

General comments:

The manuscript *Riverine biogeochemistry from the Andes to the ocean: longitudinal patterns along a Mediterranean Andean catchment in central Chile* by Derrien et al. presents important and timely findings on riverine biogeochemical dynamics in a Mediterranean Andean system. The authors provide a comprehensive longitudinal assessment across the Rapel catchment, integrating dissolved organic matter (DOM) optical properties, nutrient chemistry, dissolved metals, and microbial community composition. The dataset is extensive, the spatial coverage is strong, and the multi-compartment biogeochemical approach represents a major strength of the study. The work is highly relevant for understanding hydrological regulation and land-use pressures in Andean watersheds.

We sincerely thank the reviewer for the positive and encouraging comments on our manuscript.

While the scientific foundation of the manuscript is solid, several issues require attention before final publication. These include editorial inconsistencies, missing values, formatting errors, and areas where methodological or interpretive clarity could be improved. Addressing these points will enhance readability, coherence, and overall professionalism. In its current form, the manuscript warrants moderate revision.

A detailed point-by-point response to the reviewer's comments is provided below.

Specific comments

- Line 65 and 83: The Rapel catchment area should be consistent. You have got two different numbers/significant figures.

We thank the reviewer for highlighting this inconsistency. We have revised the Introduction accordingly to ensure consistency with the information provided in the Materials and Methods: "In this study, we investigated the longitudinal biogeochemical dynamics of the Rapel catchment in central Chile, a large Andean-to-coastal Mediterranean ecosystem covering 13700 km²".

- Line 108-114: Clarify the naming conventions, they are not very clear especially for Tinguiririca and Cachapoal subcatchment. They were described in results, but given the number of samples, a short description in the methods would be helpful for the

flow.

We thank the reviewer for this comment. We have revised the text to clarify the station code structure as follows: "To examine the complete river continuum, 25 sampling sites were selected along the catchment, from the Andes to its mouth in Navidad (Fig. 1). Of these, 11 sites were located within the Cachapoal subcatchment, 8 within the Tinguiririca subcatchment, and 6 within the Rapel subcatchment. Station names follow a standardized nomenclature in which the first letter indicates the subcatchment (C = Cachapoal, T = Tinguiririca, and R = Rapel), while the following letter(s) identify the river within the corresponding subcatchment, followed by the station number, when applicable. For example, C-C1 refers to sampling point 1 on the Cachapoal River within the Cachapoal subcatchment, whereas C-P refers to the sampling point on the Portillo River within the Cachapoal subcatchment. Thus, the station code provides information on both the subcatchment and the river where the sampling site is located."

- Line 133: Maybe specify the maximum storage duration before extraction in this sentence "Sterivex filters were frozen at -20°C."

We thank the reviewer for the suggestion. The following information has been added: "Sterivex filters were stored frozen at -20 °C for a few weeks to a maximum of 4 months before extraction".

- Line 134: Sample Analysis? "Samples collection" Section title appears twice (2.2 and 2.3).

We thank the reviewer for this comment. The section title has been changed to " 2.3 Analytical measurements".

- Line 169: "retained XX% of the raw reads." Place the missing value here.

We thank the reviewer for this comment. The missing value has been added "This process resulted in an average of $155,640 \pm 37,086$ reads per sample and retained $83.9 \pm 3.6\%$ of the raw reads".

- Line 191: "C1mh, C2th, C3p, C4trp" Component naming inconsistent across manuscript Please Standardize them. Also, the component names could also be included in section 2.3 to avoid confusion.

We thank the reviewer for catching this. The naming of the components has been reviewed and homogenized across the manuscript. Component names have also been added in section 2.3. "A 4-component model was validated (98.9% explained variance, Fig. S2) and the components were compared with similar components reported in the literature using the OpenFluor database (Murphy et al., 2014) and attributed to specific groups of fluorophores (Table S1; C1mh: Marine Humic-like, C2th: Terrestrial Humic-like; C3p: Protein-like, C4p: Protein-like)".

- Line 196: catchment levels?

Indeed, it has been corrected as follows: "Similarly, for representation purposes, the three subcatchments (i.e., Cachapoal, Tinguiririca, Rapel) and the three catchment levels (i.e., headwaters, transition zone, floodplain) were added as supplementary qualitative variables".

- Line 220: a better way might be to reference figures as- (Fig. 2a) instead of (Fig. 2 (a)) here and in the rest of the manuscript.

This way of referencing this figure has been corrected across the manuscript.

- Figure 2: revise the following sentence "Dots and lines represent the main rivers; single empty dots represent the tributaries." with something like "line and scatter plots (with filled symbols) represent the main rivers while void symbols represent the tributaries."

We thank the reviewer for the suggestion. The caption of Figure 2 has been revised as follows: "Figure 2: Dissolved Organic Carbon (DOC) concentration (a) and Total Dissolved Nitrogen (b) in the three subcatchments. Line and scatter plots (with filled symbols) represent the main rivers while open symbols represent the tributaries. In the Rapel subcatchment, the reservoir sample is shown in a lighter shade. The code names of the sampling sites are shown next to the corresponding dots. Note that the y-axis of DOC concentration has a break between 140 and 200 μM due to the marked difference between the concentration in C-Ca and R-R2 and the rest of the sites, helping in highlighting the concentration dynamics in the lower concentration sites".

Also, Given the importance of Rapel reservoir in this study, highlighting it using a different color or symbol in the figures would improve readability.

We thank the reviewer for the suggestion. The comment has been reflected in Fig. 2 and Fig.

3 using a lighter shade for the reservoir samples.

- Figure 3: revise the caption following the comment for Figure 2.

We thank the reviewer for the suggestion. The caption of Figure 3 has been modified as follows: "Figure 3: Concentration normalized fluorescence of the 4 identified components: microbial humic-like C1mh* (a), terrestrial humic-like C2th* (b), protein-like C3p* (c), and tryptophan-like C4p* (d) in the three subcatchments. Line and scatter plots (with filled symbols) represent the main rivers while open symbols represent the tributaries. In the Rapel subcatchment, the reservoir sample is shown in a lighter shade. The code names of the sampling sites mentioned within the text are shown next to the corresponding dots".

- Line 244-252: Consider adding specific excitation/emission maxima at their first appearance and check for consistency in the terms used to represent the components (i.e., C4trp vs C4p) throughout the manuscript and figures.

We thank the reviewer for catching the mistake in naming the components; it has been reviewed and homogenized across the manuscript. Components' excitation/emission maxima have been added as follows: "The PARAFAC analysis of the EEMs and comparison of the results within the Openfluor database (Table S2) resulted in the identification of two humic-like and two protein-like components. C1mh ($\lambda_{Ex}/\lambda_{Em}$ max: 315/409 nm) has characteristics that are usually attributed to humic-like compounds that have been reprocessed by the microbial community. C2th ($\lambda_{Ex}/\lambda_{Em}$ max: 260(365)/469 nm) has the typical excitation and emission maxima attributed to terrestrial humic-like compounds. C3p ($\lambda_{Ex}/\lambda_{Em}$ max: 300/348 nm) has fluorescence maxima that resemble those of protein-like compounds in water, i.e., tryptophan, but its excitation maximum occurs at longer wavelengths than the typical protein-like components of DOM. This suggests that its fluorescence may be influenced by factors such as being bonded within bigger molecules or complexed with metals (Aiken, 2014). Interestingly this component was found to be more than 98% similar (Openfluor comparison) to components identified in other regions affected by the presence of ice (Chen et al., 2018; Maurischat et al., 2022). C4p ($\lambda_{Ex}/\lambda_{Em}$ max: 275/338 nm) fluorescence maxima are those usually related to protein-like fluorescence".

- Acknowledgements: If Financial Supports section is a requirement, consider

removing the same information from Acknowledgements.

As suggested by the reviewer, the financial support information has been removed from the Acknowledgements.