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RESEARCH AND OBSERVATORY CATCHMENTS: THE LEGACY AND THE FUTURE

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Acidification recovery in a changing climate: Observations from thirty-five years of stream chemistry monitoring in forested headwater catchments at the Turkey Lakes watershed, Ontario

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Abstract

Long-term ecosystem studies are valuable for understanding integrated ecosystem response to global changes in atmospheric deposition and climate. We examined trends for a 35-year period (1982/83–2017/18) in concentrations of a range of solutes in precipitation and stream water from nine headwater catchments spanning elevation and surficial geology gradients at the Turkey Lakes watershed (TLW) in northeastern Ontario, Canada. Average annual water year (WY, October to September) concentrations in precipitation significantly declined over the period for sulphate (SO_4^{2-}), nitrate (NO_3^-) and chloride (Cl^-), while calcium (Ca^{2+}) and potassium (K^+) concentrations increased, resulting in a significant pH increase from 4.2 to 5.7. Trends in stream chemistry through time are generally consistent with expectations associated with acidification recovery. Concentration of many stream water solutes (SO_4^{2-}, Cl^-, calcium [Ca^{2+}], magnesium [Mg^{2+}] and NH_4^+ generally decreased, while others (silica [SiO_2] and dissolved organic carbon [DOC]) generally increased. Increases were also observed for alkalinity (six of nine catchments), acid neutralizing capacity ([ANC]; six of nine catchments) and pH (eight of nine catchments), while conductivity declined (six of nine catchments). Variability in trends among catchments are associated with differences in surficial geology and wetland cover. While absolute solute concentrations were generally lower at bedrock dominated high-elevation catchments compared to till dominated lower elevation catchments, the rate of change of concentration was often greater for high elevation catchments. This study confirms continued, but non-linear stream chemistry recovery from acidification, particularly at the less buffered high and moderate elevation sites. The heterogeneity of responses among catchments highlights our incomplete understanding of the relative importance of different mechanisms influencing stream chemistry and the consequences for downstream ecosystems.

KEYWORDS
acidification recovery, atmospheric deposition, climate change, concentration, elevation gradient, stream chemistry, streamflow, Turkey Lakes watershed

1 | INTRODUCTION

Acidification of terrestrial and aquatic ecosystems was a significant problem in the latter half of the 20th century (Kahl et al., 2004; Norton & Vesely, 2003) which have persisted longer in some parts of the world (e.g., China; (Liu et al., 2020)). Burning of coal and other fossil fuels in the industrialized world were key causes of high emissions of nitric and sulphuric acids into the atmosphere. This acidic pollution affected aquatic ecosystems through direct deposition onto surface waters and via chemical transformations within soil that resulted in mobilization and leaching of cations (Foster et al., 1989; Galloway et al., 1983; Nicolson, 1988). Acidification of surface waters occurred when the chemical buffering capacity of surrounding soils was insufficient to balance the level of acid deposition (Austnes et al., 2018). This resulted in increased concentrations of acidifying ions (sulphate (SO_4^{2-}), nitrate (NO_3^-)) and increased surface water base cation concentrations (calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and aluminium (Al^{3+})) followed by decreases if soil supply is depleted. Increased conductivity and decreased pH, acid neutralizing capacity (ANC) and alkalinity are consequences of these trends (Galloway et al., 1983). These changes in water chemistry induced by acidification subsequently impacted the functioning and health of biological communities living in terrestrial and aquatic ecosystems (Norton & Vesely, 2003).

The widespread acidification of surface waters led to the signing of the United Nations Economic Commission for Europe Convention on Long-range Transboundary Air Pollution in 1979 and in North America, the implementation of the Clean Air Act in the U.S. (1990 and subsequent amendments) and the Canada - U.S. Air Quality Agreement (1991). Although some reductions across eastern North America in acidic deposition had already begun in the 1980's (RMCC, 1990), these policy interventions contributed to continued reductions in SO_4^{2-} and NO_3^- deposition in regions of eastern North America from rates of 28 and 21 kg ha^{-1} y^{-1} (SO_4^{2-} and NO_3^-, respectively) in 1990 to 12 and 15 kg ha^{-1} y^{-1} in 2014, respectively (IJC, 2017). Hazlett et al. (2001) showed that forest soils at some sites across northeastern North America were showing reversal of soil acidification, but that the degree of recovery varied and could not be fully explained by deposition declines alone. These declines in deposition and soils recovery have resulted in a decline in magnitude and extent of surface water acidification over the last 20 years (Austnes et al., 2018; Dillon et al., 2007; Garmo et al., 2014; Garmo et al., 2020; Mast, 2013; Stoddard et al., 1999; Strock et al., 2014).

Despite these improvements, surface water acidification remains a significant environmental issue because the original soil buffering capacity depleted by decades of acid deposition is slow to recover (Austnes et al., 2018). Furthermore, the chemical composition of water and its recovery from acidification is a function of highly complex and coupled processes (Armfield et al., 2019). For example, acidification is known to influence DOC concentrations, potentially contributing to the water's acid–base chemistry. Sawicka et al. (2016) showed that declines in SO_4^{2-} could enhance the mobilization of DOC in surface organic horizons. Reductions in atmospheric deposition also reduces ionic strength in the soil, which can increase DOC flux (Vance & David, 1989). Episodic acidification may also occur when previously deposited and now organically-bound S is oxidized during drought periods and subsequently mobilized (de Wit et al., 2015; Eimers, Buttle, & Watmough, 2008; Watmough et al., 2016). Furthermore, climate change impacts can also affect recovery from acidification through changes to: 1. Soil conditions (soil temperature, moisture, oxidation–reduction potential (Blanco & Lal, 2008)), 2. Biogeochemical reactions (decomposition, nutrient cycling and weathering rates, e.g., Augustin et al., 2015; Durán et al., 2016, Durán et al., 2014; Gessler et al., 2017; Gislason et al., 2009), 3. Ecosystem changes (tree growth and productivity, root dynamics, litter production, e.g., Hernández-Santana et al., 2009; Rennenberg et al., 2009) and; 4. Hydrological processes (hydrologic residence times, source areas and flow pathways, e.g., Groffman et al., 2009; Houle, Khadra, et al., 2020). In addition, changes in the frequency and intensity of disturbance events associated with changes in climate (e.g., fire, insects, wind and ice storms) can influence vegetation growth and mortality and contribute to major nutrient fluxes within the ecosystem (de Wit et al., 2015). Identifying and disentangling these confounding and interacting factors affecting stream solute chemistry and recovery from acidification is challenging, but essential to understanding and predicting impacts on streams and downstream aquatic communities they support.

Within Canada, the Turkey Lakes watershed (TLW) (Webster et al., 2021) was initially established in 1979 to understand the impacts of acid rain on coupled terrestrial and aquatic ecosystems. Having monitoring data from first order streams draining catchments that vary in topography and elevation make the TLW an ideal location to examine patterns in recovery in acidification under a changing climate. Nicolson (1988) provided baseline solute fluxes in 20 first order streams over the period 1981–1984 and described the spatial heterogeneity in response across the elevation gradient. He noted that hydrogen (H^+) and ammonium (NH_4^+) output of the catchments increased with elevation; whereas conductivity, alkalinity, Ca^{2+} and NO_3^- decreased. Losses of Mg^{2+}, K^+, sodium (Na^+), SO_4^{2-} and chloride (Cl^-) were not related to elevation. It was also shown that bicarbonate (HCO_3^-) was important in balancing cation losses in low elevation basins, with thicker tills, but that SO_4^{2-} dominated in high elevation basins with shallow soils over bedrock.

Beall et al. (2001) examined longer-term (1982–1996) trends in TLW stream chemistry, showing some evidence for incomplete recovery from acidification in 13 first order streams at the TLW. In that study stream concentrations of SO_4^{2-} had decreased coincident with the decline in precipitation inputs. However, other indicators of recovery from acidification (increased pH, increased alkalinity and decreasing base cation concentrations) were not uniform across streams (Beall et al., 2001). Basins that were impacted to a lesser degree from acidification were those at the lower elevations, which tend to be dominated by relatively deeper flow paths through a carbonate rich basal till resulting in greater potential acid neutralizing capacity than high elevation catchments with shallow flowpaths over bedrock and a shallow ablation till with low amounts of carbonate

(Craig & Johnston, 1988). Higher elevation streams had lower levels of potential acid neutralizing capacity and showed some, but incomplete recovery.

In a contemporary paper to Beall et al. (2001), Jeffries et al. (2002) examine temporal trends in water chemistry of different sources at TLW, including shallow and deep ground water, two headwater streams and two lake outflows. They found increasing pH in bulk deposition, two high elevation headwater streams, a low elevation lake outflow, but not in a high elevation lake outflow or shallow or deep groundwater. Increasing alkalinity was found only in the outflow of a lower elevation lake, providing additional evidence that recovery from acidification had not occurred. Jeffries et al. (2002) also identified that droughts delayed acidification recovery by mobilizing S stored in catchment wetlands and/or soil.

Since these last trend studies were published acidic deposition has continued to decline across northeastern North America (IJC, 2017; Marty et al., 2021; Vet et al., 2014; Zhang et al., 2018), concurrent with a changing climate. The objective of this paper is to examine trends in stream chemistry at the TLW to see how recovery from acidification has progressed since previous reports. Specifically, we consider trends in anions and base cations (SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^+, Na^+, K^+, NH_4^+), integrative measures (ANC, pH, conductivity and alkalinity) and other important solutes (silica [SiO_2], dissolved inorganic carbon [DIC] and DOC). We discuss and hypothesize how rates of recovery may be accelerated or delayed by: a) changes in organic acids, b) liberation of stored SO_4^{2-}, c) alteration in flow paths and/or d) internal nitrogen (N) cycling; as a starting point in which to frame questions that will be addressed in future studies within the TLW.

2 | METHODS

2.1 | Study site

The TLW (TLW; 47°03'N, 84°25'W) is located ~60 km north of Sault Ste. Marie, Ontario (Figure 1) in the Algoma region of central Ontario (Webster et al., 2021). The TLW has a total relief of 295 m (330 to 625 m ASL). Mean daily air temperature measured at the Environment and Climate Change Canada (ECCC) Algoma station of the Canadian Air and Precipitation Monitoring Network (CAPMoN; http://data.ec.gc.ca/data/air/monitor/networks-and-studies/canadian-air-and-precipitation-monitoring-network-capmon), located just outside the watershed (47°02′06"N, 84°22′52"W), for the period 1982–2017 was 4.6°C and mean annual precipitation was 1211 mm, with approximately a third of precipitation falling as snow (Semkin et al., 2012). "Year", as used in this paper, refers to WY, defined as the period from October 1 of the previous year to September 30 of the current calendar year.

Regional bedrock is Precambrian metamorphic basalt (silicate greenstone) with some granitic outcrops, covered by a thin discontinuous two component glacial till: bouldery silt loam ablation till overlying compacted sandy loam basal till (Hazlett et al., 2001). Hillslope soil cover is orthic humo-ferric podzols (spodosols) with well-defined L and F (Oi and Oe) horizons with a combined average thickness of 0.05 m (Hazlett et al., 2001), while dispersed organic soils occupy depressions and riparian areas (Creed et al., 2008). The TLW has a mature (~ 150 years old) shade-tolerant hardwood forest cover composed of sugar maple (*Acer saccharum* Marsh., 90%), yellow birch (*Betula alleghaniensis* Britton; 9%) and various conifers (1%) (Jeffries et al., 1988) characteristic of the Eastern Temperate Mixed Forest (Baldwin et al., 2018). The catchments examined in this study are relatively undisturbed forest, with the exception of a light selective harvest ("high⁻grading") in the 1950's (Beall et al., 2001). Typically, this type of forest is harvest at approximately 80–100 years of age.

Nine first order catchments that have been monitored for streamflow and water chemistry since 1981 were used for this study. These catchments (Figure 1, Table 1) represent an elevation gradient from high elevation, bedrock-dominated catchments to low elevation, with deep ablation and basal tills. Catchments at high elevation (C47, C49 and C50) are situated on bedrock and shallow tills and stream water is characterized by low alkalinity (0.02 meq L^{-1} ± 0.02). Streams draining catchments at mid elevations (C35, C42, C46) have moderate alkalinity (0.09 meq L^{-1} ± 0.03). Catchments at lower elevation (C32, C38 and C39) are over deeper ablation and basal tills and streams have high alkalinity (mean ± SD) (0.27 meq L^{-1} ± 0.09) (Table 1).

2.2 | Climate and watershed flow data

Air temperature and precipitation were monitored at a meteorological station co-located with the CAPMoN station. Sensors deployed at the top of a 10 m tower logged air temperature every 10 min and averaged over 24-h periods to provide daily mean values. Precipitation quantity was recorded daily by using a standard rain gauge and a Nipher-shielded snow gauge. WY mean air temperature and total precipitation were computed from the daily values. Growing degree days (GDD) was calculated using a base temperature of 5°C and summed for each calendar year (not WY). As an indicator of drought stress, the Palmer Drought Sensitivity Index (PDSI) was also calculated from the meteorological measurements (Palmer, 1965). The monthly PDSI was computed using the pdsi function in the scPDSI R package (Zhong et al., 2019) assuming an available soil water capacity of 140 mm. WY mean PDSI was computed from the monthly PDSI values. Water Survey of Canada monitored streamflow at the TLW outlet on Norberg Creek (station number 02BF005; catchment area 10.4 km^2) from 1980 to 2016. Mean WY discharge was computed from the daily records and used to highlight interannual variation in streamflow.

2.3 | Bulk precipitation data

Bulk precipitation samples were collected weekly at the CAPMoN station and analysed at the Water Chemistry Laboratory at the Great Lakes Forestry Centre using standardized procedures and quality-control methods (Table S1). Concentrations of NO_3^- and NH_4^+ were measured as nitrogen (i.e., NO_3^--N and NH_4^+-N). Bulk collection consists of a mixture of wet only precipitation, an unknown and variable portion of dry deposition, but no gaseous deposition.

2.4 | Stream chemistry

Stream water samples were collected yearly since 1981 for chemical analysis, with collections every 1–2 days during high discharge periods of spring melt and on a biweekly or weekly basis for the

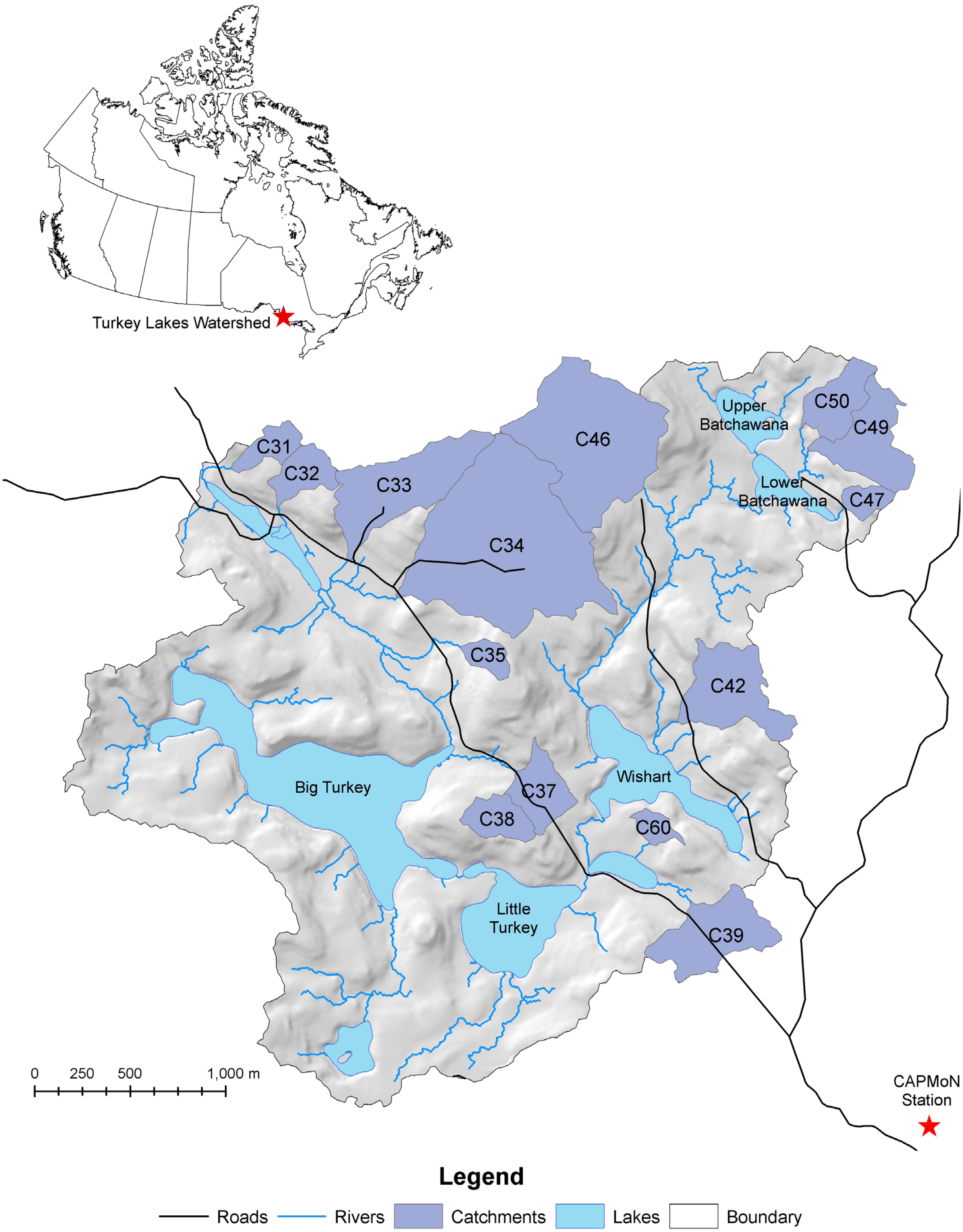

FIGURE 1 The Turkey Lakes watershed and the location of the nine 1st order catchments and the Algoma CAPMoN site

TABLE 1 Characteristics of the first order gauged catchments at the Turkey Lakes watershed (from Beall et al. (2001)). Note that C38 is classified as low and C35 as "medium" due to average elevation within the catchment

Elevation grouping	Catchment	Area (ha)	Weir elevation (m AMSL)	Total relief (m)	Wetland area (%)	Mean alkalinity (meq L^{-1})
Low	32	6.74	352	107	1	0.28
Low	38	8.5	415	34	25	0.18
Low	39	17.42	379	80	4	0.36
Medium	35	4.47	386	79	0	0.11
Medium	42	15.69	408	110	7	0.10
Medium	46	44.21	485	141	1	0.05
High	47	4.06	503	94	0	0.01
High	49	18.58	504	93	3	0.03
High	50	11.61	507	83	8	0.01

remainder of the year. Water collection for these synoptic sampling events typically occur over a 6–24 h period. During drought periods in mid to late summer streams may not flow thus samples are not collected. Samples were processed using the same procedures for bulk precipitation samples. Average WY catchment stream concentrations were unweighted mean of all synoptic stream sampling dates, acknowledging this may introduce some bias in the conclusions (e.g., Eimers, Watmough, & Buttle, 2008). Average WY ANC was the mean of ANC (meq, sum of base cations [Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+}] minus sum of acid anions [SO_4^{2-} + Cl^{-} + NO_3^{-}]) for all synoptic sampling dates.

2.5 | Trend analysis

Trends in precipitation and stream solute concentrations and metrics were assessed using Mann-Kendall monotonic trend tests and the Sen's slope linear trend coefficients (Kendall, 1955; Sen, 1968) implemented using the R 'trend' package (Pohlert, 2020). The 95% confidence intervals are computed for the Sen's slope coefficients and intervals that do not include zero indicate a statistically significant linear trend.

3 | RESULTS

3.1 | Climatic trends

Climate has not shown a straightforward linear trend over time. While temperatures have generally increased at a rate of 0.3°C per decade, periodicity in the temperature and precipitation is evident (Figure 2). Temperature, over the 35-year record, peaked in the early 2000's. Precipitation and flows show peaks in late 1990's, minimums in early 2000's and an increasing trend over the last decade. GDD increased from 1980's through to the mid-2000's at its peak, after which it has decreased (Figure 2). As indicated by the PDSI, drought years were frequent over the period 1998–2012, but wet years have become more common in recent years (2014–2017).

3.2 | Trends in precipitation chemistry

Average WY concentrations of SO_4^{2-}, NO_3^{-}, Cl^{-} and NH_4^{+} in precipitation significantly declined through the years while no significant changes were observed for Mg^{2+} and Na^{+} (Figure 3a,b). Because the NO_3^{-} decline was more pronounced than for NH_4^{+}, the proportion of the latter to total N deposition increased. Ca^{2+} and K^{+} were the only elements that showed a significant increase. As a consequence of these changing solute concentrations, precipitation pH increased by 1.5 unit, from 4.2 to 5.7, during the studied period. Trends in precipitation concentrations mirrored the trends in precipitation deposition (Figure S1a,b and Table S2, Supplementary material).

The shape of the concentration trajectory in precipitation is variable from year to year for many solutes even for those showing significant trends. Sulphate, in contrast, shows a remarkably smooth and linear decline. However, the decline in NO_3^{-}, Cl^{-} and NH_4^{+} were particularly strong after the late 1990's, early 2000's. Similarly, increases in Ca^{2+} appear around the same time. The more pronounced increase in precipitation pH during the mid-2000's matches the decreasing NO_3^{-} trend.

3.3 | Trends in stream chemistry

Stream SO_4^{2-}, Cl^{-} and NH_4^{+} concentrations declined significantly in all nine catchments (Figure 4a,b), while NO_3^{-} had significant decreases in only two high elevation catchments and a significant increase in one low elevation catchment (C39). Stream concentrations declined for Ca^{2+} in all except for the three low elevation catchments, Mg^{2+} in all catchments and K^{+} in seven catchments, while Na^{+} showed no significant changes (See Table S3 of supplementary material for p value, S and tau test statistics). As a result of changes in anions and cations, pH increased significantly in eight catchments and ANC and alkalinity in six catchments (Figure 5a,b) while conductivity decreased in six catchments. Finally, there were also significant increases (Figure 6a,b) in SiO_2 (eight catchments), DIC (four catchments) and DOC (seven catchments).

The trajectory of these trends over time varies by solute. While some responses appear linear (e.g., SO_4^{2-}), others could be

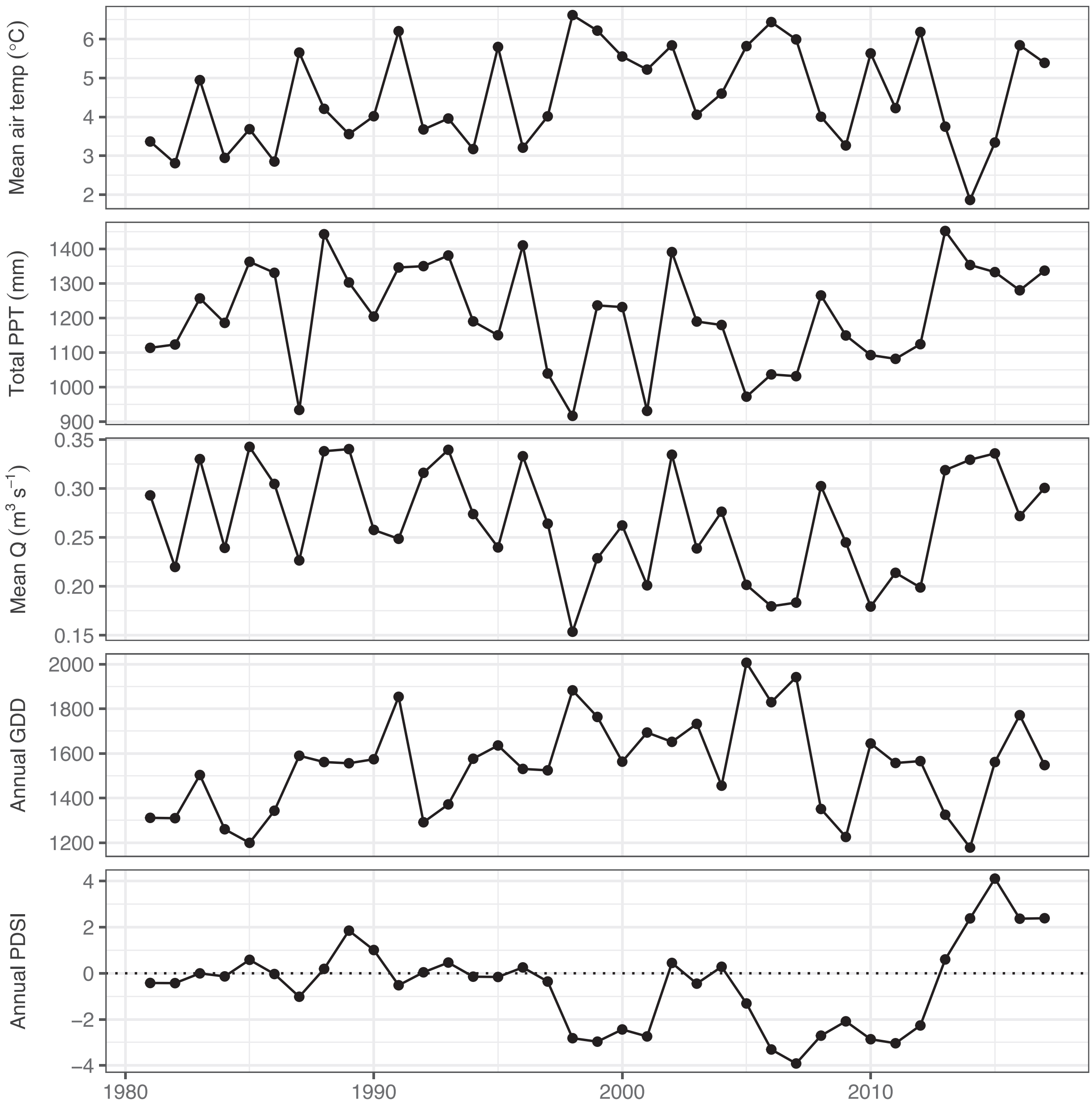

FIGURE 2 Mean water year (WY) air temperature (°C, first panel), total WY precipitation (mm, second panel), mean WY discharge from outflow of Turkey Lakes watershed ($m^3\ s^{-1}$, third panel), annual growing degree day (GDD, number of days, fourth panel) and WY PDSI (unitless, fifth panel)

represented by an exponential response (rapid earlier on and more gradual later, e.g., Cl^-) or polynomial (e.g., Na^+) (Figure 4a). For pH and conductivity, a step function increase in pH and decline in conductivity for most catchments occur during the mid-2000's (Figure 5a).

In addition to evidence for changes in some solutes over time, the stream solute concentrations differed among low, medium and high elevation sites. Lower elevation catchments typically have higher concentrations of base cations and SO_4^{2-}, higher pH, ANC, alkalinity, conductivity, DIC and SiO_2 values (Figures 4a, 5a and 6a). The rate of change (i.e., slope) of solutes over time also differed, with lower rates of change at low elevation in SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^+, pH and conductivity, but higher rates of change at low elevation in ANC and alkalinity. The presence of wetlands within catchments also influenced stream chemistry. The three catchments with wetlands (C38, C42 and C50), had higher and/or more variable K^+, DOC and SO_4^{2-} concentrations and lower and/or more variable ANC, conductivity, alkalinity and pH. This is most noticeable in C38, having the largest wetland area (25%) and more subtle in C42 and C50, with smaller wetland areas (7% and 8% respectively).

4 | DISCUSSION

4.1 | Is recovery from acidification complete?

Concentrations of acid anions in precipitation have continued to fall, with concentrations declining by 2.5 mg L^{-1} SO_4^{2-} and 0.25 mg L^{-1} NO_3^- over the 35-year record. These declines in concentration are similar in magnitude to that observed throughout eastern North

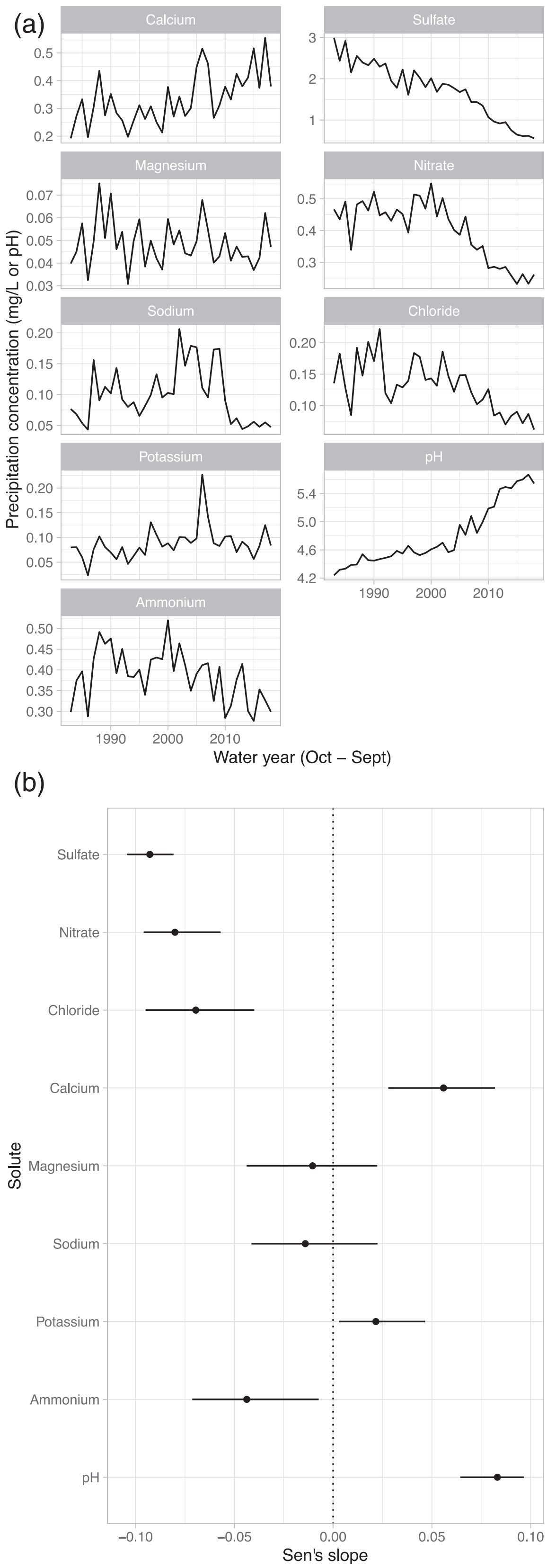

FIGURE 3 (a) Water year (WY) bulk precipitation chemistry at the Algoma CAPMoN site located at the Turkey Lakes watershed. (b) WY bulk precipitation solute concentration trends showing Sen's slope and 95% confidence interval. Significant trends occur when confidence interval does not overlap zero

America (IJC, 2017; Marty et al., 2021; Vet et al., 2014; Zhang et al., 2018). Changes in precipitation chemistry were not always mirrored in the stream chemistry. Stream SO_4^{2-} and ammonium have declined, however stream NO_3^- has decreased in two catchments, remain unchanged in others and increased in one catchment. In general, stream base cation concentrations have declined and begun to level off, despite some modest increases in precipitation, primarily driven by less leaching losses due to reductions in strong anions. Soil base cation concentrations at the site have showed no changes from the mid-1980's to the late 2000's due to high total and exchangeable base cation pools (Hazlett et al., 2011; Lawrence et al., 2015). The net result has been higher pH, ANC and alkalinity and lower conductivity.

It is clear that recovery from acidification has continued to progress since trends were last reported in Beall et al., 2001 and Jeffries et al., 2002. Most indicators (declining anions and cations, increased pH, alkalinity) point to recovery from acidic deposition (Oni et al., 2013; Watmough et al., 2005). There also appears to be a more recent acceleration of chemical recovery (most noticeable in pH and conductivity) in the mid-2000's, an observation also reported elsewhere in central Ontario by Watmough and Eimers (2020) and in other locations throughout eastern North America (Armfield et al., 2019; Augustin et al. (); Strock et al., 2014). Furthermore, conductivity appears to be still showing significant decreases in high and medium elevation sites. Only once weathering processes catch up with acidification, can the system be fully recovered (Galloway et al., 1983). Instead of recovery being "complete" we may need to assess if a new steady state condition has been achieved, which itself may be transient due to other global changes (de Wit et al., 2007; Kaste et al., 2020). Overall these observations match trends in recovery from acidification observed regionally and globally (e.g., Dillon et al., 2007; Gilliam, 2014; Gilliam et al., 2019; Mast, 2013; Stoddard et al., 1999; Strock et al., 2014).

By comparing catchments along elevation and surficial geology gradients, it is evident that recovery has been variable not only in time but also in space. The rate of recovery has been greater (slope of change) for the higher elevation catchments, whereas the lower elevation catchments had less impact of acidification due to the larger buffering capacity of deeper tills (Hazlett et al., 2011). For example, declines in SO_4^{2-} and Ca^{2+} and increases in pH and decline in conductivity have been more pronounced at the higher elevation sites. This is consistent with the idea that there is differential response to increasing or decreasing acid inputs depending on inherent site and soil conditions (Hazlett et al., 2020), even over short geographic distances.

4.2 | Influence of other processes and climate on stream recovery from acidification

Many factors also influence stream recovery from acidification, such as trends in organic acids, liberation of stored SO_4^{2-}, alterations in flowpaths and internal N cycling. Changes in climate also affect these

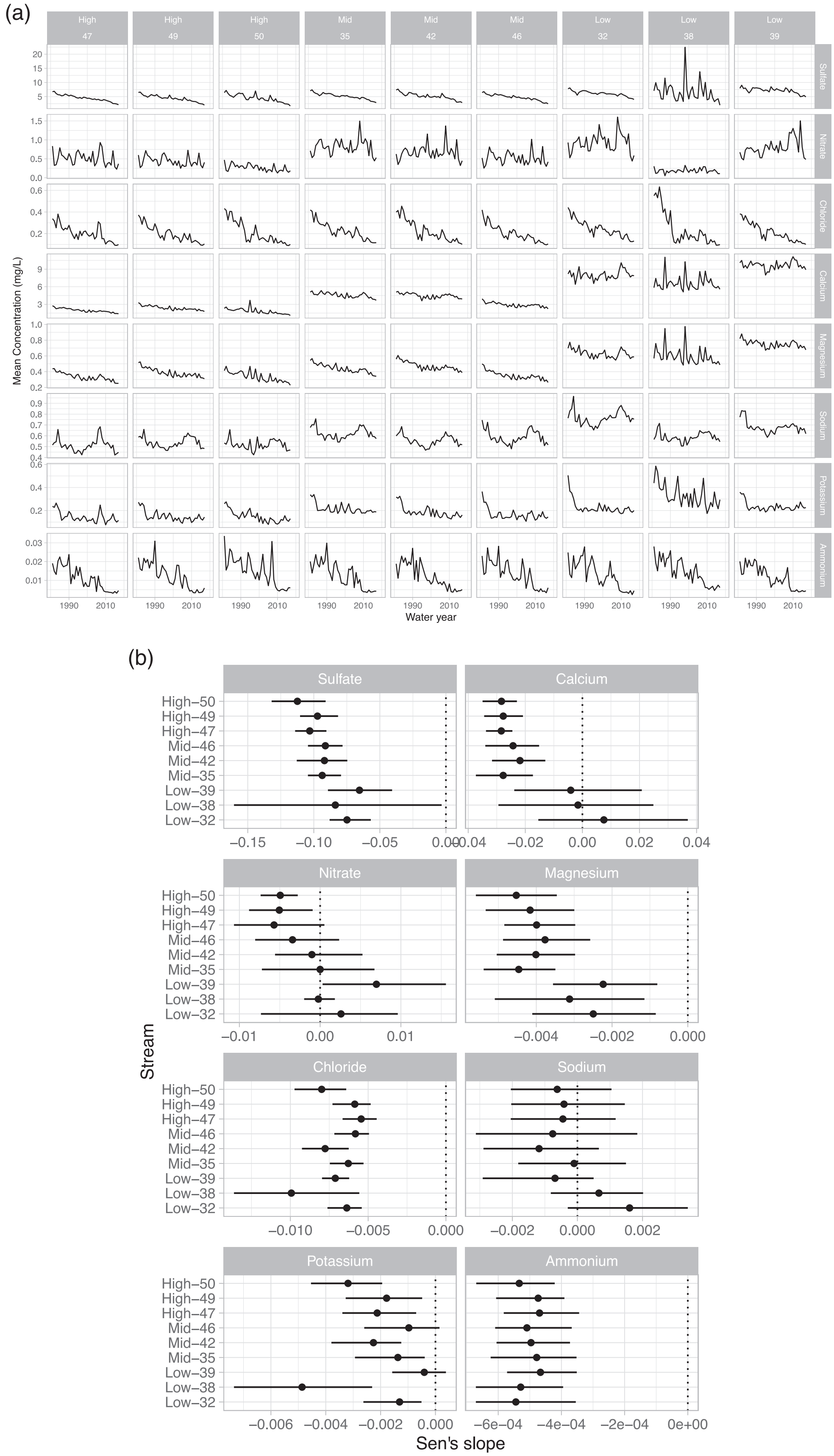

FIGURE 4 (a) Water year (WY) concentration of anions and cations in nine first order streams across low, medium and high elevation sites within the Turkey Lakes watershed. (b) WY stream anion and cation concentration trends showing Sen's slope and 95% confidence interval. Significant trends occur when confidence interval does not overlap zero

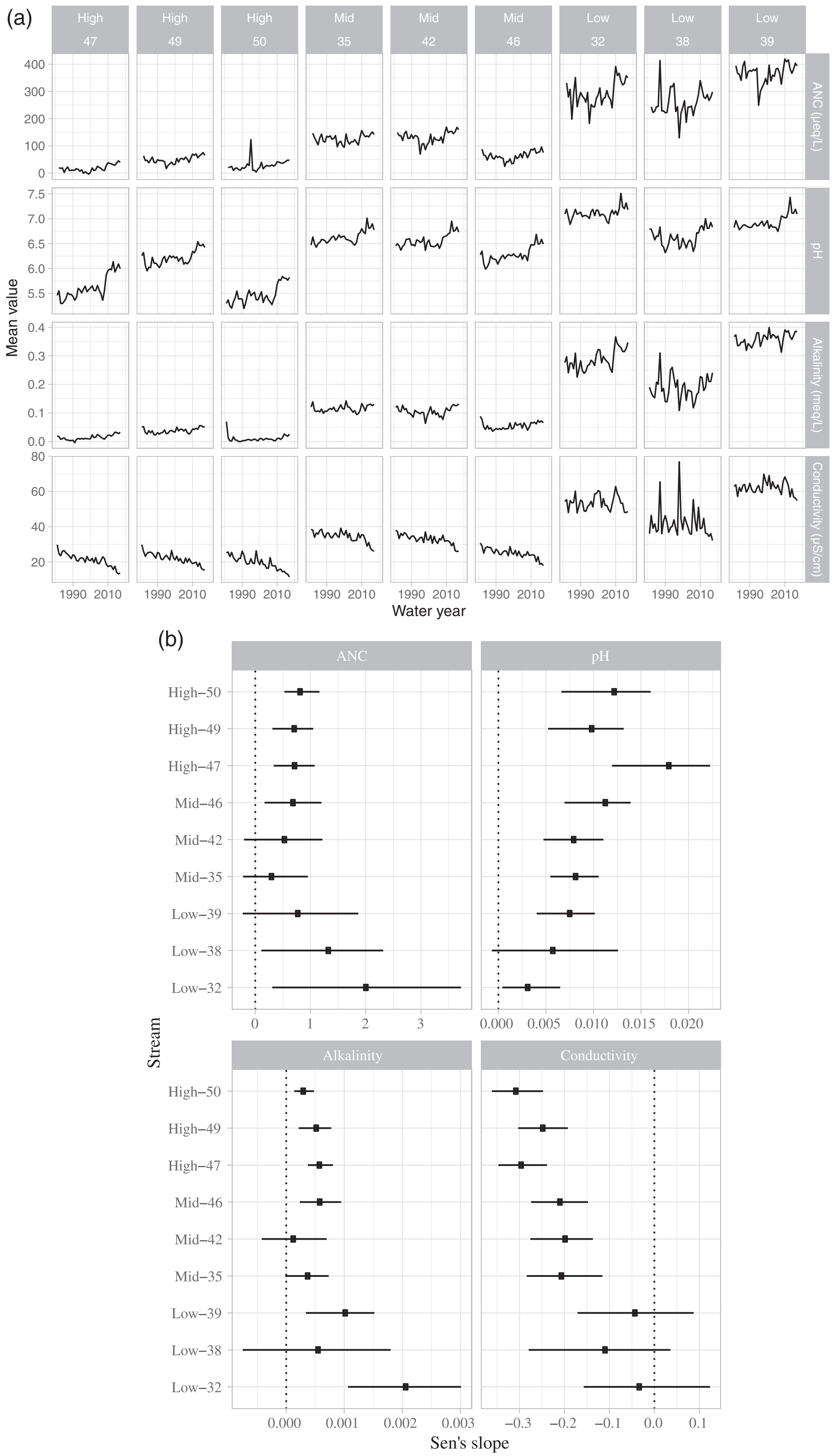

FIGURE 5 (a) Water year (WY) ANC, pH, alkalinity and conductivity in nine first order streams across low, medium and high elevation sites within the Turkey Lakes watershed. (b) WY ANC, pH, alkalinity and conductivity trends showing Sen's slope and 95% confidence interval. Significant trends occur when confidence interval does not overlap zero

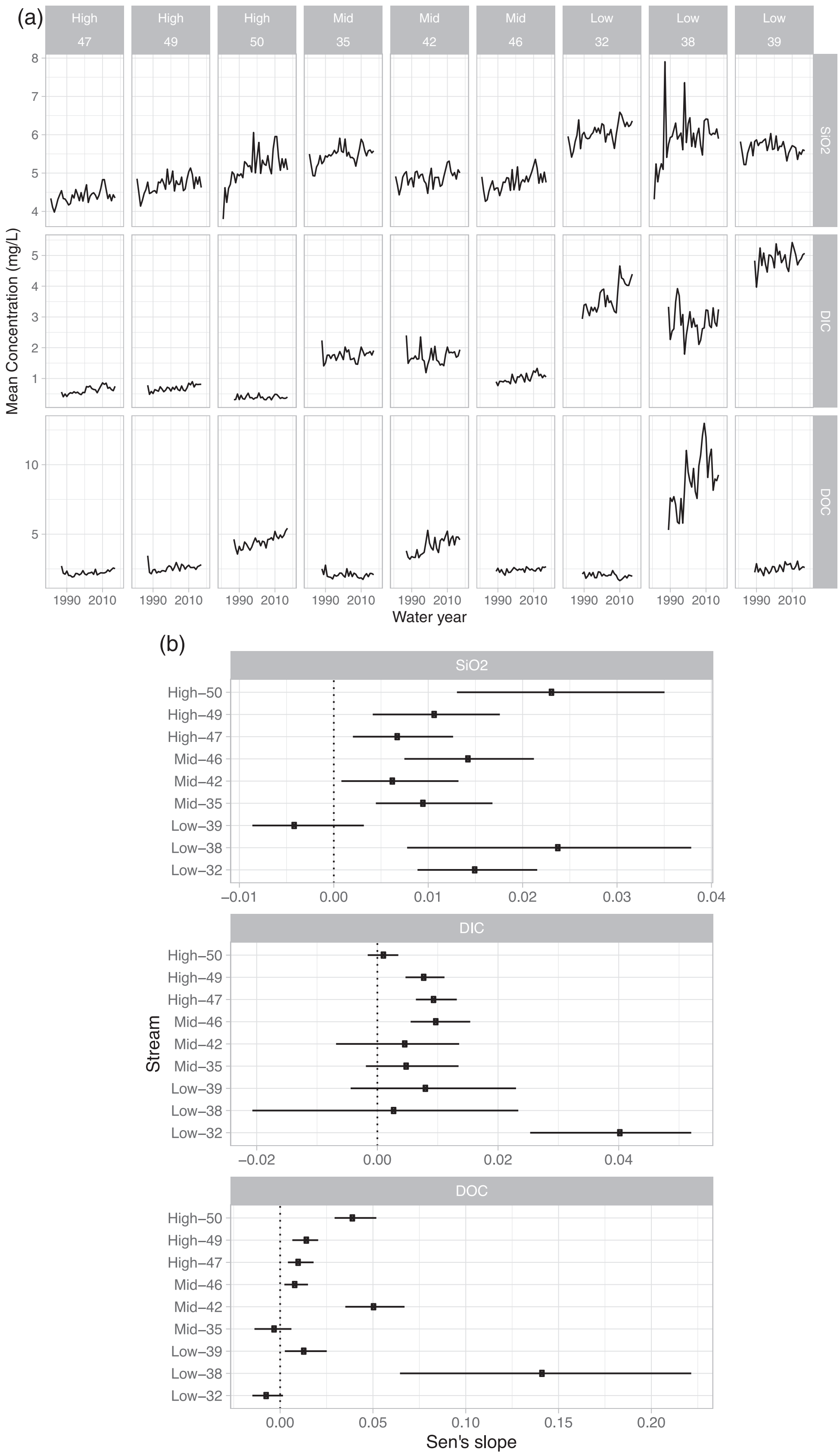

FIGURE 6 (a) Water year (WY) concentrations of SiO_2, DIC and DOC in nine first order streams across low, medium and high elevation sites within the Turkey Lakes watershed. (b) WY SiO_2, DIC and DOC trends showing Sen's slope and 95% confidence interval. Significant trends occur when confidence interval does not overlap zero

and other physical, chemical and biological processes that will influence stream chemistry. Disentangling these confounding influences on stream chemistry is challenging. Below, key processes are discussed as context for framing future research work at the TLW.

4.2.1 | Organic acids

Changes in organic acids found in DOC play a role in recovery from acidification, since natural organic acidity may delay or slow down recovery by replacing strong acid anions (Munson & Gherini, 1993). DOC increased significantly in seven of the nine catchments, with the largest increases observed in catchments with wetlands. The elevated DOC concentrations in catchments with higher wetland area likely buffered against the rise in alkalinity observed in other catchments, resulting in no change over the 35-year period.

DOC increases were also observed in catchments with little to no wetlands. Reductions in atmospheric deposition affect DOC mobility and reduces ionic strength in the soil, both which can increase DOC flux (Sawicka et al., 2016; Vance & David, 1989). However, it is difficult to separate soil pH/DOC solubility and ionic strength effects (Monteith et al., 2007) and both mechanisms could be contributing to the patterns within the TLW. More recent research has identified that recovery from acidification can also lead to the breakup of soil aggregates and the release of associated organic matter into soil solution (Cincotta et al., 2019).

Furthermore, DOC dynamics can also be influenced by changes in climate through impacts of soil temperature (particularly freezing) and soil moisture, which impacts soil carbon through processes such as root mortality and organic matter decomposition (Couture et al., 2012; Freeman et al., 2001; Lepistö et al., 2014; Oni et al., 2013; Schelker et al., 2013). Therefore, DOC patterns are complex to interpret due to multiple and interacting mechanisms involved and future work will be focused on investigating the relative importance of these mechanisms on DOC and its character within the TLW.

4.2.2 | Stored sulphate

Liberation of stored SO_4^{2-} within wetlands and riparian zones can delay acidification recovery (Aherne et al., 2008; Ledesma et al., 2016; Vuorenmaa et al., 2018). Both Beall et al. (2001) and Jeffries et al. (2002)'s observations at TLW and work of others elsewhere (e.g., Giesler, 2005; Wieder & Lang, 1988) have highlighted the important role of wetlands in delaying recovery from acidification. Wetlands can have episodic and large pulses of SO_4^{2-} in fall rains following droughty summers due to mobilization of oxidized S within the organic S pools (Eimers, Buttle, & Watmough, 2008). At TLW release of stored SO_4^{2-} is particularly pronounced for C38 (25% wetland area), but also can be seen to a smaller degree within mid elevation C42 (7% wetland) and high elevation C50 (8% wetland). In C38 these SO_4^{2-} pulses have not caused pH to decline at annual scales (although result in episodic reductions, data not shown), but may have contributed to variability and non-significant pH trend over time. As atmospheric deposition of SO_4^{2-} decreases, climate will play an increasingly important role in regulating S budgets and the amount of SO_4^{2-} mobilized form internal watershed sources (Mitchell et al., 2013). It is suggested that the magnitude of SO_4^{2-} peaks may decline if S storage declines (Walker & Johnstone, 2014). Thus although there is more severe redox-driven S acid pulses in the short term, they also more rapidly deplete the S pool resulting in faster recovery in the medium-term (Ledesma et al., 2016). Future work at TLW will investigate if the frequency and severity of S pulses is decreasing within the upland and wetland-dominated catchments.

4.2.3 | Flowpaths

Changes in hydrology and dominant hillslope flowpaths may alter stream chemistry in addition to those processes linked with acidification recovery (Armfield et al., 2019). Stream SiO_2 and DIC, which are often used as indicators of groundwater influence, showed increasing trends in eight and four catchments respectively. A recent study (Buttle et al., 2018) conducted at TLW showed that headwater streamflow decreased during the period of 1997–2007 compared to 1981–1996. Using geochemical tracers (SiO_2 and K^+), they suggest that there was a greater fraction of streamflow sourced from deeper groundwater during the 1997–2007 period due to drier surface conditions reducing inflows from shallow flowpaths. These changes in the magnitude and partitioning of flows can affect the cycling and dynamics of chemical constituents and their export (Marty et al., 2021). The relative decrease in stream water sourced from shallow flowpaths in the early to mid-2000's may have contributed to higher SiO_2 and DIC stream concentrations and may have also helped accelerate chemical recovery through delivery of water enriched with base cations (Hazlett et al., 2001). However, inferring changes in dominant flowpaths from trends in stream SiO_2 concentrations can be confounded by influences of wetlands and spatiotemporal heterogeneity in weathering kinetics (Leach et al., 2020; Scanlon et al., 2001). At TLW, previous work has highlighted that cycling of SiO_2 within wetlands may exert a greater influence on stream SiO_2 concentrations than mean catchment travel times, another proxy for dominant flowpath (Leach et al., 2020). Similarly, confounding factors influence DIC concentrations, which typically matched those of alkalinity. Increases in DIC concentration may reflect increases in soil respiration either deeper in the soil or during wetter periods of the year that could result in respired CO_2 being dissolved and degassing to the atmosphere within the streams or downstream in the lakes.

The analyses presented in this study focused on annual trends and may mask seasonal and event-scale dynamics, such as episodic acidification during spring freshet that have been observed in the northeastern United States (Burns et al., 2020; Fuss et al., 2015; Riscassi et al., 2019). Future work will try to better understand intra and inter- annual changes in flowpaths across the elevation gradient at TLW.

Changes in weathering rates may influence water chemistry and be difficult to differentiate from flowpath changes. It has been proposed that weathering rates will decrease as acid deposition decreases and soil pH increases (McHale et al., 2017), so recovery may not be as large as expected. Conversely, weathering rates are expected to increase with higher soil temperatures (Houle et al., 2010; Houle, Marty, et al., 2020). At this time there is insufficient evidence to assess if weathering rates have changed within the TLW catchments, however previous work has shown that soils at TLW have higher B horizon exchangeable Ca and base saturation (Hazlett et al., 2020) and higher total base cations (Hazlett et al., 2011).

4.2.4 | Nitrogen dynamics

Patterns in N are affected by control on internal cycling as well as acidic deposition. While stream NH_4^+ clearly shows declining trends, the pattern is less clear for NO_3^- is less clear. Stream NO_3^- trends were inconsistent, having both positive (at lower elevation) and negative (higher elevation) trends, an inconsistency also observed in other studies (Gilliam et al., 2019). One mechanism that has been proposed is that catchments with high wetland fraction are associated with low NO_3^- export (Kothawala et al., 2011), which is evident at the wetland-dominated catchments in TLW (C38, C42 and C50). Rain on snow events have also been shown to increase NO_3^- (Casson et al., 2014; Crossman et al., 2016) and it is possible that across the elevation gradient that rain on snow events may be more common at the low elevation sites. The positive trend at the nutrient rich (Hazlett et al., 2011) and higher phytomass (Morrison, 1990) lower to mid elevation catchments may reflect increasing N saturation in the ageing mature forest (Aber & Driscoll, 1997), or also increased leaching of NO_3^- due to increased mineralization and nitrification rates in the soils (de Wit et al., 2007) and sensitivity to seasonal changes in temperature (Foster, 1989). Declines at high elevation may reflect more the "flow through" effect of shallow soils over till and thus decline in acidic deposition and/or retention of NO_3^-. Further work is required to tease apart these possible mechanisms controlling N dynamics and their effect on acidification recovery.

4.3 | Other influences of a changing climate

From the perspective of the terrestrial environment, reductions in acidic pollutants will result in less leaching of essential nutrients, but climate and other factors may now exert more influence. Climate impacts on forests may also affect recovery from acidification (Gislason et al., 2009). For example, more favourable growing conditions in a CO_2 enriched world could increase vegetation demand for cations, further reducing their leaching. Alternatively, drought induced stress and mortality of trees may increase availability of cations (as well as C and N) in the soil, as may other disturbances such as insects, wind and ice storms. All of these mechanisms will influence the input of litter or woody material into dead organic matter pools (de Wit et al., 2007). As recovery (decline) in cation concentrations continue as a result of declining acidic deposition, the importance of these mechanisms may increase. Spatial variation in meteorological conditions, microclimate, vegetation productivity and soil N cycling processes (e.g., immobilization, mineralization and denitrification) will be key to asses in future studies to better understand the mechanisms controlling these observed stream patterns at the TLW.

Assessing impacts of acidification recovery in a changing climate is critical for understanding consequences to downstream aquatic communities and users. Aquatic organisms living in these streams will have conditions better reflecting pre-acidification, thus higher pH and alkalinity and lower chance of metal toxicity, but also return to lower concentrations of nutrients. However, lower flows and more frequent "no flow" days and higher stream temperatures as a result of a changing climate that were not considered as part of this analysis could have more dramatic consequences for aquatic biota beyond the chemical environment itself.

5 | CONCLUSIONS

It is clear, as has been observed elsewhere, that acidification recovery is continuing at the TLW, but it has not been linear in either time or space. There is insufficient evidence to suggest that recovery within the TLW is complete, although perhaps a new equilibrium state in conditions has been reached. A marked acceleration in recovery has been observed since 2005 and multiple mechanisms including changes in deposition, climatic influences and biogeochemical and hydrological process have likely contributed to this response. Despite large and effective efforts across Europe and North America to reduce surface water acidification, air pollution still constitutes a threat to freshwater ecosystems (Austnes et al., 2018). It is evident that many confounding mechanisms are at work in the nine catchments at the TLW examined in this study and that this investigation of patterns has produced far more questions and avenues of research than answers. Further work is required to tease apart the relative importance of various processes on stream water chemistry and how they continue to change through space and time. The TLW, being a long-term, integrated, whole ecosystem study (Webster et al., 2021) provides a unique opportunity to study how small-scale processes integrate to produce hydrochemical responses along the upland - wetland - aquatic continuum.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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