Reviewer #2, Ji-Hyung Park (AE):

Unexpectedly, two appointed referees could not provide review reports even after the extended due date. Therefore, Associate Editor provides another required report to expedite the delayed review process. – Ji-Hyung Park

General comments

This study investigates the effects of natural and altered flow regimes on DOM concentration and composition in several rivers across Northern Spain. It is a well-designed study employing a combination of analytical tools and advanced statistical approaches. The key findings on the complex linkages between flow regimes and DOM are novel and intriguing. Although the manuscript is generally well written, it also requires both clarifications of several uncertainties and improvements for a more focused discussion as follows:

REPLY: We thank Ji-Hyung Park for the positive evaluation of our work.

1. Hypotheses and key themes: This study examines the effects of altered flow regimes under two different natural settings. As the authors stated ("We hypothesize that DOM properties respond to both natural flow regimes and flow alterations. We expect the effect of flow regime alterations on the DOM regime to depend on certain characteristics of the natural flow regime."), the concentration and composition of DOM would respond to changes in natural flow characteristics without any anthropogenic perturbations to flow regimes. Therefore, the quite general hypothesis needs to be more articulated with regard to which specific DOM characteristics would respond to which specific characteristics of flow regimes (both natural and anthropogenic). Furthermore, the dams in the studied region appear located in headwaters or upper reaches. Given the fact that flow regime changes vary with dam types and locations, dam effects, as a key theme of this study, need to be explained for the prevailing dam characteristics of the study region.

REPLY: Thank you for your comments. We will revise our hypotheses to better articulate the expected DOM regimes and their expected changes due to flow alteration under the various river conditions.

In this study, our primary focus was on examining DOM regime changes under different flow regimes, in the case of 'flow regime alterations' we aimed to achieve this, irrespective of dam types or purposes. Therefore we grouped various dams under the general category of "dam effect" within the same underlying natural flow regime. A strength of the study is that it is built on a previous study allowing us to define a "natural" flow regime type even if a dam is already in place. This enables us to identify overarching trends in the DOM regime caused by dams while simultaneously acknowledging that specific regional climates likely shape flow regimes while also influence the design and operation of reservoirs..

REPLY: Despite this general overall goal, we recognize the necessity to delve deeper into the prevailing dam features of our study. We have discussed the "dam characteristics and operations" relevant to altered flow regimes in Section 3.1, where we connected these characteristics to the water demands of the region. We will expand on the common features of the dams in our study, such as their locations (e.g., predominantly in headwaters or upper reaches), the absence of hydropeaking, and their storage capacities. These details will be incorporated into the Methods section to offer a clearer context for the observed dam effects without going into the details of a site-based analysis.

2. River classification: The authors describe as if they studied 20 different rivers, but actually Fig. 1 shows 20 river locations. Some of them, as tributaries, belong to the same river basins. Around five basins are delineated on Fig. 1. Please articulate how many river basins and their tributaries were studied; and use relevant terms to distinguish mainstems and tributaries. In the same context, the river classifications in L 78-81 need revision. Some of the river sites belonging to two different systems (Atlantic and Mediterranean) are shown shoulder to shoulder on Fig. 1, making me wonder whether these sites really belong to two different "climatic regions". For instance, look at site Arlanzon. From the names, I expected that these rivers might discharge into either the Atlantic Ocean or the Mediterranean Sea. In my view, the use of these names needs to be confined to indicate something like "Atlantic-type flow regime" after defining it at its first use.

REPLY: Thank you for pointing this out. The layout and terminology we used indeed reflect some complexities, partly due to reliance on a previous study that was used to constrain our study design. In the original study by Peñas et al. (2020), Spanish river systems were classified based solely on hydrological indices, without considering their climatic region or geographical location. Subsequently, the names "Atlantic" and "Mediterranean" were assigned to two of the thereby defined hydrological groups based on their predominant flow regime characteristics: Mediterranean rivers typically experience long dry summers, while Atlantic rivers exhibit shorter summers with more moderate flow year-round. We recognize that this naming convention might not be intuitive at first glance, as it is based on hydrological patterns rather than geographic location or basin.

To address your concerns, we will clarify in the manuscript that these classifications represent "Atlantic-type" and "Mediterranean-type" flow regimes, and they are not indicative of the location of the basins they belong to.

Regarding your observation about tributaries, it is correct that some of the studied "rivers" are located within the same river basin, i.e. they share the same downstream located mainstem. However, we ensured that no study site´s catchment (and thus source of water and DOM) is nested within another one´s to maintain spatial independence. We will update the methods section to specify the number of basins and rivers included in the study and to clarify spatial independence.

3. Data interpretation: According to Table 4, DOC concentrations are significantly different only between nA and Am. Associated descriptions in Abstract and Results (L 226-230) need to be consistent with the presented results. Although the means were not significantly different, inter-regime differences distinct for some of the river sites (Fig. 4) warrant descriptions in L 226-230, particularly in relation to (any common) specific hydrologic characteristics of these sites. Statistical analyses indicated the dominant role of high-flow periods (L 311-313) in explaining variations in DOM composition. Can this be related to flow-controlled variations in DOC conc.?

Regarding the lack of dam effects on DOM composition indices, please refer to specific comments below.

REPLY: Thank you for your comments. You are correct that the DOC concentrations between nA and Am are different, as also reported in Table 4. As our primary focus was to compare rivers within the same regime or to compare the two natural regimes to emphasize their distinct characteristics, we did not want to stress this (less interesting) result. That said, for clarity and consistency, we will extend the text descriptions of these statistical results to all possible pairwise comparisons. We will also further explore some of the more distinct DOC or DOM regimes, which more prominently emerge beyond the pre-defined flow regimes, in relation to hydrological features of the respective sites (or sets of sites).

Specific comments

- Title: Do you mean that…two distinct hydrological regimes "of" Northern Spain?

REPLY: Thank you for noticing this, indeed "of" Northern Spain would fit better. We will update this.

- Line (L) 2: What have altered flow regimes?

REPLY: Many rivers specifically from this region have altered flow regimes, we will update it to "of this region" in this sentence.

- L 3 and thereafter: Please remove the comma after the subject and check grammatical errors and typos throughout the manuscript including tables and figures (for instance, superscripts such as m2 and concentration units in parentheses).

REPLY: Thank you for noticing, we will carefully scan the manuscript and correct such errors.

- L 6 "hydrological classes": As suggested by the first reviewer, please use terms consistently; in this case "flow regimes"? Definitions are required for the key terms including flow regimes, DOM regimes, and DOM turnover.

REPLY: We agree that these terms create confusion at various points in the manuscripts. We will clearly identify a set of terms early in the manuscript and also in a conceptual graph, and stick to those throughout the text. Instead of "DOM turnover" we will use "compositional shifts of DOM" in order to avoid ambiguity.

- L 8: Please do not divide this relatively short abstract into two paragraphs.

REPLY: We will combine these two paragraphs into one.

- L 12: Was this turnover rate calculated per unit carbon? Higher DOC concentrations might have led to higher turnover rates, so this needs to be clarified.

REPLY: The word "turnover" here refers to temporal changes in DOM composition. As we understood from the first reviewer's comment, our usage of the term "DOM turnover" resulted in some confusion due to the - in the field more common - interpretation of "turnover" as meaning chemical transformation. Hence, we will replace the word "turnover" by "shifts in DOM composition" and clearly indicate its meaning early in the manuscript and in a conceptual graph. With this in mind, we will indicate here clearly that the paper is not looking into "carbon turnover rates" but explores temporal shifts in DOM composition.

- L 14: What are "unusual DOM behavior"?

REPLY: We will change this to "deviations from the natural DOM behavior".

- L 19: Please specify "these" in this complex sentence.

REPLY: We will break this sentence into two and change "these" to "these natural flows".

- L 53 "DOM regime´s reaction to damming needs fine-tuning": Please rewrite this vague sentence.

REPLY: We will re-write this statement.

- L 58 "compositional turnover": Compositional changes, or variations?

REPLY: Here we refer to temporal variation of DOM composition, we will update this expression accordingly.

- L 93-94: Please provide more details about the hydroclimatic conditions for these six samplings. Later in Results and Discussion, sampling conditions need to be related to flow regimes and DOM characteristics. It would be helpful if sampling timings are indicated on Fig. 2.

REPLY: We will indicate the sampling timings in Fig.2 and in the text here. We judge the idea of indicating detailed hydroclimatic conditions for each site per sampling occasion to require too much space in the text while simultaneously not being very informative as our sites had varying conditions from dry to flooded even within the same sampling campaign. However, to give more insight into site-specific hydroclimatic conditions, we will provide discharge data per site per sampling occasion in the supplementary information.

- L 99-105: Given the importance of DOC quantification and optical characterization in this study, please provide some key QA/QC measures, including blanks, verification standards, references,,,

REPLY: We will provide more details about DOC and optical characterization of DOM in the methods section of the manuscript along with the related references. Briefly, we routinely used MQ-water as blanks for DOC measurements and optical measurements (at least one blank run every 10-15 measurements). Also, we had 3 replicates per site and occasion, each measured twice to take into account any instrumental error. To prepare standards for DOC-measurements we used potassium hydrogen phtalate (KHP). The typical limit of quantification for DOC is 0.5 mg L^{-1} and the typical analytical precision is 3 % in our TOC-V analyser.

- L 218-211: Please describe in more detail about the meaning of and how to read out the magnitude differences. It is very difficult to follow!

REPLY: We will rewrite this text section without abbreviations (or add explanations if abbreviations are unavoidable).

- L 226: It would help understand the temporal variations in DOC conc. if variations in hydrologic conditions among the six samplings were described briefly.

REPLY: Per your recommendation, we will add representative sampling dates to Fig.2. We hope this will help to understand these DOC variations as well.

- L 266-267: Interesting approach! The four regimes overlap considerably on Fig. 5a. Do some outlying sites also exhibit high DOC or any common outstanding hydrologic characteristics?

REPLY: Indeed, we have looked at whether these extreme sites/occasions coincide with high DOC values but could not find any relation. We will check this more in detail and include our findings here.

- L 307: Again this 'turnover' is an undefined, ambiguous term.

REPLY: We will change this term in the final version to "compositional shifts of DOM" as stated above.

- L 324-337: The dams studied in this study appear located in headwater streams. Dams in lowland or high-order streams might be quite different in terms of flow regimes. Please consider this stream-order effects.

REPLY: Indeed all dams are in 2nd order or 3rd order streams. We will include stream orders in the above-mentioned table for the supplementary information. We will also point to the fact that our altered flow regime sites were all impacted by headwater dams.

- Discussion is very long and repeating some results descriptions, but limited in citing other relevant studies to put the implications of the key findings in a wider regional or global context. Please consider removing repeated descriptions while focusing discussions on key implications and comparisons with previous studies.

REPLY: We will remove the repetitions from the discussion and will strive to improve comparison of our results with those of previous studies.

- L 331 (and other places): Please use two instead of 2.

REPLY: We will update this in the manuscript.

- L 351: This very long paragraph can be split here.

REPLY: We will divide this paragraph into two.

- L 373-375: Please don't repeat the descriptions already mentioned in Results.

REPLY: We will update this sentence not to repeat results.

- L 382: not "increase" but "increasing trend".

REPLY: We will update this sentence and use "increasing trend".

- L 387: How can "hydrological averaging" can increase DOC concentrations? DOC flushing mechanisms explained by Raymond et al. assume higher DOC concentrations at terrestrial sources. Increased DOC conc. in stream downstream of reservoirs should then indicate additional supplies from autochthonous sources.

REPLY: We wanted to suggest that hydrological averaging by dams that hold back flood water may lead to an increased and stable mean concentration of terrigenous DOM mobilized by floods downstream of the dam. Indeed, this requires a range of conditions, which we did not detail well enough, namely fairly high terrigenous DOM loads mobilized by floods and rather bio- and photo-resistant behaviour. Also, to affect DOC (i.e. DOM quantity), any such terrigenous DOM must still be understood in concert with autochthonous DOM produced in the reservoir. We will improve the description of our idea of "dams flattening a DOM pulse" in the revised manuscript and describe the conditions upon which it may hold. We will do so explicitly here and touch upon it further in the conclusion (per your comment L487)

- L 388-391 & 398-410: Given the significance of dam effects as a key theme, a more in-depth discussion, including comparison with previous studies on DOM characterization in other dam types (not citing only one review paper), is required to explain the observed patterns in aA and aM.

REPLY: Thank you for your suggestion. We will include a more detailed discussion of DOM regime effects in light of other studies characterizing DOM downstream of dams.

- L 392-397: Does the lack of statistical differences in DOM composition indices simply translate into no dam effects on DOM? As suggested before, a more detailed look at large within-regime variations is required to figure out some key characteristics driving the link between dam-induced alterations in hydrology and DOM. For example, you are not addressing the trophic status of your reservoirs, which may be quite different from eutrophic reservoirs.

REPLY: Indeed, an eventually observed DOM regime downstream of a dam may be driven by a large range of potential influences associated with specific dam features, e.g., location in the continuum or catchment size, reservoir size and residence time, trophic status, and operation regime. Our study and analysis design lumps together dams and reservoirs of various types, thus it was never our intention to identify how specific dam factors may influence DOM. Indeed, we also find that alteration diversifies flow regimes substantially. This diversification of flow regimes may be expected to lead to a similar diversification of DOM regimes, with potential consequence being lower statistical power to identify eventual differences to natural flow regimes. This may be true when looking at differences in means, yet we let our analysis go far beyond the analysis of “average DOM composition” by looking into potential effects of dams on temporal variation of DOM composition, i.e. a “DOM regime”. Surprisingly, we show that DOM regimes do not follow flow regimes as a consequence of alteration; a result of analysing ‘variation over time’ is that DOM regimes do not diversity but rather homogenize. Thus, we hope to be able to show that simplistic statements like “dams do not affect DOM” are not valid.

Despite our design constraints, one dam-specific factor we identified as potentially important for the DOM regime was reservoir size or storage capacity. Indeed, storage capacity and associated residence time may explain some of the observed among-river differences and we specifically discussed this in section 4.3. We will look into nutrient data and trophic status as potentially interacting with residence time to influence DOM and suggest to discuss potential effects in concert with residence time. Unfortunately, we lack more detailed information about dam operation and prefer to refrain from further speculative interpretation of our data that is not oriented along the principal design of the study. We will look into the possibility of mentioning potential effects of dam storage size in this closing sentence as well.

- L 408: Yes, but which “factors related to dam nature and operation” are critical for your rivers?

REPLY: Please see our answer to the previous comment. Besides generally alluding to a range of dam-specific features that may influence DOM regimes, we will try to identify those in our dataset and link results to particular dams. However, we believe that such an in-depth discussion of particular dams comes dangerously close to speculation and should be limited as it is not supported by our study design.

- L 413-414: Yes, temporality is critical. However, the following descriptions only focus on the statistically analyzed means. As suggested, a brief discussion can be added here to evaluate how hydrologic conditions preceding the six samplings might have (differentially) affected the observed patterns in the four systems.

REPLY: In addition to indicating the sampling dates in Fig 2 as you’ve suggested, we will add discharge on the sampling day for each site in the SI to give a clear idea on sampling day conditions per site. We will here attempt a limited discussion of how the observed hydrograph of particular rivers may be associated with the observed DOM regime. However, we point to previously already argued limitations of our study design and our limited ability to pinpoint particular dam-specific effects. Currently, we see the need to limit such argumentation based on individual discharge time series to avoid a too speculative discussion.

- L 455-: Please provide some data or literature information to link these trophic changes to autochthonous DOM production.

REPLY: Thank you for noticing, here, we will cite two references, Ulseth and Hall, 2015; Maavara et al., 2020, regarding reservoirs and residence times and reservoirs and nutrients.

- Section 4.4: The title is not in agreement with the text descriptions. This short paragraph is not redundant? Otherwise, provide a more proper discussion.

REPLY: This section closes our discussion with a last point looking at among-river variation in low regimes. We will integrate this section into the previous section.

- L 487 “longer residence times average out the naturally high turnover of DOM composition, and send relatively invariable DOM further downstream.”: This conclusion cannot explain the observed increasing DOC trend and is not in line with the following implication “increased metabolism of terrigenous DOM and increasingly higher CO_2 emissions in rivers downstream of dams”. From my own experiences in highly eutrophic, impounded systems, CO_2 emissions generally increase with the increasing supply of labile DOM (please refer to this review: https://doi.org/10.1016/j.watres.2022.119362).

REPLY: Please see our above explanation of how hydrological averaging by transiently storing flood waters in reservoirs may increase terrigenous DOM downstream of dams. We will improve our explanation of this potential mechanism and the conditions under which it may hold. Our idea of increased metabolism of this DOM is based on an improved match with microbial capabilities. We will improve the explanation of this potential mechanism. Also, we will include opposition to the case of eutrophic reservoirs, which may drive downstream metabolism and CO_2 emission by supplying labile DOM.

- Fig. 1: Given the significance of impoundments in distinguishing flow regime types, I wondered if dam locations could be indicated within each altered-regime sub-catchment.

REPLY: We will include dam locations for rivers with altered flow regimes in this Figure.

We thank Ji-Hyung Park for their insightful and constructive comments.