Environ Monit Assess (2021) 193: 212
https://doi.org/10.1007/s10661-021-08973-8

Elevated levels of sulfur, nitrogen, and fluoride in small coastal streams near an aluminum smelter in north coastal British Columbia: a reply

R. Paul Weidman · Timothy J. Maguire · Jonathan W. Moore · Scott O. C. Mundle · Daniel T. Selbie

Received: 11 February 2021 / Accepted: 24 February 2021 / Published online: 24 March 2021

Letter to the editor

[1]The Rio Tinto aluminum smelter at the terminus of the Kitimat River near the town of Kitimat in north coastal British Columbia has been in operation for over 60 years. Following a major upgrade to the facility (~$6 billion), atmospheric emissions of sulfur dioxide (SO2) from the smelter increased from ~ 6200 tonnes SO2/year in 2008–2013 to ~ 10,500 tonnes SO2/year in 2016–2018 (Rio Tinto, 2018); during the same time period emissions of nitrogen oxide (NO x) increased slightly from ~ 265 to ~ 300 tonnes NOx/year, whereas emissions of hydrogen fluoride (HF) decreased from ~ 490 to ~ 145 tonnes HF/year. Emissions of SO2 and NOx are expected to increase further with on-going development of liquefied natural gas export facilities and increased marine shipping near Kitimat (ESSA Technologies et al., 2014).

The goals of our recent study, Maguire et al. (2020; EMAS 192:568), were (1) to determine if past emissions from the smelter had elevated concentrations of major anions and cations in small streams nearby and (2) to delineate the spatial extent of any effects on stream water chemistry in the Kitimat River watershed. To do this, we examined potential differences in stream water chemistry and export of ions between exposed and reference streams in 2015 and 2016. We reported that there were elevated concentrations of sulphate (SO4−2; 5 × higher), nitrate (NO3−; 10 × higher), fluoride (F−; 12 × higher), and calcium (Ca+2;2 × higher) in six exposed streams near the smelter, relative to three proximal unexposed reference streams. Stream export of SO4−2 and Ca+2 (normalized by stream discharge and catchment area) in exposed streams was also elevated relative to reference streams by 4 × and 2 ×, respectively. Distances from the smelter where SO4−2 and Ca+2 export were elevated extended up to 16 and 8 km, respectively. These differences in water chemistry between exposed and reference streams reflect the cumulative impact of industrial atmospheric emissions deposited on the exposed portion of the Kitimat River watershed over past decades and recent years.

In their letter to the editor in this issue of Environmental Monitoring and Assessment (EMAS), Watmough et al. disagree with one statement in

R. P. Weidman (✉) · T. J. Maguire · S. O. C. Mundle
Great Lakes Institute for Environmental Research, University of Windsor, Windsor, ON , Canada
e-mail: paul.weidman@uwindsor.ca

J. W. Moore
Earth to Oceans Research Group, Simon Fraser University, BC, Burnaby, Canada

S. O. C. Mundle
Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada

D. T. Selbie
Fisheries and Oceans Canada, Science Branch, Pacific Region, Cultus Lake Salmon Research Laboratory, Cultus Lake, BC, Canada

[1] Reply to Watmough et al. February 11th, 2021

our paper where we suggested that the observed increases in ion concentrations and export "…may contribute to [biological] effects within tributaries on benthic stream communities and regionally important juvenile Pacific salmon" (Maguire et al., 2020). Watmough et al. do not disagree with our methods or findings, which indicate that smelter emissions have altered stream water chemistry within the Kitimat River watershed. However, they argue that annual SO2 deposition from the smelter is lower than average annual acid buffering capacity of the exposed streams (i.e., critical load), calculated using data from our study and the steady state water chemistry (SSWC) model (Henriksen & Posch, 2001), indicating "…there is little probability of biological impacts associated with acidification caused by SO2 emissions from the smelter." One reason for the apparent difference between these qualified statements (in quotations above) may be that Watmough et al. have focused on one potential pathway of effects via sulfur deposition, whereas we have considered multiple chemical pathways of effects on streams including sulfur, nitrogen, and fluoride.

With respect to sulfur and nitrogen, Watmough et al. have focused on calculating the average annual acid buffering capacities of streams. They emphasize that changes in long-term (years to decades) average annual pH of the exposed streams, due to elevated SO2 deposition, are predicted to be minor because most of these catchments appear to be moderately well buffered from acidification. We do not disagree with their calculation of annual acid buffering capacity of the study streams. However, the reason we did not attempt these critical load calculations in our paper was that given these small coastal tributaries are temporally highly variable with respect to their chemistry and hydrology, we think that several other factors should also be tested and considered at the same time. These factors include short-term variation (days to weeks) in stream acidity and alkalinity (e.g., Driscoll et al., 2001), which are regulated by variation in anions (including SO4−2 and NO3−), base cations (e.g., Molot et al., 1989), base cation dilution during run-off events (e.g., DeWalle & Swistock, 1994), dissolved organic matter (e.g., Buffam et al., 2007), and inputs of marine aerosols (e.g., Kowalik et al., 2007). In addition, although average NO3− concentrations among exposed streams were relatively low (80 µg NO3−/L ± 51 SD; n = 6), concentrations were 10 × higher than reference streams (8 µg NO3−/L ± 7 SD; n = 3). Relatively small increases in nitrogen inputs (e.g., doubling of anthropogenic atmospheric nitrogen deposition) can alter nutrient cycling and algal species composition in remote oligotrophic freshwater ecosystems (Elser et al., 2009; Holtgrieve et al., 2011; Wolfe et al., 2003).

Although atmospheric emissions of fluoride from the smelter have decreased in the past 10 years, fluoride levels in exposed streams are elevated near the smelter. Average concentrations of F− exceeded Canadian guidelines for the protection of aquatic life (120 µg F −/L; CCME, 2002) in five of six exposed streams (355 µg F −/L ± 173 SD; range 177–565 µg F−/L; n = 5), which was 14 × higher than the three reference streams (26 µg F−/L ± 8 SD; range 17–34 µg F−/L; n = 3). Maximum F− concentrations (i.e., 95th percentile) in the five highest exposed streams ranged up to 202–833 µg F−/L. Elevated levels of F− as low as 200 µg F−/L have been shown to negatively affect some sensitive species of benthic invertebrates (Camargo, 1996; Camargo & La Point, 1995; Camargo, 2003) and juvenile fish (CCME, 2002; McPherson et al., 2014; Pearcy et al., 2015).

In conclusion, within the bounds of the results of our paper, and the literature we have cited, our original statement—that elevated levels of sulfur, nitrogen, and fluoride "may contribute to [biological] effects" in these tributaries—was supported scientifically. We suggest that it is important to consider all three possible pathways of effects from sulfur, nitrogen, and fluoride, on annual and daily time scales, due to the potential for cumulative effects on aquatic biota, ongoing and historical industrial atmospheric emissions, and given that emissions are forecasted to increase with proposed industrial development within the region.

References

Buffam, I., Laudon, H., Temnerud, J., Mörth, C. M., & Bishop, K. (2007). Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network. Journal of Geophysical Research: Biogeosciences, 112(1). https://doi.org/10.1029/2006JG000218

Camargo, J. A. (1996). Estimating safe concentrations of fluoride for three species of nearctic freshwater invertebrates: Multifactor probit analysis. Bulletin of Environmental

Contamination and Toxicology, 56(4), 643–648. https://doi.org/10.1007/s001289900094

Camargo, J. A., & La Point, T. W. (1995). Fluoride toxicity to aquatic life: A proposal of safe concentrations for five species of palearctic freshwater invertebrates. Archives of Environmental Contamination and Toxicology, 29(2), 159–163. https://doi.org/10.1007/BF00212965

Camargo, J. A. (2003). Fluoride toxicity to aquatic organisms: A review. Chemosphere, 50(3), 251–264. https://doi.org/10.1016/S0045-6535(02)00498-8

CCME. (2002). Canadian water quality guidelines for the protection of aquatic life: Inorganic fluorides. In Canadian environmental quality guidelines (pp. 1–4). Winnipeg, Manitoba, Canada: Canadian Council of Ministers of the Environment (CCME).

DeWalle, D. R., & Swistock, B. R. (1994). Causes of episodic acidification in five Pennsylvania streams on the Northern Appalachian Plateau. Water Resources Research, 30(7), 1955–1963. https://doi.org/10.1029/94WR00758

Driscoll, C. T., Lawrence, G. B., Bulger, A. J., Butler, T. J., Cronan, C. S., Eagar, C., et al. (2001). Acidic deposition in the northeastern United States: Sources and inputs, ecosystem effects, and management strategies. BioScience, 51(3), 180–198. https://doi.org/10.1641/0006-3568(2001)051{[}0180:ADITNU]2.0.CO;2

Elser, J. J., Andersen, T., Baron, J. S., Bergström, A. K., Jansson, M., Kyle, M., et al. (2009). Shifts in lake N: P stoichiometry and nutrient limitation driven by atmospheric nitrogen deposition. Science, 326(5954), 835–837. https://doi.org/10.1126/science.1176199

ESSA Technologies, Laurence, J., Risk Sciences International, Trent University, & Trinity Consultants. (2014). KitimatAirshed Emissions Effects Assessment (pp. 1–205). Report prepared for BC Ministry of Environment.

Henriksen, A., & Posch, M. (2001). Steady-state models for calculating critical loads of acidity for surface water. Water, Air, and Soil Pollution: Focus, 1, 375–398.

Holtgrieve, G. W., Schindler, D. E., Hobbs, W. O., Leavitt, P. R., Ward, E. J., Bunting, L., et al. (2011). A coherent signature of anthropogenic nitrogen deposition to remote watersheds of the Northern Hemisphere. Science, 334 (6062), 1545–1548. https://doi.org/10.1126/science.1212267

Kowalik, R. A., Cooper, D. M., Evans, C. D., & Ormerod, S. J. (2007). Acidic episodes retard the biological recovery of upland British streams from chronic acidification. Global Change Biology, 13 (11), 2439+. https://doi.org/10.1111/j.1365-2486.2007.01437.x

Maguire, T. J., Weidman, R. P., Mundle, S. O. C., Moore, J. W., Chezik, K. A., & Selbie, D. T. (2020). Impacts of industrial atmospheric emissions on watershed export of dissolved ions in coastal streams: A Bayesian modeling approach. Environmental Monitoring and Assessment, 192(9), 1–9 + 3. https://doi.org/10.1007/s10661-020-08493-x

McPherson, C. A., Lee, D. H. Y., & Chapman, P. M. (2014). Development of a fluoride chronic effects benchmark for aquatic life in freshwater. Environmental Toxicology and Chemistry, 33(11), 2621–2627. https://doi.org/10.1002/etc.2724

Molot, L. A., Dillon, P. J., & Lazerte, B. D. (1989). Factors affecting alkalinity concentrations of streamwater during snowmelt in central Ontario. Canadian Journal of Fisheries and Aquatic Sciences, 46(10), 1658–1666. https://doi.org/10.1139/f89-211

Pearcy, K., Elphick, J., & Burnett-Seidel, C. (2015). Toxicity of fluoride to aquatic species and evaluation of toxicity modifying factors. Environmental Toxicology and Chemistry, 34(7), 1642–1648. https://doi.org/10.1002/etc.2963

Rio Tinto. (2018). Environmental Report, BC Works. *Rio Tinto Inc*, 1–57.

Wolfe, A. P., Van Gorp, A. C., & Baron, J. S. (2003). Recent ecological and biogeochemical changes in alpine lakes of Rocky Mountain National Park (Colorado, USA): A response to anthropogenic nitrogen deposition. Geobiology, 1(2), 153–168. https://doi.org/10.1046/j.1472-4669.2003.00012.x