05-04-2022

Response to Decision on manuscript hess-2021-401

Hydrology and riparian forests drive carbon and nitrogen supply and DOC:NO_3^- stoichiometry along a headwater Mediterranean stream

Editor comments to the authors

Dear authors,

First, I would like to apologize for how long the review process has been since your initial submission. One of the reviewers became unresponsive after their deadline to submit their review had passed, and it was difficult to find another reviewer to replace them. I thank you very much for your patience through all of this. Two referees have now provided comments on your manuscript and suggested ways of strengthening it: while they both found it to be of good quality, they raised that in its current state, its contribution (in terms of novelty) may be modest. Your responses, posted on the Interactive Discussion page, indicate that you have already started addressing some of these comments. I am therefore returning your manuscript for moderate revisions, and I look forward to receiving your revised manuscript. With best regards,

Genevieve Ali

[Reply]:

Dear Editor,

We appreciate your apology about the length of the review process. While it is indeed not optimal for us authors to experience long waiting times in the process, we understand editorial work is becoming increasingly challenging, particularly finding suitable reviewers, and more so in the last couple of years due to the well-known circumstances.

We are happy that both reviewers found our work of good quality and we noticed the common suggestions they had, which we have incorporated into the revised manuscript or rebut accordingly.

Please, find below our point-by-point response to the reviews in line with the comments we posted in the online Interactive Discussion, and including descriptions of the relevant changes made to the original manuscript. Note that the text in *italics refers to literal comments by the reviewers*, the text in blue contains literal quotations from the revised version of the manuscript, and line numbers refer to those in the revised, clean version.

With thanks in advance for your effort handling our manuscript,

José L. J. Ledesma and co-authors

Reviewer #1

General comments

This study analyses DOC, NO3- and the DOC:NO3- ratio along three stations in a Mediterranean headwater, and across flow conditions, during a 2-year period. Spatial variability is controlled by the presence of riparian forest and topography, while temporal variability is controlled by hydroclimatic conditions. The authors conclude that this spatiotemporal variability influences stream metabolic processes.

The manuscript is well written and the conclusions are clear. This work is within the scope of HESS but I find this is a modest contribution to the literature.

Here are three options to make a stronger paper:

- *Relax the selection criteria for the storm events to include in the PLS regression (currently only 5 observations)*
- *Include data on DOC and N composition, not only in the discussion. The discussion suggests that such data is available. Is nitrate the only N form in this stream?*
- *Include more recent data to make a more complete synthesis of research in this catchment. The references indicate that other studies have taken place in this catchment since the monitoring period 2010-2012 considered here.*

[Reply]: We are happy that the reviewer found the manuscript "well written" and the conclusions "clear" and appreciate the three suggestions to make the paper stronger. They are sensible and, in fact, we had already considered these options during the preparation of the manuscript. Below we respond to each of these suggestions separately and explain the actions that we have taken in each case.

<u>Including more storm events in the PLS regression</u>

Following the reviewer's suggestion, we relaxed the selection criteria for including storm events in our analyses. Specifically, events were included if they fulfilled three requirements: (i) a precipitation amount of at least 25 mm, as opposed to the 50 mm threshold that we had in the former version of the manuscript (note that events below the 25 mm threshold showed no groundwater table response at the temporal resolution of the study and limited stream flow responses), (ii) stream flow was classified as storm flow during the days of the event (not all events with precipitation amounts higher than 25 mm generated storm flow at the temporal resolution of the study), and (iii) a complete stream chemistry data series associated with the event for the downstream site (i.e. no gaps in chemical data for the event dates were allowed as we were ultimately interested in stream chemical responses).

Using these more relaxed criteria, we identified a total of 11 new events besides the 5 events that we had previously analyzed. We calculated the same nine hydroclimatic descriptors defining those 5 former events for the 11 new events, as well as their average DOC and NO_3^- concentrations and the relative increase in DOC and NO_3^- concentrations with respect to base flow conditions (Table R1).

Table R1. Hydroclimatic descriptors of the storm events identified during the study period (September 2010 to August 2012) at the downstream site of the Font del Regàs catchment, including duration, precipitation amount (P), accumulated precipitation seven (P-7) and 30 (P-30) days before the event, average stream flow (Q_{avg}), average groundwater table (Gw_{avg}), groundwater table range (ΔGw), slope of the linear relationship between riparian groundwater table and stream flow (slope), and average stream flow normalized to average groundwater table (Q_{avg}/Gw_{avg}). Average dissolved organic carbon (DOC) concentrations and average nitrate (NO_3^-) concentrations during each event at the downstream site and the relative increase in DOC and NO_3^- concentrations with respect to average concentrations observed during base flow conditions (within brackets) are also shown. Events are subdivided into medium (*) and large (#) storms.

Event	Period	Duration (days)	P (mm)	P-7 (mm)	P-30 (mm)	Q_{avg} (mm)	Gw_{avg} (m)	ΔGw (m)	Slope (m mm^{-1})	Q_{avg}/Gw_{avg} (mm m^{-1})	DOC (mg C L^{-1})	NO_3^- (mg N L^{-1})
*1	16-19/09/2010	4	52	9	36	0.4	0.97	0.04	0.10	0.4	1.01 (15%)	0.23 (36%)
*2	14-17/05/2011	4	30	22	122	0.7	0.90	0.02	0.15	0.8	0.99 (13%)	0.17 (5%)
*3	30/05-02/06/2011	4	36	0	69	0.6	0.92	0.02	0.15	0.6	1.19 (36%)	0.18 (7%)
*4	03-06/06/2011	4	50	36	96	0.6	0.92	0.03	0.14	0.7	0.83 (-5%)	0.17 (-1%)
*5	09-15/06/2011	7	34	66	148	0.6	0.91	0.03	0.15	0.7	1.10 (26%)	0.18 (7%)
*6	25/07-03/08/2011	10	74	4	48	0.5	0.94	0.04	0.16	0.5	0.82 (-7%)	0.18 (5%)
*7	23-30/10/2011	8	98	17	39	0.3	0.95	0.09	0.17	0.3	1.53 (75%)	0.23 (41%)
*8	21-23/03/2012	3	57	6	8	0.8	0.88	0.06	0.22	0.9	0.95 (8%)	0.36 (118%)
*9	03-05/04/2012	3	29	0	63	0.7	0.95	0.06	0.13	0.7	1.23 (40%)	0.16 (-2%)
*10	18-24/05/2012	7	49	10	62	0.5	0.97	0.04	0.02	0.5	0.82 (-7%)	0.19 (12%)
*11	04-09/08/2012	6	33	0	4	0.2	1.05	0.03	0.23	0.2	1.08 (23%)	0.18 (5%)
#1	11-14/03/2011	4	95	11	39	1.7	0.74	0.36	0.16	2.3	2.35 (167%)	0.40 (140%)
#2	14-23/03/2011	10	116	102	133	3.3	0.64	0.55	0.14	5.1	2.16 (146%)	0.33 (97%)
#3	02-12/11/2011	11	134	65	116	0.8	0.87	0.21	0.18	0.9	2.45 (178%)	0.40 (138%)
#4	14-19/11/2011	6	174	14	261	4.2	0.69	0.52	0.06	6.1	1.91 (117%)	0.29 (74%)
#5	21-30/11/2011	10	67	182	426	3.4	0.74	0.21	0.07	4.5	1.36 (55%)	0.34 (102%)

We observed large differences between the two subsets of events (the new and the former) in their precipitation and associated hydrological response and consequently classified them as ‘medium storms’ and ‘large storms’. Compared to the large storms, the medium storm events were characterized by significantly (a) lower accumulated precipitation amounts, (b) lower average stream flow, (c) deeper groundwater tables, (d) smaller groundwater table ranges (i.e. the thickness of the riparian layer that becomes hydrologically activated during the event), (e) lower stream DOC concentrations, and (f) lower stream NO_3^- concentrations (Wilcoxon rank-sum tests, $p<0.01$ in all cases; Figure R1). This analysis suggest that the differences in climatic and, especially, hydrological chatacteristics between the large and medium storm events were responsible for the marked differences in the resulting stream DOC and NO_3^- concentrations. Sepecifically, we argue that the hydrological activation of a thicker and shallower riparian layer during large storm events leads to the mobilization of relatively larger amounts of DOC and NO_3^- stored in the riparian soil compared to the amounts mobilized from the deeper and narrower layers that are hydrologically activated during medium storm events. We conclude that large and medium storm events display a distinct mechanism of DOC and NO_3^- mobilization from the riparian zone, and thus including the samples from the two type of events into the same PLS regression analysis would not help shedding light on the hydroclimatic characteristics that most effectively promote the mobilization of DOC and NO_3^- into the stream via groundwater table elevation and consequent hydrological activation of upper riparian layers, as highlighted in the conceptual model we propose in Figure 7 (now Figure 8) of the manuscript.

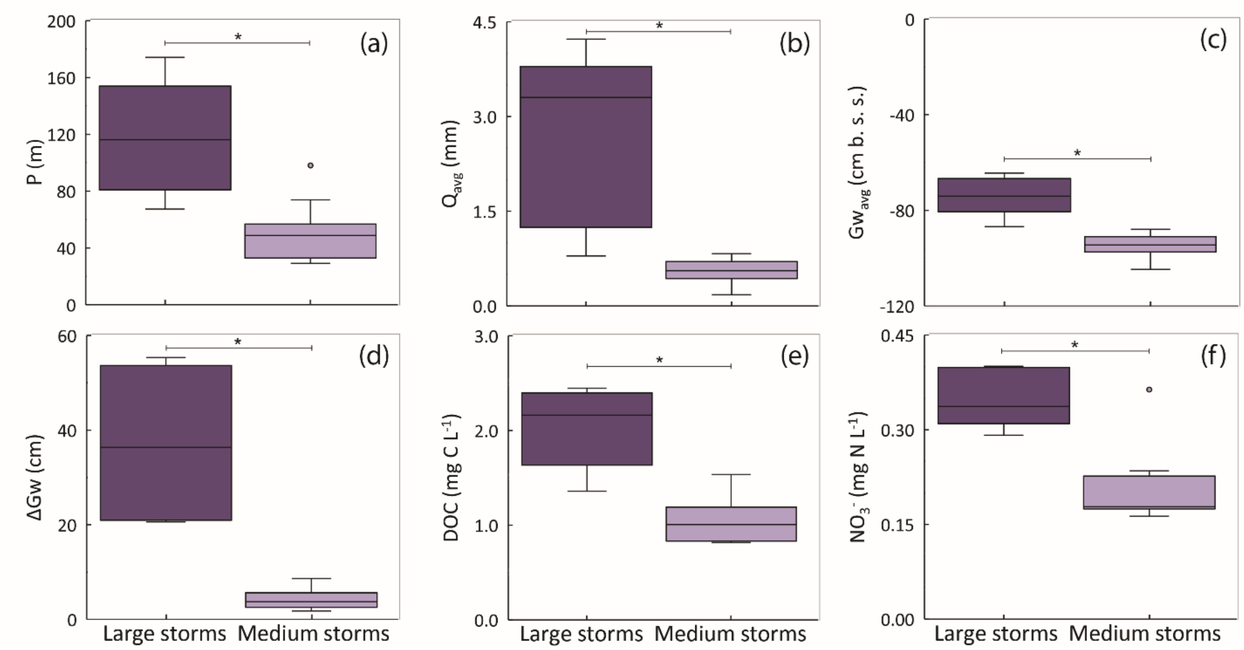

Figure R1. Box plots of **(a)** precipitation amount (P), **(b)** average stream flow (Q_{avg}), **(c)** average groundwater table (Gw_{avg}, with 0 value indicating the soil surface and negative values indicating cm below the soil surface), **(d)** groundwater table range (ΔGw), **(e)** average dissolved organic carbon (DOC) concentrations at the downstream site, and **(f)** average nitrate (NO_3^-) concentrations at the downstream site for 'large' (N = 5) and 'medium' (N = 11) storm events identified during the study period (September 2010 to August 2012). On each box, the central mark indicates the median, and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers. Results from pairwise Wilcoxon rank-sum tests are also shown, where * indicates statistical difference ($p<0.01$).

All in all, the inclusion of medium storm events is an added value to the manuscript because the new results underscore the hydrological and biogeochemical differences between the two types of events. Consequently, we have decided to keep only the five large storm events in our PLS regression model, which is the statistical analysis that supports our suggested conceptual model, and which only applies to large events where clear hydrological activation of upper riparian soil layers takes place. Hence, in the revised version of the manuscript, we have included Table R1 and Figure R1 showed here (as new Table A1 and new Figure 5, respectively), and integrated in the text all information regarding these new analyses, including additions in the Abstract (Lines 21-23: "The hydroclimatic analysis of storms suggest that large and medium storm events display a distinct mechanism of DOC and NO_3^- mobilization. In comparison to large storms, medium storm events showed limited hydrological responses that led to significantly lower stream DOC and NO_3^- concentrations"); in the Materials and Methods (Lines 180-182: "We further aimed to explore the hydroclimatic characteristics that most effectively promoted the mobilization of DOC and NO_3^- into the stream via groundwater table elevation and consequent hydrological activation of upper riparian layers during storm events"; Lines 184-186: "We then related those descriptors with the observed stream DOC and NO_3^- concentrations through a partial least square (PLS) regression model for the subset of storms for which clear hydrological activation of upper riparian soil layers occurred"; Lines 188-193: "We identified storm events based on three requirements: (i) a precipitation amount during the days included in the event of at least 25 mm (events below these threshold showed marginal groundwater table responses at the temporal resolution of the study), (ii) stream flow was classified as storm flow during the days of the event (not all events with precipitation amounts higher than 25 mm generated storm flow at the temporal resolution of the study), and (iii) a complete stream chemistry data series associated with the event for the downstream site (i.e. no gaps in chemical data for the event dates were allowed as we were ultimately interested in stream chemical responses)"; Lines 214-220: "We observed large differences between two subsets of events in their groundwater table elevation (defined by their groundwater table range ΔGw), generally associated with their precipitation amount P (R^2 = 0.67, linear regression between P and ΔGw). We classified these two subsets of events as 'medium storms' (P = 29 to 98 mm, ΔGw = 2 to 9 cm, N = 11) and 'large storms' (P = 67 to 174 mm, ΔGw = 21 to 55 cm, N = 5), and proceeded with the PLS analyses only with the subset of large storms because, unlike medium storms, they showed clear hydrological activation of upper riparian soil layers defined by ΔGw. Pairwise Wilcoxon rank-sum tests were used to compare the hydroclimatic descriptors and the stream DOC and NO_3^- concentrations between medium and large storm events"); in the Results (Lines 296-301: "Hydrological responses were considerably different between medium and large storm events. Compared to large storms, medium storms were characterized by (i) lower accumulated precipitation amounts, (ii) lower average stream flow, (iii) deeper groundwater tables, and (iv) smaller groundwater table ranges, i.e. smaller thickness of the riparian layer that becomes hydrologically activated during the event […]. Additionally, both stream DOC and stream NO_3^- concentrations were significantly lower during the medium storm events than during the large storm events"); and in the Discussion (Lines 436-446: "Based on their hydrological response to precipitation, we were able to clearly identify two subsets of events. Large storms, characterized by higher precipitation amounts, produced considerable stream flow and groundwater table responses, whereas medium storms produced only moderate responses in stream flow and limited groundwater table elevations (Fig. 5). These differences in climatic and, especially, hydrological characteristics between large and medium storm events led to marked differences in the resulting stream chemistry, with both DOC and NO_3^- concentrations being significantly higher during the large storm events. This observation is likely caused by the hydrological activation of a thicker and shallower riparian layer during large storm events that leads to the mobilization of relatively larger amounts of DOC and NO_3^- stored in the riparian soil compared to the amounts mobilized from the deeper and narrower layers that are hydrologically activated during medium storm events. These results suggest that large and medium storm events display distinct mechanisms of DOC and NO_3^- mobilization from the riparian zone and that large storms are responsible for a disproportionally larger supply of these solutes").

<u>DOM composition and other forms of nitrogen</u>

Unfortunately, we do not have data on DOM composition at daily resolution or during storm flow conditions, which prevents us for directly integrating DOM composition data into the analyses of the present study. However, during the same study period (2010-2012), we performed longitudinal surveys of DOM composition on 11 occasions during base flow conditions. The data from these surveys showed that DOM in Font del Regàs has a prominent protein-like character in both riparian groundwater and stream water (Bernal et al. 2018). In the present manuscript, we use this information by referring to the published study in order to support our idea that in-stream heterotrophic activity could be partially sustained during storm flow conditions. We have reworded the sentence in the discussion where we included this information to make clear that the data we have on DOM composition was collected during base flow and that we assume the character is maintained across flow conditions (Lines 417-420: "Further, Bernal et al. (2018) showed that DOM at Font del Regàs has a prominent protein-like character in both riparian groundwater and stream water during base flow conditions, which could favour rapid assimilation even during periods of short water residence times assuming DOM molecular composition maintains part or most of its labile character across flow conditions").

Regarding the different forms of nitrogen, NO_3^- is not the only form found at the Font del Regàs stream, but it makes up the overwhelming majority of both inorganic and total nitrogen. For the study period (2010-2012), we do have data on daily concentrations of other forms of dissolved inorganic nitrogen (DIN), including NH_4^+ and NO_2^- (partially published in Bernal et al., 2015). Overall average stream concentrations of NH_4^+ (0.010 ± 0.006 mg N L^{-1}) and NO_2^- (0.006 ± 0.005 mg N L^{-1}) are more than one order of magnitude lower than overall average stream NO_3^- concentrations (0.20 ± 0.09 mg N L^{-1}). Moreover, NH_4^+ and NO_2^- concentrations are in all cases lower than 0.02 mg N L^{-1} and show no differences between base flow and storm flow conditions. Hence, NO_3^- accounted for more than 90% of DIN during both base flow and storm flow during the study period. It its turn, dissolved organic nitrogen (DON) was always below 0.05 mg N L^{-1}, which implies that NO_3^- makes up more than 80% of the total dissolved nitrogen under all circumstances. Given that (i) NO_3^- is the major source of nitrogen for stream heterotrophic microorganisms in our system, and (ii) no significant differences were observed in other DIN forms between base flow and storm flow conditions, we decided to only analyze spatiotemporal patterns in NO_3^- concentrations. We have added this information in the revised manuscript in Lines 75-76 ("In this stream, NO_3^- is the major source of N for stream heterotrophic microorganisms, accounting for more than 90% of the dissolved inorganic N (Bernal et al., 2015) and for more than 80% of the total dissolved N (unpublished data)").

Including more recent data

Unfortunately, we do not have chemistry data beyond the studied period at the temporal (i.e. daily) or spatial (i.e. three sites along the stream) resolutions that we used in the present study. Some of the studies from the catchment that we cite, and that the reviewer refers to, did use parts of the dataset that we analyse here, though to answer different questions (e.g. Lupon et al., 2016b; Ledesma et al., 2021). In any case, these studies did not contain data beyond 2012. In some cases, the studies used data from specific experiments or campaigns that cannot be directly incorporated into our analyses. This is the case of the aforementioned Bernal et al. (2018) study, which was based on longitudinal surveys of DOM composition. In autumn 2018, we restarted the hydrological monitoring at the downstream site. Since then, DOC and NO_3^- concentrations (and consequently DOC:NO_3^- molar ratios), have only been measured sporadically. We are planning to conduct a more regular sampling of stream water at this site, but unfortunately, no additional data is available at the moment.

Specific comments

Figure 1: add location of the weather station

[Reply]: We thank the reviewer for pointing this out. We have added the location of the automatic weather station in a revised version of Figure 1.

L115 "Rating curves obtained from the relationships between stream flow and stream water level measurements were used to construct daily time series of stream flow data at each site" can you provide the rating curves in SI?

[Reply]: The rating curves were presented in the supplementary material of Lupon et al. (2016b), published also in *HESS*. We can provide them as a new figure in the Appendix of the present study if this is adequate, but we believe it is redundant to reproduce the same figure in two different papers.

L122 "the dynamics of this dataset capture well the dynamics of the groundwater table variation in the surrounding riparian area and therefore we are confident that the recorded pattern at the monitoring location was representative of the groundwater table variations in the riparian zone" please provide stronger evidence that this piezometer is representative of the whole downstream area.

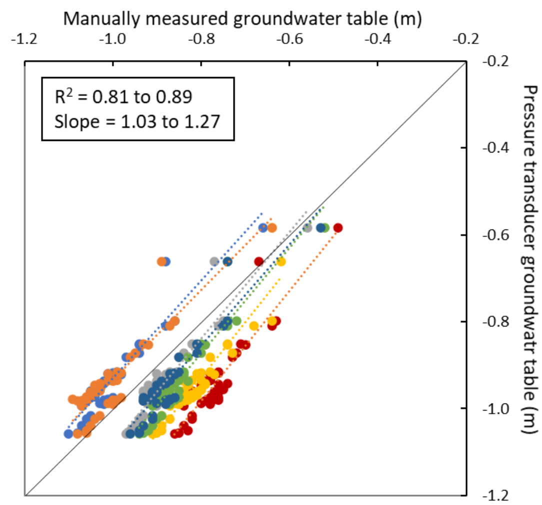

Figure R2. Comparison of pressure transducer versus manually measured groundwater tables. Measurements from each piezometer are presented in a different colour and dotted lines are linear regressions between the two variables for each corresponding colour-coded case ($p<0.01$ in all cases).

[Reply]: The evidence for this statement was presented in Ledesma et al. (2021). In addition, to the groundwater tables presented in this study (recorded at 15 min intervals using a water pressure transducer installed in a piezometer placed 2.5 m away from the stream channel), we also measured groundwater tables manually every two weeks during the same period at seven equidistant (ca. 3 m) piezometers placed ca. 2 m from the stream channel along the same area where the pressure transducer was located. We compared a total of 45 supplementary groundwater table measurements available at each of the seven piezometers with the data from the pressure transducer, and showed that groundwater table dynamics were notably similar in all cases, which supports the use of the pressure transducer data as representative of the downstream riparian areas in our study (Figure R2). In the revised manuscript, we have rephrased the sentence to make the evidence more explicit in Lines 125-129 ("In a previous study, we showed that the dynamics of the pressure transducer dataset captured well the dynamics of manually-measured groundwater table variations in seven other piezometers located in the surrounding riparian area (Ledesma et al., 2021). Therefore, we are confident that the recorded pattern at the pressure transducer location was representative of the groundwater table variations in the riparian zone soils in the lower parts of the catchment").

L174 "hydroclimatic analysis of large storm events" I understand that the authors chose to analyze the largest storm events because they probably exhibit the clearest signal, but the selection criteria here are very strict and only 5 storm events were kept for analysis. This is a very small number, even though PLS regression can handle datasets with few observations and many variables. Wouldn't it be more interesting to relax the selection criteria and include more storm events?

[Reply]: Please, see our detailed response to this issue above.

L322 "given that this is a predominantly heterotrophic system (Lupon et al., 2016c)." please explain how this was determined (most readers won't read the reference)

[Reply]: The stream is predominantly heterotrophic because daily rates of ecosystem respiration (5.0 – 10.0 g O_2 m^{-2} day^{-1}) are between 10- and 100-fold higher than daily rates of gross primary production (0.1 – 0.7 g O_2 m^{-2} day^{-1}), as we measured and reported in Lupon et al. (2016c). Following the suggestion, we have included this information in the revised manuscript in Lines 342-343 ("[…] given that this is a predominantly heterotrophic system where ecosystem respiration rates are between 10- and 100-fold higher than gross primary production rates (Lupon et al., 2016c)").

L340 "This result is in line with the idea that headwater streams can remove substantial amounts of NO3 - within relatively short distances (Peterson et al., 2001) […] providing groundwater inputs with low NO3 - concentrations driven by denitrification, as observed in temperate forest catchments (Cirmo and McDonnell, 1997)." Both instream removal and dilution from the middle part of the catchment can explain this decrease. Is it possible to estimate the share of each process?

[Reply]: In general, the data presented in this study cannot be analyzed and evaluated in a way that would allow estimating the relative contribution of these two processes to the NO_3^- decrease between the upstream and midstream sites. Nevertheless, in this case we are confident than *in-stream removal* dominates over *dilution from riparian denitrification* because denitrification is low at the riparian soils at Font del Regàs (< 3 µg N kg^{-1} day^{-1}; Poblador et al., 2017). In fact, they rather sustain large nitrification rates (1 – 2 mg N kg^{-1} day^{-1}; Lupon et al., 2016a). Yet, even if *in-stream removal* likely accounts for an important fraction of the observed NO_3^- decrease, we consider that this process alone cannot explain the entire NO_3^- reduction between the upstream and midstream sites. We have suggested potential mechanisms for the comparatively high NO_3^- concentrations in the upstream site that could add to explain the upstream-midstream pattern (Lines 365-369: "[…] it is unclear why the upstream site showed such consistently higher NO_3^- concentrations with respect to the midstream site. A combination of steeper slopes (which also favour oxygenation and potential nitrification in soil water) and a vegetation dominated by beech forest (which might uptake lower amounts of NO_3^- than the oak and riparian forests at the midstream section) might partially explain the higher NO_3^- concentrations upstream and the upstream-midstream pattern (Schiff et al., 2002; Poblador et al., 2019; Simon et al., 2021)").

L375 "The magnitude of change between flow conditions was different for DOC and NO3 - at the upstream site…" please specify which of DOC or NO3- increases more.

[Reply]: We have specified this information in the revised manuscript in Lines 398-401 ("At the upstream site, the magnitude of change between flow conditions was different between DOC (which on average increased by 66%) and NO_3^- (which on average increased by 41%), leading to an increase in the frequency of optimal DOC:NO_3^- stoichiometric conditions for heterotrophic activity during storm flow").

L395 "another study from Font del Regàs showed that DOM has a prominent protein-like character in both riparian groundwater and stream water (Bernal et al., 2018)" suggest to include this data in the analysis (not only just in the discussion) to make a more complete paper. The speciation of DOC and the N species other than nitrate should be analyzed further.

[Reply]: Please, see our detailed responses to these issues above.

Technical corrections

L110 "All data and analyses were integrated and carried out for daily resolutions, which were determined by the availability of the stream chemical data." This sentence is unclear

[Reply]: We agree, and in the revised manuscript we have changed the sentence to "All data and analyses were integrated and carried out for daily resolutions, which was the resolution of the stream chemical data" (Lines 113-114).

Reviewer #2

General comments

This manuscript explores hydrological and riparian controls on DOC and NO3- stream chemistry in an oligotrophic Mediterranean stream. Their rationale was to understand how these dynamics may impact in-stream heterotrophic activity. To do this, the authors use data collected at three sites within the catchment collected over a period 2 years (2010-2012). Their results suggest that spatial (upstream to downstream) patterns are explained by riparian geomorphology and forest coverage and that temporal variability results from hydrological variability. The manuscript is well written, figures are clear, and conclusions are straightforward and supported by data. I particularly enjoyed the use of the hydrological metrics to understand controls on lateral exchanges of DOC and NO3- between the riparian zone. That said, the contributions to the literature are modest. I wonder if the authors could strengthen the manuscript by adding data beyond 2010-2012 and include more (smaller) storm events in their PLSR analysis. Large storms are relatively rare and DOC and NO3- transport during smaller, and likely more frequent, storms may influence stream metabolism more than the larger events. Also, I suspect antecedent conditions are even more important for DOC and NO3- transport dynamics during these smaller events. I also wonder if the authors have NH4+ and/or DON concentrations and might consider looking at the DOC:DIN or DOC:TDN ratios. Perhaps NO3- is the dominant form of N and these other N forms won't impact the story much?

[Reply]: We are happy that the reviewer found the manuscript "well written" and the conclusions "straightforward and supported by data" and we acknowledge the appreciation of the use of hydrological metrics. Our detail responses to the three main points that we identified in this general comment follow below.

<u>Including more storm events in the PLS regression</u>

Please, see our extended response and description of changes made in the manuscript in relation to this issue in our reply to Reviewer #1 above.

<u>Adding data beyond 2010-2012</u>

Unfortunately, we do not have chemistry data at the temporal (i.e. daily) or spatial (i.e. three sites along the stream) resolutions that we used in the present study beyond the period that we have analysed (i.e. 2010-2012). Therefore, there is no other data outside this period that can be sensibly integrated into our analyses and we only use other studies from the catchment to support our discussion.

<u>Ammonium and DON concentrations and other carbon to nitrogen ratios</u>

The reviewer made the right point, NO_3^- is the dominant form of both inorganic and total nitrogen in our system and thus, the other forms lack relevance in the context of the story. For the study period (2010-2012), we have data on daily concentrations of other forms of dissolved inorganic nitrogen (DIN), including NH_4^+ and NO_2^- (partially published in Bernal et al., 2015). During this period, stream concentrations of NH_4^+ (0.010 ± 0.006 mg N L^{-1}) and NO_2^- (0.006 ± 0.005 mg N L^{-1}) were more than one order of magnitude lower than stream NO_3^- concentrations (0.20 ± 0.09 mg N L^{-1}). Moreover, NH_4^+ and NO_2^- concentrations were similar between base flow and storm flow conditions. Hence, NO_3^- accounted for more than 90% of DIN during both base flow and storm flow. It its turn, dissolved organic nitrogen (DON) was always below 0.05 mg N L^{-1}, which implies that NO_3^- makes up more than 80% of the total dissolved nitrogen under all circumstances. We are therefore confident that NO_3^- is the major source of nitrogen for stream heterotrophic microorganisms in our system, and this is why we decided to only analyze spatiotemporal patterns in NO_3^- concentrations. To support this choice, in the revised manuscript we have made clear that NO_3^- is the dominant form of nitrogen in Font del Regàs (Lines 75-76: "In this stream, NO_3^- is the major source of N for stream heterotrophic microorganisms, accounting for more than 90% of the dissolved inorganic N (Bernal et al., 2015) and for more than 80% of the total dissolved N (unpublished data)").

Minor concerns

Lines 25-26: The authors state "These results suggest that (i) increased supply of limited resources during storms can promote in-stream heterotrophic activity during high flows . . ." They don't actually measure this process, instead they infer it from DOC:NO3- ratios. Perhaps reword this result to be more accurate.

[Reply]: It is true that we do not explicitly measure heterotrophic activity, but we do provide data and analyses that support an "increased supply of limited resources during storms" (Lines 27-28), which is where most of the weight of this statement lies on. The subsequent implication (that this increased supply can promote in-stream heterotrophic activity) is indeed inferred from the analyses on DOC:NO_3^- molar ratios and, more importantly, from the increase in DOC and NO_3^- concentrations during storm flow compared to base flow. We have toned down the statement to be more accurate as suggested by the reviewer by using "could sustain" (Line 28) instead of "can promote".

Lines 108-110: "All data and analyses were integrated and carried out for daily resolutions, which were determined by the availability of the stream chemical data." This line is confusing, please reword.

[Reply]: We agree, and in the revised manuscript we have changed this sentence to "All data and analyses were integrated and carried out for daily resolutions, which was the resolution of the stream chemical data" (Lines 113-114).

Line 114: Please avoid use of "fortnightly" as most readers will not know what this means. Instead state the actual frequency (i.e., every two weeks).

[Reply]: This is most likely true and thus we have removed the word "fortnightly" and use "every two weeks" (Line 118) instead.

New references added to the manuscript (marked with *), references removed from the manuscript (marked with -), and references used in this response letter (not marked)

*Beiter, D., Weiler, M., and Blume, T.: Characterising hillslope-stream connectivity with a joint event analysis of stream and groundwater levels, Hydrol. Earth Syst. Sci., 24, 5713-5744, https://doi.org/10.5194/hess-24-5713-2020, 2020.

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