# Identifying global trends and drivers of freshwater aluminium concentrations using the Global Freshwater Acidification Database (GloFAD)

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> European Geosciences Union 2020 Online Annual General Assembly



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Identifying global trends and drivers of freshwater aluminium concentrations using GloFAD

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This is a self-guided presentation. The authors will be available to discuss this research during the text-based chat period on Friday May 8th, 2020 from 8:30 to 10:15 CEST.

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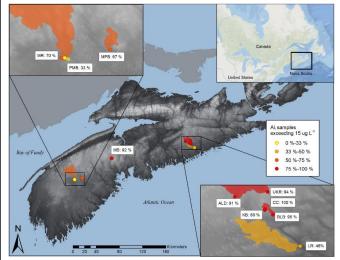


#### Problem statement

Aluminium (Al) is toxic to aquatic and terrestrial ecosystems [1]. Acid deposition is a main driver of elevated Al concentrations in Europe and eastern North America [2].

Acid deposition and associated elevated Al concentrations are partially responsible for reduced primary productivity [3], species mortality and extirpation [4], reduced bird nesting success [5], reduced forest health [6] resulting in reduced forest  $CO_2$  uptake, and human neurological and osteological diseases [7].

Although acid deposition has decreased across Europe and eastern North America [8, 9], regional studies indicate that Al concentrations remain elevated [10] and are increasing in some lakes and rivers [11]. Map showing proportions toxic inorganic monomeric Al concentrations exceeding maximum concentrations required for aquatic health in Nova Scotia Canada. Map from Sterling et al. 2019 [10].





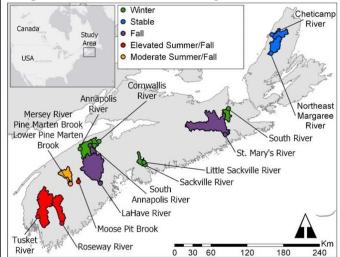


#### Background

Acid deposition causes elevated freshwater Al concentrations by depleting soil base cation stores, causing Al to be mobilized instead to neutralize negatively charged acids [12]. This model of freshwater acidification predicts, that when acid deposition declines, soil base cation stores are replenished from bedrock weathering, and freshwater Al concentrations decline [12].

Some regional studies indicate that freshwater Al concentrations remain elevated [10, 13] despite declining acid deposition [14], as is predicted by the above model. Instead, these studies show Al concentrations are driven by organic carbon (OC), as opposed to base cation concentrations [10, 13].

Based on these observations Sterling et al. propose an alternative freshwater acidification model which states that a hysteresis between base cation and OC response to declining acid deposition retards freshwater Al declines [11]. Map of seasonal Al regimes in Nova Scotia, Canada. Al concentrations in the Fall, Elevated Summer/Fall, and Moderate Summer/Fall regimes are predominantly driven by OC concentrations. Map from Rotteveel and Sterling 2020 [13].



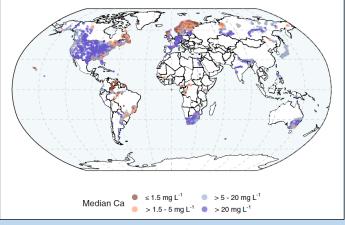




Knowledge gaps

Although the aforementioned conceptual models of freshwater acidification explain regional observations, few studies have empirically evaluated these models using large sample sizes. Without global-scale validation of these models, assessment of their validity and relevance is limited.

Furthermore, despite the threat of Al to ecosystems, Al is not frequently measured and has not been included in prior global-scale analyses or databases of acidification-related water chemistry. Map of low Ca concentrations from a global-scale study of acidification-related water chemistry. Map from Weyhenmeyer et al. 2019 [15]







Research goals and questions

#### **Research** goals

Goal 1: To develop a global database of acidification-related water chemistry.

Goal 2: To demonstrate the utility of the global database by assessing the empirical validity of conceptual models of freshwater acidification.

#### **Research questions**

Question 1: Is the conceptual freshwater acidification model proposed by Sterling et al. empirically supported?

Question 2: Where is freshwater acidification model proposed by Sterling et al. applicable?

This research is ongoing and only preliminary results are presented here. This presentation focusses on Research Goal 1, and only briefly addresses Research Goal 2.



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Overview

We compiled a global database of acidification-related freshwater chemistry.

From this database, we selected sites which had Al measurements.

For these sites, we assessed average water chemistry concentrations, their trends, and their geographic patterns.





#### Data collection

Data was compiled from openly available databases provided by national and international agencies.

The data search was targeted toward freshwater acidification-related variables in untreated surface water bodies.

The data search did not have a specific geographic focus.

#### Organization Database name United Nations International Global Water Quality Centre for Water Resources database and information and Global Change system European Environment Waterbase Agency Environment and Climate National Long-Term Water Change Canada Quality Monitoring Database United States of America National Water Quality Water Quality Database Monitoring Council McMurdo Dry Valleys Long United States of America Term Ecological Research National Science Foundation Network Jens Hartmann, Ronny Global River Chemistry Lauerwald, and Nils Database (GloRiCh) Moosdorf



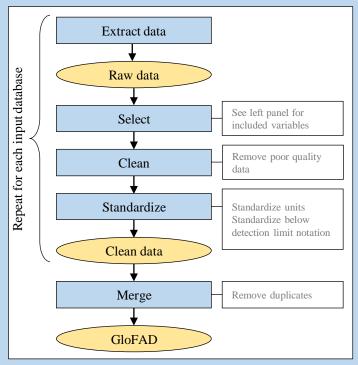


#### Data processing

Data were processed prior to inclusion in the Global Freshwater Acidification Database.

Included water body types and variables are:

- Water body types
  - Rivers, streams, canals
  - Ponds, lakes, reservoirs, impoundments
- Variables
  - Base cations (Ca, Mg, K, Na)
  - Acid anions (SO4, NO3, NO2)
  - Other anions (F, Cl)
  - Metals (Al)
  - Nutrients (P, PO4, NH4)
  - Physical (pH, temperature)
  - Other (DOC, TOC, discharge)







Data selection

The Global Freshwater Acidification Database was complete at this stage. To assess the empirical validity of conceptual models of freshwater acidification, further data selection was applied.

- Selected variables: Al, calcium (Ca), OC, pH
  - These variables were selected, as they are the variables included in the freshwater acidification model proposed by Sterling et al. [11]
  - Sulphate (SO<sub>4</sub>), the main component of acid deposition [2], was not included because it substantially reduced the sample size
- Selected date range: 2000-01-01 to 2015-12-31
  - This date range was selected, as it corresponds to that used to develop the freshwater acidification model proposed by Sterling et al. [11]
- For trend analysis
  - Minimum timeseries length: 10 years
  - Minimum dataset completeness: 3/4 of years have data
  - Minimum data collection frequency: four samples per year for riverine systems, one sample per year for lacustrine systems





Statistical analysis

Water chemistry data were non-normally distributed (positive skew), so we used non-parametric statistical tests.

- To assess average water chemistry concentrations
  - Medians
- To assess water chemistry trends
  - For timeseries without seasonality or auto-correlation: Mann-Kendall non-parametric test [16, 17]
  - For timeseries with seasonality: seasonal Mann-Kendall non-parametric test [18]
  - For timeseries with persistence (Durbin-Watson statistic < 1.5 or > 2.5): Hamed and Rao modified Mann-Kendall non-parametric test [19], considering all significant lags
- To assess relationships between water chemistry trends
  - Ordinary Least Squares (OLS) regression



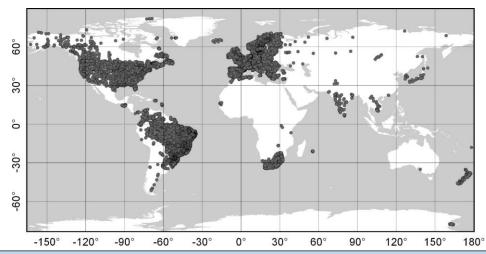


### Results

#### The Global Freshwater Acidification Database

Map of the Global Freshwater Acidification Database sample site locations. Some sites are not plotted due to unreliable location information.

Table summarizing available water chemistry and physical variables in the Global Freshwater Acidification Database.



Variable	Samples (n) Sites (n)	
Ca	713,952	20,257
Mg	698,452	19,551
K	657,921	16,340
Na	655,416	17,320
Al	155,876	6,146
F	427,538	5,723
Cl	819,501	20,254
SO <sub>4</sub>	759,157	20,424
NO <sub>3</sub>	368,870	13,227
NO <sub>2</sub>	293,858	13,037
NH <sub>4</sub>	652,117	14,460
Р	494,886	12,064
$PO_4$	486,323	8,976
pН	1,150,669	27,187
OC	523,695	14,349
Turbidity	184,413	6,256
Temp.	854,572	27,306
Discharge	3,267,779	7,199
Total	13,164,995	41,478

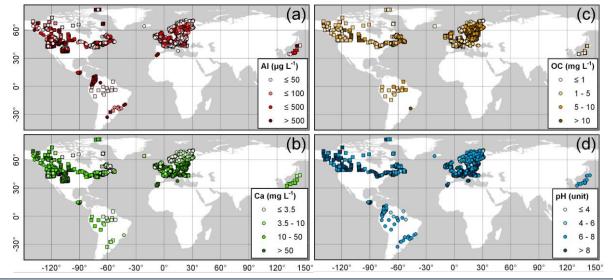




### Results

#### Water chemistry concentrations

Median concentrations between January 1<sup>st</sup>, 2000 and December 31<sup>st</sup>, 2015. For Al, Ca, and OC, circles represent total concentrations and squares represent dissolved concentrations. For pH, triangles represent field measurements, squares represent laboratory measurements, and circles represent unspecified measurements.





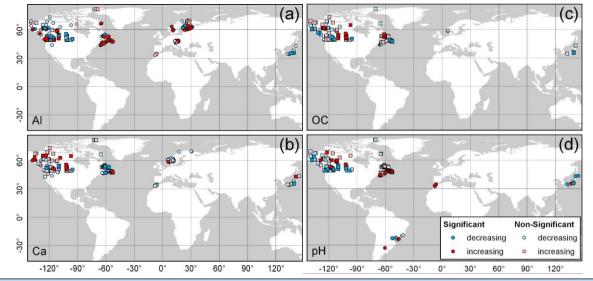
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### Results

#### Water chemistry trends

Trends between January 1<sup>st</sup>, 2000 and December 31<sup>st</sup>, 2015. For Al, Ca, and OC, circles represent total concentrations and squares represent dissolved concentrations. For pH, triangles represent field measurements, squares represent laboratory measurements, and circles represent unspecified measurements.





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## Discussion

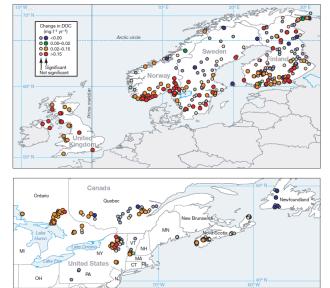
#### Geographic patterns of AI trends

There are notable hotspots of increasing Al trends in eastern Canada and Scandinavia. These trends co-occur with increasing OC trends [20] and low median Ca concentrations, as predicted by the freshwater acidification model proposed by Sterling et al.

Both of these hotspot areas are underlain by metamorphic and plutonic bedrock, which provides little Ca input to soils and freshwater systems through weathering reactions.

These preliminary results suggest increasing OC trends may be driving increasing Al trends in regions with low Ca concentrations, providing empirical support for the freshwater acidification model proposed by Sterling et al.

Increasing OC trends in northeastern North America and Europe. Map from Monteith et al. 2007 [20].





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### Discussion

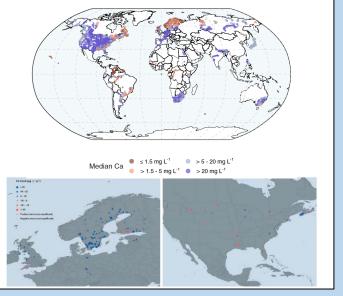
Comparison of results to prior research

The observed co-occurrence of increasing Al and OC trends in areas of low Ca is supported by prior research. Other large-sample freshwater acidification research also shows OC [20] and iron (Fe) [21]\* concentrations are increasing in acidified areas while Ca concentrations remain low [22].

Furthermore, research into the drivers of Al in Nova Scotia, Canada, one of the identified hotspot areas, indicates that OC is the main driver of total Al concentrations in many rivers [13] and is also a main driver of toxic inorganic monomeric species of Al [10].

\* Mobilization of Fe and Al from soils is similar [1].

Increasing Fe trends (bottom; map from Björnerås et al. 2017 [21]) in areas with low Ca (top; map from Weyhenmeyer et al. 2019 [22]).







### Discussion

Implications, limitations, and next steps

#### Implications

Areas with low Ca concentrations and increasing OC trends are at risk of increasing Al concentrations, threatening plants, animals, and people.

Based on our assessment, increasing Al trends may occur in any region with low Ca and increasing OC, regardless of acidification status. For example, soil Ca concentrations may decline in response to forest harvest [21] and increased atmospheric forcing may increase OC leaching to freshwaters [20].

#### Limitations

Our preliminary conclusions are limited by insufficient data for timeseries analysis in many acidified areas.

Furthermore, the Global Freshwater Acidification Database has notable data gaps on the continents of Asia, Africa, and Australia.

These data gaps limit the generalizability of our conclusions and prevent us from assessing if Al concentrations are also increasing in areas not affected by acid deposition.

#### Next steps

Thus far, our research has focused on examining the cooccurrence of increasing Al and OC trends, and their relationships to Ca concentrations.

Next, we aim to examine mechanistic drivers of Al in low Ca sites using partial least squares regression.

Further, through participating in the online European Geosciences Union 2020 Annual General Assembly, we hope to solicit additional data to fill the data gaps we have identified.





## Summary and conclusions

What can the Global Freshwater Acidification Database do for you?

The Global Freshwater Acidification Database is a global database of acidification-related freshwater chemistry. The database contains contains total, dissolved, and speciated water chemistry data across 18 variables, 41,478 sites, and 13,164,995 unique sample points. The included variables include base cations, acid anions, nutrients, and physical parameters.

The wide variety of available variables and large sample sizes in Global Freshwater Acidification Database allows users to conduct powerful and robust statistical analysis to answer global freshwater chemistry questions.

The Global Freshwater Acidification Database provides transboundary data which can be used to develop integrated water resources management strategies, contributing to the United Nations Sustainable Development Goals, specifically, the Clean Water and Sanitation Goals.

In the first ever application of the Global Freshwater Acidification Database, we test the freshwater acidification model proposed by Sterling et al. and find the conceptual model is empirically supported and is applicable to sites with increasing OC concentrations and low Ca concentrations.





### **References and Acknowledgements**

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#### Acknowledgements

The authors would like to acknowledge Franz Heubach for his support with statistical analysis, Abby Millard for her assistance with data collection, and the Natural Sciences and Engineering Research Council of Canada and the Government of Nova Scotia for funding this research.





#### Data availability and contribution

#### Data availability

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The Global Freshwater Acidification Database and the Python scripts used to generate it will be made openly available after this research has been published.

#### **Data contribution**

The authors of this research welcome suggestions of other databases for inclusion into the Global Freshwater Acidification Database.

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