

ORIGINAL ARTICLE OPEN ACCESS

Hydrologic and Landscape Drivers of Seepage Lake ANC Status in Northern Wisconsin, USA

Lucy A. Rose¹  | Nancy Serediak² | Randall K. Kolka³  | Trent R. Wickman⁴

¹Department of Forest Resources, University of Minnesota, Saint Paul, Minnesota, USA | ²Lakehead University, Orillia, Ontario, Canada | ³USDA Forest Service Northern Research Station, Grand Rapids, Minnesota, USA | ⁴USDA Forest Service Eastern Region, Duluth, Minnesota, USA

Correspondence: Lucy A. Rose (larose@umn.edu)

Received: 22 November 2022 | **Revised:** 23 May 2024 | **Accepted:** 9 December 2024

Funding: Funding was provided by the USDA Forest Service Superior National Forest and Chequamegon-Nicolet National Forest to RKK and TRW.

Keywords: acid neutralising capacity | atmospheric deposition | lake water quality | mixed effects model

ABSTRACT

In some seepage lakes, acid neutralising capacity (ANC) is regulated by precipitation chemistry and in-lake biogeochemical processes with little influence from groundwater and catchment runoff. However, additional environmental contexts, for example, landscape position and changing precipitation dynamics, may also contribute to variability in ANC across lakes over time. We used a mixed effects model to assess the influence of changing precipitation patterns and the chemistry of hydrologic inputs on ANC in seven northern Wisconsin, USA seepage lakes from 1984 to 2018. We observed differential ANC responses across lakes to the concomitant changes in precipitation acidity and post-drought oxidative acidity pulses from adjacent wetland soils. Although all study lakes lie within a 4 km² area, mean lake ANC values ranged from $32.8 \pm 25.2 \mu\text{eq L}^{-1}$ to $71.9 \pm 26.8 \mu\text{eq L}^{-1}$ and were inversely related to lake landscape position. Lakes with higher mean ANC also showed lower relative variability over time, suggesting that these lakes were better buffered than those with lower ANC. Mixed effects modelling explained 50% of the ANC variability across all lakes, while model explanatory power ranged from 39% to 71% when ANC was assessed within individual lakes. The range of modelled ANC accuracy highlights the complex nature of biogeochemical regulation in individual seepage lakes, despite their shared geographic setting. Our study demonstrates the utility of mixed effects modelling for repeated measures analysis, emphasising the necessity of long-term studies to evaluate seepage lake ANC responses to changing hydrologic and biogeochemical inputs.

1 | Introduction

Freshwater lakes acidify when acid inputs exceed lake buffering capacity. The ecological condition of surface waters is often assessed through measurement of this acid neutralising capacity (ANC) with system-specific ANC targets greater than zero defined to ensure the protection of aquatic habitats (Adams 1991; Sullivan et al. 2012). Acid neutralising capacity in surface waters often serves as the basis for pollutant critical load

thresholds (Adams 1991; Pardo 2010; Sullivan et al. 2012; U.S. EPA 2016). Despite greater regulation of stationary air pollutant sources to reduce atmospheric sulphate and nitrate deposition in the United States (Stoddard et al. 2003; Burns et al. 2011) and Canada (Watmough, Eimers, and Baker 2016), some freshwater systems have shown only modest recovery in ANC or pH in recent decades (Jeffries, Clair, et al. 2003; Eimers et al. 2007; McDonnell et al. 2014; Watmough, Eimers, and Baker 2016; Watmough and Eimers 2020).

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2025 The Author(s). *Lakes & Reservoirs: Science, Policy and Management for Sustainable Use* published by John Wiley & Sons Australia, Ltd.

A particular challenge in predicting lake acidification responses to changing acid deposition regimes is the identification of relevant biogeochemical sources and processes. For example, several studies have reported robust long-term recovery of lake ANC in response to reduced atmospheric sulphate deposition rates (Driscoll et al. 2003; Stoddard et al. 2003; Strock et al. 2014), whereas other researchers have reported minimal or delayed effects of those same atmospheric deposition trends on lake ANC in different settings (Clair, Dennis, and Vet 2011; Watmough and Eimers 2020; Marty et al. 2021). Notably, many of the lakes exhibiting gradual or delayed ANC responses occur in low-relief glaciated landscapes, surrounded by organic matter-rich wetland catchments; this suggests a confounding influence of organic acidity on ANC status in these lakes (Jeffries, Brydges, et al. 2003; Clair, Dennis, and Vet 2011). Such disparate lake responses highlight the need to consider a broad range of biogeochemical and hydrologic drivers to understand the mitigating and exacerbating factors of lake ANC status.

While national monitoring networks such as the National Atmospheric Deposition Program (NADP) in the United States have enabled researchers to directly assess ecosystem responses to long-term acid deposition reductions (Stoddard et al. 2003; Burns et al. 2011; Hobbs, Lynch, and Kolka 2017), characterising the temporal patterns of acid inputs from other, more transient sources has proven difficult. This challenge is especially acute in the context of poorly buffered seepage lakes, which can be disproportionately influenced by atmospheric and catchment inputs with minimal groundwater interaction (Webster et al. 2006) when they occur in high landscape positions or high in the groundwater flow field (Cheng and Anderson 1994; Kratz et al. 2006). As a result, the hydrologic and biogeochemical source contributions to these systems can be temporally variable (Krabbenhoft and Webster 1995; Watras et al. 2014). Episodic acidification in these lakes can also occur as a result of inputs from catchment sources such as wetlands, complicated by the effects of climate and local hydrology (Webster, Brezonik, and Holdhusen 1993; Eilers and Bernert 1997; Devito, Hill, and Dillon 1999). Baker et al. (1991) proposed that lake acidification can be deposition, catchment or organic acid dominated, requiring the identification of all significant input sources as contributing factors. Clearly, the transient nature of hydrologic and biogeochemical inputs to some seepage lakes necessitates a detailed understanding of the processes affecting ANC status in these systems. This is particularly true in light of the potentially significant shifts in hydrologic regimes predicted under future climate scenarios (Reidmiller et al. 2019).

To investigate the hydrologic and biogeochemical drivers of ANC status in northern seepage lakes, we developed a mixed effects model to assess the importance of atmospheric and catchment contributions to lake ANC during the open water season. We compared modelled ANC estimates to long-term (1984–1995 and 2007–2018) records of lake ANC in seven seepage lakes located in the Rainbow Lake Wilderness (RLW) area of north-western Wisconsin, USA. The modelling results presented here highlight the dynamic effects of atmospheric and catchment contributions to these lakes over time and the role of landscape position as a regulator of overall lake sensitivity to acid inputs from atmospheric and catchment sources.

2 | Materials and Methods

2.1 | Study Site and Sample Collection

The RLW is a 2585 ha parcel of land in the Washburn/Great Divide Unit of the Chequamegon-Nicolet National Forest in Bayfield County, Wisconsin, USA (Figure 1). It is designated a Class I area by the Clean Air Act; therefore, assessment of impacts from new industrial-related air emissions on air quality-related values is required. It is also designated as a wilderness area by the USDA Forest Service primarily due to its numerous pristine lakes. Lakes in the RLW are primarily small seepage lakes that are currently unaffected by significant development; remnants of an old railway bed and former logging roads persist in the area and are now used as hiking trails. Forest vegetation has recovered following intensive logging and forest fires in the early 1900s, with regenerated forest cover largely comprised of a deciduous-dominated mix of sugar maple (*Acer saccharum*), aspen (*Populus* spp.), red maple (*Acer rubrum*), basswood (*Tilia* spp.), oak (*Quercus* spp.) and hickory (*Carya* spp.) interspersed with coniferous red pine (*Pinus resinosa*), northern white cedar (*Thuja occidentalis*), white pine (*Pinus strobus*), jack pine (*Pinus banksiana*), spruce (*Picea* spp.) and balsam fir (*Abies balsamea*) (Haugen 1998).

The flat to gently rolling topography of the study area reflects the complex history of glaciation in northern Wisconsin more broadly (Fitzpatrick et al. 2015). At least seven postglacial shorelines have been identified across the Bayfield Peninsula associated with the gradual decline in water levels in Lake Superior (Fitzpatrick et al. 2015). This has resulted in a series of alternating clay and sand layers throughout the area, contributing to isolated pockets of perched groundwater tables that can be disconnected from the deeper groundwater flowpaths by more than 30 m (Fitzpatrick et al. 2015). Upland soils (typically Spodosols) in the study lake catchments are characterised as sandy with low clay content and very high infiltration capacity, whereas soils in low-lying areas are primarily Histosols with high organic content subject to frequent saturation (NRCS Soil Survey Staff 2021).

The seven lakes included in our study lie approximately along a spatial gradient of both land surface elevation and distance from the regional groundwater divide, in alignment with the local groundwater flow field (Figure 1; Graham et al. 2019). While all of the study lakes are classified as seepage lakes, the true extent of groundwater connectivity to individual lakes is unclear given the paucity of groundwater measurements in the study area (Fehling et al. 2018; Graham et al. 2019). The layering of postglacial shoreline deposits and the potential for localised perched water tables throughout the Bayfield Peninsula add additional complexity to the estimation of groundwater connectivity in the study area (Fitzpatrick et al. 2015).

The seven seepage lakes considered in this study have been intermittently monitored by the USDA Forest Service since 1984, mainly during the open water season. Lake monitoring data have typically included colour, pH, ANC and dominant ions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , SO_4^{2-}) although not all measurements are collected in every year. Lake ANC (μeq

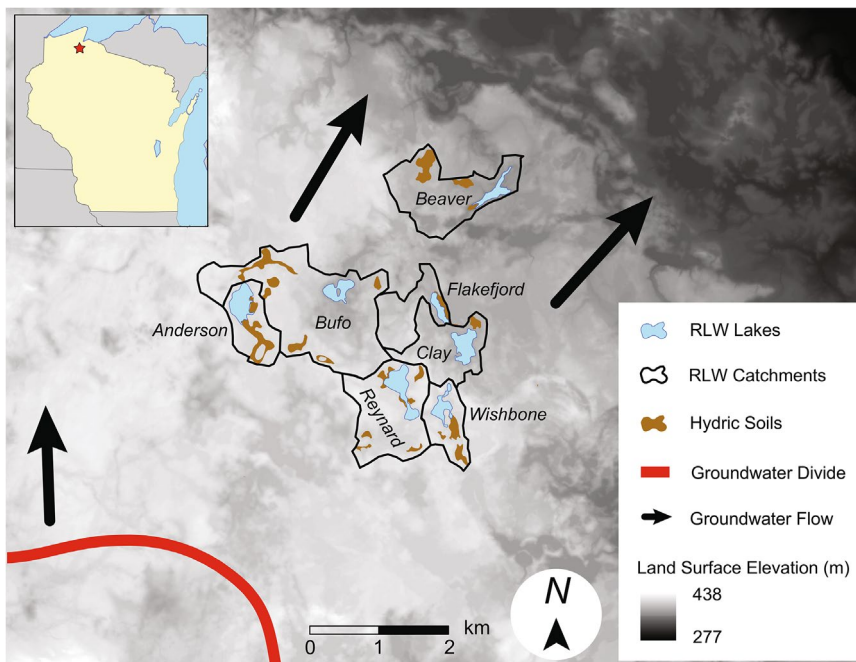


FIGURE 1 | Location of study lakes and catchments in the Rainbow Lake Wilderness (RLW) area. Red line shows the nearby groundwater divide (recharge zone) and black arrows indicate the direction of groundwater flow away from the recharge zone from Graham et al. (2019). Hydric soils used in the estimation of organic acidity inputs to lakes are shown in brown for each catchment. Map shading indicates the local land surface elevation gradient. The red star on the inset map shows the location of RLW in northwestern Wisconsin.

L^{-1}) for this study was determined using a Gran titration on unfiltered water samples (Wilde et al. 1998). Gran titrations are recommended for samples with low anticipated buffering capacity and when contributions to alkalinity are from mineral acids, organic acids or other non-carbonate sources (Wilde et al. 1998). During the years 1996–2006, an incorrect titration endpoint was used for ANC determination; samples from these years were therefore omitted and only data from 1984 to 1995 and 2007 to 2018 were included in our analysis. After 2016, a different analytical laboratory was used for ANC determination on lake samples. Although both pre-2016 and post-2016 laboratories used the same analytical method for ANC determination, a sharp decrease in ANC occurred in some lake samples after 2016. No meteorological anomalies (e.g., excessive drought or heat, heavy rainfall) occurred in northern Wisconsin during this time period, so it is possible that the change in laboratory during this time may have introduced an analytical artefact. In addition to this long-term water chemistry sampling, an additional water sample was collected once from each lake in August 2021 (Anderson, Bufo, Clay, Reynard, Wishbone lakes) or October 2023 (Beaver and Flakefjord lakes) for determination of water isotopic composition (δ^2H and $\delta^{18}O$ of water) at the USDA Forest Service Northern Research Station Forestry Science Laboratory in Grand Rapids, Minnesota, USA. To assess the relative importance of precipitation and groundwater contributions to the study lakes, we compared lake water isotope values to previously reported δ^2H and $\delta^{18}O$ ranges for 17 local groundwater samples in the Washburn-Great Divide Unit of the Chequamegon-Nicolet National Forest (Fehling et al. 2018) and 14 summer precipitation samples in northern Wisconsin (Kendall and Doctor 2004).

2.2 | Spatial Analysis

A geographic information system (GIS) was constructed using Quantum GIS (QGIS) (Quantum GIS Development Team 2012). Lake bathymetry was digitised from scanned copies of the State of Wisconsin Lake Survey Series contour maps and projected to NAD 1983 Wisconsin Transverse Mercator. The GIS layers for soils, vegetation and elevation were obtained from various sources through the USDA-NRCS Geospatial Data Gateway (NRCS Soil Survey Staff 2021). The assembled GIS data were used to calculate areas and volumes of relevant geophysical features (Table 1); calculated values were then used as deposition weighting factors for interpolated precipitation and catchment runoff data. All watersheds were delineated by Mr. Dale Higgins, USDA Forest Service Hydrologist (retired) with the Chequamegon-Nicolet National Forest, as the low relief and hummocky terrain of the RLW area confounded digital elevation model-based watershed delineations.

2.3 | Model Parameter Estimation

The potential drivers of lake ANC dynamics considered in our analysis included total monthly acid deposition to each catchment ($\mu eq\ month^{-1}$), total monthly organic acidity in modelled runoff from saturated hydric soils ($\mu eq\ month^{-1}$; runoff events were grouped based on whether or not they immediately followed drought conditions to assess the potential influence of oxidative acidity generation) and time (expressed as the number of months since the initiation of sampling in May 1984, ranging from 0 in May 1984 to 398 in August 2018).

TABLE 1 | Physical features of the RLW lakes. Saturated soils percentages are the sum of all hydric soils within each lake catchment.

Lake	Perimeter (m)	Surface area (m ²)	Volume (m ³)	Maximum depth (m)	Catchment area (m ²)	Hydric soil (% of catchment area) ^a
Anderson	2435	129,112	1,635,931	12.2	1,638,366	29.7
Beaver	2452	69,578	683,172	11.9	685,624	8.0
Bufo	1557	82,096	427,373	11.9	428,930	6.6
Clay	2092	129,960	1,849,634	13.7	1,851,726	3.0
Flakefjord	1197	41,895	294,387	6.1	295,584	6.0
Reynard	2511	143,442	1,276,521	13.7	1,279,032	6.4
Wishbone	2330	70,482	661,783	12.2	664,112	14.5

^aHydric soil estimates from Wisconsin Department of Natural Resources Surface Water Data Viewer GIS tool (<https://dnr.wisconsin.gov/topic/SurfaceWater/swdv>).

We used a charge balance approach to quantify monthly atmospheric acid deposition to the lakes and catchments:

$$\text{Acidity } (\mu\text{eq L}^{-1}) = \frac{2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] - (2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{NH}_4^+])}{(1)}$$

Ions in Equation (1) are routinely measured in wet deposition samples collected as part of the NADP National Trends Network monitoring program (National Atmospheric Deposition Program 2011). Precipitation chemistry data were averaged from the two nearest long-term monitoring stations (W136 and W137), and local RLW precipitation amounts were estimated to calculate monthly deposition acidity fluxes from May 1984 to August 2018. Using GIS, we located the centroid of the minimum bounding box surrounding the catchments for all seven lakes and estimated precipitation volumes for the RLW area, interpolated to the centroid (46.40354 latitude, -91.19487 longitude) using the Parameter-elevation Regressions on Independent Slopes Model, or PRISM (PRISM Climate Group 2012). Ion deposition to lakes was multiplied by catchment area to calculate area-weighted monthly acid deposition fluxes. Dry deposition fluxes are not included as part of routine NADP monitoring, although in 2000 NADP began reporting annual total S and N deposition across the United States by combining modelled dry deposition estimates with routine measurements of wet S and N deposition at monitoring sites (Schwede and Lear 2014). For the portion of our study period from 2007 to 2018, we downscaled the annual NADP estimates of dry S and N deposition to a monthly timestep (assuming equal rates of dry deposition across all 12 months of a calendar year) and calculated the total S and N deposition across each lake watershed as the sum of monthly dry deposition estimates and wet deposition measurements. For study years prior to 2000, we used proportional dry deposition contributions to total atmospheric deposition of 25% and 20% for S and N, respectively, based on measurements of total and dry only S and N deposition measured by Baumgardner et al. (2002) at a northern Wisconsin monitoring site. Baumgardner et al. (2002) estimated mean annual total sulphur and nitrogen deposition (dry + wet) and mean annual dry sulphur and nitrogen deposition from 1990 to 1993 and 1997 to 2000, making them a more temporally appropriate match for the portion of our study period from 1984 to 1995. Using these estimates of dry S and N deposition, as well as our monthly wet SO_4^{2-} and

NO_3^- deposition data from NADP, we calculated total monthly S and N deposition across each lake watershed area. As S and N historically constitute the largest dry deposition inputs in our study area, we only considered wet deposition inputs of the remaining ions in our charge balance model.

Organic acidity inputs to lakes from hydric soil runoff were estimated using a ‘fill and spill’ approach, as topographic relief is minimal in the study area and saturated hydric soils generally coincide with areas of low slope (0%–3%). From May 1984 through August 2018, we calculated the cumulative water volume (m³) to a depth of 20 cm potentially available for runoff from saturated hydric soils each month; this depth was chosen because even dry conditions do not lower water levels more than approximately 30 cm in hydric soils due to increases in water tension (NRCS Soil Survey Staff 2021). Monthly cumulative water volume was calculated as the difference between area-weighted precipitation inputs and total monthly evapotranspiration (estimated using a simplified Penman equation [Valiantzas 2006]). When the estimated cumulative water volume was positive, we assumed that all runoff from the upper 20 cm of the hydric soil profile reached the lake. To estimate the total organic acid equivalents in runoff from wet hydric soils, we used the organic acidity concentration of 112 $\mu\text{eq L}^{-1}$ reported by McLaughlin and Webster (2010) for pore-water at 25 cm depth in a northern Ontario peatland. Assuming a triprotic model (Driscoll, Lehtinen, and Sullivan 1994), this organic acidity estimate yields a DOC concentration of approximately 25 mg L^{-1} ; this concentration is within the range of pore-water DOC concentrations (16–101 mg L^{-1} , median 57 mg L^{-1}) measured across 17 peatland sites in northern Wisconsin by Buffam et al. (2010). Estimated organic acidity was multiplied by runoff volume estimates to quantify the total organic acid equivalents contributed to each lake from saturated hydric soils each month. In the Beaver Lake and Bufo Lake catchments, saturated hydric soils are not proximal to the lake perimeter as is the case for the other lakes (Figure 1). For these two lakes, a distance decay weighting approach was used to accommodate the reduction in acid pulse impacts along longer flowpaths (Canham et al. 2004). Acid inputs were multiplied by the inverse of the shortest line length between the two nearest edges of saturated hydric soil and lake surface polygons. As saturated hydric soils in the Bufo Lake catchment are linked in an arc (Figure 1), only the nearest leading edge of the closest polygon was used to calculate the weighting measure.

We defined drought periods as those months when estimated evapotranspiration rates exceeded precipitation inputs; cumulative water volume estimates were negative, and hydric soils were assumed to dry out during these months. We estimated the amount of additional acidity potentially generated due to oxidation of reduced sulphur in these dried soils (Wood 1989; Devito, Hill, and Dillon 1999; Eimers et al. 2007; Vermaat et al. 2016). We assumed that the acidity generated by these oxidation reactions was mobilised to lakes during runoff-generating events immediately following these dry periods. To quantify the acidity generated by drying of hydric soils, we used the estimate of $16.3 \mu\text{eq m}^{-2}$ of oxidative acidity reported by Wood (1989) for dry peatland soils. When monthly cumulative water volume was negative, we used Equation (2) to estimate the area of dried hydric soil in each lake catchment and multiplied this estimate by $16.3 \mu\text{eq m}^{-2}$ (Equation 3) to calculate the amount of oxidative acidity flushed to lakes when subsequent cumulative water volume estimates were positive.

$$\text{DHS} = \frac{\text{CWV} \times \text{HSA}}{\text{HSV}} \quad (2)$$

where: CWV, cumulative water volume deficit in m^3 ; DHS, area of dried hydric soil in m^2 ; HSA, total hydric soil area in m^2 ; HSV, total hydric soil volume at threshold in m^3 .

$$\text{OA} = \text{DHS} \times 16.3 \mu\text{eq m}^{-2} \quad (3)$$

where: OA, oxidative acidity in μeq .

Although acidity can also be generated at several steps in the nitrogen cycle, nitrogen uptake and retention by vegetation in ombrotrophic peatlands is typically high (Wood 1989). As such, our estimates of catchment acidity export do not incorporate acidity generated via nitrogen cycling.

We treated the time variable—quantified as the number of months since the initiation of sample collection in May 1984—as a fixed effect in all model parameterisations, allowing us to test for interactions between time and other fixed effect predictors (described below). Time was defined as an ordinal variable to better align the repeated measures time-series nature of the dataset with the irregular monthly sampling frequency inherent to the study design, and to better reflect the gap in available ANC data from 1996 to 2006.

2.4 | Model Development and Assessment

The repeated measures nature of our study, which also incorporated measurements across multiple lakes, necessitated a mixed effects modelling approach to appropriately reflect the variance structure of the dataset. We followed a model selection procedure similar to those outlined by Zuur et al. (2009) and Harrison et al. (2018) to determine the optimal parameterisation of fixed and random effects for our dataset.

Linear mixed effects models are widely used in econometrics and the social sciences, and are seeing more widespread

application in the natural sciences (Harrison et al. 2018). The primary advantage of mixed effects models is the inclusion of ‘random effects’ to account for the lack of independence among measurements taken within groups (lakes, in our case) while simultaneously estimating the effect of model predictors (‘fixed effects’) on the response variable across all groups. In the initial model selection process, the fixed effect structure for lake ANC included the following predictors: total monthly atmospheric acid deposition, organic acidity from saturated hydric soils, organic acidity from dried hydric soils, and time, as well as the interactions of all non-time fixed effects with time. Additionally, we considered three possible random effect structures: no random effect (analogous to an ordinary least squares regression approach), a random effect of lake with random intercepts, and a random effect of lake with uncorrelated random slopes and intercepts. From these potential fixed and random effects structures, the optimal model was selected by comparing Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) scores for all models, with the lowest scores indicating the optimal random effect structure (Zuur et al. 2009). Fixed effect parameters were retained in the model based on a p -value threshold of $p < 0.05$ for the parameter t -statistic. The appropriateness of the mixed effect model approach was validated by examining the intra-class correlation coefficient, with a coefficient value greater than zero indicating that observations within a group are correlated, supporting the inclusion of a random effect (Zuur et al. 2009). Additionally, model residuals were checked for violations of linear regression assumptions (e.g., homoscedasticity, normality of residuals) and for serial autocorrelation. We assessed the accuracy of model estimates by regressing model-predicted ANC values against measured values and evaluating the strength of linear fits based on regression R^2 and p -values.

2.5 | Statistical Analyses

All statistical analyses were conducted using R version 4.0.3 (Venables and Smith 2020). We used packages ‘nlme’ and ‘plm’ for mixed effects model specification and testing of model assumptions. Package ‘stats’ was used to evaluate the linear fits between measured and model-estimated lake ANC values within individual lakes and across all lakes. We note that the datasets used for model specification and evaluation include only those measurements that occurred from 1984 to 1995 and 2007 to 2018, due to the aforementioned issue with laboratory ANC determination from 1996 to 2006. Because precipitation amount and chemistry were measured continuously at nearby NADP sites throughout the 1984–2018 study period, we evaluated temporal trends in atmospheric acid deposition and organic acid inputs to lakes during all months from May 1984 through August 2018 using Mann-Kendall trend tests in packages ‘NADA2’ and ‘modifiedmk’. Due to the censored nature of the hydric soil runoff estimates (i.e., many zeros in the dataset during months with no runoff) and the presence of serial correlation in the post-drought runoff data, a modified Mann-Kendall test described by Hamed and Rao (1998) was used to evaluate the trend in organic acidity in post-drought hydric soil runoff.

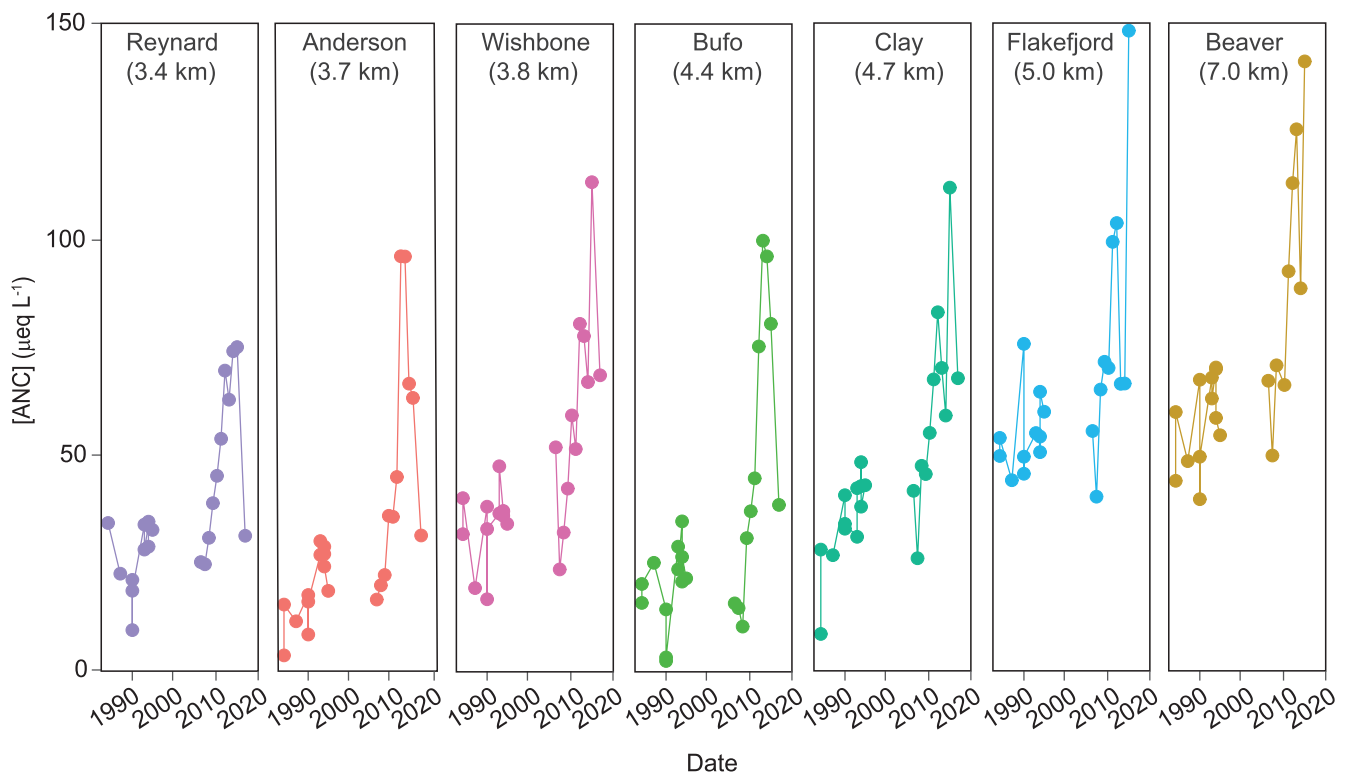


FIGURE 2 | Measured ANC in study lakes during sampling events between May 1984 and August 2018. Lakes are ordered by distance from the nearby groundwater divide (recharge zone); distances are indicated with lake name.

TABLE 2 | Mean ANC and coefficients of variation for study lakes.

Lake	Mean ANC ($\mu\text{eq L}^{-1}$)	ANC coefficient of variation
Anderson	32.8	0.77
Bufo	33.8	0.82
Reynard	37.6	0.49
Wishbone	46.6	0.48
Clay	47.5	0.46
Flakefjord	66.3	0.38
Beaver	71.9	0.37

3 | Results

3.1 | Temporal and Spatial Patterns in Measured Lake ANC Values

Although the irregular timing of sample collections precluded a true time-series analysis of lake ANC, visual inspection of individual lake ANC patterns suggests increasing ANC in all lakes over time (Figure 2). Mean lake ANC ranged from 32.8 $\mu\text{eq L}^{-1}$ in Anderson Lake to 71.9 $\mu\text{eq L}^{-1}$ in Beaver Lake (Table 2) and showed a significant negative correlation with in-lake relative ANC variability (as quantified by the coefficient of variation (CV); $r = -0.82$, $p = 0.02$, $n = 7$). The absolute variation in ANC (as quantified by the standard deviation; Table 2) was not correlated with mean ANC, showing no systematic increase or decrease with changing mean ANC across lakes. These

relationships suggest that within-lake ANC variability was not responsible for the differences in mean ANC we observed across the study lakes, and that differences in mean lake ANC did not necessarily scale with the degree of within-lake ANC variability over time.

Mean lake ANC also showed significant relationships with metrics of landscape position and lake morphology. When Bufo Lake was excluded, there was a significant negative relationship with land surface elevation ($R^2 = 0.75$, $p = 0.03$, $n = 6$; Figure 3) and a significant positive relationship with the ratio of catchment area to lake surface area ($R^2 = 0.86$, $p = 0.01$, $n = 6$; Figure 3). These relationships became non-significant when the mean ANC for Bufo Lake was included in the regressions ($R^2 = 0.40$, $p = 0.12$, $n = 7$ for land surface elevation; $R^2 = 0.04$, $p = 0.66$, $n = 7$ for catchment area to lake surface area ratio). Both lake elevation and the ratio of catchment area to lake surface area have been used as broad-scale indicators of lake biogeochemical status (Webster et al. 1996, 2000; Kratz et al. 1997; Riera et al. 2000). Similarly, the distance of each lake from the regional groundwater divide was also positively related to mean lake ANC across all lakes ($R^2 = 0.70$, $p = 0.02$, $n = 7$; Figure 3). Although the strong relationship between mean lake ANC and the distance from the regional groundwater divide suggests that groundwater inputs may differentially influence ANC across the study lakes, the strong divergence of Bufo Lake from the relationship between mean lake ANC and catchment to lake surface area ratio and lake elevation may result from complex surface and subsurface dynamics in the RLW. For example, the low relief and hummocky terrain of the RLW area precludes digital approaches to watershed delineation, necessitating personal experience and expert

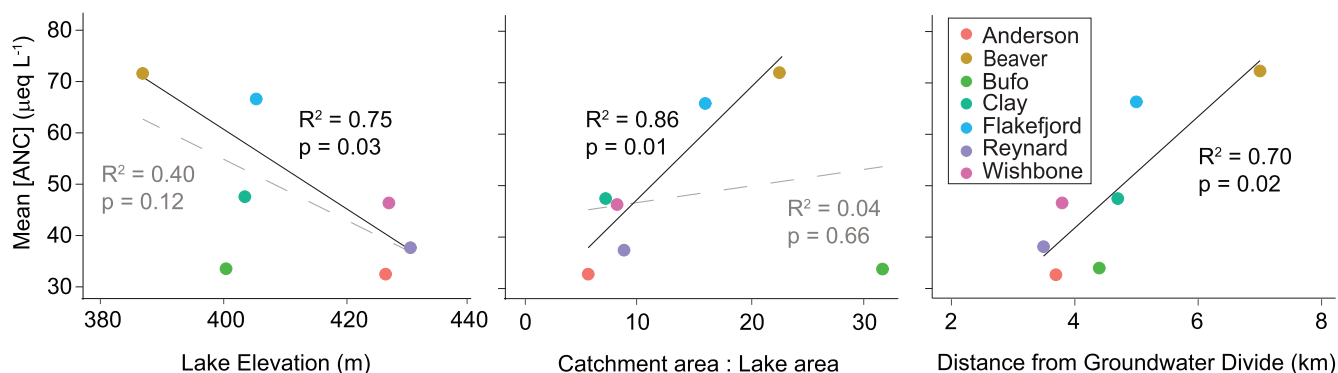


FIGURE 3 | Mean lake ANC vs. landscape characteristics in the RLW. Dashed grey lines and grey text represent regression fits with all lakes included; solid black lines and black text represent regression fits with Bufo Lake excluded.

knowledge for watershed delineation. In addition, patterns in the water isotopic compositions ($\delta^2\text{H}$ and $\delta^{18}\text{O}$ of H_2O) of lake water, local groundwater and local summer precipitation further support the idea that Bufo Lake may be less influenced by groundwater inputs than would be expected based on the elevational position of the lake or its distance from the groundwater divide (Figure 4). Although the elevation of Bufo Lake is most similar to that of Clay and Flakefjord Lakes, suggesting the potential for groundwater inputs (Figure 3), the isotopic composition of Bufo Lake is nearly identical to that of Reynard Lake, which is the lake nearest to the regional groundwater divide and is, like Bufo Lake, characterised by a low mean ANC (Figures 3 and 4).

3.2 | Selection of the Optimal Lake ANC Response Model

Among the three models considered in our analysis, the random intercept model had both the lowest AIC value (3504, compared to 3627 and 3516 for the no random effect and random slope and intercept models, respectively) and the lowest BIC value (3534, compared to 3654 and 3564 for the no random effect and random slope and intercept models, respectively; Table 3). The random effects structure of the final model therefore included random intercepts only.

The main effects of atmospheric acidity, organic acidity runoff from saturated hydric soils, organic acidity runoff from dried hydric soils following drought, and time were each statistically significant in the model (Table 4). However, as none of the interactions with time were statistically significant, no interaction terms were included in the final model.

After removing the non-significant interactions from the model structure, the final random intercept model included main effects for atmospheric acidity and both categories of organic acidity, and time. The intraclass correlation coefficient for the final model was 0.73, indicating that measurements within lakes were strongly correlated and thus validating the appropriateness of the mixed effect modelling approach for our dataset. Visual inspection of residual autocorrelation plots showed no strong tendency toward positive or negative serial autocorrelation, and model residuals were homoscedastic,

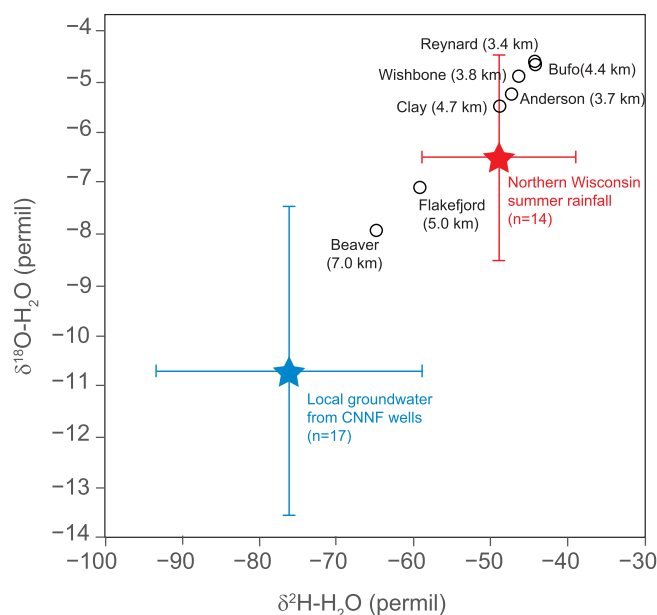


FIGURE 4 | Dual isotope plot of hydrogen vs. oxygen isotopic composition of lake water (black circles), local groundwater (blue star and lines) and summer precipitation (red star and lines). The blue star shows the mean composition of 17 groundwater samples collected from wells located throughout the Washburn/ Great Divide Unit of the Chequamegon-Nicolet National Forest (Fehling et al. 2018). The red star shows the mean composition of 14 summer precipitation samples collected throughout northern Wisconsin (Kendall and Doctor 2004). Vertical and horizontal blue and red lines indicate the ranges of reported isotope values for groundwater and precipitation endmembers, respectively. Distance values after lake names indicate the distance of each lake from the local groundwater divide.

indicating that the final model did not violate these linear regression assumptions.

3.3 | Temporal Changes in Model Predictors of Lake ANC

Mann-Kendall trend tests indicated a significant decrease in the acidity of atmospheric deposition over the study period, with a Kendall τ value of -0.36 ($p < 0.001$; Figure 5, Table 5).

TABLE 3 | Random effects structures, model formulations, AIC and BIC values for tested models.

Random effects structure	Generalised model formulation	AIC	BIC
OLS regression (no random effects)	$y_i = \beta_0 + \beta_1 X_i + e_i$	3627	3654
Random effect of lake, random intercepts	$y_i = \beta_0 + L_{0i} + \beta_1 X_i + e_i$	3504	3534
Random effect of lake, random intercepts, uncorrelated random slopes	$y_i = \beta_0 + L_{0i} + (\beta_1 + L_{1i}) X_i + e_i$	3516	3564

Note: y_i = ANC in lake i ; β_0 = population intercept; L_{0i} = intercept of lake i ; β_1 = population slope; L_{1i} = slope of lake i ; X_i = matrix of fixed effects for observations in lake i ; e_i = residual error.

TABLE 4 | Coefficients (standard error) and p -values for random intercept model parameters.

	Coefficient (std.err.)	p
Intercept	25,690.00 (11,990.00)	0.070
Fixed effect		
Total atmospheric acidity (eq)	2.226 (1.232)	0.072
Organic acidity in saturated soil runoff (eq)	−1.911 (0.570)	0.001
Post-drought organic acidity in runoff (eq)	−1.967 (0.566)	0.001
Time (mos. Since sampling onset)	128.000 (14.360)	<0.001
Total atmospheric acidity × time	−0.003 (0.003)	0.353
Organic acidity in saturated soil runoff × time	0.002 (0.002)	0.355
Post-drought organic acidity in runoff × time	0.001 (0.002)	0.559

Trends in organic acid flushing from hydric soils to lakes varied depending on lake and precipitation regime. Estimated organic acidity contributions from runoff events immediately following drought increased significantly in all RLW lakes except Bufo Lake over the study period; post-drought organic acidity contributions decreased over time in Bufo Lake (Figure 5, Table 5). Conversely, organic acidity contributions following all other runoff events (i.e., events not following drought) differed among lakes, with a significant positive trend only occurring in Anderson Lake and non-significant positive or negative trends in all other lakes (Figure 5, Table 5).

3.4 | Model Estimates of Lake ANC

When evaluated across the entire set of study lakes, model-predicted lake ANC values compared well with the measured lake ANC values ($R^2=0.50$, $p<0.001$, Figure 6a). However, at the scale of individual lakes, the accuracy of model-predicted ANC values was highly variable, but statistically significant

in all lakes. Although modelled ANC values compared well to ANC measurements, an excessively high modelled ANC value for Flakefjord Lake resulted in a larger divergence from the 1:1 line of measured vs. modelled-predicted ANC values in that lake (Table 6, Figure 6b).

4 | Discussion

4.1 | Lake ANC Responses to Changing Precipitation Chemistry

The long-term decline in wet atmospheric deposition acidity from 1984 to 2018 (Figure 5) largely reflects the dramatic reductions in SO_x and NO_x emissions across the United States following implementation of the Clean Air Act Amendments of 1990 (Stoddard et al. 2003; Burns et al. 2011). Lake monitoring in acid-sensitive regions of the United States—which encompass nearly all of the Upper Midwest and New England, and much of the Appalachian and Adirondack Mountain ranges (Stoddard et al. 2003)—has revealed a steady increase in the ANC status of many lakes, concomitant with the long-term decline in acid deposition (Stoddard et al. 2003; Kahl et al. 2004; Driscoll et al. 2016). However, ANC recovery trends in other lakes have been less straightforward in response to decreasing deposition acidity (Jeffries, Clair, et al. 2003; Clair et al. 2007; Strock et al. 2014; Watmough and Eimers 2020). In the seven RLW lakes monitored in our study, the overall increase in ANC was modest compared to ANC increases reported for other acid-sensitive regions (Kahl et al. 2004; Waller et al. 2012; Driscoll et al. 2016), but the generally similar patterns in ANC response across all seven lakes in our study (Figure 2) suggest that changing acid deposition chemistry over time was an important driver of ANC response in these seepage lakes.

4.2 | Changing Precipitation Regimes and Organic Acidity Fluxes

Despite the long-term decline in atmospheric deposition acidity, ANC recovery has been modest in our study lakes and in lakes throughout the Upper Midwest and southeastern Canada compared to many other acid-sensitive regions (Jeffries, Brydges, et al. 2003; Jeffries, Clair, et al. 2003; Clair et al. 2007). The extensive wetland cover and prevalence of organic matter-rich soils throughout much of the low-relief, glaciated landscape of the Upper Midwest and southeastern Canada may contribute to this differential response across regions and landscape types (Clair et al. 2007). In a study of organic matter-driven nutrient loading in the same RLW lakes investigated in our study,

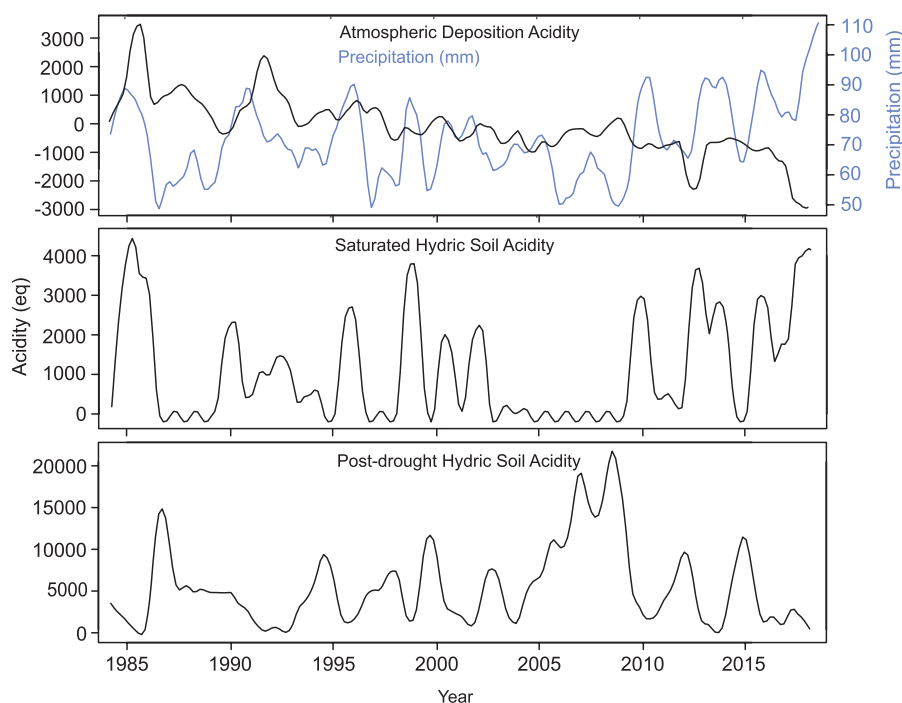


FIGURE 5 | Annual average precipitation and atmospheric and organic acidity trends for Anderson Lake, shown as 12-month moving averages. Atmospheric acidity trends were similar in all lakes; trends in organic (hydric soil) acidity were similar for all lakes except Bufo Lake. Bufo Lake showed minor or non-significant trends in organic acidity.

TABLE 5 | Kendall τ slope values (p -values) for atmospheric deposition acidity, organic acidity runoff following drought, and organic acidity runoff following non-drought periods during the study period.

Lake	Atmospheric deposition acidity	Post-drought organic acidity	Non-drought organic acidity
Anderson	−0.36 (<0.001)	0.09 (0.01)	0.09 (0.03)
Beaver	−0.36 (<0.001)	0.21 (<0.001)	−0.01 (0.78)
Bufo	−0.36 (<0.001)	−0.13 (0.001)	0.02 (0.55)
Clay	−0.36 (<0.001)	0.21 (<0.001)	−0.01 (0.78)
Flakefjord	−0.36 (<0.001)	0.21 (<0.001)	−0.01 (0.78)
Reynard	−0.36 (<0.001)	0.21 (<0.001)	−0.01 (0.78)
Wishbone	−0.36 (<0.001)	0.21 (<0.001)	−0.01 (0.78)

Corman et al. (2018) reported significant declines in lake sulphate concentrations from 1984 to 2016, but observed no trend in pH over the same time period. However, declining sulphate concentrations in all lakes were associated with significant increases in lake colour, or ‘browning’ (Corman et al. 2018), suggesting that any potential increase in lake pH (or ANC) following reductions in atmospheric sulphate deposition may have been offset by the effect of increased acidity contributions to the lakes from wetland runoff. Decreasing ionic strength of precipitation inputs may have also facilitated increased solubility of soil organic matter in the study watersheds over time (Lawrence and Roy 2020; Monteith et al. 2023), contributing to the increased DOC delivery to and browning of the study lakes as reported by Corman et al. (2018). Regardless of the mechanism behind the increased lake browning, previous studies have demonstrated that organic acids can directly regulate lake ANC status depending on the composition of organic acidic functional

groups (Driscoll, Fuller, and Schecher 1989; Clair, Dennis, and Vet 2011; Marty et al. 2021).

The effect of pulsed acid inputs from wetlands to lakes following oxidation (drying) events has been previously studied in weakly buffered systems throughout North America (Dillon, Molot, and Futter 1997; Devito, Hill, and Dillon 1999; Jeffries, Brydges, et al. 2003). Under dry conditions, lower water tables facilitate the oxidation of reduced sulphur compounds stored in previously anoxic soils; once oxidised, this sulphate can be mobilised to receiving waters during subsequent wetland runoff events (Dillon, Molot, and Futter 1997; Devito, Hill, and Dillon 1999). Eimers et al. (2003) reported high sulphate concentrations in streams draining wetlands following drying and re-wetting cycles, and Aherne, Futter, and Dillon (2008) suggested that lake recovery from acidification can be hampered by climate effects, with sulphate export increasing following drought events.

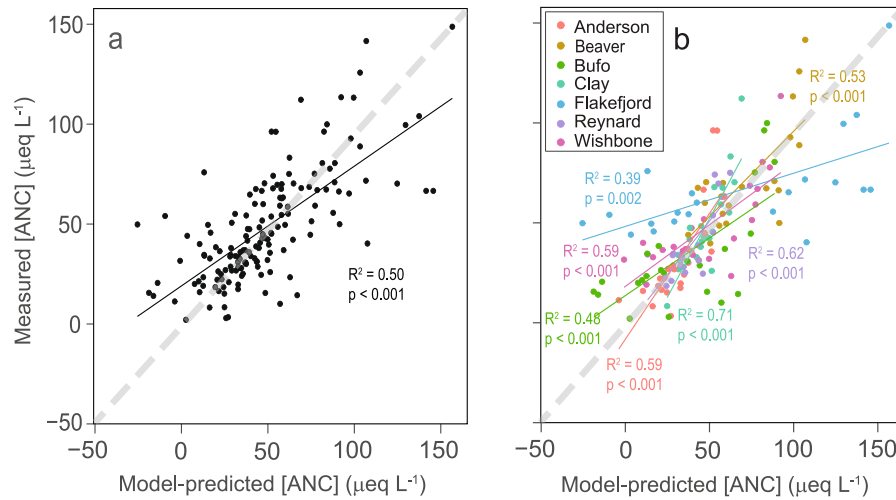


FIGURE 6 | Linear fit between measured and model-predicted ANC (a) across all study lakes and (b) in individual lakes. Grey dashed line indicates the 1:1 line.

TABLE 6 | Intercepts, slopes, R^2 and p -values for individual lake regressions of modelled vs. measured ANC values.

Lake	Intercept	Slope	R^2	p
Anderson	-8.23	1.25	0.58	<0.001
Beaver	10.93	0.85	0.53	<0.001
Bufo	14.02	0.56	0.48	<0.001
Clay	-26.70	1.58	0.71	<0.001
Flakefjord	48.01	0.27	0.39	0.002
Reynard	-2.41	1.06	0.62	<0.001
Wishbone	17.84	0.62	0.59	<0.001

Similarly, Kerr et al. (2012) observed significant increases in stream sulphate response following seasonal drying; the degree of response was positively related to the percent saturated area and percent of catchment area in wetland coverage; our results also reflect these catchment drivers, as illustrated by the significant positive trends in the estimated post-drought oxidative acidity contributions to most lakes from dried hydric soils over the study period (Table 5). Our observations add to the body of literature emphasising the importance of wetlands as potential episodic sources of acidity to lakes under both drought and non-drought conditions (Figure 5).

4.3 | Lake Morphology, Position and Resilience to Acid Inputs

The strong relationships we observed between mean lake ANC values and landscape and lake morphological characteristics, along with the lower ANC variability in lakes with higher mean ANC (Figure 3, Table 2) demonstrate the influence of landscape-scale gradients on ANC status in RLW lakes. The spatial pattern in overall ANC status across our study lakes is related to variations in the degree of groundwater connectivity among these lakes. This influence of groundwater is demonstrated by the gradient in water isotopic composition shown in Figure 4, where the

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ composition of water in higher mean ANC lakes was more similar to the isotopic composition of local groundwater, whereas the lakes with lower mean ANC and higher topographic position had isotopic compositions more similar to a precipitation source. Driscoll et al. (2016) reported widespread increases in 48 Adirondack lakes in response to declines in regional acid deposition rates, with mounded seepage lakes among the fastest to respond due to the predominance of precipitation as a hydrologic source. Our results are similar to those reported by Driscoll et al. (2016), as the lakes with less groundwater influence (low mean ANC lakes) showed more relative variability in ANC across the study period than higher mean ANC lakes, which were more buffered from changing deposition inputs because of their connection to groundwater. Kahl et al. (2004) noted a similar response in the Upper Midwest of the U.S., describing the behaviour of seepage lakes in this region as ‘pass-through systems’ that are highly responsive to changing atmospheric deposition rates, similar to the low mean ANC lakes and in contrast to the high mean ANC lakes in our study. Lake morphology (e.g., mean and maximum depth, perimeter length, surface area) and landscape position (e.g., position within the local groundwater flow system, land surface elevation) are important regulators of water quality and aquatic habitat, particularly in the glaciated landscapes of the Upper Midwest (Schnoor, Nikolaidis, and Glass 1986; Kratz et al. 1997; Riera et al. 2000; Martin and Soranno 2006; Webster et al. 2006). These physical characteristics can influence lake ANC status in both direct and indirect ways. For example, the degree to which a lake maintains connectivity to the local groundwater system is, in part, a function of its landscape position (Webster et al. 1996; Riera et al. 2000; Martin and Soranno 2006). However, the presence of localised perched water tables within and surrounding the study area (Fitzpatrick et al. 2015) may also foster spatially and temporally heterogeneous groundwater connections, adding complexity and nuance to the relationship between lake ANC status and landscape drivers such as lake elevation and catchment size. Additional tools such as water stable isotope analysis can clarify the role of subsurface hydrologic processes and inform our understanding of land surface and subsurface drivers of lake biogeochemical processes. Lake morphometry characteristics such as maximum and average depth can also indirectly affect in-lake

biogeochemical processes via their influence on water temperature and stratification, which affect biogeochemical mixing (Cornett 1989; Baines et al. 2000; Richardson et al. 2017). Similarly, lake orientation, shape and surface area can influence lake fetch, with implications for hydrologic and biogeochemical mixing (Robertson and Imberger 1994; Richardson et al. 2017). Lake sensitivity to external climatic drivers such as drought can also be mitigated or exacerbated by lake morphology and landscape position; evaporation rates may be greater in high surface area lakes, or shallow lakes may be more frequently affected by drought-induced water table drawdowns (Webster et al. 2000; Magnuson, Benson, and Kratz 2004).

Such landscape and lake morphological characteristics have clear implications for the connectivity of lakes to groundwater (Webster et al. 2006) and, consequently, overall lake ANC status. The spatial patterns and relationships with landscape and lake morphological features observed in our study may reflect a gradient of groundwater connectivity across the RLW; future research should focus on better quantifying variations in this likely important driver of lake ANC status. Lakes with higher mean ANC and lower overall ANC variability (e.g., Beaver and Flakefjord) may have a more consistent connection to groundwater due to their lower position on the landscape, whereas groundwater connectivity in lakes with lower mean ANC and higher relative ANC variability (e.g., Anderson, Reynard, Bufo) may be more transient or completely absent. The wide range in accuracy of model-predicted ANC values we observed within individual study lakes suggests a spatial gradient in lake ANC responses. Lakes situated higher on the landscape and positioned higher in the local groundwater flow systems may be more strongly influenced by acidity inputs from atmospheric deposition and wetland runoff (Schnoor, Nikolaidis, and Glass 1986), as these lakes showed better agreement between measured and modelled ANC values. Conversely, ANC in lakes positioned lower on the landscape and local groundwater flow system may be more strongly influenced by biogeochemical sources and processes insufficiently characterised by our model, that is, larger groundwater inputs and in-lake biogeochemical processes. This would account for both the less robust model fits in these lakes as well as their generally higher ANC and lower overall ANC variability. Although we lacked data that would allow us to quantify the rates of groundwater inputs and in-lake biogeochemical processing in individual lakes, hydrochemical tracers (e.g., source water ion ratios, water isotopes) might aid the quantification of these potential contributors to and drivers of lake ANC status.

5 | Conclusion

This study demonstrates the relationships among long-term changes in wet deposition chemistry, climate-mediated biogeochemical processes in hydric catchment soils, and landscape-scale drivers on seepage lake ANC responses in the Upper Midwest. Our mixed effect modelling approach revealed a shift in the relative contributions of acidity from atmospheric and catchment sources to RLW seepage lakes over time, and the wide range of model-predicted ANC across our study lakes suggests a gradient of lake-groundwater interactions across the RLW. Our results demonstrate that some poorly buffered northern

Wisconsin seepage lakes may be vulnerable to transient acidification events following drying of hydric soils; this effect may be particularly acute in lakes situated in higher landscape positions. In addition, landscape position likely functions as a direct control on the ANC status of RLW lakes through regulation of lake-groundwater connectivity (Webster et al. 2006) and as an indirect control by influencing lake morphology and catchment characteristics (Kratz et al. 1997, 2006; Riera et al. 2000). The critical convergence of hydric soil, catchment hydrology, deposition, and drought influences on lake ANC responses must be considered when assessing the biogeochemical status of seepage lakes in poorly buffered glaciated landscapes. Importantly, lake landscape position and the likelihood of shifting precipitation patterns should also be incorporated into evaluations of lake acidification risk when hydric soils have the potential to serve as a direct source of oxidative acidity to lakes.

Acknowledgements

Funding was provided by the USDA Forest Service Superior National Forest and Chequamegon-Nicolet National Forest to RKK and TRW, and by the Natural Sciences and Engineering Research Council of Canada to NS. The authors thank Dale Higgins, Jim Mineau, Sue Reineke and Sara Sommer for their help with this project.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- Adams, M. B. 1991. "Screening Procedure to Evaluate Effects of Air Pollution on Eastern Region Wildernesses Cited as Class I Air Quality Areas." Vol. 151. US Department of Agriculture, Forest Service, Northeastern Forest Experiment Station.
- Aherne, J., M. N. Futter, and P. J. Dillon. 2008. "The Impacts of Future Climate Change and Sulphur Emission Reductions on Acidification Recovery at Plastic Lake, Ontario." *Hydrology and Earth System Sciences* 12, no. 2: 383–392.
- Baines, S. B., K. E. Webster, T. K. Kratz, S. R. Carpenter, and J. J. Magnuson. 2000. "Synchronous Behavior of Temperature, Calcium, and Chlorophyll in Lakes of Northern Wisconsin." *Ecology* 81, no. 3: 815–825.
- Baker, L. A., A. T. Herlihy, P. R. Kaufmann, and J. M. Eilers. 1991. "Acidic Lakes and Streams in the United States: The Role of Acidic Deposition." *Science* 252: 1151–1154.
- Baumgardner, R. E., T. F. Lavery, C. M. Rogers, and S. S. Isil. 2002. "Estimates of the Atmospheric Deposition of Sulfur and Nitrogen Species: Clean Air Status and Trends Network, 1990–2000." *Environmental Science & Technology* 36: 2614–2629.
- Buffam, I., S. R. Carpenter, W. Yeck, P. C. Hanson, and M. G. Turner. 2010. "Filling Holes in Regional Carbon Budgets: Predicting Peat Depth in a North Temperate Lake District." *Journal of Geophysical Research: Biogeosciences* G1: 115.
- Burns, D. A., J. A. Lynch, B. J. Cosby, M. E. Fenn, J. S. Baron, and U. S. EPA Clean Air Markets Division. 2011. *National Acid Precitation Assessment Program Report to Congress 2011: An Integrated Assessment*. Washington, DC: National Science and Technology Council.

- Canham, C. D., M. L. Pace, M. J. Papaik, et al. 2004. "A Spatially Explicit Watershed-Scale Analysis of Dissolved Organic Carbon in Adirondack Lakes." *Ecological Applications* 14, no. 3: 839–854.
- Cheng, X., and M. P. Anderson. 1994. "Simulating the Influence of Lake Position on Groundwater Fluxes." *Water Resources Research* 30, no. 7: 2041–2049.
- Clair, T. A., I. F. Dennis, D. A. Scruton, and M. Gilliss. 2007. "Freshwater Acidification Research in Atlantic Canada: A Review of Results and Predictions for the Future." *Environmental Reviews* 15: 153–167.
- Clair, T. A., I. F. Dennis, and R. Vet. 2011. "Water Chemistry and Dissolved Organic Carbon Trends in Lakes From Canada's Atlantic Provinces: No Recovery From Acidification Measured After 25 Years of Lake Monitoring." *Canadian Journal of Fisheries and Aquatic Sciences* 68, no. 4: 663–674.
- Corman, J. R., B. L. Bertolet, N. J. Casson, S. D. Sebestyen, R. K. Kolka, and E. H. Stanley. 2018. "Nitrogen and Phosphorus Loads to Temperate Seepage Lakes Associated With Allochthonous Dissolved Organic Carbon Loads." *Geophysical Research Letters* 45, no. 11: 5481–5490.
- Cornett, R. J. 1989. "Predicting Changes in Hypolimnetic Oxygen Concentrations With Phosphorus Retention, Temperature, and Morphometry." *Limnology and Oceanography* 34, no. 7: 1359–1366.
- Devito, K. J., A. R. Hill, and P. J. Dillon. 1999. "Episodic Sulphate Export From Wetlands in Acidified Headwater Catchments: Prediction at the Landscape Scale." *Biogeochemistry* 44, no. 2: 187–203.
- Dillon, P. J., L. A. Molot, and M. Futter. 1997. "The Effect of El Nino-Related Drought on the Recovery of Acidified Lakes." *Environmental Monitoring and Assessment* 46, no. 1: 105–111.
- Driscoll, C. T., K. M. Driscoll, H. Fakhraei, and K. Civerolo. 2016. "Long-Term Temporal Trends and Spatial Patterns in the Acid-Base Chemistry of Lakes in the Adirondack Region of New York in Response to Decreases in Acidic Deposition." *Atmospheric Environment* 146: 5–14.
- Driscoll, C. T., K. M. Driscoll, K. M. Roy, and M. J. Mitchell. 2003. "Chemical Response of Lakes in the Adirondack Region of New York to Declines in Acidic Deposition." *Environmental Science and Technology* 37: 2036–2042.
- Driscoll, C. T., R. D. Fuller, and W. D. Schecher. 1989. "The Role of Organic Acids in the Acidification of Surface Waters in the Eastern US." *Water, Air, and Soil Pollution* 43, no. 1–2: 21–40.
- Driscoll, C. T., M. D. Lehtinen, and T. J. Sullivan. 1994. "Modeling the Acid-Base Chemistry of Organic Solutes in Adirondack, New York, Lakes." *Water Resources Research* 30, no. 2: 297–306.
- Eilers, J. M., and J. A. Bernert. 1997. "Temporal Trends and Spatial Patterns in Acid-Base Chemistry for Selected Minnesota Lakes." *E & S Environmental Chemistry*.
- Eimers, M. C., P. J. Dillon, S. L. Schiff, and D. S. Jeffries. 2003. "The Effects of Drying and Re-Wetting and Increased Temperature on Sulphate Release From Upland and Wetland Material." *Soil Biology and Biochemistry* 35, no. 12: 1663–1673.
- Eimers, M. C., S. A. Watmough, J. M. Buttle, and P. J. Dillon. 2007. "Drought-Induced Sulphate Release From a Wetland in South-Central Ontario." *Environmental Monitoring and Assessment* 127, no. 1–3: 399–407.
- Fehling, A. C., K. R. Bradbury, A. T. Leaf, et al. 2018. "Characterization of Groundwater Resources in the Chequamegon-Nicolet National Forest." Wisconsin: Washburn/Great Divide Unit, Wisconsin Geological and Natural History Survey.
- Fitzpatrick, F. A., M. C. Peppler, D. A. Saad, D. M. Pratt, and B. M. Lenz. 2015. "Geomorphic, Flood, and Groundwater-Flow Characteristics of Bayfield Peninsula Streams, Wisconsin, and Implications for Brook-Trout Habitat." Scientific Investigations Report 2014–5007. U.S. Geological Survey.
- Graham, G. E., A. C. Fehling, M. B. Gotkowitz, and K. R. Bradbury. 2019. "Hydrogeologic Atlas of Bayfield County, Wisconsin." Technical Report 005. Wisconsin Geological and Natural History Survey.
- Hamed, K. H., and A. R. Rao. 1998. "A Modified Mann-Kendall Trend Test for Autocorrelated Data." *Journal of Hydrology* 204, no. 1–4: 182–196.
- Harrison, X. A., L. Donaldson, M. E. Correa-Cano, et al. 2018. "A Brief Introduction to Mixed Effects Modelling and Multi-Model Inference in Ecology." *PeerJ* 6: e4794.
- Haugen, D. E. 1998. "The Forest Resources of the Chequamegon-Nicolet National Forest." US Department of Agriculture, Forest Service, North Central Research Station.
- Hobbs, T., J. Lynch, and R. Kolka. 2017. "Site-Specific Critical Acid Load Estimates for Forest Soils in the Osborn Creek Watershed, Michigan." Gen. Tech. Rep. NRS-171. Newtown Square, PA: US Department of Agriculture, Forest Service, Northern Research Station. 49 p. 171: 1–49.
- Jeffries, D. S., T. G. Brydges, P. J. Dillon, and W. Keller. 2003. "Monitoring the Results of Canada/USA Acid Rain Control Programs: Some Lake Responses." *Environmental Monitoring and Assessment* 88, no. 1–3: 3–19.
- Jeffries, D. S., T. A. Clair, S. Couture, et al. 2003. "Assessing the Recovery of Lakes in Southeastern Canada From the Effects of Acidic Deposition." *AMBIO* 32, no. 3: 176–182.
- Kahl, J. S., J. L. Stoddard, R. Haeuber, et al. 2004. "Have US Surface Waters Responded to the 1990 Clean Air Act Amendments?" *Environmental Science & Technology* 38, no. 24: 484A–490A.
- Kendall, C., and D. H. Doctor. 2004. "Stable Isotope Applications in Hydrologic Studies." In *Surface and Ground Water, Weathering, and Soils*, edited by H. D. Holland and K. K. Turekian, 319–364. Amsterdam, the Netherlands: Elsevier.
- Kerr, J. G., M. C. Eimers, I. F. Creed, et al. 2012. "The Effect of Seasonal Drying on Sulphate Dynamics in Streams Across Southeastern Canada and the Northeastern USA." *Biogeochemistry* 111: 393–409.
- Krabbenhoft, D. P., and K. E. Webster. 1995. "Transient Hydrogeological Controls on the Chemistry of a Seepage Lake." *Water Resources Research* 31, no. 9: 2295–2305.
- Kratz, T., K. Webster, C. Bowser, J. Magnuson, and B. Benson. 1997. "The Influence of Landscape Position on Lakes in Northern Wisconsin." *Freshwater Biology* 37, no. 1: 209–217.
- Kratz, T. K., K. E. Webster, J. L. Riera, D. B. Lewis, and A. I. Pollard. 2006. "Making Sense of the Landscape: Geomorphic Legacies and the Landscape Position of Lakes." In *Long-Term Dynamics of Lakes in the Landscape: Long-Term Ecological Research on North Temperate Lakes*, edited by J. J. Magnuson, T. K. Kratz, and B. J. Benson. 49–66. New York, NY: Oxford University Press.
- Lawrence, G. B., and K. M. Roy. 2020. "Ongoing Increases in Dissolved Organic Carbon Are Sustained by Decreases in Ionic Strength Rather Than Decreased Acidity in Waters Recovering From Acidic Deposition." *Science of the Total Environment* 766: 142529.
- Magnuson, J. J., B. J. Benson, and T. K. Kratz. 2004. "Patterns of Coherent Dynamics Within and Between Lake Districts at Local to Intercontinental Scales." *Boreal Environment Research* 9, no. 5: 359–369.
- Martin, S. L., and P. A. Soranno. 2006. "Lake Landscape Position: Relationships to Hydrologic Connectivity and Landscape Features." *Limnology and Oceanography* 51, no. 2: 801–814.
- Marty, C., L. Duchesne, S. Couture, C. Gagnon, and D. Houle. 2021. "Effects of Climate and Atmospheric Deposition on a Boreal Lake Chemistry: A Synthesis of 36 Years of Monitoring Data." *Science of the Total Environment* 758: 143639.
- McDonnell, T. C., T. J. Sullivan, P. F. Hessburg, et al. 2014. "Steady-State Sulfur Critical Loads and Exceedances for Protection of Aquatic

- Ecosystems in the US Southern Appalachian Mountains.” *Journal of Environmental Management* 146: 407–419.
- McLaughlin, J. W., and K. L. Webster. 2010. “Alkalinity and Acidity Cycling and Fluxes in an Intermediate Fen Peatland in Northern Ontario.” *Biogeochemistry* 99, no. 1: 143–155.
- Monteith, D. T., P. A. Henrys, J. Hruška, et al. 2023. “Long-Term Rise in Riverine Dissolved Organic Carbon Concentration Is Predicted by Electrolyte Solubility Theory.” *Science Advances* 9: eade3491.
- National Atmospheric Deposition Program. 2011. “National Atmospheric Deposition Program 2010 Annual Summary.” NADP Data Report 2011-01. Illinois State Water Survey, Urbana IL.
- NRCS Soil Survey Staff. 2021. Natural Resources Conservation Service, United States Department of Agriculture. “Web Soil Survey.” <http://websoilsurvey.sc.egov.usda.gov/>.
- Pardo, L. H. 2010. “Approaches for Estimating Critical Loads of Nitrogen and Sulfur Deposition for Forest Ecosystems on US Federal Lands.” General Technical Report NRS-71. Newtown Square: USDA Forest Service, Northern Research Station.
- PRISM Climate Group. 2012. “PRISM Climate Data.” Oregon State University. prism.oregonstate.edu.
- Quantum GIS Development Team. 2012. “Quantum Geographic Information System.” qgis.osgeo.org.
- Reidmiller, D. R., C. W. Avery, D. R. Easterling, et al. 2019. “Fourth National Climate Assessment. Volume II: Impacts, Risks, and Adaptation in the United States.” Washington, D.C.: U.S. Global Change Research Program.
- Richardson, D. C., S. J. Melles, R. M. Pilla, et al. 2017. “Transparency, Geomorphology and Mixing Regime Explain Variability in Trends in Lake Temperature and Stratification Across Northeastern North America (1975–2014).” *Watermark* 9, no. 6: 442.
- Riera, J. L., J. J. Magnuson, T. K. Kratz, and K. E. Webster. 2000. “A Geomorphic Template for the Analysis of Lake Districts Applied to the Northern Highland Lake District, Wisconsin, USA.” *Freshwater Biology* 43, no. 3: 301–318.
- Robertson, D. M., and J. Imberger. 1994. “Lake Number, a Quantitative Indicator of Mixing Used to Estimate Changes in Dissolved Oxygen.” *Internationale Revue der Gesamten Hydrobiologie Und Hydrographie* 79, no. 2: 159–176.
- Schnoor, J. L., N. P. Nikolaidis, and G. E. Glass. 1986. “Lake Resources at Risk to Acidic Deposition in the Upper Midwest.” *Journal (Water Pollution Control Federation)* 58: 139–148.
- Schwede, D. B., and G. G. Lear. 2014. “A Novel Hybrid Approach for Estimating Total Deposition in the United States.” *Atmospheric Environment* 92: 207–220.
- Stoddard, J. L., J. S. Kahl, F. A. Deviney, et al. 2003. *Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990*. Research Triangle Park, NC: US Environmental Protection Agency.
- Strock, K. E., S. J. Nelson, J. S. Kahl, J. E. Saros, and W. H. McDowell. 2014. “Decadal Trends Reveal Recent Acceleration in the Rate of Recovery From Acidification in the Northeastern US.” *Environmental Science & Technology* 48, no. 9: 4681–4689.
- Sullivan, T. J., B. J. Cosby, C. T. Driscoll, T. C. McDonnell, A. T. Herlihy, and D. A. Burns. 2012. “Target Loads of Atmospheric Sulfur and Nitrogen Deposition for Protection of Acid Sensitive Aquatic Resources in the Adirondack Mountains, New York.” *Water Resources Research* 48, no. 1: W01547.
- U.S. EPA. 2016. “National Lakes Assessment 2012: A Collaborative Survey of Lakes in the United States.” EPA 841-R-16-113. US Environmental Protection Agency, Washington, DC.
- Valiantzas, J. D. 2006. “Simplified Versions for the Penman Evaporation Equation Using Routine Weather Data.” *Journal of Hydrology* 331, no. 3–4: 690–702.
- Venables, W. N., and D. M. Smith. 2020. *An Introduction to R, Version 4.0.3 (0)*. R Development Core Team.
- Vermaat, J. E., J. Harmsen, F. A. Hellmann, et al. 2016. “Annual Sulfate Budgets for Dutch Lowland Peat Polders: The Soil Is a Major Sulfate Source Through Peat and Pyrite Oxidation.” *Journal of Hydrology* 533: 515–522.
- Waller, K., C. T. Driscoll, J. Lynch, D. Newcomb, and K. Syracuse. 2012. “Long-Term Recovery of Lakes in the Adirondack Region of New York to Decreases in Acidic Deposition.” *Atmospheric Environment* 46: 56–64.
- Watmough, S. A., C. Eimers, and S. Baker. 2016. “Impediments to Recovery From Acid Deposition.” *Atmospheric Environment* 146: 15–27.
- Watmough, S. A., and M. C. Eimers. 2020. “Rapid Recent Recovery From Acidic Deposition in Central Ontario Lakes.” *Soil Systems* 4, no. 1: 10.
- Watras, C. J., J. S. Read, K. D. Holman, et al. 2014. “Decadal Oscillation of Lakes and Aquifers in the Upper Great Lakes Region of North America: Hydroclimatic Implications.” *Geophysical Research Letters* 41, no. 2: 456–462.
- Webster, K. E., C. J. Bowser, M. P. Anderson, and J. D. Lenters. 2006. “Understanding the Lake-Groundwater System: Just Follow the Water.” In *Long-Term Dynamics of Lakes in the Landscape: Long-Term Ecological Research on North Temperate Lakes*, edited by J. J. Magnuson, T. K. Kratz, and B. J. Benson, 19–48. New York, NY: Oxford University Press.
- Webster, K. E., P. L. Brezonik, and B. J. Holdhusen. 1993. “Temporal Trends in Low Alkalinity Lakes of the Upper Midwest (1983–1989).” *Water, Air, and Soil Pollution* 67, no. 3–4: 397–414.
- Webster, K. E., T. K. Kratz, C. J. Bowser, J. J. Magnuson, and W. J. Rose. 1996. “The Influence of Landscape Position on Lake Chemical Responses to Drought in Northern Wisconsin.” *Limnology and Oceanography* 41, no. 5: 977–984.
- Webster, K. E., P. A. Soranno, S. B. Baines, et al. 2000. “Structuring Features of Lake Districts: Landscape Controls on Lake Chemical Responses to Drought.” *Freshwater Biology* 43, no. 3: 499–515.
- Wilde, F. D., D. B. Radtke, J. Gibbs, and R. T. Iwatsubo. 1998. *National Field Manual for the Collection of Water-Quality Data*, 9. US Geological Survey Techniques in Water-Resources Investigations, Book. Denver: U.S. Department of the Interior, U.S. Geological Survey.
- Wood, J. A. 1989. *Peatland Acidity Budgets and the Effects of Acid Deposition*. Ottawa, Ontario, Canada: Ecological Application Research Division, Environment Canada.
- Zuur, A., E. N. Ieno, N. Walker, A. A. Saveliev, and G. M. Smith. 2009. *Mixed Effects Models and Extensions in Ecology With R*. New York: Springer Science & Business Media.