

I think the authors have demonstrated a good understanding of processes across a large catchment. I was very interested in this work and the results. Overall, I think the paper is well written, with only a few sentences that need clarification. I think the majority of my comments are detail-oriented, but there are a few key things missing from the paper that I would recommend including in revisions:

- Discussion of the flow conditions during the sampling time period
- Statistics testing the downstream patterns in DOC, TDN, and fluorescence metrics
- More thorough incorporation of the ANOVA/Kruskal-Wallis (K-W) test results
- How did you define where the headwaters, transition zone, and floodplain are? How did you calculate the distance from the glacier?
- Please see my comments on salinity vs TDS vs conductivity – if all three of these are listed separately they should be derived from different measurements, rather than an estimate from a conductivity sensor.

L43 paragraph – the RCC is an important foundation for this work, but in this paragraph I would make how the variables you measured relate to the RCC more clear.

L52 – Cite some of the serial discontinuity research like Stanford & Ward 1983, 2001; Ward & Stanford; Ellis & Jones 2013; Poole 2002

L84 – make sure you define a.s.l.

L89 – this isn't clear – is 310 km the entire length of flowpath? Or this distance between the dam and the ocean?

L95 – I'm assuming these average annual discharges are at the confluence of the two rivers? Please specify where if not.

L96 – reunited or just united?

L100 – I'm not sure that "at lower elevations" is specific enough to describe where these native vegetation communities are, as from my understanding, the agricultural areas are at lower elevation from these.

L104 – Do you have a source describing the metal inputs from the mines?

L111 – Are sites R-R1 and R-R2 reservoir samples?

Fig 1 – This map is clear visually, and I like that it shows the elevation, since this is a key part of how you define the different zones within the catchment. However, I do think it may be helpful to try to include the land use data in the main text (e.g. SI Fig 1). I recognize this may

not be possible to incorporate into the Fig. 1 map without negatively impacting the legibility. However, it may be helpful to include high level annotations of the cities, the Rapel reservoir, and maybe even outlines of the land use zones. Ultimately I think this edit is a matter of personal opinion, but at the very least I would define the headwater, transition zone, floodplain on the map.

Fig 1 – What is this other lake upstream of T-Ch? On the map it looks to be about the same size as the Rapel Reservoir by surface area.

L 123 – What were the flow conditions during your period of sampling? Did you do anything to make sure flow was consistent across days? How do you think that sampling during snowmelt influenced your results?

L124- Based on your variation in temperature in the results, I would recommend reporting your conductivity values as specific conductance.

L144- Did you do an inner filter effect correction? If so, make sure it's listed here.

L204 – Unless I missed it, I didn't see salinity mentioned in your methods? Is this in parts per thousand?

L210 – Is the conductivity measurement coming from the same sensor as the salinity measurement? Same with the TDS measurement. I am not familiar with the Hanna probe, but I know with some instruments conductivity, salinity, and TDS all come from the same conductivity sensor. If so, I would report only one.

L212 – elevated compared to what?

L213 – Did you test this EC pattern with the ANOVA/K-W?

L214 – What do you mean here by continental stations?

Section 3.1. and 3.2. – Here you have mostly qualitative descriptions of the data, it would be good to incorporate the ANOVA/K-W in Section 3.1. and apply stats to say if something was actually significantly increasing or decreasing along the flowpath in Section 3.2.

Figure 2 – How did you define distance from glacier base and the locations of the transition zones? You don't discuss glaciers in your site description, where are they? What glacier are you using for the downstream sites (e.g. Rapel), where presumably there are multiple glaciers in the headwaters? Are the tributaries plotted based on their confluence with the main stem? These same questions go for Figure 3.

L264 – again, I’m looking for some sort of statistical trend analysis here. I agree with your qualitative descriptions of these patterns, but it would be good to look at the significance of the downstream trends.

Fig 3 – I think there’s a discrepancy between your units in Figure 3 ($\times 10^2$ R.U. μM^{-1}) vs in the text (R.U. μM^{-1}).

L297 – I don’t think that you have evidence here to “confirm” that the copper concentrations are due to the mining; perhaps you can say “potentially related”

L300 – What do you mean by “lower” and “intermediate” metal concentrations? Did you use the ANOVA/K-W test here to compare the subcatchments?

L320 – By “lower zone” do you mean the Rapel subcatchment? I would make sure you’re referring to these zones consistently throughout. I think how you break down the site groups in Figure 4 is clear, and can be a guiding example throughout the text. I think what’s missing in the map is the Headwaters/Transition Zone/Floodplain.

Figure 5 – Can you visually add the results here from your ANOVA/K-W test? E.g. labeling the significant groups a/b/c (this website contains examples: <https://statdoe.com/one-way-anova-and-box-plot-in-r/>)

L356-358 – I think this relationship is a really interesting finding.

Figure 6 – are the replicates analytical replicates? This wasn’t discussed previously. Also, are the tributaries included in here? Since you made a distinction with the tributaries in figures 2 and 3 you may also consider doing it here, where you can trace site by site.

L380-382 What do you mean by “different y-axis scales between the protein components and the humic ones”?

L393 – why would the volcanic environment lead to more protein-like DOM?

L397 – what are the common characteristics specifically?

L407-408 – If this were a pristine catchment, would you still expect terrestrial OM to accumulate along the continuum?

L419-423 – Can you link some of these differences between the reservoir to other studies comparing reservoirs vs streams? I would expect them to operate pretty differently.

L427 – Reference indicating these taxa are reflective of these conditions?

Paragraph at Line 401 – Can you break this up into shorter paragraphs with some overview sentences? Currently it is hard to digest in one long paragraph. Maybe have one paragraph describing what is going on in each subcatchment/zone?

L431 – have there been any studies at the Alhue stream showing it has high concentrations and can be a source? Is this stream the orange/beige part of the map?

L461- Be more specific here than “upper Andean sectors” – do you mean you observed more variability in these upper areas?

L475 – Even though this type of headwater to ocean study is uncommon, there must be studies looking at how dams impact the downstream properties of organic matter. Are your results typical?

L493-495 and L 511-516– Do you have references for these statements? I don’t think that these statements (particularly regarding changes to climate/hydrology) are clearly supported by your results, which measured only one time period.

General questions for the discussion - How does the rain/snow regime influence the differences you might see between the upland headwaters and further downstream, particularly since you sampled during a time period with snow runoff?

What would you expect to see if you compared first order streams in the upper Andean zone with low order streams at a lower elevation?

How does the strong altitudinal gradient influence the transferability of the results from this study?