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ACs - Reply on RC2

Marc Diego-Feliu et al.

Author comment on "Extreme precipitation events induce high fluxes of groundwater and associated nutrients to coastal ocean" by Marc Diego-Feliu et al., Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2021-594-AC2, 2022

Anonymous referee #2

We sincerely thank anonymous reviewer 2 for their helpful and constructive comments. In his/her remarks, the reviewer expressed the need for clarifying the assumptions and limitations related to the quantification of SGD and nutrient fluxes through the Ra mass balance. Especially, the reviewer focused on the steady-state assumption and on the lack of consideration of runoff as a source of Ra isotopes and nutrients to the coastal ocean. See his/her general comment below:

"The authors used a radium survey to assess inputs of submarine groundwater discharge (SGD) to the Mediterranean Sea in northeastern Spain following an extreme precipitation event and at base flow. They showed that terrestrial water inputs increased by an order of magnitude 4 days after the storm and returned to base flow conditions another 4 days later. The episodic terrestrial and marine nutrient inputs associated with this one event likely accounted for more than 10% of the dissolved inorganic nitrogen, dissolved inorganic phosphorus, and dissolved silicate inputs to the coast for the whole year. This highlights the importance of extreme events for nutrient inputs to the coast.

The study will be of great interest to those who study nutrients in coastal waters. It is one of a relatively small number of studies to quantify changes in submarine groundwater discharge and associated nutrients during large recharge/rainfall events. I have minor suggestions to improve the clarity of the manuscript. The most important is the need for the authors to more clearly communicate the assumptions in their Ra and nutrient budget analyses within the methods and discussion, rather than the appendix. In my view, the most severe limitations are the steady-state assumption and the lack of consideration of runoff as an input.

Regarding runoff, flow occurred in at least some of the ephemeral streams at T1, T2, and T3 during the October 2019 event (L 372). This is important information and should be stated in the main text rather than the appendix. Was runoff water sampled for Ra isotopes and nutrients? The authors argue they can neglect runoff in their Ra and nutrient budgets because the Ra delivered by overland flow may have decreased by 90% at the time of the P1 sampling, but if the total delivery was large, 10% of that total delivery could still be sizeable. Ideally the authors would perform some calculations to examine the potential scale of the runoff contribution. Did the authors collect any runoff samples for Ra isotope and nutrient analysis? The volumetric flux of runoff is likely unknown, but an

estimate could probably be made based on typical runoff ratios for the region and the known catchment area. Without this kind of a calculation, the assumptions and limitations of lacking these runoff measurements should be clearly discussed. Care should be taken in attributing all terrestrial water inputs to groundwater (as in L 210) and all terrestrial nutrient inputs to groundwater (as in L 228). A large amount of sediment-water interactions would be expected in a flowing, turbid ephemeral stream under an extreme precipitation event, so the contribution of runoff to radium isotopes and nutrients should not be readily discounted without further analysis."

According to the reviewer's suggestions, in the new version of the manuscript, we will address in detail the runoff produced by the EPE and we will introduce the following information in the text:

- The description of the EPE that occurred in October 2019, including the runoff associated with this episode, will be introduced in the main text of the manuscript rather than in the appendix.
- An estimate of runoff during the EPE based on a soil mass balance will be included in the new version of the manuscript.
- An estimate of the Ra flux associated with the episode will also be included in the new version of the manuscript
- The influence that runoff may have had on the calculations of SGD and nutrient fluxes will be discussed in the main text and in the appendix of the new version of the manuscript.

Description of the flash flood events in the Argentona ephemeral stream

The hydrological regime of Mediterranean ephemeral streams has been described in detail in many research articles due to the hazardous characteristics of its associated flash flood events (e.g., Ballesteros et al., 2018; Camarasa-Belmonte and Tilford, 2002; Colombo and Rivero, 2017). Surface runoff in the Argentona ephemeral stream only occurs after heavy rainfall events characterized by its short duration and great intensity. The conceptual hydrograms corresponding to these events are well known and have been described in detail, especially in the grey literature (Cisteró and Camarós, 2014; Riba, 1997). According to these hydrograms, the flood events consist of different stages, which take place in a few hours (2 to 6) depending on the intensity and duration of the EPE: (1) some minutes after the precipitation has started a thin layer (some cm) of 'dirty' water (from the surroundings) flow superficially towards the sea, (2) after some minutes to hours, a cleaner water mass, which carries heavier materials overcomes the first one, (3) the flood level increases progressively towards a maximum discharge rate, which remains constant for a short period of time, and (4) the water level decreases gradually until completely disappearing (Cisteró and Camarós, 2014). Water velocities in one of the heaviest precipitation events that occurred in the Argentona ephemeral stream (180 mm in 24 h) were calculated to be on the order of 2.7 to 3.8 m s⁻¹ (Martín-Vide, 1985). This information is now presented in the description of the study site of the new version of the manuscript (Section 2.1):

"In this region, most of the ephemeral streams are hydraulically disconnected from their alluvial aquifers and, therefore, surface runoff takes place only after the most significant rain events, which are characterized by short duration and high rainfall intensity. The nature of floods associated with EPEs are well known and has been described in detail, especially in the grey literature (Cisteró and Camarós, 2014; Riba, 1997). Floods associated with the EPE events consist of different stages, which take place within a few hours (2 to 6 h) depending on the intensity and duration of the EPE: (1) a thin layer (a few centimeters) of "dirty" water (from the surrounding area) flows towards the sea a few minutes after the onset of rainfall, (2) then, after some minutes to hours, a cleaner water mass

carrying heavier materials, flows along the ephemeral stream; (3) the flood level increases progressively towards a maximum discharge rate, which remains constant for a short period of time (some hours), and (4) the water level decreases gradually until completely disappearing (Cisteró and Camarós, 2014). Water velocities in one of the heaviest precipitation events that occurred in the Argentona ephemeral stream (180 mm in 24 h) were calculated to be on the order of 2.7 to 3.8 m s⁻¹(Martín-Vide, 1985)."

Surface runoff in the Argentona ephemeral stream on October 22nd, 2019

Surface runoff has been estimated by soil mass balance (based on the type of soil, land use, geology, precipitation, slope, etc.) during the rainfall event of October 22nd, 2019. The soil mass balance has been used for a calibrated regional groundwater numerical model of the southern section of Maresme county. The model is not publicly available, as it has been developed for a specific work of the Spanish railway public company (ADIF). According to the soil mass balance, surface runoff associated with this EPE was about 1 hm³. This information is now mentioned in Section 3.1 Meteorological and hydrological context:

"Estimating the runoff velocity and discharge in the study site is difficult because in the mid-19th century a set of galleries and dams were constructed at the upper part of the Argentona ephemeral stream (municipality of Dosrius) to collect groundwater and surficial water from this area. The effect that these structures may have on surface runoff is uncertain. However, a soil mass balance (based on the type of soil, land use, geology, precipitation, slope, etc.) of the lower part of the Argentona ephemeral stream has been used to provide a semi-quantitative estimate of surface runoff during the October 22nd, 2019 rainfall event. The soil mass balance has been used for a calibrated regional groundwater numerical model of the southern section of Maresme county. The model is not publicly available, as it has been developed for a specific work of the Spanish railway public company. According to the soil mass balance, surface runoff associated with this EPE was about 1 hm³. "

Radium inputs due to surface runoff

Proper monitoring of Ra isotopes activities and nutrient concentrations in runoff water during the EPE that occurred in October 2019 was not done. This is due to the difficult sampling situation and the dangers inherent to flood events. However, a single surface water sample was taken at the initial stage of the flood, when the amount of water flowing represented only a thin layer of water (some cm). A first-order assessment of the Ra flux associated with surface runoff in the study site was performed by using the ²²⁴Ra and ²²⁸Ra activities of this water sample and the calculated runoff discharge. To assess the influence of this Ra input on our estimates of groundwater discharge, we have used a non-stationary Ra mass balance, which considers (1) a punctual surface input of Ra, (2) the offshore exchange of Ra, and (3) radium decay:

$$A(t) = A_{runoff} \exp(-t(1/T_F + \lambda))$$
. Eq. 1

where A [Bq] is the radium activity in seawater at a specific time (t [d]), A_{runoff} [Bq] is the activity delivered by the punctual input through surface runoff and it is calculated by multiplying the total surface runoff (Q [m³]) by the specific activity of Ra in surface water (a [Bq m⁻³]), T_F is the flushing time of radium, and λ is the decay constant of each radionuclide. Notice that for ²²⁸Ra, mixing with offshore water may be the predominant output and decay losses can be neglected. Equation 1 has been used to determine the activity of both Ra isotopes in seawater in the two subsequent samplings performed after the EPE and compared with the seawater Ra inventories found during these two

samplings.

The relative significance of runoff derived from the EPE in the Ra inventories based on the above calculations is 2 and 1% for ²²⁴Ra, and 1 and 8% for ²²⁸Ra at the first and second sampling, respectively. Notice that these values are low and comparable with the common uncertainties derived from the measurement of Ra isotopes. It should be also noticed that the calculated Ra inputs through surface runoff are likely overestimated since the surface water sample was collected at the beginning of the flood and it is representative only of the initial thin and 'dirty' water (with more particles per mass of water) flow and not of the 'cleaner' water mass, which represents most of the total runoff discharge. Therefore, we do believe that this punctual source of Ra is negligible and may not affect the estimations regarding SGD and nutrient fluxes made in this article. In the new version of the manuscript we will mention that the estimates may be slightly biased towards higher SGD and nutrient fluxes due to the lack of consideration of surface radium and nutrient inputs (see extract Section 4.1.2).

"It should also be noticed that estimates presented in this study should be taken as semi-quantitative in view of the biases, limitations, and uncertainties discussed in detail in appendix A (e.g., endmember selection, steady-state assumption, lack of consideration for runoff)."

We also included the discussion about the role of runoff in the quantification of SGD and nutrient inputs in the appendices:

"Ra inputs from runoff water were also discarded for the sampling conducted in March 2020 (BF) due to the total absence of surface water inputs during the sampling period. In October 2019, 4 days before the first sampling conducted at the study site, runoff occurred in direct response to an EPE (~90 mm). However, considering the flushing time of Ra isotopes in the coastal system (see S1.2.2), the Ra delivered by this punctual runoff may have decreased by >90% for the first sampling (P1) and by >99% for the second sampling (P2), due to decay (for ²²⁴Ra) and mixing with offshore waters. However, the relative contribution that runoff may have had on Ra inventories during the first two samplings was calculated using the Ra activities of the runoff sample collected during the beginning of the EPE, and the calculated runoff discharge by using a soil mass balance. Although the estimates may be uncertain, the results indicate that the relative significance of runoff derived from the EPE in the Ra inventories were 2 and 1% for ²²⁴Ra, and 1 and 8% for ²²⁸Ra at the first and second sampling, respectively. Notice that these values are low and comparable with the common uncertainties derived from the measurement of Ra isotopes. It should be also noticed that the calculated Ra inputs through surface runoff are likely overestimated since the surface water sample was collected at the beginning of the flood and it is representative only of the initial thin and 'dirty' water (with more particles per mass of water) flow and not of the 'cleaner' water mass, which represents most of the total runoff discharge. Therefore, Ra runoff input was discarded as a major source of Ra isotopes to the coastal ocean during the sampling periods."

Regarding stationary or transitory conditions of the Ra mass balance, we consider that (1) using a non-stationary Ra mass balance would have required monitoring the activities of Ra isotopes over the sampled period, a sampling effort that was not possible to conduct, and (2) the assumption of steady state may result in conservative estimates of SGD induced by EPEs relative to that in baseflow conditions. We have indicated the assumption taken for solving the model throughout the manuscript (Section 4.1.2 and 4.2.3) and in the appendices (see extract below):

"A.2.3 Steady state conditions

Steady state conditions (i.e., tracer inventories do not vary with time; da/dt = 0) are often assumed in Ra mass balances (e.g., Alorda-Kleinglass et al., 2019; Beck et al., 2008; Rodellas et al., 2017). This assumption implies that Ra inputs and outputs are balanced for a time period equivalent to the tracer residence time in the system (Rodellas et al., 2021). In Maresme County, the tracer residence time ranged from 1.6 to 2.6 days for ²²⁴Ra and from 2.4 to 5.6 days for ²²⁸Ra. The tracer residence time can be estimated by dividing the radium inventory in surface waters by the sum of all losses (i.e., radioactive decay and exchange with offshore waters) (Rodellas et al., 2021). The assumption of steady state may therefore not be valid due to the significant difference between Ra activities from the first and second samplings (P1 and P2; Fig. 3), which were carried out only 4 days apart. Notice however that using a non-stationary Ra mass balance would have required monitoring the activities in coastal waters of Ra isotopes over the sampled period to understand its temporal patterns. Moreover, assuming steady state instead of a decrease of activities in coastal waters () (the pattern that was observed in the EPE from 2019; Fig. 3), results in conservative estimates of SGD induced by EPE relative to that in baseflow conditions."

Technical edits:

Here we discuss the technical edits of reviewer 2:

"The spatial relationships in the study could be clarified in a couple of places. For example, L 99 and Figure 1 refer to the Medistraes project or site. Is Medistraes an alternate name for the Argentona site? If so, it would be clearer in the figure and text to just refer to the site location by one name (or else label Medistraes project on Figure 1b). L 157 refers to "groundwater from the site of the Argentona ephemeral stream." I would suggest calling this the "Argentona site" and refering to Figure 1c-d for clarity."

We agree with the reviewer on the need for standardization of the terms used to describe the study site. From now on, in the new version of the manuscript, we will refer to the Argentona site when talking about the site located at the lower part of the Argentona ephemeral stream.

"L 85-Please provide the percentile for a 90-mm event here and reference Figure 2a."

In the new version of the manuscript, we provided the percentile for the 90 mm event in the new as suggested by the reviewer:

"Three samplings were conducted in the southern section of Maresme County during 2019 and 2020. The two first samplings (hereinafter P1 and P2, chronologically) were performed shortly after an EPE with an accumulated precipitation rate of ~90 mm in one day, which corresponds to the 99.6 wet-day percentile (Fig. 2a)."

"L 239: It should be noted this is not necessarily a good assumption, as shown by studies like Weintein et al., 2011; Sawyer et al., 2014, Wong et al., 2020, and many others, but it is understood that it is not very feasible to mobilize a high-resolution sampling effort near the sediment-water interface on the tail of an extreme precipitation event, and this is what would be needed to alleviate the assumption."

A clearer description of the assumptions and limitations associated with the quantification will be provided throughout the new version of the manuscript (see example below,

Section 4.1.3). See also the response to reviewer 1 regarding the endmember selection.

"Since it was not possible to directly collect the discharging groundwater, by using onshore samples we are implicitly assuming that no nutrient transformation occurred between the sampling point and the discharge point, within the subterranean estuary (Cook et al., 2018). This assumption is perhaps one of the main sources of uncertainty in the reported nutrient fluxes as it has already been shown by many authors (Sawyer et al., 2014; Weinstein et al., 2011; Wong et al., 2020). It should also be noted that these SGD-derived nutrient estimates may be biased due to the groundwater endmember selection, since nutrient concentrations in discharging groundwaters may vary during EPE due to dilution, increasing lixiviation of fertilizers, or enhancement of biogeochemical reactions in the mixing zone of coastal aquifers (Spiteri et al., 2008). Although all the assumptions made for nutrient fluxes quantification may result in high degrees of uncertainty, the results presented in this study enable the assessment of EPE significance as a major driving force transporting nutrients to the coastal ocean."

"Figure 5: Rather than showing the portion of nutrient fluxes attributed to terrestrial and marine SGD with bullseyes, consider coloring the bars below directly (i.e. stacked dark and light blue bars) to condense the information into one graphic style."

Figure 5 has been modified in order to separate the pie charts and the bar plot into two subplots. However, we decided not to use stacked bar plots because the logarithmic scale hampers the recognition of the percentages.

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