issue raised by reviewer 1. The data is now included (amendment to Table 1), see also above response to #10 (reviewer 1).

S#15: P12448 L26. Detailing the water balance in the lagoon would be helpful ie. The amount of water coming in and the amount of water going out. If the water balance is not equal over the particular tidal cycle where the Rn was measured, this can have significant impacts on the mass balance and should be accounted for.

R: This has been comprehensively done by Andre Pacheco and colleagues (see Pacheco et al, 2010, cited in P12440 L6 and P12449 L3, for example). The residual tidal prism is very small in spring tides (see Figure 4 and Table 4 of their paper). Both radon surveys were conducted in Spring-tide conditions (both tidal amplitudes are now specified in the new additions to Table 1, for comparison). The two mass balances are directly comparable. This information has been incorporated into the mass balances we did, as explained in P12449 L3-6. As a result, the net exchange of radon between the lagoon and the Atlantic (see Table 1) is negligible and doesn't affect the mass balance, as we discuss in P12449 L6-9.

S#16: P12450 L1. Throughout the Stable Isotope Hydrology section, it needs to be clear which samples were collected during the 222Rn surveys and timeseries and if the collection times were different how applicable is it to compare signatures at the different times and how the signatures compare to the 222Rn concentrations/export/import/mass balance.

R: This is a fair comment and has now been addressed, by inclusion of a summary of the relevant sampling information on the new Table 2, and a new section (under 3.2) on the inter-comparability of results. The new section on inter-comparability and the additional data provided might contribute to clarify the issue.

S#17: P124550 L14 Please define the acronyms used in figure 4 and 5 in the caption ie.WMMWL

R: Done.

S#18: P12455 L5. Change "discriminate between potential source functions of SGD." To "discriminate between potential sources of SGD."

R: Done.

S#19: P12455 L9. Change "potential source functions" to "potential sources"

R: Done.

S#20: P12455 L9. As per the general comments, clarification on the recirculation endmember needs to be addressed. Does the beach groundwater endmember represent fully equilibrated re-circulated seawater or new seawater with a very low residence time that has yet to fully equilibrate. The authors assume it is fully equilibrated, but it needs to be discussed why they believe this is so.

R: See in the introductory paragraphs, response to #2. If we assume that the water (from the lagoon, only partly open seawater) infiltrates the unsaturated zone of the beach during flood and is flushed through the permeable zone of the beach driven by tidal pumping, then as part of this endmember, we get radon produced from the sediments during the residence time of the water in the beach plus the radon which was already in the water before recycling through the beach sediments. This recirculation pump is constant, i.e. the residence time of the water in the beach is constant over time, so the added fraction of radon from sediments may be seen as constant. Therefore, we don't require or assume that it is fully equilibrated.

Under the assumptions above, and those pertinent to the calculation of the contribution of re-circulated water to the SGD in the lagoon (lifetime of radon), we always get the same amount of radon from this production in the sediments as long as the recirculation time scales are seen to be constant. So we have an endmember which is probably partly equilibrated (because the residence time within the beach is probably too short for full equilibration to occur) but which is constant; and this endmember was measured, several times (Table 1)

S#21: P12455 L15. Add in "The corresponding volumetric discharges, if each of these potential sources is considered in turn to be the only source of SGD to the lagoon are.."

R: Done (see note on edited manuscript).

S#22: P12455 L25. Again this highlights the temporally dynamic nature of the lagoon and comparison of parameters across different campaigns must be discussed.

R: This has now been done. See response to comment S#16, detailing the new section on inter-comparability of campaigns, and additions to Table 1 as well as the new Table 2.

S#23: P12456 L2. Please describe this mechanism (with references) in more detail as I find this explanation highly unlikely. As 222Rn is essentially sourced from sediments and porewater 222Rn is regularly many magnitudes higher in porewater than surface water, surface water contributing 222Rn to the porewater is not feasible. At a guess I would say that wind and current evasion is likely underestimated. Providing more detailed explanation of the terms used in evasion calculations and uncertainties around those estimates may help determine if this is the case.

R: This comment is not entirely clear to us. We assume that the reviewer is requesting further explanation of beach hydrology and beach groundwater dynamics, as this explains the loss of radon from the system found at high tide (explained in P12456, L1-19).

Since the late 1940's, there has been a multitude of studies focusing on hydraulic behavior of beaches, including modeling studies describing flow dynamics above and below the beach water table. Given the abundance of materials, these cannot be cited entirely here and this issue is not the main focus of the paper – it is well-established knowledge, at least on the issue mentioned by the reviewer. However, a comprehensive review of beach groundwater dynamics is given by Diane Horn (Horn, D.P., 2002. Beach groundwater dynamics. Geomorphology 48: 121-146), and more recent work with focus on SGD can be consulted for example in Heiss et al (2014): Heiss, Ullman, Michael: Swash zone moisture dynamics and unsaturated infiltration in two sandy beach aquifers, Estuarine Coastal and Shelf Science 143: 20-31, or Ibanhez & Rocha, 2014 and 2015 (below).

Briefly, the water table on beaches divides them into two main areas, depending on prevalent pore pressure: the area below the water table, which is permanently saturated and where pore pressures are positive, and the area above the water table (sub-atmospheric), where sediment is unsaturated and pore pressure is negative. The size of these areas across a vertical beach section changes in cyclic fashion according to tide level – during flood, water infiltrates into the unsaturated portion of the beach (recharge), usually at the upper levels of the beach slope, and during ebb, this water flows seaward mainly through the pores driven by the hydraulic gradient established between the beach water table and the sea level at any one point in time during discharge (discharge). Infiltration of water into the unsaturated zone of the beach during flood tide is an advective process, i.e., water physically infiltrates the unsaturated portion of the beach, taking up empty pore space left behind by the previous discharge cycle. This water will eventually discharge through the lower portion of the beach at low tide. This cycle is referred as tidal pumping and is the reason for seawater recirculation through beaches. Hence, when water infiltrates the unsaturated portion of the beach, it injects into the beach any accompanying solutes, and even some particulates that are critical in determining the biogeochemical role of tidal pumping (see for instance Ibanhez and Rocha, 2014 and 2016). This process also affects stable isotope signatures of porewater, as explained for example in P12458, L2-9).

Hence during flood, lagoon water with dissolved radon infiltrates the unsaturated zone of the beaches within the lagoon, removing this radon from the surface lagoon pool, as we explain, with calculations based on our data, in P12456, L1-19. This is not a mixing process between surface lagoon water and saturated beach porewater as the reviewer seems to have understood – it is a removal of surface water and its radon from the surface water pool and into the area below the sediment surface. Mixing occurs within the beach pore space after recharge and the water discharged at the lower portion of the beach slope during low tide incorporates both water infiltrated during the previous high tide and water that had remained in the beach for a longer period of time. We therefore are at loss as to how to make the mechanics of this process more clear.

Ibanhez JSP & Rocha C (2014). Effects of recirculation of seawater enriched in inorganic nitrogen on dissolved organic carbon processing in sandy seepage face sediments. Marine Chemistry 166: 48-58

Ibanhez JSP & Rocha C (2016). Oxygen transport and reactivity within a sandy seepage face in a mesotidal lagoon (Ria Formosa, Southwestern Iberia). Limnology and Oceanography, 61: 61-77

S#24: P12456 L22 Would "is" be a better choice of words here than "could"?

R: We are not sure – but we wished to keep with the narrative type discussion, where we progress from the unknown into finally taking a supported conclusion as to how conflating the two SGD modes because of the lack of distinction of sources may affect the N balance estimates for the system. So we would maintain the 'could'.

S#25: P12456 L20 Again the "two different periods" are not clearly defined previously in the manuscript.

R: We are not sure about this comment. The page and line mentioned do not contain the sentence the reviewer alluded to. However, we hope that following the changes

to the manuscript and highlighted in our responses to the other comments, the issue of comparability is resolved.

2.3. Response to comment #C6634 (reviewer 3)

We would like to thank the reviewer for the clear, detailed commentary arising necessarily from an in-depth review of the manuscript. As with the other referees (we note that there are points in common), this has benefitted us greatly. The reviewer makes three general comments, and a number of other suggestions. In the interest of clarity and to facilitate cross-referencing, we have transcribed them into the response and have numbered them according to the original order and type. The response addresses these individually.

General Comments:

G1. "This is an important paper. As the authors recognize, problem of selecting end-member concentrations has plagued SGD studies since their inception both in transforming Rn (and Ra) data into water fluxes and in calculating contaminant deliver via SGD. The stable isotope strategy presented here is an innovative approach. I would emphasize the method rather than "the overarching aims of the study to identify the sources of SGD…" (p. 12438 1, line 28). As a demonstration of the method, one might have hoped for a simpler study site, but perhaps, the complications at the Ria Formosa Lagoon serve to demonstrate the utility of the approach."

R: It is very generous of the reviewer to give us this mark of approval on our work. Sincere thanks. Having said that, the suggestion appended is indeed an important and valued one. Our perspective is that if the approach works in such a complex system, and actually highlights aspects of the system that took decades of research to uncover by traditional hydrodynamic and modeling analysis, then it certainly would be of value to the community. Considering also comments along the same vein by the other reviewers, we attempted to rewrite the last two paragraphs of the introduction to hopefully highlight the study and its consequential findings a bit more.

G2. "Given the sophisticated geochemistry, I found the treatment of the tidal hydraulic overly simplistic. Although I'm willing to concede that the residual tidal exchange is unimportant in the Rn budget, I had little confidence in the results. The tides deserve a more complete treatment in the description of the study site. The tide may indeed be a "traveling wave" (p. 12445 line 7) but I would not be surprised that, in such a tortious lagoon, it is not; and why use 12 hours as the semi-diurnal period when it's no more calculation effort to use the actual semi-diurnal period (p. 12445 l 21). The issue of the exchange of water among the three inlets (p 12461 l 6-15) is important and should be described earlier in the description of the study area."

R: Andre Pacheco and colleagues (see Pacheco et al, 2010, cited in P12440 L6 and P12449 L3, for example) conducted a comprehensive analysis of inlet hydrodynamics in the Ria Formosa in the context of multi-inlet system morphological stability. The residual tidal prism is very small in spring tides (see Figure 4 and Table 4 of their paper). There is an internal residual flow eastward within the lagoon, which they showcase based on careful analysis of system hydrodynamics, and we independently uncover with a basis on the stable isotope hydrology data (in section 5.2, specifically P12460 L29, P12461 L1-15), the radon

distribution between low and high tide (P12461 L16-28), and confirm its coherence with insights provided by their work in P12461 L16-25.
With regards to the exchange fluxes of radon, both radon surveys were conducted in Spring-tide conditions (both tidal amplitudes are now specified in the new additions to Table 1, for comparison). The two mass balances are therefore directly comparable. This information has been incorporated into the mass balances we did, as explained in P12449 L3-6. As a result, the net exchange of radon between the lagoon and the Atlantic (see Table 1) is negligible and doesn't affect the mass balance, as we discuss in P12449 L6-9. Given that the Rn budget is controlled essentially by internal lagoon processes, and not by the exchange of its water with the Atlantic, we then treat the entire system as our domain neglecting spatial variability for the purpose of budgeting.
Using 12 hours as the semi-tidal period is a mathematical simplification, for ease of use by others (formula 4c becomes easy to use and recall, under the assumptions of negligible exchange with the outer domain over the lifetime if radon). Either way, it doesn't affect the result at all, since the exchange flux is orders of magnitude lower than the other fluxes as depicted in Table 1 and discussed in section 4.1.2. We also show the lack of distinction between the two SGD estimates, obtained respectively by treating the whole domain as one and using all the data, and using the travelling wave approach and tidal stage inventories in separate in section 4.1.3.

G3. "The "freshwater lens" (p. 12455 l 10) is not described. Is it possible that differences in tidal phase across the outer barrier is driving water between the ocean and lagoon under the barrier? (I believe this has been shown to happen in some sites in Florida and Venice). And what about the extensive marshlands in the lagoon (grey areas in Figure 1)? How does drainage on, off and through the marshland figure into the budget?"

R: This is part of the M12 aquifer (Section 4.2.2, P12451 L19-24). The difference in tidal phase driving water between the ocean and the lagoon is always a possibility. Indeed, there is a seminal paper on this very issue (Bokuniewicz & Pavlik, 1990: Groundwater seepage along a barrier island, Biogeochemistry 10: 257-276) that illustrates the debate perfectly. The question is whether this is saltwater (i.e., re-circulated lagoon water) or freshwater. If it is freshwater (it certainly isn't the case for 2009-2010 as we show), we had previously (see Rocha et al 2009) conducted an analysis of potential hydraulic gradient created by this tidal difference and compared that with that created by the piezometric levels on the continental side of the lagoon, within the same aquifer. We found the hydraulic gradient from land to be the more important force driving the flow. However, it is almost certain from a rational perspective that this oscillation of tidal phase contributes to porewater (beach groundwater) mixing within the beach aquifer. Which brings us to the second point: If it is re-circulated lagoon water that overlays the freshwater beneath, and therefore potentially the dominant fraction of SGD (in the absence of a terrestrial hydraulic gradient driving fresh groundwater flow from the M12 aquifer through the seepage face), this tidal phase gradient-driven mixing and driving force would only contribute to the SGD mode we describe.

With regards to the marshland contribution to the radon budget: at the request of reviewer 1, we added some detail on the way samples where obtained for the measurement of diffusive fluxes of radon (P12444 L7 and subsequent lines) to employ in the budgeting analysis (see note on edited manuscript). The section now reads: 'Sediment-water diffusive fluxes of radon were measured as described in Corbett et al. (1998) in samples (n=16) collected throughout the lagoon and directly analysed in the laboratory upon collection. To obtain these samples, undisturbed

sediment cores (35 cm length) were collected using polycarbonate core liners (∅ 5.5 cm) in both sub-tidal (n=8) and intertidal environments (n=8), with each environment sub-sampled for sandy and muddy sediments in equal proportions. Resulting fluxes from all analyzed cores where then averaged and the latter value, with its associated uncertainty, used in subsequent mass balance calculations.' Most of the intertidal areas mentioned are covered in a muddy-silty layer as typical of intertidal marshland, and these were sampled. Hence part (necessarily, as we cannot assume under this budget framework that we are covering all bases completely and have to accept some uncertainty) of the contribution of Rn to the budget is already accounted for, since the diffusive fluxes comprise an average of those measured in sandy and muddy-silty areas, with the associated uncertainty of the mean is also propagated into the calculation. The area employed to upscale this data to basin scale is the Mean Tidal Area, which would cover most of the marshland sections of the map. Since for impermeable sediments we accept that no significant convective or advective water inputs occur (given the poor hydraulic conductivity of the muddy coverage), we accept that most of this contribution will be accounted for in our budget.

Minor suggestions:

1. I found confusing the use of two names interchangeable for each inlet (p. 12440 l2) especially when only one name is given in Figure 1. Is this necessary?

R: This is a fair comment, and has been put forward by the other reviewers as well. We addressed the issue in the following manner:
a) Figure 1 was redrafted, and now incorporates two panels, with one covering the entire extent of the system, where all the inlets are depicted.
b) There is a now a list of all the inlet denominations, with their anglicized and their Portuguese names associated with the new panel in Figure 1.
With regards to inter-changeability of names, we assume this is more of an effort to first make reading and memorization for non-Latin speakers that might find the accentuation of the Portuguese words difficult to accommodate (hence Barra-Nova rather than Faro-Olhão, for example). This might be entirely pedantic, but would also bring to the fore the local denominations, rather than those publicized in the international literature.

2. Page 12448 line 8. Because the ocean waters are Rn-poor why is the mean Rn activity higher on the flood? Here's where a more careful explanation of the tidal hydraulics might have helped.

R: Firstly, we do not treat the system as completely isolated from the adjoining coastal water mass (i.e., by employing the tidal prism method, where all water leaving the system never returns, etc). See Section 5.2, specifically P12460 L3-7, where we quite clearly state that the adjacent coastal water is affected by the mixture of lagoon water, affected by terrestrial sources and surface evaporation, and offshore seawater. This is clear from the isotope data presented in figure 4a.
Secondly, we provide further discussion on P12460-12461 in this regard. In lines 20-25 (P 12460), we infer a hydraulic connection between the Ramalhete Channel, the Ancão inlet and water masses in the eastern sector of the lagoon, as ebb progresses into flood, from the isotopic data (Fig 6a and 6b). This implies, as we then state in L29 (P12460) and then L1-6 (P12461) part of the water flowing out at ebb through the Ramalhete Channel and into the Ancão basin (where stations 3B, 4B and 5B are) is kept in the system, and hence its radon is added to theat produced by beach discharge during ebb within the lagoon – this can be through reinsertion of the

water during flood through the Barra Nova inlet toward the east, after this water masses leaves through the Ancao inlet (given the eastward along shore currents), or via a loop within the western sector (Ancão basin into the Faro Channel again and from there eastward). Because the Barra Nova inlet is flood dominated, while the others are ebb dominated, the circulation through the lagoon progresses with a westward loop (Barra Nova – Ancão inlet) and a similar loop eastward (Barra Nova – Armona Inlet) taking place and connecting hydraulic flow through these three main inlets and residual flow moving slowly eastward, which is consistent with hydrodynamic studies (Pacheco et al 2010), as we refer. See also first paragraph of the response to general comment 2 (G2, above).

3. Figure 3. It might be more instructive to plot Rn-flux versus the water depth rather than to plot both against time. The figure suggests a more complicated tidal modulation than the simplified flood-ebb analysis used earlier.

R: Indeed, but it would not add in our view any more of substance to the paper. It does suggest more complicated tidal modulation over the whole system, given that this is data from the main inlet, which is flood dominated – this is an aspect that we discuss further in P12460-61, and in the response to comment 2 above.

4. P 12451 l 25. "LEL" is not on these figures (until you get to Figure 6).

R: Here we just mention that the groundwater samples from both aquifer M10 and 12 plot along Local Evaporation Lines (defined in L25) with slopes as indicated. This intends to show that there is interaction with the atmosphere (hence evaporation) even in the groundwater flow paths. The LELs depicted in Figure 6 are surface water evaporation lines.

5. P. 12455 lines 3 and 7. Are "end-member source" and "source functions" synonyms or the authors mean some (subtle) difference between the two phrases.

R: No, there are subtle differences and we would seek to maintain these as much as possible. The subtlety arises from the perceived mode of variability of the source composition (or absence of variability) when reading its description – if it is described tout-court as a "source" one would more easily associate this, strictly speaking, to a continuous, constant composition; However, the source-function terminology carries the association with a variable end-member composition, either in time or space, that could be described by a mathematical function, for instance. The latter is more realistic.

6. Table 1 Tidal Flux. Does this make sense? More water cannot be moving in than is moving out. If the ocean water is Rn-poor how can the import of Rn be higher than the export?

R: yet, it does make sense – in a multi-inlet system. The Barra Nova (Faro-Olhão) inlet is flood dominated, while the other inlets are ebb dominated. See response to comment 2 above, and relevant discussion in P12460-61.

Next Page: Marked manuscript.

Assessing land-ocean connectivity via Submarine Groundwater Discharge (SGD) in the Ria Formosa Lagoon (Portugal): combining radon measurements and stable isotope hydrology

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Abstract

Natural radioactive tracer-based assessments of basin-scale Submarine Groundwater Discharge (SGD) are well developed. However, SGD takes place in different modes and the flow and discharge mechanisms involved occur over a wide range of spatial and temporal scales. Quantifying SGD while discriminating its source functions therefore remains a major challenge. Yet, correctly identifying both the fluid source and composition is critical. When multiple sources of the tracer of interest are present, failure to adequately discriminate between them leads to inaccurate attribution and the resulting uncertainties will affect the reliability of SGD solute loading estimates. This lack of reliability then extends to the closure of local biogeochemical budgets, confusing measures aiming to mitigate pollution.

Here, we report a multi-tracer study to identify the sources of SGD, distinguish its component parts and elucidate the mechanisms of their dispersion throughout the Ria Formosa — a seasonally hypersaline lagoon in Portugal. We combine radon budgets that determine the total SGD (meteoric + recirculated seawater) in the system with stable isotopes in water (δ^2H, $\delta^{18}O$), to specifically identify SGD source functions and characterize active hydrological pathways in the catchment. Using this approach, SGD in the Ria Formosa could be separated into two modes, a net meteoric water input and another involving no net water transfer, i.e., originating in lagoon water re-circulated through permeable sediments. The former SGD mode is present occasionally on a multiannual timescale, while the latter is a dominant feature of the system. In the absence of meteoric SGD inputs, seawater recirculation through beach sediments occurs at a rate of ~1.4x10^6 m^3 day^{-1}. This implies the entire tidal-averaged volume of the lagoon is filtered through local sandy sediments within 100 days (~3.5 times a year), driving an estimated nitrogen (N) load of ~350 Ton N y^{-1} into the system as NO_3^-. Land-borne SGD could add a further ~61 Ton N y^{-1} to the lagoon. The former source is autochthonous, continuous and responsible for a large fraction (59%) of the estimated total N inputs into the system via non-point sources, while the latter is an occasional allochthonous source capable of driving new production in the system.

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1. Introduction

Freshwater inputs into the coastal zone are important pathways for the transfer of land-borne solutes and particulates into the sea. Even if channeled freshwater flows such as rivers are relatively well-gauged world wide, sub-surface sources are more difficult to quantify in coastal settings. This difficulty has hindered the understanding of current drivers of coastal ecosystem decline (Carpenter et al. 1998; Finkl and Krupa 2003). Indeed, on a global scale, an estimated 6 % of the freshwater input into the sea, carrying an anticipated 52% of the total dissolved salts crossing the land-ocean interface, was estimated to occur via SGD-Submarine Groundwater Discharge by Zektser and Loaiciga (1993). This early estimate has since been updated by Kwon et al (2014), who show that global SGD is 3-4 times greater than the freswater flow into the oceans by rivers. This revision means that SGD is by far the largest contributor of terrestrial solutes to the global ocean, hence implying that some global biogeochemical budgets of major elements need revision. Yet, mass flows defining the contribution of SGD to coastal biogeochemical budgets are difficult to quantify in a systematic way (Burnett et al. 2001a).

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To understand the contribution of groundwater/seawater interactions to marine biogeochemistry (Moore 1996; Moore and Church 1996; Church 1996, Moore 2006), the definition of SGD encompasses any flow of water across the sea floor, regardless of fluid composition or driving force (Burnett et al. 2003). This is because reactivity of solutes when meteoric and sea water mix and travel through porous media significantly alters the composition of the discharging water with respect to both original contributions (Moore 1999; Moore 2010). Submarine Groundwater Discharge is therefore not limited to fresh groundwater discharge but includes seawater recirculation through coastal sediments (Li et al. 1999) and seasonal repositioning of the salt/freshwater interface (Michael et al. 2005; Edmunds 2003; Santos et al. 2009). All of these promote changes to the rates of transfer, mixing and chemical reaction at the subterranean estuary (Moore 1999; Charette et al. 2005; Charette and Sholkovitz 2006; Robinson, et al. 2007) altering the original chemical signatures in a non-uniform way at system scale (Slomp and van Cappellen 2004; Spiteri et al. 2008).

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Tracer-based assessments of basin-scale SGD are well developed (Burnett et al. 2001a,b; Burnett et al. 2003; Burnett et al. 2008), but because the flow and discharge mechanisms involved cover a wide range of spatial and temporal scales (Bratton 2010; Santos et al. 2012), quantifying SGD while discriminating its source functions is still a challenge (e.g., Mulligan and Charette 2006). Indeed, the most common approaches to estimate SGD are: a) radioactive tracer studies specifically looking at radon (^{222}Rn, $T_{1/2}$= 3.8 days) (Burnett et al. 2001a,b) and radium isotopes (Moore and Arnold 1996); b) direct measurement of discharge fluxes over small areas (Lee 1977, Michael et al 2003, Taniguchi et al 2003); and c) modeling. Direct measurements offer limited spatial coverage and are labor intensive (e.g., Leote et al. 2008), making reliable flux estimates at the system scale difficult. Modeling approaches depend on the water and/or salt budgets, hydrograph separation techniques, or descriptions of interfacial flow dynamics based on Darcy's law. Frequently, however, they incorporate assumptions of a steady state inventory and homogeneity of hydraulic conductivity over large scale-lengths and fail to include seawater recirculation. In addition, there is often a mismatch between spatial and/or temporal scale of the model outputs and those necessary to close coastal biogeochemical budgets (Prieto and Destouni 2010).

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Radioactive tracer studies produce spatially integrated estimates of flux (Cable et al. 1996; Moore 1996), while simultaneously dampening the effects of short-term variability (Burnett et al. 2001a). However, while radon budgets produce an estimate of 'total' SGD, i.e., freshwater inputs + re-circulated seawater (Mulligan and Charette 2006), radium budgets primarily assess the salty component of SGD given that radium is normally absent in fresh groundwater but might be mobilized from sediment particles in case of saline water influence (Webster et al. 1995). Even so, the variety of ubiquitous temporally and spatially variable sediment-water exchange mechanisms that also act as sources of radon (Cable et al. 2004; Martin et al. 2004; Colbert, et al. 2008a,b) and short-lived radium isotopes to surface waters (Webster et al. 1994; Hancock and Murray 1996; Hancock et al. 2000; Colbert and Hammond 2007; Colbert and Hammond 2008; Gonneea et al. 2008) cannot be ignored. Correctly identifying both the

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fluid source and composition is thus an important task (Mulligan and Charette 2006; Burnett et al. 2006). When multiple tracer sources of interest are present, failure to adequately discriminate between them will lead to inaccurate attribution and the resulting uncertainties will affect the reliability of SGD solute loading estimates.

Indeed, as noted by Beck et al. (2007), SGD-borne chemical load into coastal systems is usually predicted by combining measurements of source composition with SGD estimates. Linking these two datasets requires care and is underpinned by our ability to correctly identify and quantify the different SGD pathways into any one system. This is because the final SGD solute-load estimate not only depends on how accurate our recognition of the SGD source functions is, but also on the ability to track their path within the system, since this is required to evaluate the biogeochemical history of the source components prior to their mixture into receiving waters. Not fulfilling this requisite therefore constitutes the major obstacle to prognosticate upper boundary or 'potential' SGD-related impact, and more importantly, confidently attribute causality. Indeed, the endmember is usually the greatest source of uncertainty in any tracer or solute mass balance. It follows that determining the endmember concentration in the area(s) most likely to be the source(s) of groundwater would decrease uncertainty in SGD estimates, on the one hand, and in biogeochemical budgets derived from those estimates on the other. The current panorama of SGD research at the system scale therefore begs the question of which end-member to use when selecting a source solute concentration in attempts to quantify pollutant fluxes associated with SGD.

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We contribute an answer to this conundrum with a study conducted in a seasonally hypersaline lagoon in southern Portugal where we combine two datasets: radon surveys are used to determine total SGD in the system while stable isotopes in water (^{2}H, ^{18}O) are used to specifically identify SGD sources and characterize active hydrological pathways. We show that, in combination with radon budgeting, stable isotope hydrology is a reliable tool to identify different SGD sources in a very complex coastal system, even though it hasn't been used to this end before. This underuse of the methodology has two main reasons. The first is a disciplinary divide: the technique has been the domain of freshwater hydrologists; correlations between $\delta^{18}O$ and $\delta^{2}H$ are central to research into the effect of evaporation and mixing on surface waters (Gat et al. 1994, Gibson and Edwards 2002) and contribute to the disentanglement of different water sources affecting catchments (Rodgers et al. 2005). The other is the paucity of paired $\delta^{18}O$ – $\delta^{2}H$ data on coastal seawater (e.g., Rohling 2007), even if stable isotope datasets might help constrain the origins of freshwater inputs into the ocean when coupled with salinity data (Munksgaard et al. 2012, Schubert et al 2015), or as part of a methodological arsenal in SGD studies combining physical and chemical measurements with radioactive and stable isotope tracers (e.g., Povinec et al 2008). Hence we also bridge the disciplinary gap between marine chemists and hydrogeologists currently extant in SGD studies by using a combined approach merging techniques from both disciplines.

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The occurrence of SGD comprising significant freshwater contributions was first detected in the Ria Formosa in 2006–2007 and subsequently described as a prominent source of nutrients, in particular nitrogen derived from fertilizers, to the lagoon (Leote et al. 2008; Rocha et al. 2009; Ibánhez et al. 2011, 2013). However, the unpredictable nature of freshwater availability in the region, coupled with a mixed-source (i.e., a variable mix of groundwater abstraction and surface water collected in reservoirs) management of public water supply to meet demand (Monteiro and Costa Manuel 2004; Stigter and Monteiro 2008), made it unclear whether meteoric groundwater would be a persistent feature of SGD in the system. This made it difficult to clarify the contribution of SGD to the nitrogen budget of the Ria Formosa, with obvious consequences to environmental management strategies. The overarching aims of the study were therefore to identify the sources of SGD, distinguish its component parts and elucidate the mechanisms of their dispersion throughout the Ria Formosa. The outcomes are then employed to distinguish and quantify nitrogen loads carried into the lagoon by different SGD modes.

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2. Study Site

2.1. Geomorphology and Hydrodynamics

Located in South Portugal (36°58'N, 8°02'W – 37°03'N, 7°32'W), the Ria Formosa (Fig. 1) is a leaky (Kjerfve 1986) lagoon system separated from the Atlantic by a multi-inlet barrier island cordon. The system covers a surface area of ~111 km^2 and has an average depth of 2 m. The tide is semi-diurnal with average ranges of 2.8 m for spring tides and 1.3 m for neap tides (Vila-Concejo et al. 2004; Pacheco et al. 2010a). The maximum average tidal volume as estimated by the Navy Hydrographical Institute (IH 1986) is ~140×10^6 m^3. Lagoon water is exchanged with the Atlantic Ocean through six tidal inlets with an average tidal flux of ~8×10^6 m^3 (Balouin et al. 2001). Estimates for the submerged area amount to ~55km^2 at high spring tide and between 14 and 22 km^2 at low spring tide (IH, 1986). From west to east (Fig. 1), inlets (*Barra*, in Portuguese) are identified as Ancão, Faro-Olhão (*Barra Nova*), Armona (*Barra Velha*), and Fuzeta, Tavira and Lacem. Barra Nova, Barra Velha and Ancão jointly capture ~90% of the total tidal prism: 61%, 23% and 8% of the total flow during spring tides and 45%, 40% and ~5% during neap tides, respectively (Pacheco et al. 2010). With the exception of the Barra Nova all inlets are ebb dominated with residual circulation directed seaward (Dias and Sousa 2009).

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Comment [17]: C5845-T2; See redrawn Figure 1.

2.2. Hydrogeological setting

The regional climate is semi-arid, with average annual temperature of 17 ºC and averages of 11°C and 24°C during winter and summer. The surrounding watershed covers 740 km^2 and receives effective precipitation of 152 mm/year (Salles 2001), corresponding to an annual rainfall amount of ~1.2×10^6 m^3. There are five minor rivers and fourteen streams discharging into the lagoon. Most are ephemeral and dry out during the summer, the exception being the River Gilão, which intermittently discharges almost directly into the Atlantic through the Tavira inlet at the eastern limits of the system.

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Three aquifer systems (Fig. 1) border the Ria Formosa (Almeida et al. 2000). These are the Campina de Faro (M12), Chão de Cevada – Quinta João de Ourém (M11) and São João da Venda – Quelfes (M10). The main lithologies supporting these units are Plio-Quaternary, Miocene and Cretaceous formations, comprising respectively Pliocene sands and gravels, Quaternary dunes and alluvial deposits; sandy limestones of marine facies; and limestones and detritic limestones. The oldest formation dips to the south, and is found at depths in excess of 200 m near the city of Faro. It is overlain by the Miocene formation extending below the Ria Formosa into the Atlantic Ocean. Sand dunes, sands and gravels of the Plio-Quaternary cover the Miocene and Cretaceous formations within the coastal area. The Campina de Faro (M12, Fig. 1, 86.4 km^2) comprises a superficial unconfined aquifer (Pleistocene deposits) with a maximum thickness of 30 m and an underlying Miocene confined multi-layered aquifer, which Engelen and van Beers (1986) suggest discharges directly into the Atlantic Ocean bypassing the lagoon. The unconfined Pleistocene aquifer is hydraulically connected to the underlying Miocene aquifer. The São João da Venda-Quelfes aquifer (M10, Fig. 1, 113 km^2) includes a surface 75 m thick layer of Wealdian facies and an underlying Cretaceous layer of loamy limestone. It contacts with the M12 (Campina de Faro) aquifer and the M11 (Chão de Cevada-Quinta João de Ourém) to the south, and the main flow direction on the eastern side is towards the southeast. Groundwater flow is divergent toward the southeast and the southwest from a central point (Almeida et al. 2000).

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In the 1980's nitrate contamination from inorganic fertilizers was detected in both Quaternary and Miocene sub-units of the Campina de Faro (M12) aquifer (Almeida and Silva 1987). Average concentrations where 8.3 mmol L^{-1} with some samples containing in excess of 28.6 mmol L^{-1}. More recently, Lobo-Ferreira et al (2007) calculated an average concentration of 2.1 mmol L^{-1} over the entire aquifer, an estimate that is consistent with the long-term (1995–2011) average (n=31) of 1.87 ± 0.35 mmol L^{-1} nitrate concentration reported from public groundwater quality data (http://www.snirh.pt) in a monitoring borehole in Montenegro, close to the boundary with the Ria. During 2006–2007, nitrate and ammonium concentrations of up to 187 and 40 μmol L^{-1} respectively were measured in SGD collected by seepage meters deployed at the littoral zone of the barrier islands. The upper bound mean nitrate concentration in the freshwater component of SGD was estimated at ~0.4 mmol L^{-1} (Leote et al. 2008).

3. Methods

3.1. Radon measurements

3.1.1. Lagoon radon inventory during ebb and flood

Water radon (^{222}Rn) content was measured continuously in-situ using two electronic Durridge RAD-7 radon-in-air monitors deployed in tandem on a moving rubber boat during winter (December 2009) and spring (May 2010). Each monitor was coupled to an air-water equilibrator (Durridge RAD-Aqua Accessory) via its own air loop. Non-cavitating centrifugal pumps were used to flush water from ~50 cm below the water surface directly into the equilibrators, at a flow rate of 1.8–2.5 L min^{-1}. HOBO™ temperature sensors and a CTD diver (Schlumberger™) continuously recorded the temperature in the mixing chambers and the salinity and temperature of the water being pumped. Counting interval was set at 20 minutes on each RAD-7 monitor, with the two machines staggered by a 10-minute period, allowing for simultaneous replication of 20-minute integration periods over the route and increased temporal resolution. Full equilibration between the air within the air-loop and the pumped seawater was achieved before surveys started. Sampling began near low tide and continued without interval for 24 hours. The survey path, recorded with an on-board GPS unit, and the timing were designed to cover the main navigable sectors of the whole lagoon at different tidal stages (ebb and flood) within the course of two complete tidal cycles. In-water radon activity was calculated from the temperature and salinity dependant gas/water equilibrium (Schubert et al. 2012). Radon activities obtained this way were then corrected by the local ^{226}Ra supported activity, to obtain excess (i.e., unsupported) radon activities. For mass balance purposes, the excess radon inventories were calculated by multiplying the unsupported radon activity from the continuous measurements by the local bathymetric depth, and then normalized to mean tidal height (Burnett and Dulaiova 2003).

3.1.2. Tidal variability of Radon activity at fixed locations

Time series of radon activity were obtained synchronously at two fixed locations within the Faro channel (Fig. 1), during June 2010. The locations were chosen in order to gain insight into the exchange of radon between the lagoon and the adjacent coastal zone through the Barra Nova (Fig. 1) and between the inner reaches of the lagoon and the latter via the Faro channel (Quatro Águas, Fig. 1). Radon activity was measured as described previously, with the added deployment of a CTD diver (Schlumberger™) recording depth, salinity and temperature at the bottom of the channel. The Barra Nova tidal cycle data was then used to calculate the net exchange of radon with the adjacent coastal zone through the main inlet, assuming a vertically well-mixed water column. Exchange of radon through the inlet cross section driven by oscillating tidal flow was determined by first calculating the instantaneous directional flux, $F_{Rn}(\Delta t)$, where Δt is the counting interval, $A_{Rn}(\Delta t\,)$ the activity of radon integrated across the counting interval and dh/dt the change in tidal height (r.m.s.l.) occurring over that interval:

$$F_{Rn}(\Delta t) = \left(\frac{dh}{dt}\right) \times ARn(\Delta t) \qquad (1)$$

The total radon flux was obtained for both the flood and ebb periods by integrating the instantaneous directional fluxes calculated for each counting period (Eq. 1) over time. Radon outflow (when fluxes were negative) and inflow (when positive) are hence obtained for each complete semi-tidal period. Difference between successive outflow and inflow periods gives us the net transfer across the channel during a complete tidal cycle. Data for a minimum of three successive complete tidal cycles, giving three different values for net transfer, were used, and the exchange values determined for each cycle were then averaged to obtain the net exchange flux along the channel at each sampling site.

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3.1.3. Complementary radon measurements

Measurements of air temperature, wind speed and atmospheric radon activities were taken on land, while the lagoon radon survey progressed. Atmospheric evasion losses (radon degassing flux) were calculated as described in Burnett and Dulaiova (2003), using the equations given in Macintyre et al. (1995) and Turner et al. (1996). Sediment-water diffusive fluxes of radon were measured as described in Corbett et al. (1998) in samples (*n*=16) collected throughout the lagoon and directly analyzed in the laboratory upon collection. To obtain these samples, undisturbed sediment cores (35 cm length) were collected using polycarbonate core-liners (∅ 5.5 cm) in both sub-tidal (n=8) and intertidal environments (n=8), with each environment sub-sampled for sandy and muddy sediments in equal proportions. Resulting fluxes from all analyzed cores where then averaged and the latter value, with its associated uncertainty, used in subsequent mass balance calculations.

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3.1.4. SGD flux estimates based on Rn mass balances

Lagoon Radon budget under steady state assumptions

The advective flux of radon associated with SGD is determined by the closure of a radon budget incorporating all known sources and sinks of radon in the system (Burnett and Dulaiova 2003). Mass conservation accounting for the change in inventory of radon was expressed as:

$$\left(\frac{dI_{Rn}}{dt}\right) = Rn_{dif}f - Rn_{dg} - Rn_{dy} + (Rn_{imp} - Rn_{\exp}) + Rn_{adv} \qquad (2)$$

where I_{Rn} is the radon inventory measured within the Ria Formosa, *t* the time, Rn_{diff} the Radon flux across the sediment water interface by diffusion, Rn_{dg} the radon degassing flux, i.e., atmospheric evasion, Rn_{dy} the radon decay flux in the lagoon (i.e., the internal sink), Rn_{exp} and Rn_{imp} the exchange fluxes across inlets, seaward (export) and landward (import), respectively, and Rn_{adv} the advective Radon flux putatively associated with SGD. Usually, an additional term accounting for the radon influx via river flow is added if the water and particulate flux associated with river discharge is significant. However, the only perennial river in the Ria Formosa is the Gilão, located in the eastern limit of the lagoon. Salinity measured at the estuary mouth was 29.6 (Table S1), which in combination with its location implied very low if any inputs of freshwater carrying radon into the system so we neglected the term.

Assuming steady state of all sinks and sources over the lifetime of radon in the system, then:

$$\left(\frac{dI_{Rn}}{dt}\right) = 0, (Rn_{imp} - Rn_{\exp}) = Rn_{net} \Rightarrow Rn_{adv} = Rn_{diff} - Rn_{dg} - Rn_{dy} + Rn_{net} \qquad (3)$$

where Rn_{net} is the residual Radon exchange flux with the ocean.

Mass balance of radon during ebb and flood

Inventories of radon in the lagoon were determined during ebb and flood. Taking the tide as a travelling wave, the change in inventory of radon as the tide floods and ebbs has to be balanced by all known radon fluxes occurring within the traversed system during the travel period. If we then take the mean tide level (MTL) as a reference, it follows that the Rn_{adv} term may be calculated for different periods: the period (*T*) at which the tidal height in the lagoon is below MTL (Rn_{adv} $(T<MTL)$), i.e., the trough of the tidal wave or low tide, and the one when it is above MTL (Rn_{adv} $(T>MTL)$), corresponding to the peak of the wave, or high tide. Assuming constant mean amplitude for the tidal wave the corresponding mass conservation equations may be written as follows:

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$$Rn_{adv}(T < MTL) = \frac{If - Ie}{\Delta t} - (R_{diff} - Rn_{dg} - Rn_{dy} + Rn_{net}) \qquad (4a)$$

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$$Rn_{adv}(T > MTL) = \frac{Ie - If}{\Delta t} - (R_{diff} - Rn_{dg} - Rn_{dy} + Rn_{net}) \qquad (4b)$$

where *If* and *Ie* are the flood and ebb inventories of radon in the lagoon, Δt the period of the wave (~0.5 day) and Rn_{adv} $(T<MTL)$ and Rn_{adv} $(T>MTL)$ the radon advective fluxes associated with each semi-period (trough and peak stages, respectively). The corresponding continuity equation, describing the net advective flux of radon on a daily basis (note that for semi-diurnal tidal periodicity we assume 1 day ~ 2 tidal periods), is then:

$$\frac{Rn_{adv}}{2\Delta t} = \frac{Rn_{adv}(T < MTL)}{2} + \frac{Rn_{adv}(T > MTL)}{2} \tag{4c}$$

3.2. Stable isotope hydrology

Sampling location and timing

Water samples for stable isotope analysis were collected in triplicate from all possible water sources to the lagoon (end-members) during winter on various occasions between 2007 and 2011 (Table 2 and S1). These include: the marine end-member, sampled in 2009; groundwater from local aquifer units (M10, M12, unconfined aquifer lenses in the Barrier island) taken from boreholes and wells (Fig. 1), in January 2007 and December 2009 and 2010; precipitation, taken at the city of Faro in December 2009; beach porewater collected in January 2007, December 2010 and January 2011. In 2007, samples where extracted from 50 cm below the sediment-water interface at various locations along the Ancão peninsula's inner dune cordon (Fig 1), while in 2010 and 2011 they originated from various depths in the sediment (2 to 7 m below r.m.s.l.) and where collected using a cross-shore array of nested, multi-level sampling piezometers (Fig 1) installed in the inner margin of the outer dune cordon in January 2010 at the point of maximal freshwater seepage rates found in 2007. Surface water reservoirs near Quinta do Lago used for irrigation and settling lagoons in the wastewater treatment plant near the city of Faro (WWTP) where sampled in July 2007, the river Gilão (Fig 1), in December 2010, and surface water from the lagoon was sampled during flood tide (western sector, Fig 1) in January 2007 and during both high and low tide in December 2009.

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Comment [24]: C5845-T9. See changes to Fig 1. Also, changes to site description.

For the latter, quasi-synoptic distributions of $\delta^{18}O$ and $\delta^{2}H$ in water at different tidal stages were obtained. For this purpose, we followed the division of the lagoon into two sectors, comprising western and eastern areas (see Fig. 1), with the separation line lying between the city of Faro and the Barra Nova. This division was based on the known divergent flow of groundwater in the M12 and M10 aquifers from a central point (Rio Seco – Chelote line, Fig 1) as described (see Section 2.2) in Almeida (2000). High-powered boats were deployed, one

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Comment [25]: C5845-T10. See changes to Fig 1 (new panel, with all the inlets named)

from the city of Faro, on the 2nd December 2009 and the other from the city of Olhão, on the 5th December 2009 (Fig 1). The boats followed the tide outflow (or inflow) while covering all the pre-defined sampling points (western sector stations 1-5 and 1B to 5B, eastern stations A to I, Fig. 1). Each region of the lagoon was covered at each tidal stage in no more than two hours around slack tide. Coastal seawater adjacent to the Ria Formosa was sampled two nautical miles (~3.8 km) offshore from the town of Quarteira to the west and from the Barra Velha (Armona inlet, Fig. 1, reference J).

Sampling and analytic methodology

Water was directly filtered through Rhizon SMS™ membranes into sterile glass Vaccutainer™ vials in the field. Subsequently, the cap area including the rubber septum was sealed with a layer of hot glue encased in Parafilm™. The vials were kept preserved at 4°C until analysis could occur (typically within six months from the date of collection). Samples were sent for standard analysis of $\delta^{18}O$ and $\delta^{2}H$ to GEOTOP Canada (Micromass IsoprimeTM dual inlet coupled to an Aquaprep TM system), Durham University (LGR - liquid water isotope analyser, DT100) and at UFZ's stable isotope laboratory facilities in Halle, Germany (Laser cavity ring-down spectroscopy (Laser CRDS) Picarro water isotope analyzer L-1120i). Following standard reporting procedures (Craig 1961a), delta values (δ) are reported as deviations in permil (‰) from the Vienna Standard Mean Ocean Water (V-SMOW), such that $\delta_{sample} = 1000((R_{sample}/R_{V\text{-}SMOW})-1)$, where R is the relevant isotopic ratio (i.e., either $^{2}H/^{1}H$ or $^{18}O/^{16}O$). The mean analytical uncertainty is reported for each data point as ± 1 standard deviation (s.d.) of the mean of *n* analysis results obtained for *n* replicate samples in ‰ for $\delta^{18}O$ and for $\delta^{2}H$ (see Table 2). Each laboratory uses stringent protocols and reporting of stable isotope values using internationally calibrated standards; hence, reported stable isotopes values of water between the different labs used in this study are directly comparable.

Inter-annual comparability of isotopic data

Sampling campaigns where carried out strategically following a field-adaptive protocol. Of primary concern was to capture the extent of temporal end-member

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Comment [26]: C5845-9; C6187-1, S16 (Entire new section introduced, see also new Table 2)

variability in isotopic signature under maximum freshwater flow (hi-flow) conditions, in order to a) guarantee coherence of source compositions to feed into mixing models when necessary while assessing the hydrology of the lagoon over wider temporal scales and b) minimizing logistics and costs while guaranteeing inter-comparability. For this purpose, winter season was chosen given that ~61% of the mean annual precipitation falls on the region between November and February (34% in the months of December and January). Stable isotope sampling in winter had the added advantage of minimizing kinetic effects over stable isotope signatures given the lower evaporation potential. Sampling in winter 2007 was exploratory, with two main objectives: firstly, to characterize isotopic signature of M12 groundwater and surface lagoon waters in the western sector, particularly in the area that could be potentially influenced by both SGD and the WWTP outflow under maximum dilution potential (hence high tide), and secondly, conduct an exploratory survey of potential seepage areas along the Ancão peninsula, keeping in mind that the location of at least one of the important SGD seepage sites was known (Leote et al, 2008). Detection of the isotopic signature of groundwater in porewaters at the seepage face at stations Pw_e and Pw_f (Table S1) led to the installation at their location of a nested piezometer transect array in January 2010. This was subsequently used to obtain porewater samples in the 2010/11 winter season (December 2010 and January 2011).

To capture inter-annual variability, the M12 aquifer was sampled twice (winters of 2007 and 2009), with the provision of one common location (Ramalhete) for cross-referencing. Following the same reasoning, the M10 aquifer was sampled in December 2010 while simultaneously sampling Rio Seco (belonging to M12, Table S1). This ensured inter-comparability between groundwater isotopic signatures in 2009 and 2010. Campaigns were planned in advance considering the precipitation over the region to ensure similarity in the hydrological regime and ultimately guaranteeing inter-comparability of results. The sampling itself took place in dry conditions as much as possible, and never after intensive rain that could have promoted flooding (Table 2, Fig 4d). For example, while January 2007 was a dry month (8.8 mm) compared to the historical average (138 mm), the accumulated precipitation during the previous 3 months was 369.7 mm, consistent with the historical average (Table 2). By contrast, both December 2009 and 2010 were relatively wet months (392.2 and 269.6 mm), but followed relatively dry 3-month periods (Table 2). So porewater samples were also taken in January 2011, hence complementing winter 2010/2011. January 2011 followed a wet three-month period (414.7 mm) and was hence comparable with January 2007, also relatively dry but on the back of three wet months (369.7 mm cumulative). The combined dataset therefore contains results from repeated measurements for end-member isotopic composition under hi-flow conditions, across different years. These are in addition compared to historical data (table S1, Figure 4), leading to a temporally coherent quantitative overview of stable isotopic hydrology over the catchment.

4. Results

4.1. Radon

4.1.1. Spatial and temporal distribution

The activity ranges and spatial distribution of ^{222}Rn were similar in winter and spring. Because the weather was stormy during winter sampling, the uncertainties associated with determination of the radon evasion fluxes affecting the overall lagoon radon inventory were much higher than in spring (see Table 1). Indeed, using a mass-balance used estimate fluxes has been shown sensitive to parameterization of gas exchange (k) with the atmosphere, with potential uncertainties reaching 58% (Gilfedder et al, 2015). Hence only the spring survey data is presented and discussed. Excess radon activities measured in water varied between 3.5 and 37 Bq m^{-3}, with a narrower range (5-25 Bq m^{-3}) measured during ebb. The highest activities within the western sector during this stage (>25 Bq m^{-3}) were measured close to the city of Faro and in the Ramalhete channel, and close to the city of Olhão (~20 Bq m^{-3}) in the eastern sector. Radon activities generally declined from the northwest to the southeast during ebb tide, with the lowest values (~5 Bqm^{-3}) found in the Olhão channel

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Comment [27]: C5845-10. Table 1 now contains data from the Winter campaign, section updated accordingly.

northeast of the Barra Nova. Conversely, the lowest activities during flood (~5 Bq m^{-3}) were measured close to the Ancão inlet and at the outer end of the Faro channel, suggesting radon-poor coastal water intrusion during flood tide. The mean radon activities throughout the lagoon were 19.3 ± 4.74 and 15.59 ± 4.54 Bq m^{-3} respectively during flood and ebb. Relative accumulation of radon occurred at specific locations in the lagoon (Fig. 2a,b). The highest local water column inventories (318 and 267 Bq m^{-2} during flood and ebb, respectively) were found in the Faro channel, covering stations 3 to A during ebb and 4 and 5 during flood. The eastern sector water column inventories were much higher during flood than during ebb. Given the non-random spatial distribution of radon, the median of each dataset was used to calculate whole-lagoon inventories. The MAD (median absolute deviation, Hampel 1974) was then used to propagate uncertainty in the radon budget calculations (Table 1). Radon inventories (median ± MAD) were 54.2 ± 17.8 and 74.0 ± 17.6 Bq m^{-2} respectively during ebb and flood (Table 1).

4.1.2. Along-channel tidal radon fluxes

Radon activity at Quatro Águas and Barra Nova was strongly anti-correlated with water level. At Quatro Águas, radon activities varied between 0 and 40 Bq m^{-3} while at Barra Nova they varied between 1 and 31 Bq m^{-3}. Tidal variability at these two points was therefore consistent with the ranges in radon activities found during the lagoon survey. Time series of instantaneous Rn fluxes obtained as described by Eq. 1 are depicted for both locations in Fig. 3. The plots show consistency in the magnitude of upstream and downstream radon fluxes (grey area under the curves) through successive tidal cycles. The net daily tidal exchanges of radon through the Barra Nova and the Quatro Águas site (8.0 ± 0.5 × 10^4 and 9.9 ± 2.0 × 10^3 Bq d^{-1}, respectively) were both directed landward. This finding is consistent with the Barra Nova being a flood-dominated inlet (channeling ~64% of the flood and ~59% of the ebb prism of the Ria Formosa during spring tides: Dias and Sousa 2009; Pacheco et al. 2010b). To calculate the total residual exchange of radon between the Ria Formosa and the adjacent coastal area, we assumed the radon flux occurring at the other inlets to be proportional in equal measure to the individual residual tidal prisms. After adjustment to the lagoon surface area at MTL the net exchange was just -9.3 (± 1.6) × 10^{-4} Bq m^{-2} d^{-1} (Table 1), so small as to be well within the uncertainty of all other quantities in the mass balance, implying that the radon inventory within the lagoon is controlled by internal fluxes.

4.1.3. SGD estimates based on radon mass balance

Solving eq. 3 for a radon inventory of 65.9 ± 19.6 Bq m^{-2} (Table 1) gave a result for Rn_{adv} of 7.14 ± 5.18 Bq m^{-2} day^{-1}, which adjusted to the submerged area at mean tide level (Tett et al. 2003) gives an SGD derived radon flux of 4.14 (± 3.00) × 10^8 Bq day^{-1} for the entire lagoon. Alternatively, the advective radon fluxes calculated as per equations 4a and 4b for low and high tide periods were respectively 46.8 ± 38.8 and -32.5 ± 27 Bq m^{-2} day^{-1}. The positive and negative signs imply an advective flux of radon (Rn_{adv}) into the lagoon water column at low tide, while a net loss occurs during high tide. The resultant net Rn_{adv} (Eq. 4c) occurring during a full tidal period is 7.15 ± 8.4 Bq m^{-2} day^{-1}, statistically equivalent to the flux calculated via the assumption of steady state of the system over the lifetime of radon on a daily timescale (Eq 3), and yielding an equivalent SGD-derived radon flux of 4.14 (± 4.87) × 10^8 Bq day^{-1} for the entire lagoon.

4.2. Stable Isotope hydrology

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Comment [28]: C5845-14. Section re-written for clarity. See also redrafted section 3.2, and additional material in Table 2.

4.2.1. $\delta^{18}O$ versus δ^2H relationships in the catchment

Water stable isotope compositions obtained during this study, as well as Global Network of Isotopes in Precipitation (GNIP) (IAEA/WMO 2013) and other literature-sourced data (Carreira 1991) are listed in Table S1. During the 2007 and 2009 winter surveys only unit M12 was sampled for fresh groundwater, but both the M12 and M10 aquifer units were sampled in winter 2010. Nonetheless the compositional range of fresh groundwater samples was quite similar: the most depleted values reported had a $\delta^{18}O$ value of -5.09 ‰ (Pechão Gimno, M10) and a δ^2H value of -27.79 ‰ (Gambelas, M12) while the most enriched had a $\delta^{18}O$ value of -3.46‰ (Rio Seco, M12) and a δ^2H value of -21.45 ‰ (Zona industrial, M12). The compositional ranges of ~1.63 ‰ for $\delta^{18}O$ and ~6.34 ‰ for $\delta^{2}H$ for groundwater were much narrower than those found in GNIP records for the city of Faro (respectively ~8.43 ‰ and ~57.3 ‰). Nevertheless (Fig. 4a), the amount-weighted average isotope composition of precipitation inputs into the Ria Formosa catchment ($\delta^{18}O$ = -4.8 ‰ and $\delta^{2}H$= -27.13 ‰) taken from the GNIP dataset (1978–2001) plots slightly above the Global Meteoric Water Line (GMWL, Clark and Fritz 1997) and below the Western Mediterranean Meteoric Water Line (WMMWL, Celle-Jeanton et al. 2001). In conjunction with the average isotopic composition of groundwater in the catchment, that of seawater (Carreira 1991) and adjacent coastal water, a precipitation-seawater mixing line (PP-SW Mix, Fig 4) may be defined ($\delta^{2}H = 5.37 \times \delta^{18}O - 1.7$, r^2=0.99). The slope of this mixing line is similar to that found by Munksgaard et al. (2012) for the Great Barrier Reef (i.e., 5.66). Additional relationships framing the isotopic composition of the waters in the catchment in δ-space include the Local Meteoric Water Line (LMWL), defined by Carreira et al. (2005) as $\delta^{2}H = (6.44 \pm 0.24) \times \delta^{18}O + (3.41 \pm 1.13)$ and the Eastern Mediterranean Meteoric Water Line (EMMWL, Gat and Carmi, 1970). This is introduced as an extreme boundary to the isotopic composition of precipitation in southern Portugal. Indeed, rain with high *d-excess* originating either from the eastern Mediterranean or aligned with extreme precipitation events might fall in the region (see Fig. 4c), particularly during summer and/or autumn (e.g., Frot et al. 2007).

4.2.2. $\delta^{18}O$ and $\delta^{2}H$ in groundwater

In winter 2007, the stable isotope composition of groundwater in M12 reveals slight evaporative enrichment by comparison to the GMWL and LMWL, plotting along the precipitation seawater mixing line (Fig. 4b). The isotopic compositions of surface waters (WWTP settling lagoons and lagoon surface waters) and porewaters plotted between the LMWL and the PP-SW mixing line (Fig. 4b), suggesting their composition was controlled by the interplay between the mixture of sea and groundwater and evaporation–condensation cycles occurring along the hydrological travel path. In winter 2009 however, the range of isotopic compositions of surface water samples (~2.87 ‰ for $\delta^{18}O$ and ~3.96 ‰ for $\delta^{2}H$) was significantly different (see inset, Fig. 4c). Their composition then fell between the WMMWL and the PP-SW mixing line. Even though the number of samples taken in winter 2007 was lower than those taken later and tide-specific sampling was absent, comparison of samples taken in both winters at high tide slack (Table S1; Stations 2, 3, 4, A and 3B) shows the isotopic composition of water in the Ramalhete and Faro channels was distinct — the observed difference in range cannot therefore be attributed to the sampling strategy. Groundwaters across the catchment could be divided into three distinct groups: samples from Pechão Gimno, Pechão Serra and Pechão Zona industrial (Table 2), all from unit M10, plot above the GMWL and the LMWL, while samples taken from the unconfined aquifer wells in the outer barrier islands belonging to the unconfined M12 aquifer (i.e., Deserta, Table S1), plot distinctly below the PP-SW mixing line. In between, M12 samples plot along (Ramalhete) and below the PP-SW Mixing line (Costa, Chelote, Rio Seco). Samples from unit M10 plot along a local evaporation line (LEL) with slope ~4.5 while samples from unit M12, excluding the ones located within the Ria Formosa, plot along a LEL with slope ~4.1.

4.2.3. Isotopic composition of beach porewater

The pore water isotope compositions differed significantly between the winter of 2007 and that of 2010/2011. Beach groundwater was sampled both during spring and neap tides from sediment depths ranging from 50 cm to 3.5 m below MTL across a beach profile from the upper to the lower intertidal during the latter period. $\delta^{18}O$ ranged from 0.96 ‰ to -0.20 ‰ and $\delta^{2}H$ from 2.5 ‰ to 8.5 ‰ and plotted close to the LMWL (Fig. 5a) along an evaporation line defined by $\delta^{2}H = (4.02 \pm 0.56) \times \delta^{18}O + (4.51 \pm 0.31)$, n=24, r^2=0.702, not shown). The slope of this LEL is slightly lower than those of the groundwater LELs (4.1 for the M12 and 4.5 for the M10). The data fell into three distinct groups (Fig. 5a,b) according to the relative position of the sampling point within the beach section. The first group of samples (average $\delta^{18}O$ of 0.0 ± 0.13 ‰ and $\delta^{2}H$ of 3.5 ± 0.93 ‰, n=5) corresponded to the unsaturated and intermediate zones (upper intertidal), while the second (average $\delta^{18}O$ of 0.4 ± 0.31 ‰ and $\delta^{2}H$ of 6.1 ± 0.47 ‰, n=10) and third groups (average $\delta^{18}O$ of 0.7 ± 0.18 ‰ and δ^2H of 8.0 ± 0.37 ‰, n=9) were isotopically heavier and included in that order pore water from the deeper (>2m below the surface) and shallower (<1m below the surface) areas of the beach section. The respective average pore water stable isotope compositions plotted close to the LMWL (Fig. 5a), showing enrichment in opposition to distance from the surface in the saturated zone and depletion in the unsaturated recharge zone, probably due to capillarity effects (Barnes and Allison 1988). The dependence of d-excess (Dansgaard 1964) on $\delta^{18}O$ (Fig. 5b) illustrates the deviation of porewater composition from Craig's (1961b) GMWL ($\delta^2H = 8 \times \delta^{18}O + 10$) along significantly linear slopes dependent on local evaporation conditions. Indeed, porewater *d-excess* from deeper within the beach plots along the line defined by $d = -6.7 (\pm 0.27) \times \delta^{18}O + 5.57 (\pm 0.13)$ (n=10, r^2=0.987, P<0.0001) while that from shallower areas plots along the line defined by $d = -7.1 (\pm 0.69) \times \delta^{18}O + 7.28 (\pm 0.52)$ (n=9, r^2=0.937, P<0.0001). These define slopes in δ-space close to 1 and are consistent with the flow paths taken by beach groundwater between the seawater infiltration point at the higher beach face (higher *d-excess*) and the exfiltration point at the seepage face (lower *d-excess*). For the intermediate group of samples, longer flow paths (larger *d-excess* range) and less evaporative enrichment (lower average $\delta^{18}O$) are consistent with tidal-forced circulation at larger depths within the beach face. Conversely, shorter flow paths (relatively narrow *d-excess* range) and more evaporative enrichment (higher average $\delta^{18}O$) characterize shallower circulation pathways.

Interannual variability was also significant. The range of ~1.16 ‰ for $\delta^{18}O$ and ~6.03 ‰ for δ^2H found in 2009–2011 was 50% and 36%, respectively, of the 2007 range, in spite of a common sampling location. Furthermore, isotopic compositions for pore water collected in 2007 plotted in δ-space clearly in between the LMWL and the PP-SW mixing line (Fig. 4b), while the 2010–2011 samples overlap the LMWL (Figs. 4c and 5a). This occurs in spite of fewer samples being taken in 2007 and their depth of 50 cm below the surface, in contrast with the wide range of sediment depths sampled during 2009–2011. Paired ranges of pore water salinity also differ, varying between 21 and 36 in

2007 and between 36 and 43 in 2010 and 2011. These results suggest different water source functions were present during each sampling period.

4.2.4. Tidal variability of surface water $\delta^{18}O$ and $\delta^{2}H$

Tides have a significant effect on the range of isotopic composition of surface water within the lagoon (see Fig. 6). In both lagoon sectors, the isotopic compositional range of water was much wider at low tide (Fig. 6a) than at high tide (Fig. 6b) but this variability was more apparent in the western sector. During low tide there $\delta^{2}H$ ranged from 5.3 ‰ (Station 2B) to 7.9 ‰ (Station 2) and $\delta^{18}O$ from -0.82 ‰ (Station 2B) to 2.05 ‰ (Station 3). By contrast, $\delta^{2}H$ ranged from 5.1 ‰ at Station 3B to 7.3 ‰ at 4B, while $\delta^{18}O$ varied from -0.16 ‰ (Station 4) to 0.86 ‰ (Station 1B and 2B). The water mass at Station 2B was most depleted in ^{18}O during low tide (Fig. 6a) and the most enriched in ^{18}O during high tide (Fig. 6b) but remains at the lower end of the $\delta^{2}H$ range covered by all collected samples during both tidal stages. Aspects of tide-induced circulation are also revealed when the western and eastern sectors are compared for identical tidal stages (Fig. 6a,b). During low tide (Fig. 6a), the isotope compositions of water collected at the Ramalhete channel and the associated Ancão basin (Stations 1B to 5B, Fig. 1) plot to the left of the LMWL, with the most isotopically depleted water found in Station 2B and the most enriched found at Station 1B. Conversely, water samples collected in the Faro channel (Stations 1 to 5) plot to the right of the LMWL. The situation is reversed during high tide (Fig. 6b), with isotopic compositions of water from Stations 1B to 4B plotting to the right of the LMWL, as a result of mixing with sea and coastal water and all others plotting to the left (mixing with internal lagoon water, including pore water).

Two mixing lines, [MX-1: $\delta^{2}H = (0.97 \pm 0.08) \times \delta^{18}O + (5.70 \pm 0.09)$, $r^2=0.871$, $n=21$; MX-2: $\delta^{2}H = (1.02 \pm 0.12) \times \delta^{18}O + (7.13 \pm 0.10)$, $r^2=0.842$, $n=16$)] and an evaporation line (LEL-1: $\delta^{2}H = (3.88 \pm 0.26) \times \delta^{18}O + (3.26 \pm 0.27)$, $r^2=0.969$, $n=9$) are defined by the paired $\delta^{18}O$ and $\delta^{2}H$ values of the surface and pore waters at low tide (Fig. 6a). The MX-1 line represents the isotopic composition of pore water taken from the deeper section (2–3.5 m below the sediment surface) of the beach water table (Fig. 5) and surface waters from Station 2B in the Ramalhete Channel, the outer eastern sector locations in the lagoon (Stations A–E and J, Fig. 1) and water from the Faro channel (Stations 1–4, Fig. 1). The MX-2 line represents the isotopic composition of pore water taken from the shallower section (0.5–1.5 m) below the sediment surface) of the beach water table (Fig. 5) and surface waters of the Ramalhete Channel (1B, Fig. 1), the Ancão channel close to the inlet (Stations 3B–5B, Fig. 1) and the landward stations of the eastern sector (Stations F–H, Fig. 1). LEL-1 describes all isotopic signatures of water collected in the eastern sector and intersects the LMWL amongst the most depleted pore water samples extracted from the beach (Fig. 6a) corresponding to the unsaturated zone. During high tide, water found at Stations A, B and C (Fig. 1) retains similar isotopic compositions (Fig. 6b) to the water mass found at the same locations during low tide (Fig. 6a).

5. Discussion

5.1. Radon source attribution

In order to derive an SGD rate for the Ria Formosa we divide the end-member source activity by the advective radon flux (4.14 ± 3.00 × 10^8 Bq day^{-1}) calculated from the mass balance. However, because radon budgets include ^{222}Rn sourced in seawater recirculation, the discharging fluid composition is important to discriminate between potential sources of SGD. In fact the two modes of SGD may be separated according to whether they drive a net influx of freshwater to the system (Santos et al. 2012). Indeed, there are three identified potential sources for advective radon input to the lagoon, i.e. Table 1, water in freshwater lenses under the outer barrier islands (outer reaches of the M12 aquifer) represented by the Deserta well (mean 0.95 salinity), porewater in sandy beaches (mean 40.6 salinity) mobilized by tidal pumping (seawater recirculation), and finally, meteoric water travelling through the subterranean pathway (M12 aquifer), represented by samples taken from the Ramalhete borehole (mean 5.06 salinity). The corresponding volumetric discharges, if each of these potential sources is considered in turn to be the only source of SGD into the lagoon are 4.42 (± 4.25) × 10^6 m^3 day^{-1}, 1.36 (± 1.28) × 10^6 m^3 day^{-1} and 6.26

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(± 4.63) × 10^4 m^3 day^{-1}, corresponding respectively to ~3.16, ~0.97 and ~0.04% of the mean daily flood prism (1.40 × 10^8 m^3). When defining the radon source function, salinity is occasionally used as the discriminating parameter because of its conservative nature (Crusius et al. 2005; Swarzenski et al. 2006; Stieglitz et al. 2010). Yet, the low estimated SGD to tidal prism ratio combined with saline intrusion into the local aquifers (Silva et al. 1986; Table S1) advises against this option as the estimated discharge volumes would not have a discernable impact on the overall salinity of the Ria Formosa, leaving us without a way in which to verify the reliability of the choice. Furthermore, porewater salinity at the site where the piezometer transect is located (Fig. 1) was always very high (>35; Table S1) but could be as low as 21 in 2007, suggesting different SGD modes might be active in different years. *So how do we confidently identify the source of radon?*

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Our mass balances (see section 4.1.3) for each tidal stage suggest that radon is removed from the water column during the flood period. In the absence of any other realistic explanation we might accept that it had to be advected into the unsaturated intertidal zone during beach recharge. The daily flux of radon into unsaturated sandy sediments would then amount to 16.25 ± 13.5 Bq m^{-2} day^{-1}. Conversely, the input of radon into the water column during ebb was 23.4 ± 19.4 Bq m^{-2} day^{-1}. Because the mean radon inventory during high tide was 19.3 ± 4.74 Bq m^{-3}, a flux of 16.25 ± 13.5 Bq m^{-2} day^{-1} into unsaturated sediments would equate to a beach recharge rate of ~1.2 m day^{-1}. This figure is consistent with the discharge rates measured during 2006 by Leote et al. (2008) at the lower intertidal, which reached 1.9 m day^{-1}. If we therefore assume that beach discharge balances recharge on a volumetric basis at daily timescales, then the area of water infiltration would be ~1.13 × 10^6 m^2. Given the porosity of sandy beach sediments on site of ~0.3–0.4 (Rocha et al. 2009), recharge would only occur through about 7.5–10% of the maximum surface intertidal area of the lagoon (see section 2.1). Hence tidal pumping is a realistic explanation for the radon advected into the water column on a daily basis. Still, the radon data alone does not provide irrefutable proof that SGD estimated through the radon mass balance for June 2010 originates from seawater recirculation through beaches and pore water exchange mechanisms.

This proof is important: an example of how an unsupported choice of radon end member might significantly affect quantification of nitrate loading to the lagoon through SGD could be given at this stage to illustrate the effects of the lack of irrefutable source attribution. The mean nitrate concentration (in mg/L, spring tides, 2009 to 2011) was 0.1 for the lagoon water column, 0.81 for beach pore waters, 2.22 in the Deserta well, and 130 for the Campina de Faro aquifer (M12). Our discharge estimates based on the radon balance, would then result in potential average SGD borne nitrate loading to the Ria Formosa of 0.96, 9.8 and 8.14 Tons N day^{-1}, if the source of excess radon was respectively seawater recirculation through beach sands or fresh groundwater originating from either the lens under the dune cordon or the landward section of M12 aquifer. Two cautionary notes on these numbers should be obvious: (a) the latter would drive net N additions to the lagoon water budget while the former would not, implying that (b) the loadings based on directly multiplying fresh SGD by the average nutrient concentrations found in the end member samples ignore any transformations occurring within the interface before the mixture arrives at the lagoon proper, and therefore are likely to be overestimated.

Ferreira et al. (2003) estimated total N fluxes to the lagoon at 1028 Tons N/y (2.82 Tons N day^{-1}), with 58% (1.64 Ton N day^{-1}) originating from diffuse sources. Simple extrapolation from our data would suggest that ~34% of the total N fluxes to the lagoon, and ~59% of the non-point source loading, would arise from seawater recirculation through beaches, while the meteoric SGD sources would multiply the total N loading into the system by a factor of 6 or 5 on a daily basis, depending on the composition of fresh groundwater. These two latest figures compound our cautionary notes above. Furthermore, during winter 2010 and 2011, when pore water salinities were very high, nitrate available in pore waters at the littoral fringe was likely sourced from benthic mineralization of local organic matter (autochthonous source) and not in fresh groundwater input. Conversely, because nitrate contamination of the Campina de Faro aquifer is anthropogenic, freshwater inflow via SGD into the lagoon would also define the associated nitrate inputs as allochthonous, or “new” contributions to the system’s nutrient budget. Depending on SGD source therefore, there would be an order of magnitude difference between allochthonous and autochthonous sources of nitrate into the lagoon, even if the former might be overestimated as discussed. Accurately identifying the SGD source function would therefore be absolutely necessary to understand the biogeochemical workings of the lagoon, but this is not possible with the radon data alone, even in combination with the salinity data.

However, the stable isotope signatures of surface water bring clarity to the problem. The Local Evaporation Line (LEL-1, Fig. 6a) fitted by linear regression of the samples taken within the eastern sector at low tide intersects the LMWL close to the average isotopic signature of beach pore water in the unsaturated zone (Figs. 5a and 6a). This indicates the original composition of the surface water before evaporation and mixing takes place within the lagoon. The origin of the surface water is the recharge into the unsaturated beach area, which then reveals isotopic enrichment in proportion to its permanence within the system and the consequent extent of evaporative loss. Indeed, water in the upper intertidal at low tide will see its isotopic signature depleted within the sedimentary matrix — in the unsaturated zone, the isotopic concentration decreases quickly from a maximum at the zone of evaporation (phreatic surface) within the sediment matrix to a minimum close to the surface because of the movement of water vapor through the pores toward the surface (Barnes and Allison 1983, 1988). While this is clear for the eastern sector, within the western sector there is another surface source of water (WWTP) that further complicates the picture. This water joins the lagoon close to Station 2B (Fig. 6a). So, the pore water in the unsaturated sediments mixes over time with the lagoon recharge at high tide and water already present within the tidal wedge (c.f. Robinson et al. 2007), whereupon it leaves during beach discharge at low tide, either through shallow or deeper flow paths (Fig. 5b) and mixes with other meteoric sources and seawater (MX-1, MX-2, Fig. 6a).

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For the period between the winter of 2009 and that of 2010/2011 therefore, the combined stable isotope and radon tracer approach allows definite attribution of the SGD source into the Ria Formosa. SGD arises from seawater recirculation through the permeable beach sediments of the lagoon driven by the tide. In the absence of meteoric SGD inputs, a significant amount of the tidal prism (~1%) circulates through local sandy sediments driven by tidal pumping, at a rate of ~1.4 x10^6 m^3 day^{-1}. This implies that the entire tidal-averaged volume of the lagoon (140 x 10^6 m^3) is filtered through its sandy beaches within 100 days, or about 3.5 times a year. Based on our nutrient data, the average nitrate loading driven by this SGD mode to the Ria Formosa can now be confidently put at an average of 0.96 Ton N day^{-1}, ~59% of the non-point source nitrogen loading estimated by Ferreira et al. (2003).

Salinity (see Table S1) does not correlate well with both $\delta^{18}O$ and δ^2H, though, particularly for samples with $\delta^{18}O$ >1 ‰ and/or δ^2H >1 ‰ and S >37 ‰. With reference to surface water $\delta^{18}O$ values these comprise the most isotopically enriched waters found during low tide respectively the innermost stations in the eastern sector (Stations G, H and F; Figs. 1 and 6a) and at locations within the Faro channel (Stations 1–4; Figs. 1 and 6a) as discussed earlier. It is also the case for most pore water samples. Indeed, even if the mean composition of pore-water from different sections of the beach plots along well-defined mixing and evaporation lines (Fig. 5a,b), the average salinities of each group do not change significantly with $\delta^{18}O$ enrichment (40.2 ± 1.78, 40.6 ± 2.57 and 40.6 ± 2.07 respectively). While this observation is consistent with theory (Craig and Gordon 1965) and previous analysis on the covariance of $\delta^{18}O$, δ^2H and salinity in seawater (Rohling 2007), it also implies that the joint use of these tracers to infer the relative contribution of different source functions has to be done with care in semi-confined coastal water bodies subject to significant evaporation. As further support to this observation, we note that the mixing lines (MX-1 and MX-2, Fig 6 a) between the pore-water within the beach tidal wedge and the most enriched waters found in the western sector ($\delta^2H = (0.97 \pm 0.08) \times \delta^{18}O + (5.70 \pm 0.09)$, $r^2=0.87$, $n=21$) and between the Ramalhete Channel and Ancão Basin (Stations 3B, 4B, 5B) and the water mass near Olhão at Stations G and H ($\delta^2H = (1.02 \pm 0.18) \times \delta^{18}O + (7.13 \pm 1.01)$, $r^2=0.84$, $n=16$) are virtually the same as that characteristic of the modern surface ocean ($\delta^2H = 1.05 \times \delta^{18}O + 6.24$, $r^2=0.21$, *n*=62) within a comparable salinity range (Rohling 2007). This observation suggests in coastal ocean regions and areas of restricted exchange like lagoons, the stable isotope signature of seawater reflects important contributions arising from pore-water exchange driven by tidal pumping, amongst other mechanisms. Identifying and discriminating these contributions brings insights also into the hydrological paths active within these systems and therefore provides an invaluable tool to support reliable biogeochemical budgets.

5.2. Hydrological pathways and dispersion of SGD in the Ria Formosa Lagoon

The amount-weighed isotopic composition of precipitation over Faro (GNIP: IAEA/WMO, 2013) plots (Fig. 4a) at the intercept point of the GMWL, the LMWL (slope ~6.4) and the precipitation-seawater mixing line (slope ~5.4). The isotopic signature of precipitation hence plots close to that of groundwater, indicating that local aquifers are directly recharged by precipitation, in agreement with prior reports (Engelen and van Beers 1986). The isotopic composition of surface waters also reveals that the lagoon and the adjacent coastal water may be classified as a coastal boundary zone similar to that described elsewhere (Blanton et al. 1989; Blanton et al. 1994; Moore 2000), in which the isotopic signatures result from the mixing between offshore seawater and continental meteoric sources affected by surface evaporation.

Accordingly (Fig. 6), the stable isotope composition of water within the lagoon varies with tidal stage and will be affected on the one hand by the magnitude, origin and pathways taken by the meteoric inputs and on the other by internal mixing, driven by lagoon hydrodynamics and by the local evaporation regime. Nevertheless, the pore water end-member is part of the surface water mixture on both sampled periods, although in different ways: some pore waters (Pw_e and Pw_f; see Table 2) collected at the same site were significantly more depleted in both ^{18}O and ^{2}H during 2007 (Fig. 4b) when compared to 2009–2011 (Fig. 4c) and these are characterized by comparatively low salinities (21 and 23, Table 2). Station 2B is the closest to the Faro WWTP outlet; during low tide the water mass joining the lagoon mixture there has an isotopic signature close to the Western Mediterranean Water Line (Fig. 6a), suggesting that a meteoric source of water joins the lagoon there presumably as part of the WWTP discharge. On the other hand, the exchange in position of the isotopic signature of water at Stations 1–5 and 1B–3B with reference to the LMWL in $\delta^{18}O$ – $\delta^{2}H$ space during flood (Fig. 6b) suggests a hydrodynamic connection between the Ramalhete Channel, the Ancão inlet and the water masses on the eastern sector. This connection would occur via the Faro-Olhão inlet and associated channels as ebb progresses onto flood, linking both the stations closest to the city of Olhão (Stations E, F, G) and the ones closer to the coastal ocean (Stations A, B, C), to the water masses originally present in the western sector. Indeed, Stations 1 to 4 in the Faro channel display depletion of ^{18}O during high tide (Fig. 6b) by comparison to low tide (Fig. 6a). This provides evidence that the meteoric source present within the Ramalhete channel also influences the water in the Faro channel during high tide. Furthermore, the isotopic data suggest that part of the water mass out flowing through the Ramalhete channel during ebb tide (Stations 2B–5B) eventually end up being present at Stations F, G and H close to the city of Olhão via the inner portion of the system (Station 1B), having mixed with shallow beach groundwater (MX-2 in Fig. 6a) while water from the same region might also be led to Stations A, B and C in the eastern sector via Station 5 after mixing through the beach water table (MX-1 in Fig. 6a,b). The dominant alongshore drift in the area is eastward, and in fact, Pacheco et al. (2010) show that a strong hydraulic connection exists between the the Ancão, Barra Nova (Faro-Olhão) and Armona (Barra Velha) inlets, whereby the excess flood prism at Barra Nova is directed toward both the Ancão and the Armona ebb-dominated inlets. The combination of data indicates that the body of water ebbing in the first instance through the Ramalhete channel is partially retained within the system and ends up in the Faro channel before the subsequent flood moves it eastward, either via an internal pathway eastward from the Ancão inlet basin and/or externally, looping back into the lagoon via the Faro-Olhão inlet after exiting through the Ancão inlet (Fig. 6a,b).

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The combination of flood lag-time between the Ancão and Barra Nova inlets, the eastward alongshore drift and the meteoric source of water at the WWTP plant outlet (closest to Station 2B) creates the characteristic inversion observed in $\delta^{18}O$-$\delta^{2}H$ relationships and highlighted in Fig. 6a,b. This circulation path inferred from the isotopic composition of water is also consistent with the radon data, since the radon enriched water masses found in the Ramalhete and Faro channels (Fig. 2a) during low tide would eventually be transported toward the eastern sector via the distribution of the excess flood prism at Faro-Olhão (Pacheco et al. 2010). This would help explain why the radon inventory in the eastern sector is higher during flood tide (Fig. 2b), and why the net exchange of radon is directed into the lagoon at both Quatro-Águas and Barra Nova (Table 1), as part of the radon associated with beach seepage would be retained in the lagoon and/or transported back into the system via the Barra-Nova after exiting through the Ancão inlet.

5.3. Inter-annual comparison of lagoon hydrology using Deuterium excess

Because of the relatively higher enrichment in ^{18}O compared to ^{2}H in the residual water (Gat 1996), deuterium excess (*d-excess* = *d* = $\delta^{2}H - 8 \times \delta^{18}O$) decreases in water as evaporation progresses (i.e., as $\delta^{18}O$ increases). It follows therefore that a plot of *d-excess* versus $\delta^{18}O$ (in a similar fashion to Fig. 5b for pore water) might reveal the path taken by a particular water mass within a catchment area, because, (a) the magnitude of the fractionation imposed by evaporation along the travel path affects the *d-excess* of residual water (setting the slope of paired *d*-$\delta^{18}O$ relationships), and (b) water of different origins would have different *d-excess* values. The slope of the *d*-$\delta^{18}O$ covariance line shows the deviation of isotopic compositions from Craig's meteoric water line (Craig 1961b). Therefore its magnitude in absolute terms is proportional to the extent of evaporative enrichment, a function of the exposure time of the water to evaporation. Conversely, following the line along decreasing $\delta^{18}O$ values would lead us to the original isotopic composition of the water, set before the evaporative regime changed. These characteristics allow us to disentangle and identify the main hydraulic pathways active in the Ria Formosa and compare the two periods under scrutiny to reveal the distinct nature of SGD within the system (Figs. 5b and 7a,b).

Accordingly, four significant d-$\delta^{18}O$ correlation lines are identified in the basin (Fig. 7). In 2007, two pathways (P1 and P2) connecting the composition of M12 groundwater with water sampled in the lagoon are revealed: P1, with $d = (-1.10 \pm 0.02) \times \delta^{18}O + (4.41 \pm 0.1)$, $r^2=0.997$, $n=6$, $P{\sim}0$; and P2, with $d = (-1.85 \pm 0.05) \times \delta^{18}O + (0.72 \pm 0.11)$, $r^2=0.992$, $n=14$, $P{\sim}0$). These relations reveal the two different pathways into the Ria followed by groundwater from the M12 aquifer in 2007 (Fig. 7a). The surface water circulation pathway (P1) originates when water from the public supply (sourced in local aquifers) is treated at the WWTP and subsequently discharged into the lagoon, whereupon it circulates into the Ancão basin mixing with coastal and seawater. This pathway is consistent with the internal circulation path discussed earlier. In contrast, the groundwater pathway (P2) followed by water originating in the same aquifer crosses the subterranean estuary and emerges later (d-$\delta^{18}O$ correlation slope magnitude is higher than P1) within the lagoon where it mixes with surface waters, including seawater and the WWTP outlet emissions (Fig. 7a). Hence the isotope data conclusively show two aspects of the local water balance in 2007: on the one hand, water for public consumption was essentially extracted from groundwater sources while on the other SGD into the lagoon comprising a net water input into the system was present.

The situation later (2009–2011) was substantially different (Fig. 7b). Two major hydraulic pathways are shown in the isotopic data (P3, P4); P3, with $d = (-7.8 \pm 1.2) \times \delta^{18}O - (22.76 \pm 5.04)$, $r^2=0.813$, $n=10$, $P=0.0002$; and P4, $d = (-7.43 \pm 0.18) \times \delta^{18}O + (6.45 \pm 0.18)$, $r^2=0.979$, n=37, $P{\sim}0$. These highlight other aspects of the local water balance. Firstly, P3 suggests that groundwater from the M10 aquifer mixes with water in M12, and that the local groundwater flow follows a Northeast to southeast general direction (*c.f.* location of M10 and M12 in Fig. 1), eventually communicating under the Ria Formosa with freshwater lenses present in the barrier islands, where the *d-excess* signature of groundwater is lowest. Secondly, P4 shows that water used for public consumption in the catchment was mainly withdrawn from a direct meteoric source (position of rainwater signature, Fig. 7b). This water, upon leaving the WWTPs then mixes with surface and re-circulated seawater establishing the mixing line for the lagoon (Figs. 6a and 7b). It is also evident that the surface water samples collected in the lagoon in 2007 plot close to the P4 line, suggesting that the magnitudes of the factors driving evaporation and internal circulation in the lagoon are generally stable on a multiannual basis. This comparative approach confirms, additionally, that the subterranean pathway was not present in 2009–2011, and hence SGD at this time was comprised entirely of saline water re-circulated through the sandy beaches by tidal pumping.

The difference observed in water sources for public water supply and their isotopic signature in the catchment and subsequently released through the WWTPs into the lagoon is consistent with the changes occurring in the regional water management strategy: while water to meet irrigation and public consumption demand relied almost entirely on groundwater abstraction until the 2000's (Stigter et al. 2006), from this period onwards it was to be drawn almost exclusively from surface reservoirs North of the littoral zone. However, a substantial number of the local groundwater captions remained active in support of irrigation, while some of the major municipal captions had to be re-activated after the 2005 drought (EM-DAT 2013) to support consumption demand when surface reservoirs became depleted. In fact, because of the unpredictability of scarcity periods, the current operational thinking tends toward mixing both water sources to face demand, with the primary source being surface water reservoirs (Monteiro and Costa Manuel 2004; Stigter and Monteiro 2008). Our approach clearly indicates that this is the case for 2009–2011 as the WWTP plant water signal shows the water being discharged as meteoric in origin (Figs. 6a and 7b). Following the implementation of a mixed source water supply chain, the activity of the SGD subterranean pathway into the Ria becomes dependent on whether groundwater levels in M12 are sufficient to establish a hydraulic gradient driving the flow as was apparently the case in 2007 (Fig. 7a). Increased water mining and reduced aquifer recharge would

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provide the counterbalance by reducing groundwater levels and consequently the hydraulic gradient driving SGD of meteoric origin into the system via the subterranean estuary.

6. Concluding Remarks

We compared hydrological scenarios in a semi-arid coastal lagoon across two different periods, aiming to distinguish SGD modes and correctly identify end-member contributions to the water mixture within the system. While it has been established that radon mass conservation allows for the determination of total SGD, i.e., meteoric plus re-circulated water flow, we show that combining this information with stable isotope hydrology contributes to define and distinguish origins and pathways followed by SGD into the system. While $\delta^{18}O$ and *d-excess* paired data helped define the active hydrological pathways in the Ria Formosa, $\delta^{2}H$ *versus* $\delta^{18}O$ plots provided insights into water source functions and their dispersion through the lagoon. Using our combined approach, SGD occurring in the Ria Formosa could be separated into a discharge incorporating net meteoric water input into a receiving ecosystem (2007) and an input with no net water transfer (2009–2011). We conclude that whilst the Ria Formosa receives SGD through tidal pumping (as in 2009–2011), it is also occasionally subject to SGD inputs of meteoric origin (as in 2007) directly associated with the contaminated M12 aquifer.

In the absence of meteoric SGD inputs part of the tidal prism (1.3%) circulates through local sandy sediments driven by tidal pumping, at a rate of ~1.4 x 10^6 m^3 day^{-1}. This implies that the entire tidal-averaged volume of the lagoon (140 x 10^6 m^3) is filtered through its sandy beaches within 100 days, or about 3.5 times a year, driving an estimated load of ~350 Ton N y^{-1} into the lagoon. Conversely, using the estimates for the upper bound of N concentration found in the freshwater component of SGD during 2006 (0.4 mmol L^{-1}) and the associated SGD-borne freshwater discharge of ~1.1×10^7 m^3 y^{-1} estimated by Leote et al. (2008) based on seepage meter measurements, meteoric SGD inputs could add a further ~61 Ton N y^{-1} to the lagoon. If for the former the source is autochthonous and responsible for a rather large fraction (59%) of the estimated nitrogen inputs into the system via non-point sources (Ferreira et al. 2003), leaving no direct mitigation options in the context of environmental management — it isn't so for the latter, as specific measures could be implemented in support of mitigation (e.g., Almasri and Kaluarachchi 2004). Nevertheless, the potential loadings delivered from two distinct vectors differ in magnitude, frequency and origin, and could therefore cause different ecosystem-level impacts. Hence while simple or weighted averages of end member radon activities might be useful under well defined circumstances (Crusius et al. 2005; Swarzenski et al. 2006; Kroeger et al. 2007; Blanco et al. 2011) in radon budgets to evaluate SGD as a potential pollutant source in comparison to other vectors (local surface drainage, riverine input, etc), these are of little value to effectively provide environmental managers with the causal chain alluded to in the introduction: without actual source identification and attribution, there is little that can be done to manage potential pollutant loading of coastal ecosystems via SGD.

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Figure Captions

Figure 1. Map showing location of the sampling sites within the Ria Formosa and its geographical context. The top panel shows the full geographical extent of the system, with the operational separation of the region of interest into western and eastern lagoon and the names of all the inlets; The lower panel shows an amplified map of the region of interest, including major channels, locations of sampling and tidal stations, as well as boundaries of the aquifers bordering the lagoon (M10, M11, M12).

Figure 2. Map showing the distribution of Radon inventories (Bq/m^2) within the main channels, during ebb (Panel a) and flood (Panel b), for the radon survey conducted in 2010. For more details regarding the radon budget in both December 2009 and June 2010, see Table 1.

Figure 3. Tidal variability of instantaneous radon fluxes, respectively at the inner at the Barra Nova inlet (Panel a) and Quatro-Águas station (Panel b), for the radon survey conducted in 2010. For more details on calculation methods, please see Section 3.1.2.

Figure 4. Catchment isotope hydrology. Anticlockwise, from top left: panel a shows the main meteoric water lines framing the isotopic composition of precipitation within the catchment, including the precipitation-seawater mixing line (PP-SW Mix, section 4.2.1.). Panel b plots the isotopic compositional range of water samples taken during 2007, while Panel c plots the isotopic compositional range of water samples taken during the period 2009–2011; the lagoon surface water samples (inset) are shown in more detail on Fig. 6. Panel d provides the complete record of daily precipitation over the region for the period 2006-2013 for contextual support (see also Table 2 for summarized data). EMMWL: Eastern Mediterranean Meteoric Water Line (Gat and Carmi 1970); WMMWL: Western Mediterranean Meteoric Water Line (Celle-Jeanton et al 2001); GMWL: Global Meteoric Water Line (Clark and Fritz, 1997); LMWL: Local Meteoric Water Line (Carreira et al 2005)

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Figure 5. Isotopic composition of pore water extracted in winter 2010/2011 (Table S1) at different levels depth below the surface at the saturated zone and the dynamics of the beach groundwater table. Panel a frames the compositional range and the subdivision of the isotopic characteristics through three groups, corresponding to different circulation paths within the beach (for explanation, see Section 4.2.3). Panel b frames the same samples in a *deuterium excess* (*d*) versus $\delta^{18}O$ plot, illustrating the progression of evaporative enrichment throughout the three zones and its relationship with the LMWL (Local Meteoric Water Line, Carreira et al 2005). Crosses and attached error bars represent average compositions for each group. Error bars represent ± 1 s.d.. PP-SW Mix: Precipitation-Seawater Mixing line (section 4.2.1.); EMMWL: Eastern Mediterranean Meteoric Water Line (Gat and Carmi 1970); WMMWL: Western Mediterranean Meteoric Water Line (Celle-Jeanton et al 2001); GMWL: Global Meteoric Water Line (Clark and Fritz, 1997)

Figure 6. Tidal variability of the isotopic composition of surface waters in the lagoon, framed by significant local evaporation (LEL), mixing (MX), and meteoric lines as well as the average composition of adjacent coastal water and seawater (historic data). Panel a: Low tide, and panel b: High tide. For more details, see Sections 4.2.4. and 5.2.

Figure 7. Hydrological pathways within the Ria Formosa, as defined by stable isotope data. Panel a: 2007 situation — SGD with net input of meteoric water present; Panel b: 2009–2011 — SGD essentially derived from tidal pumping. Detailed explanations are available in Section 5.3.

Tables

Table 1. Excess ^{222}Rn inventories and relevant fluxes supporting the radon mass balance for the Ria Formosa in winter 2009 and summer 2010 (see Sections 4.1 and 5.1). Notes: [a]Calculated with formulas 4a and 4b, Section 3.1.4.2; [b]Calculated with Formula 3, Section 3.1.4.1; *Referenced to lagoon surface area at MTL, calculated using the residual exchange measured at Faro-Olhão adjusted to the residual tidal prisms for all the inlets reported in Pacheco et al. (2010) and cross-section area for all the inlets. Minus sign signifies net export (seaward). **Per unit cross-sectional channel area

	Winter 2009	**Summer 2010**
Tidal Amplitude [m]	2.73	2.51
Wind speed [ms^{-1}]	8.4±8.0	6.3±1.2
Inventories	**^{222}Rn inventory ± MAD [Bq m^{-2}]**	
Ebb stage[a]	55.6±30.9	54.2±17.8
Flood stage[a]	73.8±31.5	74.0±17.6
All data[b]	66.1±34.7	65.9±19.6
Fluxes	**^{222}Rn flux ± σ [Bq m^{-2} day^{-1}]**	
Diffusion	5.7±1.9	5.9±1.7
Degassing	1.7±1.8	1.1±0.7
Decay	12±6.3	11.9±1.6
Residual Exchange*	-5.26(±1.03)×10^{-4}	-4.74(±0.79)×10^{-4}
Tidal Flux**	**^{222}Rn flux ± σ [Bq m^{-2} day^{-1}]**	
Quatro-Águas		
Export	-	85.4±11.1
Import	-	98.6±16.1
Residual	-	13.2±2.8
Barra-Nova		
Export	57.0±6.4	49.8±1.1
Import	65.5±4.2	65.0±4.2
Residual	8.5±1.1	15.2±1.0
Potential Rn sources	**Salinity**	**Activity ± σ [Bq m^{-3}]**
Deserta (Well)	0.95	93.8±59.5
Beach porewater	40.6	304±182
Ramalhete (borehole)	5.06	6625±996

Table 2. Precipitation records over the region during the sampling campaigns described by this study, as measured at the São Brás de Alportel meteorological station (www.snirh.pt, Ref 31J/C). Monthly precipitation is contrasted with rainfall during the sampling campaigns and compared with historical monthly averages in order to evaluate the relative wetness of the periods in the wider temporal context. Accumulated precipitation during the 3 months prior to the month fieldwork took place is also shown and similarly compared to the historical record average. For a more detailed contextual assessment, the chronological record of daily precipitation for the period 2006-2013 is shown in Fig 4, panel d, with the sampling periods overlain for easy reference when evaluating the stable isotope hydrology of the catchment defined by this study and previous research. Under 'Sampling', and 'Type', the type of endmember collected for stable isotope analysis is shown, except when radon survey campaigns were executed in parallel – in this case '*Radon survey*' is added to the column. More details on the individual samples are shown in Table S1.

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Date	Sampling		Precipitation [mm]				
			Survey	Month		Previous 3 months	
mm/yy	Period	Type	Total	Survey month	Historical average	Total	Historical average
Jan 07	3rd-6th	<u>Groundwater</u> • M12 aquifer • Beach porewater	0.1	8.8	138	369.7	369
July 07	1st-3rd	<u>Groundwater</u> • Beach drainage <u>Surface water</u> • WWTP • Lagoon West	0.0	0.5	3	83.7	125
Dec 09	1st-8th	*Radon survey* <u>Groundwater</u> • M10 aquifer • M12 aquifer <u>Surface water</u> • Lagoon East • Lagoon West • Seawater <u>Other</u> • Precipitation	10.3	392.2	160	93.6	232
May/June 10	28th-7th	*Radon survey*	0.0	24.1	16	88.6	207
Dec 10	8th-16th	<u>Groundwater</u> • Beach porewater <u>Surface water</u> • River Gilão	0.5	269.6	160	147	232
Jan 11	3rd-12th	<u>Groundwater</u> • Beach porewater	18.7	48.5	138	414.7	369

New/altered Figures (1&4) – all others remain the same

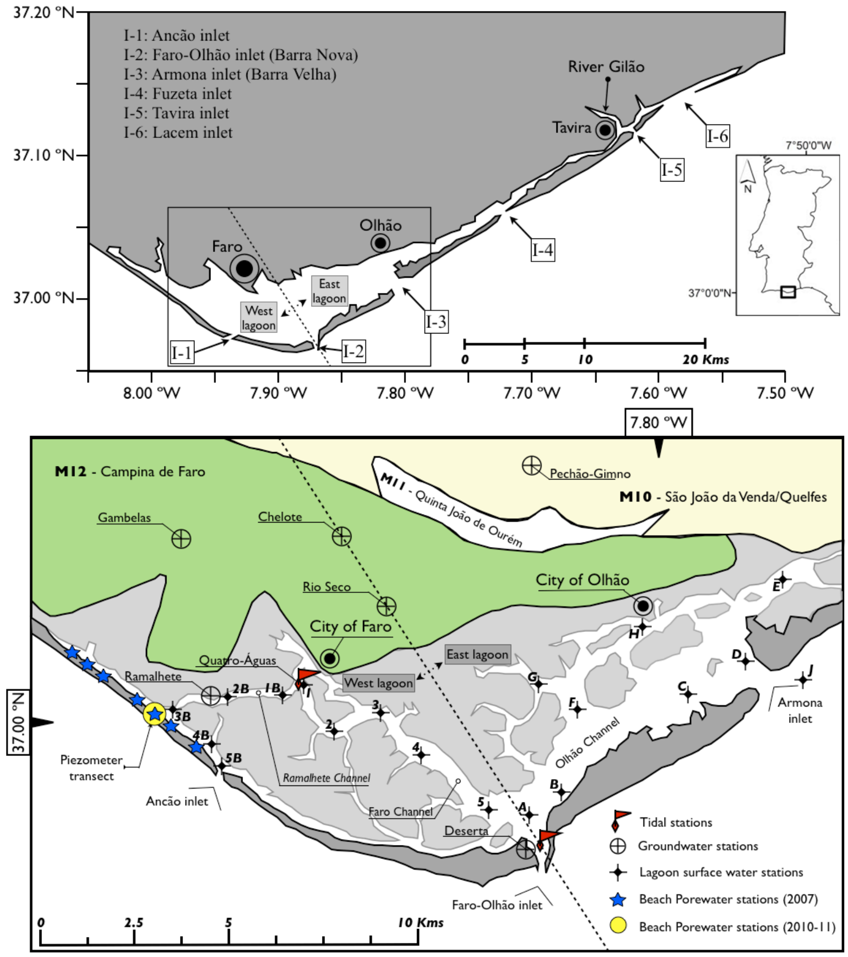

Figure 1

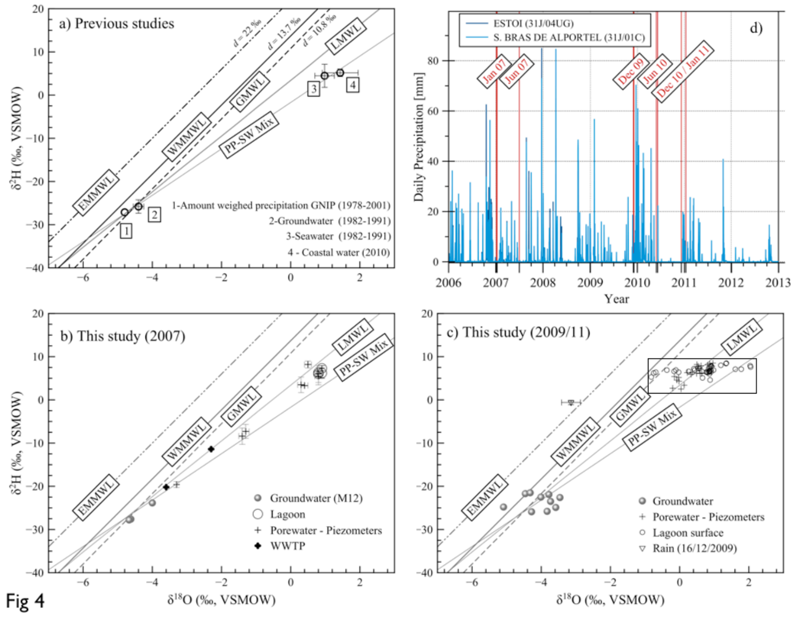

Fig 4

Figure 4