Hydrology and
Earth System
Sciences
Discussions

Interactive comment on "Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers" *by* Shannon Sterling et al.

Shannon Sterling et al.

shannon.sterling@dal.ca

We thank Anonymous Referee #2 for the thoughtful review of our manuscript. Below we respond (in bullets) to Anonymous Referee #2's comments (in quotes).

"Overall the paper presents an interesting dataset for a topic that probably hasn't received as much attention as it should have. The paper in its present form is largely site-specific case study, highlighting high concentrations of Al that exceed toxicity limits across several river basins, despite reductions in acid sources.

I think the paper can be suitable for publication, following some revision. The intro-

duction sets a good background and context, but the methods and results could be mistaken for a monitoring report and could be enriched to better highlight the novelty in approach and the significance of the findings.

There are three main points I think could be considered to improve the paper:

I think the paper is missing a conceptual model. The mechanisms that could explain the observations are well described, but a conceptualisation of how they are inter-related could help frame the paper and give it a more general focus, making it more than just presentation of a site specific dataset – this is something that could be considered as a diagram for the discussion, and would help as a synthesis of the observations."

- We agree. We have added a conceptual model. The paper is strengthened as a result. The conceptual model proposes new hypotheses to explain the insights into the drivers of toxic aluminium that we have learned from our study. Specifically, it proposes an explanation as to why, contrary to the existing conceptualizations of Ali concentrations being highest during spring peak flow, Ali concentrations are highest during summer low flow. And our Generalized Linear Mixed Model reveals, contrary to the standard conceptualization that DOC is inversely correlated with Ali, that DOC is strongly positively associated with Ali, suggesting that the increased recruitment of Al in soils by DOC may outweigh DOC's protective effects in waterbodies.

"Related to the above, the paper could enrich the link to hydrology – seasonality is discussed at one point, but could this be expanded to better frame in context of catchment behaviour? I feel that after reading this paper, the take away message was that concentrations are high, above toxicity limits, which makes it perhaps more suited to an environmental quality journal, but what seems to be missing is how hydrology may be mediating concentrations and speciation. Again, this is where a conceptual model may help."

- We agree. We have added a conceptual model and its discussion to the manuscript, illustrating how stormflow vs baseflow mediates concentrations and speciation.

"The statistics seems like it could benefit from a multi-variate approach to looking for patterns – currently the reliance on a series of independent correlations makes it hard to understand if there any interactions between variables. Use of GLMM is suggested at one point as a recommendation, but it's not clear why it wasn't done. For a paper in a top science journal, a full analysis of the data should be undertaken to come to a conclusion and show the results, rather than describe a possibility of showing something. In any event maybe there are other techniques that could be applied to better explain the variability?"

- Thank you for this insight. We have added a multivariate approach by developing a GLMM; the results support our conceptual model.

"Specific Comments

- Line 39-40. Sulfur emission reductions are mentioned here. But the paragraph opens straight away with acidification. Whilst most HESS readers I think will be familiar with the context, there may be readers without familiarity of this chemistry. I would therefore recommend extending the opening sentences to introduce the origin of acidification
- Following the above, the paper also maybe assumes the reader is familiar with the link between acidity and Al. Is this link predictable or depends on geology? Improving these contextual statement in the opening to highlight how sulfur, acid and aluminium are related I think will help entrain readers (though I notice some coverage of this at the end of the intro)."

- We agree and have extended the opening sentences to introduce the origin of acidification, and have expanded the description of the link between acidity and Al.

"- Ln 46 – What is SWNS?"

- Thank you for catching this undefined acronym. It has been removed.

"- Ln 61 – Gibbsite is mentioned here. It would help to highlight the approximate pH where this kicks in (âĹij4.5?), and maybe replace "formation" with "precipitation" in case

people are not aware it is a solid phase."

- Thank you for catching this ambiguity. We have highlighted that gibbsite is formed at pH 6.0-8.0 at 25oC and approaching 6.5-8.5 at cooler temperatures (5oC) (Lydersen et al., 1990).

"- Ln 70 – This sentence seems like it should have come earlier (see initial comment): "Lowered pH increases Al solubility and observations confirm that Ali concentrations are negatively correlated with pH". Currently this paragraph on Al sources, comes after a paragraph on speciation and toxicity."

- Agreed, and fixed.

"- Line 96 – Should the ":" be a ";"?"

- Two independent clauses – yes, it should be a ";". Fixed.

"- Line 101 – I don't recall NS is defined by this point."

- We have added a definition of this acronym (Nova Scotia).

"- Line 110 – Here the aim of the paper is outlined, but it is a bit vague – there is a general desire to "increase understanding . . . " – could this be more specific? Ideally it would be good if the questions could also link to hydrology . . . eg is Al linked to hydrologic dynamics?"

- We have added more specific research questions linking hydrology to the observed chemical patterns.

"- Line 147 – The description of statistics is brief. It looks like univariate statistics were done. It seems like the sort of dataset which requires a multivariate approach? PCA?"

- Thank you for this insight. We have added a multivariate approach by developing a GLMM and have presented the results in the manuscript.

"- Line 149 – the last sentence introduces the term toxic threshold, but it doesn't follow

from the previous sentences. Are you setting a threshold to determine exceedance frequency? Or are other metrics related to toxicity computed? - This toxicity value of 15 is mentioned, but I think it needs more justification and a clear rationale – is it acute or chronic, what is the origin and basis of this number?"

- We have added a clarification of the origin and basis of the water quality threshold of 15 ug/L used in this manuscript; it is drawn from the FAO European Inland Fisheries Advisory Commission (EIFAC) water quality criteria for freshwater fish (Howells et al., 1990, Chemistry and Ecology). In the pH range of the 4.5-5.8, exposure of salmonids to concentrations of Ali around 10 to 15 μg L-1 for less than 14 days were found to acutely impair the sea-water tolerance of salmon smolts (Staurnes et al., 1995; Howells et al., 1990; Dennis and Clair, 2012; Kroglund et al., 2012).

"- Figure 1 & 2. I would have thought concentrations should come before the fraction % of samples above 15, as the latter has a higher level of interpretation."

- We agree that current Figure 2 should go before Figure 1; further, to reduce redundancies, we have combined Figures 1 and 2 into one figure with two panels.

"- Line 189 – Seems like a significant finding – could this be better highlighted as specific focus when framing your research question in the introduction, and also highlighting in the abstract?"

- Reviewer #1 pointed out that the lack of correlation between pH and Ali is likely due to a low pH range in observations. We have added this point to the discussion. We have also highlighted other mechanisms that may cloud the strength of the inverse relationship between pH and Al: Al buffering in base cation-poor soils such as in Nova Scotia, increased DOC solubility at higher pH, increasing Al solubility in soils. In contrast, our finding that DOC is significantly and positively correlated with Ali, rather than inversely - as has been stated in the literature (e.g., Gensenmer and Playle, 1999), is important. This finding has important policy implications. For decades, policy makers in Nova Scotia assumed that the high levels of DOC in Nova Scotian rivers protected

C5

wild Atlantic salmon populations from aluminum. We have improved the highlighting of this significant finding in the conceptual model, research question and in the abstract.

"- Line 221 – it is suggested in the results that you should do a GLM model – why don't you do it in this study and present it here? I would have thought that for a hydrology focused journal, understanding the link between seasonality in hydrology and pH / Al relationship would be an important area to explore in detail, rather than just hint at it?"

- We agree. We have developed a GLMM to explore these ideas in more detail and have presented the results in the revised manuscript. The model results reinforce that DOC concentrations are positively associated with cationic aluminum on a seasonal basis.

"- Conclusions – this is a good summary, but framed as 4 short paragraphs. I felt this could be more refined, maybe as just a single paragraph that flows better. Recommendations for further research on recovery approach's may be useful?"

- We agree. We have changed the conclusion to a single paragraph and have added recommendations for further research on recovery approaches.