



# Chemical Effects of Snowmelt on an Alpine Lake in the Wind River Range, WY

T. R. Ganz · J. McMurray · K. Covey ·  
C. Bettigole · G. Benoit

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**Abstract** Nitrogen deposition from air pollution is increasingly reaching alpine lakes where the addition of nitrate and ammonium to sensitive surface waters can cause acidification and/or eutrophication. Thirty years of sampling in the Wind River Range, WY, has shown some lakes increasing in nitrogen. We sought to (1) determine if nutrient concentrations in Deep Lake increase during snowmelt when atmospheric deposition is released from the snowpack and (2) assess if the sampling season, location, meteorological factors, and time of day samples are collected influence lake chemistry metrics, to inform monitoring. We analyzed water samples from the outlet of

Deep Lake in peak snowmelt (June) and from the inlet, outlet, and middle of Deep Lake when the basin was snow free (August). In June, outlet samples were more acidic, and nitrogen content was three times August levels. Acid neutralizing capacity (ANC) declined with snowmelt. August inlet samples were higher in nutrients than outlet and mid-lake samples. Our results indicate that atmospheric pollution in the snowpack enters the lake with snowmelt. Although Deep Lake has not acidified, ANC levels indicate a risk of episodic acidification if nitrogen deposition continues to increase. When monitoring lakes at risk for episodic acidification, sampling during the late snowmelt pulse should be prioritized. Simplified sampling protocols may be used in some lakes, as epilimnion and outlet samples were nearly identical. The time of day and cloud cover did not affect lake chemistry, while wind speed and precipitation weakly increased August ANC and June pH, respectively.

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T. R. Ganz (✉)  
School of Environmental and Forest Sciences, University of Washington, Box 352100, Seattle, WA 98195-2100, USA  
e-mail: [trganz@uw.edu](mailto:trganz@uw.edu)

T. R. Ganz · G. Benoit  
Yale School of the Environment, Yale University, New Haven, CT, USA

J. McMurray  
Bridger Teton National Forest, United States Forest Service, Jackson, WY, USA

K. Covey · C. Bettigole  
Skidmore College, Saratoga Springs, NY, USA

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## 1 Introduction

Over the past 150 years, global human production of reactive nitrogen has increased from 15 to 210 Tg N/year, compared to 120 Tg N/year historically produced by natural processes alone (Bobbink et al., 2010; Galloway et al., 2003, 2008). Globally,

anthropogenic nitrogen primarily comes from the production of fertilizers via the Haber–Bosch process, followed secondarily by the cultivation of nitrogen-fixing plants, and fossil fuel combustion, although additional sources contribute and vary regionally in importance (Galloway et al., 2003). Atmospheric nitrogen pollution is reaching remote high-elevation areas of the western USA and depositing on aquatic and terrestrial ecosystems through dry and wet deposition. Atmospheric nitrogen deposition is now the primary source of nitrogen to some systems (Bobbink et al., 2010; Galloway et al., 2003, 2008; Vitousek et al., 1997). In aquatic systems, increased nitrogen deposition alters biogeochemical cycling and may cause eutrophication, episodic acidification, decreased lake pH, and altered community composition of diatoms (Baron et al., 2000; Elser et al., 2009; Fenn et al., 2003).

Lakes in high-elevation alpine environments of the Rocky Mountains commonly have dilute water chemistry and low levels ( $< 100 \mu\text{eq/L}$ ) of acid neutralizing capacity (ANC) as a result of their limited vegetation, steep terrain, and exposed bedrock basins with thin soils, and thus are susceptible to impacts from increasing inputs of acidic solutes (Bergström & Jansson, 2006; Musselman & Slauson, 2004; Nanus et al., 2012; Williams et al., 2017). High-elevation environments often receive greater loads of atmospheric deposition due to higher amounts of annual precipitation than low elevation sites, although deposition rates can vary substantially depending on local topographic and meteorological patterns and the amount of other types of deposition such as dry, fog, or cloud (Hoffman et al., 2019; Nanus et al., 2017; Weathers et al., 2006). While the vast majority of lakes globally are phosphorus limited (Schindler, 1977), high-elevation lakes in the western USA are historically nitrogen limited, or co-limited by nitrogen and phosphorus (Lewis & Wurtsbaugh, 2008; Morris & Lewis, 1988; Saros et al., 2011; Smith et al., 2003; Williams et al., 2017).

Increasing nitrogen deposition across the Rocky Mountains has led to increased lake productivity, shifting lakes toward eutrophication. Nitrogen deposition can also contribute to chronic or episodic acidification through decreasing ANC, especially in sensitive lakes (Baron et al., 2011; Reuss & Johnson, 2012). Such inputs have the potential to impact populations of fishes and amphibians, as has been

documented in other geographic regions (Burns, 2004; Camargo & Alonso, 2006). Fenn et al. (2003) define nitrogen saturation as the long-term shift from nitrogen limitation of ecological processes, coinciding with decreased nitrogen retention capacity in the system. When nitrogen deposition is in excess, diatom communities in aquatic systems are the first to respond. Nitrogen deposition has also been linked to negative impacts in lichen, bryophytes, mycorrhizal fungi, and then plants, shrubs, and trees (Baron et al., 2000; Burns, 2004; Camargo & Alonso, 2006; Geiser et al., 2019; Horn et al., 2018; Wolfe et al., 2001). Atmospheric deposition of nitrogen across the Greater Yellowstone Ecosystem, USA, is currently estimated to range from  $< 1.4$  to  $7.5 \text{ kg N/ha/year}$ , and current research estimates that 30% of Greater Yellowstone lakes may be impacted by excess atmospheric nitrogen deposition (Burns, 2003; Nanus et al., 2017). Critical loads are a quantitative estimate of exposure to one or more pollutants (typically  $\text{kg/ha/year}$  for N) below which no harmful effect to a specified resource is expected to occur according to present knowledge (Nilsson & Grennfelt, 1988). Saros et al. (2011) estimated that exceeding a critical load of  $1.4 \text{ kg N/ha/year}$  of wet deposition would drive a change in diatom communities in alpine areas of the Greater Yellowstone Ecosystem, and exceeding a total deposition load (wet + dry) of  $4.0 \text{ kg N/ha/year}$  risks episodic acidification and nutrient enrichment (Baron et al., 2011; Hundey et al., 2016; Saros et al., 2005; Williams & Tonnesen, 2000).

A variety of research programs monitor alpine lakes, although samples tend to be collected periodically but infrequently (i.e., on a seasonal basis), or synoptically across a geographic range. To our knowledge, there have been no studies investigating the fine-scale temporal variation (i.e., daily—hourly) in lake chemistry which is necessary to contextualize broader trends and inform sampling strategies. Additionally, the influences of local and immediate weather factors such as cloud cover, precipitation, and wind on surface water chemistry measures remain largely unexplored at fine time scales. The snowmelt period is particularly important to understanding the variation in lake chemistry and the sensitivity to these changes because Rocky Mountain snowpacks may store atmospheric deposition for up to 9 months of the year. Seasonally, alpine lakes are expected to peak in nutrient and chemical content during snowmelt

as the snowpack releases accumulated dry and wet atmospheric deposition, which has been observed at coarser temporal scales (weekly—seasonally) across the Rocky Mountains from Loch Vale, CO, to the Snowy Range, WY, and the Uinta Mountains, UT (Brooks et al., 1999; Burns, 2004; Campbell et al., 1995; Denning et al., 1991; Hundey et al., 2016; Ingersoll et al., 2016; Mast et al., 2014; Reuss et al., 1995). Conversely, total nitrogen concentration was found to be highest in the summer at the Green Lake 4 catchment, a high-elevation (3515 m) Long-term Ecological Research site along the continental divide of the Rocky Mountains, 30 km west of the city of Boulder, CO (Mladenov et al., 2012). Samples from this site are collected weekly and thus may not capture the highest nitrogen concentration of the snowmelt pulse (Liu et al., 2004; Mladenov et al., 2012).

Local weather, such as cloud cover, precipitation, and wind, has the potential to alter lake chemistry at a fine scale, both directly through the transport of pollutants and indirectly by influencing snowmelt flux and in-lake processes. Atmospheric pollutants can be transported by clouds and deposited on the lake surface (Weathers et al., 2000, 2006) while increased cloud cover can cool temperatures, delaying snowmelt and reducing the transport of pollutants to the lake. Wet deposition (i.e., precipitation) delivers inorganic nitrogen and in some Rocky Mountain lakes is the main source of chloride, sulfate, nitrate, and ammonium (Baron & Campbell, 1997; Baron et al., 1995; Benedict et al., 2013a; Campbell et al., 2000; Clow & Drever, 1996; Heath & Baron, 2014). Because precipitation-born pollutants deposit directly to the lake surface, recent rain could influence epilimnion samples. Shifts in wind direction can alter the regional sources of pollutants and deposition rates, as has been documented in Rocky Mountain National Park (Benedict et al., 2013b), or drive lake surface mixing. Because these factors remain largely unstudied, it remains unknown if they should be accounted for in lake sampling protocols.

There is a current lack of understanding of (1) the fine-scale temporal variability in lake chemistry over hours and days and with meteorological variation that is necessary to contextualize long-term trends and (2) the extent of lake inputs during peak snowmelt when atmospheric deposition is released to sensitive high-elevation ecosystems while they are most sensitive,

which we address here (Baron et al., 2011; Williams & Tonnessen, 2000). Alpine lakes within federally designated Wilderness and other remote areas are particularly difficult to access during the peak of spring snowmelt, and thus, our study offers important and novel insights for such systems, and context for optimizing lake monitoring protocols.

On the western flank of the Wind River Range of the Bridger-Teton National Forest is the Bridger Wilderness, a federally designated Class I Wilderness Area, which land managers are legally required to protect from degradation of air quality related values (AQRV) (Clean Air Act, 1970). Zhang et al. (2018) recently estimated that modeled atmospheric deposition contributed between 2.32 and 3.56 kg N/ha/year of total nitrogen at Black Joe Lake in the southern Wind River Range. Black Joe Lake is located < 2 km northeast of our study site at Deep Lake. Total nitrogen deposition on the Bridger-Teton National Forest has been modeled between 2.20 and 4.79 kg N/ha/year (Leora Nanus, personal communication). This rate could be exceeding the estimated critical load for nitrogen-driven changes in diatom community structure by up to 0.8 N/ha/year, suggesting that atmospheric deposition may be driving changes in the nitrogen concentration and the diatom community of some Wind River Lakes (Baron et al., 2011; Saros et al., 2011; Zhang et al., 2018). Although some of the alpine lakes in the Wind River Range have been monitored annually since 1984, there is limited understanding of the spatial and temporal chemical changes these lakes undergo at peak snowmelt, when access and sampling are particularly difficult but the lakes are most vulnerable to nitrogen inputs (Fenn et al., 2003).

In this study, we investigate the spatial and temporal dynamics of water chemistry at Deep Lake, Wind River Range, WY, during snowmelt, collecting temporally fine-scale samples for 2 weeks in June (peak snowmelt) and a week in August when the basin was snow free. Our goals were first to determine the variability in water chemistry between seasons, sampling locations, day-to-day, time of day, and meteorological changes to inform future lake monitoring programs. Second, we sought to identify the extent of the pulse of nutrients into the lake as snowmelt released stored atmospheric deposition and determine if the lake may be at risk of episodic nitrification or acidification.

From these investigations, we make recommendations as to how managers can better monitor alpine lakes to capture vulnerable periods. We expected that the period of peak snowpack melt would release a pulse of accumulated atmospheric pollutants, including total nitrogen, particularly nitrate, which we expected to depress pH even as we expected ANC to simultaneously rise when dust was released from the snowpack (Brahney et al., 2015a, 2015b; Rhoades et al., 2010). We expected an imbalance in the chemical budget of the lake and predicted that the lake inlet would be higher in concentrations of nitrogen and cations, yielding an increase in ANC despite a paradoxical decrease in pH. We predicted that cloud cover, precipitation, and wind could alter lake chemistry samples. Finally, we expected the diurnal hydrograph to show an increase in cations late in the day when snowmelt flow is highest. Understanding the variability in lake chemistry between season, sampling locations, considered weather patterns, and time of day is critical to explain long-term chemical changes in alpine lakes and in planning future lake monitoring.

## 2 Methods

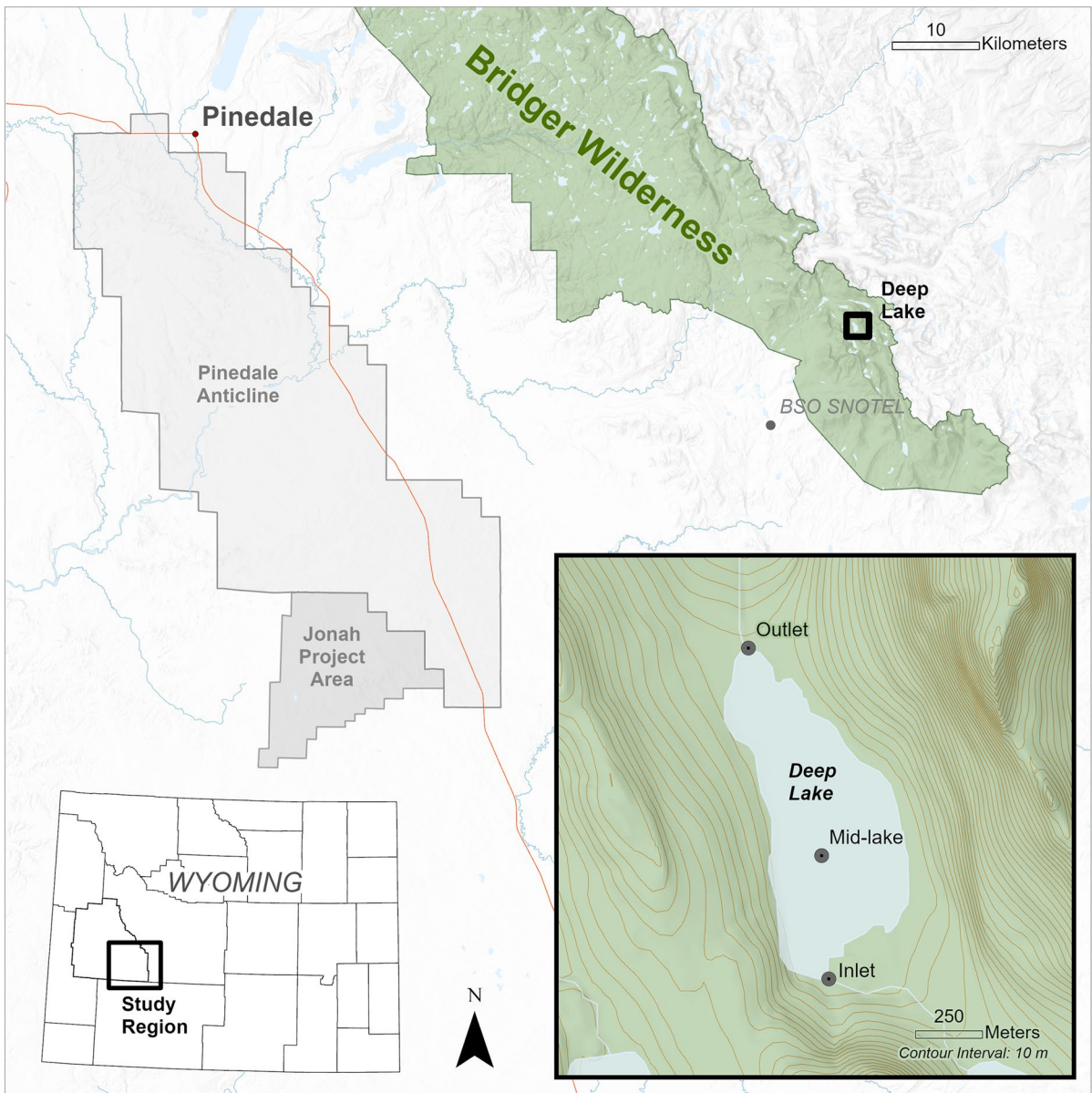
### 2.1 Site Description

The Wind River Range extends roughly 250 km, forming the continental divide through west-central Wyoming as part of the Rocky Mountains and the southeastern arm of the Greater Yellowstone Ecosystem (GYE). Rugged, glacially sculpted terrain, a high density of alpine lakes (over 1500 lakes across 173,374 ha; Grenon et al., 2010; McMurray et al., 2013), cold temperatures, thin or absent soils, and a short growing season (less than 40 consecutive nights above freezing per year) characterize the Wind River Range (<https://wrcc.dri.edu/narratives/WYOMING.htm>). Archean granitic rock, granitic gneiss, and migmatites are predominant across the range (Frost et al., 1998). Precipitation comes primarily in the form of snow and averages 100–130 cm total annual water equivalent at the lower-to-mid elevations and reaches up to 150 cm or more along the continental divide (Hall et al., 2012). An estimated two-thirds of the annual precipitation runs off as stream flow, with the rest attributed to evapotranspiration (Foster & Hall, 1981; Hall et al., 2012). While the exact proportion

of annual water derived from snow in the Wind River Range is undocumented, snowfall, snow cover, and the timing of snowmelt have been identified as the primary drivers of stream discharge for the region, emphasizing the dominance of snow in these hydrologic systems (Hall et al., 2012, 2015). Snowmelt from the western slopes of the Wind River Range drains to the Green River, providing water to the largest tributary of the Colorado River.

Two oil and gas extraction sites, the Pinedale Anticline and Jonah Project Area (Fig. 1), are located 40 km west and upwind of the southwestern Wind River Range in nearby Boulder, WY, and have been identified as a source of reactive nitrogen to the southern Wind River Range, contributing the highest volume of nitrogen pollution in winter months (Zhang et al., 2018). The Jim Bridger coal plant 110 km to the south may provide an additional local source of reactive nitrogen to the mountain range. These extraction sites are sources of nitrogen in the form of nitrate, but they may also be a source of ammonia to the Wind River Range (Brahney et al., 2015a, 2015b; McMurray et al., 2013). Additional sources of nitrogen to the GYE also come from regional and long-distance transport from agriculture, fire, and other sources (Zhang et al., 2018).

Deep Lake (elevation 3218 m; 42.719084°N, 109.172130°W; Fig. 1) basin has a 190-ha watershed that lies in the southwestern Wind River Range within the Bridger Wilderness and is estimated to be 90% barren, 7% grass, and 3% forest (Brahney, 2012). Parent material in the basin is predominantly granitic, which breaks down slowly and thus has limited contribution of base cations to the total ANC (Brahney, 2012; Mast et al., 1990, 2001; Turk & Spahr, 1991). Like many high alpine lakes in the Wind River Range, the inlet and lake surface remain frozen through June, and water enters the lake diffusely from all sides as snow melts. In August, water primarily enters the lake through one main inlet, though groundwater contribution is possible but unknown (Fig. 1). Deep Lake is 24.5 ha in area and 27.0 m deep (Grenon et al., 2010). Deep Lake is not fed by any glaciers or permanent snowfields, and all inputs thus reflect annual snowmelt, current precipitation, or possibly ground water which we were unable to examine. Given the watershed area and rates of evapotranspiration, and assuming 110 cm total annual water equivalence,



**Fig. 1** Sampling sites at Deep Lake, and the greater context of the region, illustrating the location of the Big Sandy Observation (BSO) SNOTEL site and the proximity of the Bridger Wilderness to the Pinedale Anticline and Jonah Project Area

mean annual runoff is estimated to be  $1.4 \times 10^6 \text{ m}^3$  (Foster & Hall, 1981; Hall et al., 2012).

Outflow from the lake can reflect the chemistry of the epilimnion when the lake is stratified, or a mix of layers following lake turnover (Hutchinson, 1975). Thus, water chemistry at the outlet can be a function of input occurring over multiple years. Assuming the average depth is half the maximum depth of the

lake, lake volume is calculated to be  $3.3 \times 10^6 \text{ m}^3$  and mean residence time in Deep Lake is estimated to be 2.3 years, by Eq. (1) (Hutchinson, 1975; Winchester, 1968).

$$\begin{aligned} &\text{Water residence time (yrs)} \\ &= \text{Lake Volume (m}^3\text{)}/\text{Mean Annual Runoff (m}^3\text{/year)} \end{aligned} \tag{1}$$

Detailed bathymetry of the lake is not available to form a more accurate estimate. We selected a value of one-half because of the steepness of the surrounding terrain (Fig. 1). Our approximation is probably an upper limit to the volume of the lake, and consequently, the water residence time. It is important to note that traditional thinking about water residence time can be somewhat misleading for a water body like Deep Lake. In this system, almost all of the flow occurs during the short period of snowmelt. If this discharge continued throughout the year, water residence time would be much shorter. Instead, for most of the year, discharge is close to zero and the water in the lake through the colder months has a much longer effective residence time. Though it was not observed in the course of our study, in many years, the outlet of Deep Lake dries up from late summer through autumn. Taken together, this means that all of the lake water that we measured (outlet and mid-lake) had an effective water residence time that was much shorter than the average residence time of all water in the lake. It is possible to estimate the magnitude of these effects. When the lake is stratified, we measured the epilimnion to be 9 m thick, and water residence time for this layer alone is 1.4 years. Furthermore, if most of the flow through the lake occurs in 3 of the 12 months, then this number reduces to an effective water residence time during the time we sampled of about 4 months.

Snow depth, snow-water equivalent, and precipitation data referenced in this analysis were from the National Resources Conservation Service Big Sandy Opening snow-telemetry (SNOTEL) site (elevation 2770 m; 42.64580°N, 109.25965°W) located 10.6 km southwest of Deep Lake (National Water & Climate Center, 2016). Annual precipitation at this site was reported to be 107% of average by the June sampling period and 97% of average by the August sampling period (National Water & Climate Center, 2016).

## 2.2 Study Design

Sampling of Deep Lake occurred during two time intervals in the summer of 2016: (1) peak snowmelt (June 1–18) and (2) peak primary production (August 7–13). In June, we collected grab samples of water at the outlet twice per day, in the morning (7:00–9:00) and evening (17:00–19:00) for 19 days along with one cycle of samples collected at the outlet every hour for

24 h (8:00 June 9, 2016, to 8:00 June 10, 2016). We were unable to collect water samples from the mid-lake surface and lake inlet in June because those sites were frozen. In August, water samples were collected at the outlet, mid-lake, and inlet twice per day for 7 days, in the morning (7:00–10:00) and in the evening (17:00–19:00) as weather conditions allowed. A 24-h sampling cycle was not conducted in August.

All samples were collected from the epilimnion at 10-cm depth and filtered with 0.45- $\mu$ m nominal pore size Polyethersulfone Sterile Syringe Filters (N.A. PN 28,145–505) VWR® attached to BD 60-ml Luer-Lok™ syringes (REF 309,653) VWR®. We collected 100 ml of filtered water via two syringe pulls and stored the water in 125-ml polyethylene bottles, allowing 25 ml of headspace in the bottle to prevent rupture when they were frozen for long-term storage. Neither acid nor other preservatives were added to the bottles. Bottles and syringes were rinsed with lake water (collected about 3 m downstream of the sampling location), and syringes were not reused after sample collection. Samples were kept at approximately 1–3 °C while in the field by submersing them in meltwater downstream of the sampling site. The bottles were immediately frozen following transport from the field until they were thawed for analysis. Water temperature and pH were measured at each sample collection using an Oakton® pH 150 Waterproof Portable pH/mV/Temperature Meter (EW-35614–90).

For every sampling event, we observed meteorologic conditions, recorded wind speed, and proportion of cloud cover following the Bridger-Teton National Forest Wind River Mountains Air Quality Monitoring Program Methods Manual (U.S. Department of Agriculture, Forest Service, 2002). We also qualitatively recorded any precipitation since the last sampling period noting no precipitation as 0, precipitation since the last sampling event as 1, and precipitation during the sampling event as 2.

A Solinst® Levelogger® Jr. Edge M5 (110,241) was submerged 0.4 km downstream of the lake outlet and recorded pressure every 5 min for the duration of the sampling periods. An adjacent, terrestrial Solinst® Levelogger® Edge M5 (110,023) simultaneously recorded changes in atmospheric pressure. Using the difference between the two devices, we calculated downstream water depth at 5-min intervals, corrected for variation in barometric pressure.

In August, we recorded temperature and pH every meter to 19-m (the maximum reach of our measuring equipment) at mid-lake to evaluate depth profiles and identify a thermocline with a YSI® 556 Hand-held Multi Parameter Instrument (556–01). The thermocline is a boundary between the epilimnion and hypolimnion, which limits mixing between the layers and allows flow to occur within the epilimnion (Lerman et al., 1995). An inflection point in the temperature gradient is used to identify the epilimnion, and a lake is considered strongly stratified when there is a temperature gradient of  $>4$  °C between the surface and 60% of its depth (16.0 m for Deep Lake) (Landers et al., 1987; Lerman et al., 1995).

### 2.3 Chemical Analysis

We used an ICP-OES Optima 3000 (Perkin Elmer, Waltham, MA) to measure concentrations of strong base cations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ ), an Ion Chromatograph (IC) DX500 (Dionex, Sunnyvale, CA), to measure strong acid anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{Cl}^-$ ), and an Astoria 2 Flow Analyzer (Astoria Pacific, Clackamas, OR) to measure ammonium, total nitrogen, and total phosphorus. ANC was determined by gran titration. Duplicates were collected in the field for one-tenth of all samples, and 10% of collected water samples were split and run as lab replicates for QA/QC purposes. Blanks of deionized water were stored in sample collection bottles, frozen with field samples for storage, and also analyzed for QA/QC, but not transported into the field. Strong base cation concentrations were calculated as the sum of the normal (eq/L) concentrations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ . The strong acid anion concentrations were taken to be the sum of the normal (eq/L) concentrations of  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ .

The ratio of nitrogen to phosphorus was calculated from the molarity of each sample as an indicator of nutrient limitation in the lake. In an analysis of 2053 lakes and nearly 90 nitrogen and phosphorus lake enrichment experiments from Norway, Sweden, and the Rocky Mountains, USA, Elser et al. (2009) found that lakes in low-nitrogen deposition areas had molar total nitrogen to total phosphorus ratios below 44.2 and were generally nitrogen limited, whereas lakes above total nitrogen to total phosphorus ratio of 110 were consistently in high deposition areas and limited by phosphorus. Similarly, a synthesis of 221 lakes

from 14 countries found that nitrogen limitation was consistent when the total nitrogen to total phosphorus ratio was below  $\sim 31$  and total phosphorus was above 0.003 mg P/L (Downing & McCauley, 1992). Dissolved inorganic nitrogen to total phosphorus ratios have been suggested as a better indicator of nutrient limits on phytoplankton growth, and by this metric, nitrogen limitation transitions to phosphorus limitation when molar dissolved inorganic nitrogen to total phosphorus ratios shift from 3.3 to 7.5, with higher ratios typical of alpine lakes with moderate levels of nitrogen deposition (Bergström, 2010).

We focused our analysis on testing for changes in concentrations of total nitrogen, total phosphorus, titrated ANC, and the sums of the strong base cations and strong acid anions. To assess differences in these lake chemistry metrics, we ran ANOVAs testing the effect of sampling season (outlet samples only), sampling location (August only), and time of day the sample was collected. We used simple linear regression to determine if ion concentrations became more dilute during June sampling interval at the lake outlet over time. In lake monitoring programs, researchers often wonder if meteorological factors influence the chemistry of epilimnion samples, and thus should be accounted for in sampling protocols. We used general linear regression to test the influence of cloud cover, precipitation, and wind speed on major lake chemistry parameters in both June and August. We took  $p < 0.05$  as our threshold for significance for all analyses.

Reported uncertainties for summary values by location, season, and time of day are given as the standard deviation. Uncertainties for measurements of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ , total nitrogen, total phosphorus, and titrated ANC were taken as the square root of the mean of the squares of the difference in replicates for each measure. Uncertainty values for the sum of the strong base cations and strong acid anions were taken to be the square root of the sum of the squared uncertainties of their components.

### 3 Results

In total, we collected and analyzed 88 individual samples, of which 51 were collected in June at the lake outlet and 37 were collected in August from the

outlet, inlet, and mid-lake. Of the 51 June samples, 25 were collected at the outlet during the diel cycle of sampling (8:00 June 9, 2016, to 8:00 June 10, 2016). Severe thunderstorms prevented us from collecting evening samples on 3 occasions in June. We included 8 samples from the diel sampling period which fell into the morning and evening sampling time ranges in our analyses comparing water chemistry by time of day ( $n=34$ ). August sampling included 13 inlet samples, 11 mid-lake samples, and 13 outlet samples. Strong winds and impending lightning storms twice prohibited mid-lake sample collection in August.

Deep Lake samples were characterized by dilute concentrations of nutrients, circumneutral pH levels, and low levels of ANC (Table 1). Across the entire study, total nitrogen ranged from  $<0.05$  to  $0.26$  mg N/L, while total phosphorus ranged from  $<0.001$  to  $0.016$  mg P/L. Of the 88 total samples, 9 were below the detection limit for total nitrogen ( $0.05$  mg N/L), and 13 were below the detection

limit for total phosphorus ( $0.001$  mg P/L). robust ROS correction for left-censored data of total nitrogen and total phosphorus did not affect summary statistics within the range of standard error, and thus, we used uncorrected values (Bolks et al., 2014). From June to August, pH ranged from 6.4 to 7.6 with a median of 6.7. Titrated ANC was measured to range from 35 to  $153 \mu\text{eq/L}$  with a mean of  $73 \pm 22 \mu\text{eq/L}$ . The sum of the strong base cations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ ) ranged from 57 to  $169 \mu\text{eq/L}$  with a mean of  $112 \pm 23 \mu\text{eq/L}$ . Calcium was the largest contributor to the cations and varied the most, ranging from a minimum of  $48 \mu\text{eq/L}$  to a maximum of  $134 \mu\text{eq/L}$  with a mean of  $85 \pm 18 \mu\text{eq/L}$  through the season (Fig. 2). The sum of the strong acid anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) ranged from 27 to  $61 \mu\text{eq/L}$  with a mean of  $42 \pm 6 \mu\text{eq/L}$ . Sulfate was the dominant anion ranging from 16 to  $47 \mu\text{eq/L}$  with a mean of  $30 \pm 8 \mu\text{eq/L}$  and was responsible for the seasonal change in anion concentration (Fig. 2).

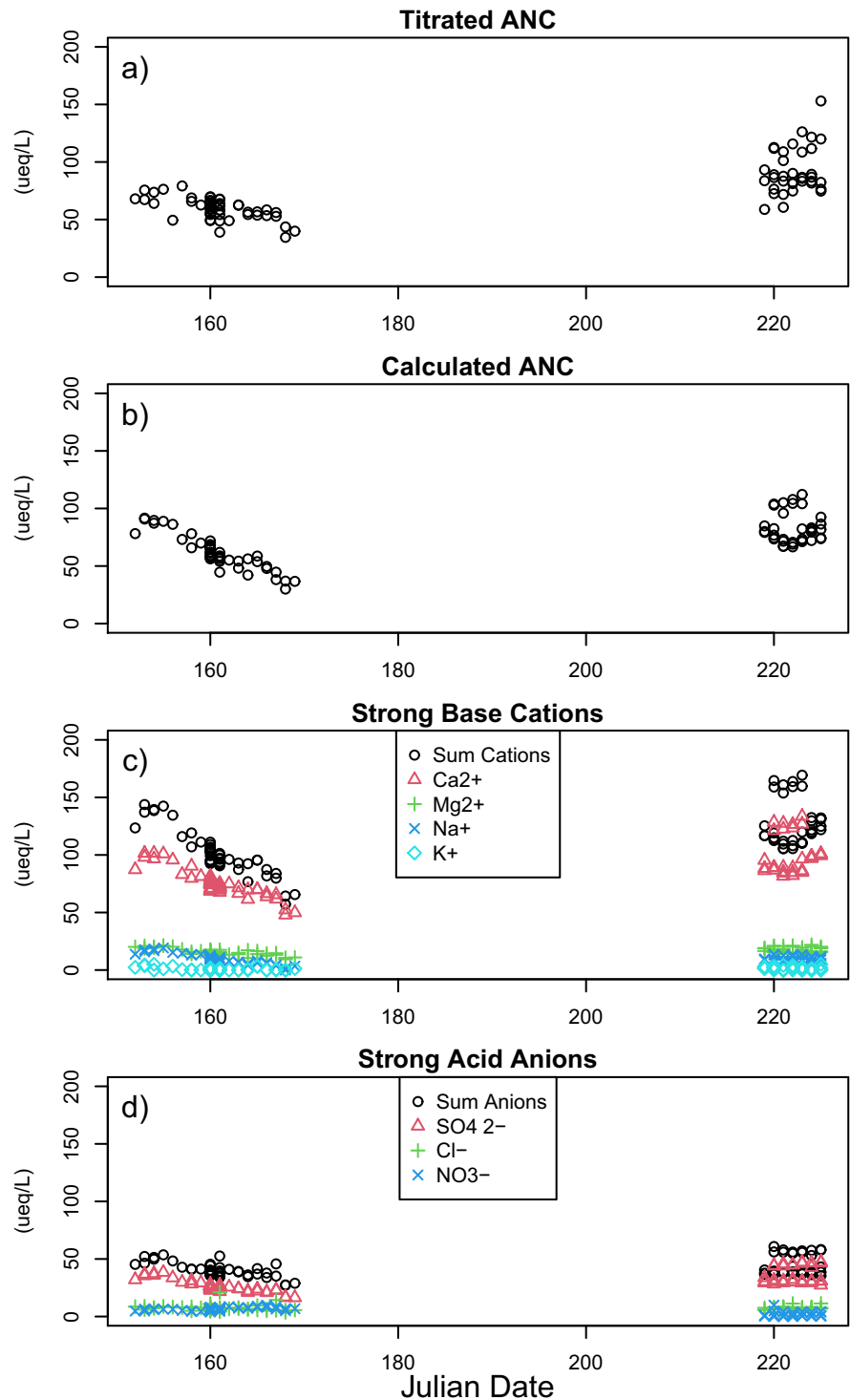
**Table 1** Summary of water chemistry results for the full sampling season, detailing (a) the range of measured values and their averages; (b) comparison by season; (c) mean/median (pH) by location in August; and (d) mean/median (pH) values from the 24-h cycle. Values are reported as mean  $\pm 1$  standard

error, except in the case of pH, which are presented as median (1st quartile, 3rd quartiles), and minimum and maximum values, where error was calculated by propagation of error from the precision of measurement of the constituent values

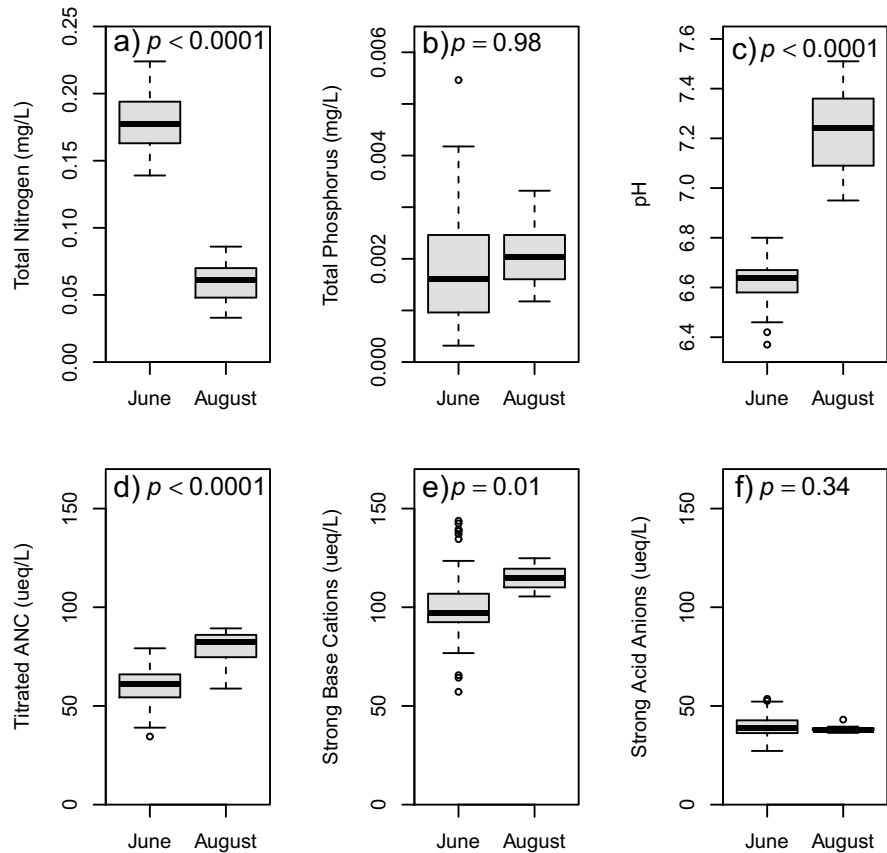
	<i>n</i>	Total N mg/L	Total P mg/L	pH	Titrated ANC $\mu\text{eq/L}$	Strong base cations $\mu\text{eq/L}$	Strong acid anions $\mu\text{eq/L}$
a) All samples							
Mean	88	0.14	0.002		73	112	42
Median (pH)				6.7			
SD	88	0.06	0.002		22	23	8
1st, 3rd quartiles (pH)				6.6, 7.2			
Minimum	88	$<0.05$	$<0.001$	6.4	$35 \pm 10$	$57 \pm 5$	$27 \pm 5$
Maximum	88	$0.26 \pm 0.01$	$0.016 \pm 0.001$	7.6	$153 \pm 10$	$169 \pm 5$	$61 \pm 5$
b) Season							
June outlet	51	$0.18 \pm 0.03$	$0.002 \pm 0.002$	6.6 (6.6, 6.7)	$60 \pm 9$	$101 \pm 19$	$40 \pm 6$
August outlet	13	$0.06 \pm 0.02$	$0.002 \pm 0.001$	7.2 (7.1, 7.4)	$80 \pm 9$	$114 \pm 6$	$38 \pm 2$
<i>p</i> -value		$<0.0001$	0.98	$<0.0001$	$<0.0001$	0.01	0.34
c) Location—August only							
Inlet	13	$0.11 \pm 0.03$	$0.004 \pm 0.001$	7.3 (7.2, 7.4)	$113 \pm 17$	$149 \pm 16$	$55 \pm 5$
Outlet	13	$0.06 \pm 0.02$	$0.002 \pm 0.001$	7.2 (7.1, 7.4)	$80 \pm 9$	$114 \pm 6$	$38 \pm 2$
Mid-lake	11	$0.06 \pm 0.01$	$0.002 \pm 0.001$	7.1 (6.9, 7.4)	$82 \pm 9$	$116 \pm 7$	$39 \pm 2$
<i>p</i> value		$<0.0001$	$<0.0001$	0.1	$<0.0001$	$<0.0001$	$<0.0001$
d) Diel cycle							
24 h	25	$0.18 \pm 0.04$	$0.002 \pm 0.003$	6.6 (6.6, 6.7)	$60 \pm 9$	$99 \pm 6$	$39 \pm 10$



**Fig. 2** Titrated ANC (a), calculated ANC (b), strong base cations (c), and strong acid anion (d) concentrations shown to decrease at the outlet through the snowmelt season in June. Calculated ANC was taken to be the sum of the strong base cations minus the sum of the strong acid anions. Titrated ANC decreased significantly through June ( $r^2=0.42, p<0.0001$ ) as ion concentrations become more dilute. Concentrations of strong base cations noticeably decreased through June ( $r^2=0.84, p<0.0001$ ) due to significant decreases in  $\text{Ca}^{2+}$  ( $r^2=0.83, p<0.0001$ ),  $\text{Mg}^{2+}$  ( $r^2=0.64, p<0.0001$ ),  $\text{Na}^+$  ( $r^2=0.84, p<0.0001$ ), and  $\text{K}^+$  ( $r^2=0.16, p=0.003$ ). Strong acid anions become significantly more dilute through June ( $r^2=0.49, p<0.0001$ ).  $\text{SO}_4^{2-}$  decreased significantly through June ( $r^2=0.82, p<0.0001$ ) whereas  $\text{NO}_3^-$  ( $r^2=0.20, p<0.001$ ) increased through June.  $\text{Cl}^-$  decreased, but not significantly ( $r^2=0.02, p=0.4$ ). In August, ANC and strong base cations were higher than those at the end of the snowmelt period in June, whereas strong acid anions were largely unchanged



**Fig. 3** Total nitrogen (a) was significantly higher in June than that in August while total phosphorus (b) did not differ between seasons. Median pH (c), titrated ANC (d), and strong base cations (e) were significantly lower in June than those in August. Strong acid anions (f) did not differ between seasons. All seasonal comparisons are between outlet samples only, because inlet and mid-lake samples were not collected in June



### 3.1 Seasonal Variation

Samples collected at the outlet in June (during snowmelt) were higher in nitrogen and lower in pH and ANC than those at the outlet in August when the basin was nearly snow free (Fig. 3; Table 1). In June, average total nitrogen was  $0.18 \pm 0.03$  mg N/L, significantly higher ( $p < 0.0001$ ) than the August concentration at the outlet of  $0.06 \pm 0.02$  mg N/L. Total phosphorus was not different by season ( $p = 0.98$ ) with average outlet concentrations of  $0.002 \pm 0.002$  mg P/L in June and  $0.002 \pm 0.001$  mg P/L in August. Both values were very close to the detection limit of 0.001 mg P/L. Measured pH was significantly lower in June ( $p < 0.0001$ ) with a June median of 6.6 compared to a median of 7.2 in August. Mean ANC was significantly lower during snowmelt ( $p < 0.0001$ ) with a mean concentration of  $60 \pm 9$   $\mu\text{eq/L}$  in June compared to  $80 \pm 9$   $\mu\text{eq/L}$  in August. Mean concentrations of strong base cations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$ ) were slightly but significantly lower in June at

the outlet ( $101 \pm 19$   $\mu\text{eq/L}$ ;  $p = 0.01$ ) than those in August at the outlet ( $114 \pm 6$   $\mu\text{eq/L}$ ), although the difference primarily reflects a decline toward the end of June; the maximum concentration of strong base cations on 2 June ( $143 \pm 19$   $\mu\text{eq}$ ) exceeded the maximum concentration of strong base cations at the outlet on 13 August ( $125 \pm 6$   $\mu\text{eq/L}$ ) (Fig. 2). Strong acid ions ( $\text{NO}_3^-$ ,  $\text{SO}_4^-$ , and  $\text{Cl}^-$ ) were not significantly different by season and averaged  $40 \pm 6$   $\mu\text{eq/L}$  in June and  $38 \pm 2$   $\mu\text{eq/L}$  in August. June concentrations of strong acid anions decreased minimally through snowmelt (Fig. 2).

Ion concentrations become more dilute as snow melted (June 1–18) and ANC decreased significantly at the outlet ( $r^2 = 0.42$ ,  $p < 0.0001$ ) (Fig. 2). Significant decreases in  $\text{Ca}^{2+}$  ( $r^2 = 0.83$ ,  $p < 0.0001$ ),  $\text{Mg}^{2+}$  ( $r^2 = 0.64$ ,  $p < 0.0001$ ),  $\text{Na}^+$  ( $r^2 = 0.84$ ,  $p < 0.0001$ ), and  $\text{K}^+$  ( $r^2 = 0.16$ ,  $p = 0.003$ ) yielded a decline in base cations ( $r^2 = 0.84$ ,  $p < 0.0001$ ), though the trend was primarily driven by  $\text{Ca}^{2+}$ . Strong acid anions likewise decreased through June ( $r^2 = 0.49$ ,  $p < 0.0001$ ), primarily due to

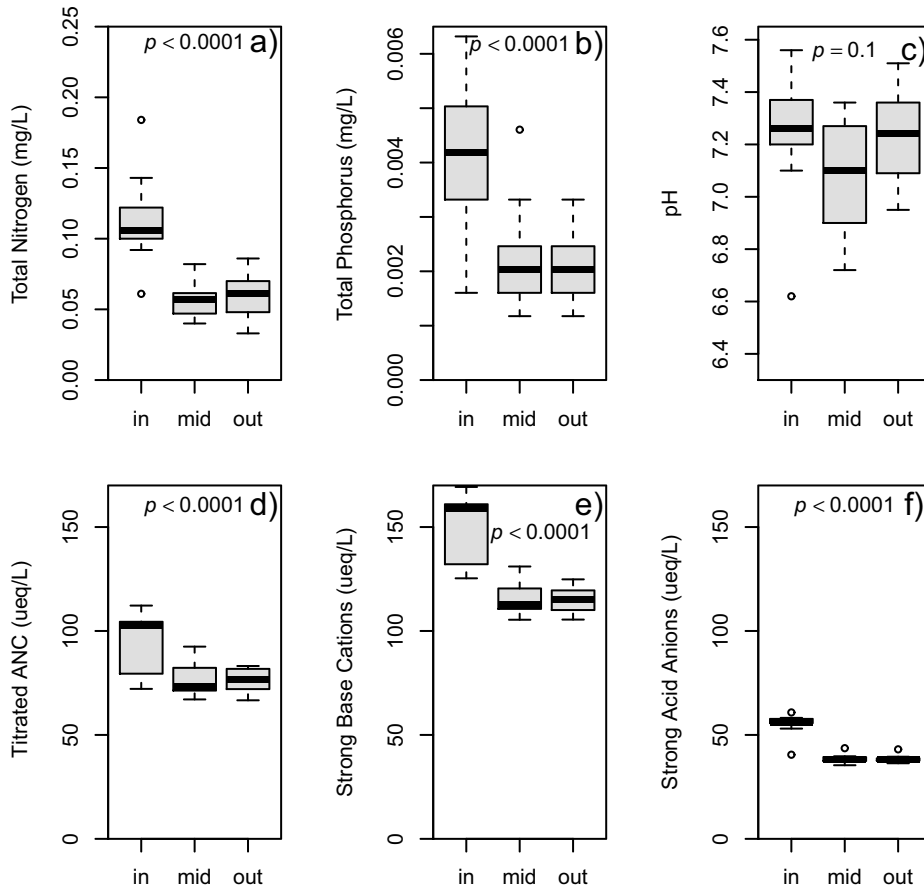
a decline in  $\text{SO}_4^{2-}$  ( $r^2=0.82$ ,  $p<0.0001$ ) and despite a slight but significant increase in  $\text{NO}_3^-$  ( $r^2=0.20$ ,  $p<0.001$ ).  $\text{Cl}^-$  did not change significantly ( $r^2=0.02$ ,  $p=0.4$ ) (Fig. 2). These trends imply that higher snowmelt flows diluted ANC and most ion concentrations in the lake before ANC and ions returned to higher concentrations by August (Fig. 2).

August depth profiles show that the lake was strongly stratified, with a 9-m-thick epilimnion and a thermocline that extended from there to at least 19 m below the surface (the maximum depth reached by our measuring equipment; Online Resource S1) (Landers et al., 1987). Depth profiles were not collected in June because the lake was 95% covered in ice, and the middle of the lake was not safely accessible.

### 3.2 Spatial Variation

We analyzed the August samples to determine if water chemistry differed by sampling location (inlet, outlet, and at the mid-lake where samples were collected from the epilimnion) (Fig. 4; Table 1). Since June samples could only be collected at the outlet, they were not included in the spatial analysis. Overall, the inlet samples had significantly higher concentrations of total nitrogen, total phosphorus, titrated ANC, cations, and anions than the outlet or mid-lake samples, but pH did not vary by sampling location. We found no statistical difference between mid-lake and outlet samples for all reported chemical components (Fig. 4; Table 1).

Inlet samples were significantly higher in nitrogen ( $p<0.0001$ ;  $0.11 \pm 0.03$  mg N/L) than



**Fig. 4** In August, inlet samples were significantly higher in concentrations of total nitrogen (a), total phosphorus (b), titrated ANC (d), strong base cations (e), and strong acid anions (f) than mid-lake or outlet samples. Median pH was lower at the mid-lake than that at the inlet or outlet (c), but the difference was not significant

ons (f) than mid-lake or outlet samples. Median pH was lower at the mid-lake than that at the inlet or outlet (c), but the difference was not significant

outlet ( $0.06 \pm 0.002$  mg N/L) and mid-lake samples ( $0.06 \pm 0.01$  mg N/L). Total phosphorus was significantly higher at the inlet ( $p < 0.0001$ ;  $0.004 \pm 0.001$  mg P/L) as compared to outlet and mid-lake concentrations ( $0.002 \pm 0.001$  mg P/L), which were near the detection limit ( $0.001$  mg P/L). Titrated ANC differed significantly by location ( $p < 0.0001$ ). Mean inlet ANC was  $113 \pm 17$   $\mu\text{eq/L}$  compared to a mean outlet ANC of  $80 \pm 9$   $\mu\text{eq/L}$  and a mean mid-lake ANC of  $82 \pm 8$   $\mu\text{eq/L}$  (Fig. 4; Table 1). Strong base cations were significantly different by location ( $p < 0.0001$ ) where mean values were the highest at the inlet ( $149 \pm 16$   $\mu\text{eq/L}$ ) as compared to the outlet ( $114 \pm 6$   $\mu\text{eq/L}$ ) and mid-lake ( $116 \pm 7$   $\mu\text{eq/L}$ ) concentrations. The mean value for strong acid ion concentration was likewise significantly higher at the inlet ( $p < 0.0001$ ;  $55 \pm 5$   $\mu\text{eq/L}$ ) than that at the outlet ( $38 \pm 2$   $\mu\text{eq/L}$ ) and at mid-lake ( $39 \pm 2$   $\mu\text{eq/L}$ ). Measured pH values were not significantly different by location ( $p = 0.1$ ) with median values of 7.3 at the inlet, 7.2 at the outlet, and 7.1 at mid-lake. The simplest interpretation of our spatial data is that outlet samples generally can be characterized as displaced, shallow, mid-lake water.

### 3.3 Diurnal Variation

During snowmelt, level loggers measured a variation of up to 10 cm in depth over the course of the day downstream of the lake outlet, peaking in the evening and reaching its lowest point in the morning, which coincides with expected daily snowmelt cycles (Online Resource S2) (Caine, 1992; Dunne & Black, 1971; Slaymaker, 1974). While a rating curve was not developed for the site, we estimated changes in flow based on a mean stream width of 3 m where the level loggers were deployed. During snowmelt, the steam was approximately 20 cm deep at minimum flow and 37 cm at maximum flow, such that daily outflow varied by as much as 30 to 50% with the 10-cm diel change in depth. Data from the 24-h sampling cycle (Table 1) showed there was no difference in lake chemistry by time of day or with downstream water

depth. During the 24-h period, the average value for total nitrogen was  $0.18 \pm 0.04$  mg N/L, for total phosphorus  $0.002 \pm 0.003$  mg P/L, ANC was  $60 \pm 9$   $\mu\text{eq/L}$ , strong base cations were  $99 \pm 6$   $\mu\text{eq/L}$ , strong acid anions were  $39 \pm 10$   $\mu\text{eq/L}$ , and median pH was 6.6 (Table 1).

As with the 24-h sampling cycle, total nitrogen, total phosphorus, titrated ANC, strong base cations, and strong acid anions did not differ between time of day sampled for the June and August periods. The August pH data (Table 2; Online Resource S3) show that at the inlet, morning pH (median pH=7.2) was significantly lower ( $p = 0.04$ ) than evening pH (median pH=7.4). The same trend held at the outlet where there was a significantly lower ( $p < 0.001$ ) morning pH (median pH=7.1) compared to the evening (median pH=7.4). Median pH at the mid-lake did not differ ( $p = 0.5$ ) between morning (median pH=7.1) and evening (median pH=7.0). August pH values in aggregate show morning pH (median pH=7.1) were significantly lower ( $p = 0.01$ ) than evening pH (median pH=7.3).

### 3.4 Meteorological Impacts

We investigated the effects of cloud cover, precipitation, and wind speed on lake chemistry for the June and August sampling windows using general linear models to determine if these factors should be accounted for in sampling protocols. Cloud cover had no significant effect on water chemistry, and precipitation only had a weakly positive effect on pH in June ( $p = 0.03$ ; Online Resource S4). Wind speed only had a weakly positive effect on titrated ANC in August ( $p = 0.03$ ; Online Resource S4). Overall, meteorological factors had no to minimal significance and had little influence on lake chemistry patterns in this study. Considering that we ran 12 models (2 sampling periods  $\times$  6 chemistry parameters) with 3 predictors each, these two weakly significant findings carry little weight and may be a type I error. Overall, we show that meteorologic factors had minimal influence on

**Table 2** August pH, presented as median (1st quartile, 3rd quartiles), compared by time of day for different sampling locations

	Inlet pH	Mid-lake pH	Outlet pH	All pH
Morning	7.2 (7.1, 7.3) ( $n = 7$ )	7.1 (7.0, 7.2) ( $n = 6$ )	7.1 (7.0, 7.2) ( $n = 7$ )	7.1 (7.0, 7.3) ( $n = 20$ )
Evening	7.4 (7.3, 7.4) ( $n = 6$ )	7.0 (6.8, 7.2) ( $n = 5$ )	7.4 (7.3, 7.5) ( $n = 6$ )	7.3 (7.2, 7.4) ( $n = 17$ )
<i>p</i> value	0.04	0.5	<0.001	0.01

lake chemistry parameters, and monitoring protocols probably do not need to account for daily to hourly changes in weather.

### 3.5 Nitrogen and Phosphorus

During snowmelt, the total nitrogen content of water exiting the lake at the outlet (Fig. 5; Table 3) was primarily in the form of nitrate, which was three times higher than ammonium. In contrast, August nitrate and ammonium levels were similar at the lake outlet and mid-lake, but nitrate was higher than ammonium at the inlet (Fig. 5; Table 3). In June, average total nitrogen of lake water at the outlet was measured to be  $0.18 \pm 0.03$  mg N/L of which nitrate was  $0.09 \pm 0.02$  mg  $\text{NO}_3\text{-N/L}$  and ammonia was  $0.028 \pm 0.005$  mg  $\text{NH}_4^+\text{-N/L}$ . In August, average total nitrogen at the outlet was  $0.06 \pm 0.02$  mg N/L with  $0.008 \pm 0.005$  mg  $\text{NO}_3\text{-N/L}$  and  $0.012 \pm 0.004$  mg  $\text{NH}_4^+\text{-N/L}$ . Similarly, total nitrogen in the mid-lake samples measured  $0.06 \pm 0.01$  mg N/L on average with  $0.006 \pm 0.004$  mg  $\text{NO}_3\text{-N/L}$  and  $0.015 \pm 0.006$  mg  $\text{NH}_4^+\text{-N/L}$ . Inlet concentrations of total nitrogen were higher ( $0.11 \pm 0.03$  mg N/L) than other August sampling locations, primarily due to an increased concentration of nitrate ( $0.06 \pm 0.03$  mg  $\text{NO}_3\text{-N/L}$ ) while ammonium ( $0.015 \pm 0.006$  mg  $\text{NH}_4^+\text{-N/L}$ ) was similar across sampling locations.

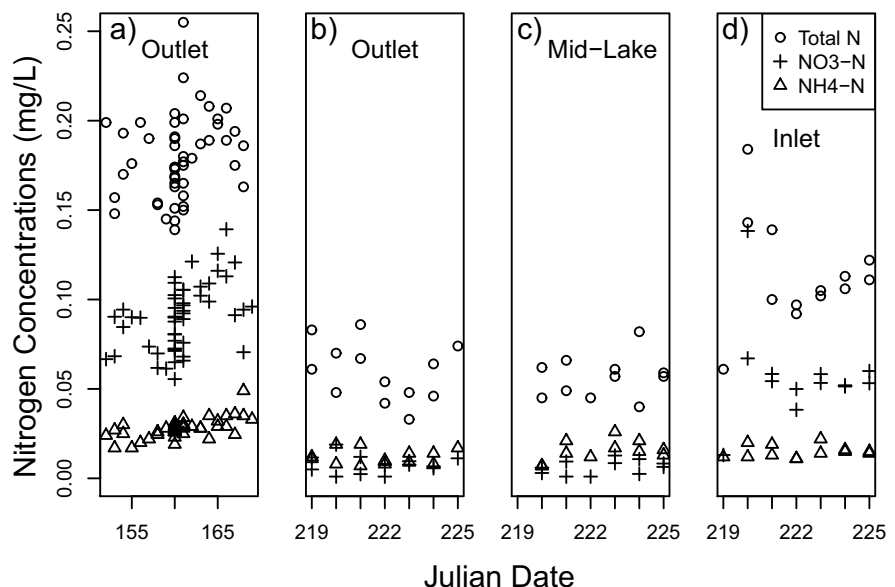
**Table 3** Total nitrogen, nitrate, and ammonium by season and by sampling site, reported as mean  $\pm 1$  standard error. Total nitrogen includes organic nitrogen, which was not measured but is assumed to account for the difference between total nitrogen and inorganic nitrogen

	<i>n</i>	Total N mg/L	$\text{NO}_3\text{-N}$ mg/L	$\text{NH}_4^+\text{-N}$ mg/L
June outlet	51	$0.18 \pm 0.03$	$0.09 \pm 0.02$	$0.028 \pm 0.005$
August all locations	37	$0.08 \pm 0.03$	$0.02 \pm 0.03$	$0.014 \pm 0.005$
August outlet	13	$0.06 \pm 0.02$	$0.008 \pm 0.005$	$0.012 \pm 0.004$
August mid-lake	11	$0.06 \pm 0.01$	$0.006 \pm 0.004$	$0.015 \pm 0.006$
August inlet	13	$0.11 \pm 0.03$	$0.06 \pm 0.03$	$0.015 \pm 0.003$

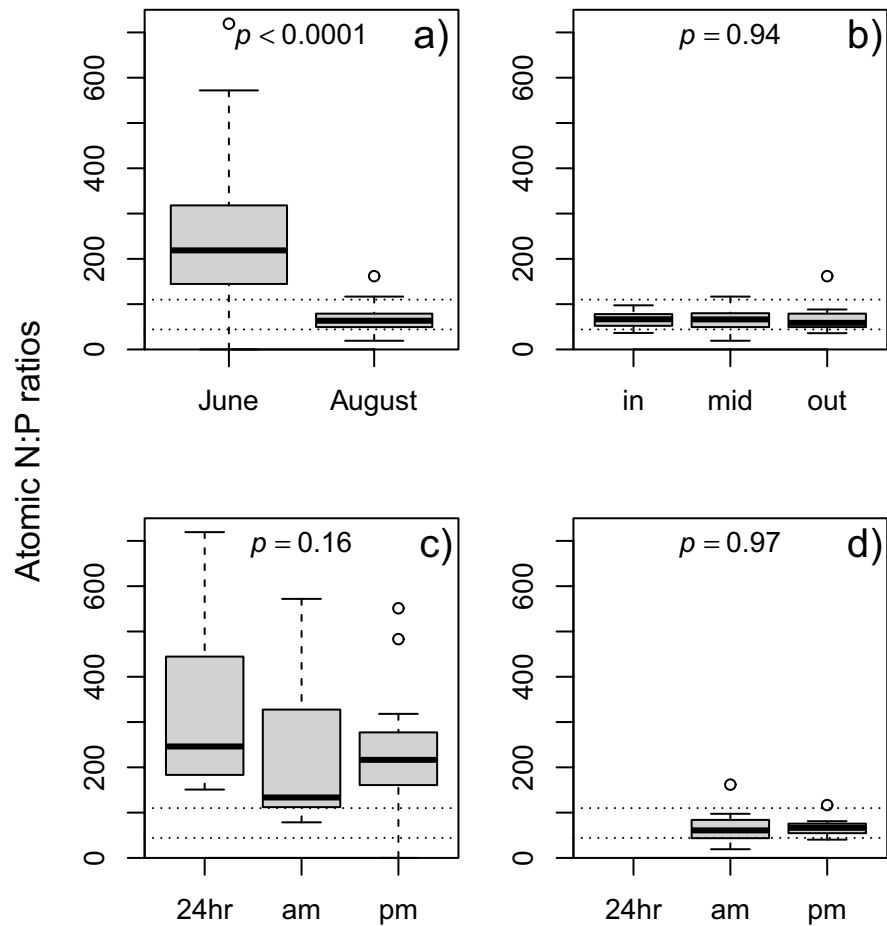
The amount of organic nitrogen can be estimated by the difference between total and inorganic forms. In June at the outlet, organic nitrogen thus averaged 0.062 mg N/L. In August, it was 0.040, 0.039, and 0.035 mg N/L at the outlet, mid-lake, and inlet, respectively, and comprised the majority (about 2/3) of all the nitrogen in the lake.

Molar ratios of total nitrogen to total phosphorus ranged from 19 to 720 (Fig. 6). Total phosphorus was below the detection limit (0.001 mg/L) in 13 measurements, and 9 samples were below the detection limit for total nitrogen (0.05 mg/L). Correcting summary statistics with the robust ROS methods did not

**Fig. 5** Outlet samples during snowmelt (a) were significantly higher in nitrate concentration than when the basin was snow free at the outlet (b) ( $p < 0.0001$ ). In August, the inlet (d) has a higher concentration of nitrate and total nitrogen than outlet (b) and mid-lake (c) ( $p < 0.0001$ )



**Fig. 6** Nitrogen to phosphorus (N:P) ratios (atomic) demonstrate that the system is nitrogen saturated and phosphorus limited in June, but co-limited by nitrogen and phosphorus in August (a). Sampling location in August (b) did not influence nitrogen to phosphorus ratios, nor did the time of sampling in June (c) or the time of sampling in August (d). Below a ratio  $\sim 44$ , identified by the lower dashed line, freshwater lakes are generally nitrogen limited, whereas they tend to be phosphorus limited above  $\sim 110$ , identified by the higher dashed line, and co-limited between these thresholds (Elser et al., 2009). Correcting summary statistics by means of the robust ROS method to take into account left-censored data did not substantially change nitrogen to phosphorus ratios



significantly change total nitrogen to total phosphorus ratios, thus uncorrected values are reported (Bolks et al., 2014). In June, the molar ratio of total nitrogen to total phosphorus averaged  $255 \pm 150$ , whereas the August molar ratio averaged  $66 \pm 25$ . Nitrogen to phosphorus ratios did not vary statistically by the time of day they were sampled in June or August, or the location of sampling in August (Fig. 6). Deep Lake was well above the 110 threshold identified by Elser et al. (2009) for phosphorus limitation and nitrogen saturation in June and was in the intermediate zone (44 to 110) in August, suggesting co-limitation by nitrogen and phosphorus in the late summer. Likewise, this interpretation of nutrient limitation in Deep Lake is corroborated by the  $\sim 31$  total nitrogen to total phosphorus ratio and 0.003 mg P/L thresholds identified by Downing and McCauley (1992). Considering the ratio of dissolved inorganic nitrogen to total phosphorus, Deep Lake samples were  $99 \pm 85$  in June and

$13 \pm 7$  in August, suggesting phosphorus limitation across the seasons and represent values indicative of moderate nitrogen deposition sites (Bergström, 2010).

#### 4 Discussion

Lake chemistry at Deep Lake varied significantly temporally and spatially during our study. As predicted, the lake samples collected during the snowmelt period had higher total nitrogen, primarily in the form of nitrate which coincided with decreased pH as compared to the snow-free season. This supported our hypothesis that snowmelt would release a pulse of stored nutrients to the lake. Contrary to our hypothesis, however, ANC declined as snowmelt progressed, indicating the expected cation pulse from dust release was not realized. We also expected the diurnal hydrograph to show an increase in cations late in the day

when snowmelt flow was highest, but we saw no trend over the 24-h sampling cycle conducted in June, nor did any lake chemistry parameter vary by time of day for June or August, except pH in August. June ANC was lower on average than ANC in August, making the lake particularly vulnerable to episodic acidification from anion inputs such as nitrogen. Ion concentrations, especially calcium and sulfate, decreased with snowmelt (Fig. 2), presumably as they became more dilute with the addition of new meltwater to the system. Either the dust was released in the earliest phases of snowmelt and became diluted with the increased water flux of melting snow, or the components of ANC were already present in the lake before snowmelt began and became diluted by snowmelt.

We also predicted that there would be an imbalance in the chemical budget of Deep Lake, and we found support for this hypothesis as lake inflow was higher in concentrations of nitrogen, cations, and ANC than samples collected at the outlet and mid-lake in August. We further predicted that the nutrient load would decrease pH despite the increase in ANC, but there was no statistical difference between pH at the lake inlet compared to the epilimnion (mid-lake and outlet samples). Apparently, the increase in ANC in August was sufficient to buffer the increased nutrient load. Samples collected from the mid-lake and the outlet showed no statistical difference in any lake chemistry parameter and represent a well-mixed epilimnion. Spatial comparisons were only made in August as the inlet in June was frozen and hazardous to access, which prevented sampling.

Ultimately, we found that while season influenced total nitrogen, pH, and strong base cations, the time of day and changes between days were unimportant considerations for these variables. However, ANC, strong base cations, and strong acid ions decreased steadily as snowmelt progressed and samples became more dilute, presumably due to an increase in water flux from snowmelt. Changes in weather had little influence on measures of lake chemistry. These findings highlight two major themes for monitoring alpine lakes in the Wind River Range, and high-elevation water-bodies in general: (1) snowmelt nutrient loading contributing to observed regional trends of increasing nitrogen and decreasing pH over many years has the potential to shift nutrient limitation and puts lakes at risk of exceeding critical loads for ecosystem health and (2) the need to better account for

changes in lake chemistry that can occur during peak snowmelt flows, a period which may be challenging to capture. In light of these two points, we discuss the lake dynamics and sources of atmospheric deposition which explain the trends we observed and discuss the risk of exceeding critical loads in Deep Lake and other alpine lakes. We conclude by summarizing the implications of our findings for monitoring alpine lakes where episodic acidification or nutrient loading is of concern.

#### 4.1 Lake Dynamics

The chemical dynamics in Deep Lake are coupled with its water flow paths. In June, the lake is largely ice covered. As snow melts, it enters the lake from all sides, not just the main inlet. Between June and August, as surface waters warm and become less dense, there is likely a period of whole-lake mixing as the surface temperature passes through the 4 °C density maximum. Unfortunately, we were unable to capture lake dynamics during this period. As revealed by flow out of the lake in August, which declines as temperatures drop at night, inflowing water is recently melted and probably near the freezing point. Influent water likely sinks to the level deeper in the lake that matches its own temperature and density (Hutchinson, 1975), displacing overlying water upwards. The net result is that, even during stratification, water added to the lake spends a period of time in the basin similar to the average water residence time. Similarly, displaced water leaving the lake's outlet may have been in the lake for many months, a year, or even more.

Differences in outlet water chemistry between June and August may reflect (A) changes in water that entered the lake between those two dates, (B) changes in surface waters driven by biogeochemical processes over the time period (especially photosynthesis), and (C) changes in water chemistry occurring over longer periods of time and that are preserved in deeper layers in the stratified lake and mixed to the surface during spring/summer overturn. Shifts in surface water entering the lake during these warm months might represent interactions between snowpack chemistry and the watershed substrate (soil and rock) over which it flows.

Nitrate levels at the outlet declined, whereas pH, ANC, and strong base cations all increased in August

relative to June (Fig. 3). During the 18-day sampling period in June, ANC and base cations were declining before the increase that occurred sometime before August measurements (Fig. 2). Most likely, the June decline reflects the role of snowmelt in diluting solute concentrations in that period, whereas the increase later in summer may have been caused by spring/summer mixing. Primary production consumes nitrate and may raise pH under ambient acid–base conditions but has only a small effect on ANC or base cation concentration (Morel & Hering, 1993), suggesting the observed changes in lake chemistry were significantly influenced by mechanisms (A) and (C). Mechanism (A) ultimately reflects changes occurring outside of the lake as there is no apparent internal source of base cations. Aside from sulfate which decreased through snowmelt, strong acid anion concentrations were relatively unchanged in the lake through our study, whereas the strong base cations decreased during snowmelt before increasing to higher levels in August and have no evident internal source. Storage of atmospheric deposition in the snowpack can be a primary source of sulfate to alpine regions of the Rocky Mountains, while chloride concentrations in the snowpack tend to be minimal (Turk & Spahr, 1991; Turk et al., 2001). Thus, the variations in strong base ions and sulfate over the summer, and lack thereof for chloride, almost certainly reflect exogenous processes.

One possibility is that early snowmelt includes a pulse of solutes preferentially released with first melt (Likens & Bormann, 1995) that declines through June and becomes diluted by increased water flow into the lake, whereas rising air temperatures in July and August promote weathering release of cations from watershed soils and rocks. This pattern suggests exogenous drivers of lake chemistry, with local substrate weathering as the most likely source of these solutes in August. Because the basin is predominately granitic and slow to weather (Brahney, 2012), such contributions are still quite small, as reflected in the low concentrations of strong base cations in the lake in August (mean values of  $149 \pm 16 \mu\text{eq/L}$  at the inlet,  $114 \pm 6 \mu\text{eq/L}$  at the outlet, and  $116 \pm 7$  at mid-lake).

#### 4.2 Sources

Water chemistry in high alpine lakes in the Wind River Range may be influenced by a combination

of deposition from air pollution, deposition from natural dust, bedrock weathering, and other biogeochemical processes (Brahney et al., 2014; Zhang et al., 2018). Nitrate contributes up to half of total nitrogen, and up to 2/3 of inorganic nitrogen at Deep Lake (Fig. 5; Table 3). The proportion of nitrate is of particular concern given its role in the eutrophication process. Nitrate concentrations in alpine lakes are primarily associated with fossil fuel combustion and anthropogenic use of fertilizers following nitrification (Hundey et al., 2014, 2016; Mast et al., 2001; Peterson et al., 1998). Zhang et al. (2018) modeled deposition of reactive nitrogen across the GYE and found that agriculture was the largest contributor of total reactive N deposition (34%), followed by oil and gas (>10%) in the southern Wind River Range, of which nearly half comes from local sources. Similarly, in alpine lakes of the Uinta Mountains of Utah, at least 70% of atmospherically deposited aquatic nitrate derives from anthropogenic sources, with an estimated 60% from agricultural sources and approximately 10% resulting from fossil fuel combustion (Hundey et al., 2016). Since 1984, the number of natural gas-producing wells in Sublette County, WY, has increased eightfold, gas production has increased 26-fold (Wyoming Oil & Gas Commission, 2017), and  $\text{NO}_x$  has concordantly increased relative to the amount of activity on the Pinedale Anticline (Soltis & Field, 2012). Two oil and natural gas fields (the Jonah and Pinedale Anticlines) are located less than 40 km upwind of the lake and are a probable point source for pollutants (Fig. 1) (McMurray et al., 2013). Nitrogen concentrations in lichens from the western slopes of the Wind River Range decreased exponentially with distance from active drilling sites of the Jonah Field and Pinedale anticlines, highlighting the role of natural gas and oil production as a source of local nitrogen pollution (McMurray et al., 2013). Despite the relatively small contribution fossil fuel combustion makes to nitrogen deposition in the GYE, increases in oil and gas development could be enough to push lakes above critical loads and trigger episodic acidification or eutrophication.

In other systems, climate change has been linked to increases in lake water nitrogen concentrations resulting from glacial melt and the loss of large permanent snowfields (Heath & Baron, 2014), though neither source is present in the Deep Lake basin to contribute solutes. It is more likely that the increase in nitrate



and decrease in pH over the past 30 years is due to atmospheric deposition (Grenon et al., 2010). However, changing conditions in the future could exacerbate the effects of nitrogen deposition from anthropogenic sources and must remain in consideration for future monitoring in the region.

In alpine lakes, ANC may be linked to the weathering of granitic parent material in the basin or upstream, aeolian dust that is stored in the snowpack through winter, and dry and wet deposition when the lake is ice free (Clow et al., 2016; Landers et al., 1987; Rhoades et al., 2010). Due to the slow weathering geology of Deep lake, and that of many high alpine headwater lakes, there is limited material in situ to buffer against acidification, and the consistent exceedance of critical loads in nitrogen raises concerns of eutrophication and acidification if observed trends continue (Brahney, 2012; Mast et al., 1990, 2001; Nanus et al., 2017). The decline of strong base cations, particularly  $\text{Ca}^{2+}$ , observed over the course of snowmelt (Fig. 2) likely represents the release of accumulated dust in the snow followed by the dilution of solutes with increased snowmelt water flow, as has been found elsewhere in the Rocky Mountains (Brahney et al., 2014; Meszaros, 1966; Mladenov et al., 2012; Sequeira, 1982). Interestingly, phosphorus concentrations did not show similar dilution trends with snowmelt, and there was no statistical difference between June and August outlet samples that would highlight a release from snowpack as a primary source. This counters evidence by Brahney et al. (2014) from the Wind River Range and Deep Lake demonstrating that dust and atmospheric deposition are primary sources of phosphorus to alpine lakes in the region. However, 15% of our phosphorus levels were below the detection limit, and it is possible that the difference was not detectable at such low levels. Alternatively, the snowpack may not retain phosphorus to the same extent as nitrogen and components of ANC, in-lake processes regulate phosphorus concentrations, or phosphorus stored in the snowpack is metabolized before entering the lake in June. Phosphorus has been identified as a limiting nutrient for red snow and glacial algae, and it is possible that phosphorus from atmospheric deposition is consumed by algae in the snowpack before reaching the lake (Lutz et al., 2015; McCutcheon et al., 2021). Although algae were not noted in the Deep Lake basin during the study, red snow algae are common

across the Wind River Range and may have occurred at levels too low to visually observe in the Deep Lake basin, particularly if it is nutrient limited.

#### 4.3 Critical Loads and Ecosystem Response

When critical loads of nitrogen are exceeded in surface waters, diatom communities are often the first organisms to respond (Baron et al., 2000; Camargo & Alonso, 2006). In the Rocky Mountains, studies of sensitive high alpine lakes have estimated critical loads associated with changes in diatom communities to be as low as 1.4–1.5 kg N/ha/year of wet deposition (Baron et al., 2011; Saros et al., 2011). Such critical loads are among the lowest in the USA, and thus, these lakes are important indicators for agencies charged with managing air pollution impacts (Pardo et al., 2011; Williams et al., 2017). Within the Rocky Mountains, high-elevation lakes surrounded by steep and rocky terrain with minimal vegetation, such as Deep Lake, tend to have lower critical loads and receive higher levels of deposition relative to surrounding lower, flatter, and more vegetated terrain (Nanus et al., 2012, 2017).

Critical load exceedances of total nitrogen deposition for nutrient enrichment are estimated to be common in the Wind River Range with the magnitude of exceedance in some locations  $>4$  kg N/ha/year (McMurray et al., in press), a level that has been associated with episodic acidification in other regions, such as the Colorado Front Range and identified by Baron et al. (2011) as the threshold for nitrogen-driven acidification (Nanus et al., 2012; Williams & Tonnessen, 2000). CASTNET (<https://www.epa.gov/castnet>) data from nearby Pinedale, WY, show dry nitrogen deposition rates above 2 kg N/ha/year since 2000 with total deposition (wet+dry) rates in Pinedale estimated to be 2.56 kg N/ha/year in 2016, the year of our study. Deposition increases with elevation and it is likely that deposition at Deep Lake is greater, as supported by measured rates of total nitrogen deposition ranging from 2.0 to 4.5 kg N/ha/year in total deposition between 1990 and 2008 at Black Joe Lake, which is located  $<2$  km north-east of Deep Lake (Grenon et al., 2010). Bulk collectors at Black Joe Lake revealed increasing trends of total nitrogen deposition to the lake between 1986 and 2008, with a maximum total (wet+dry) deposition of 4.0–4.5 kg N/ha in 2007 for the period

(Grenon et al., 2010). At Deep Lake, a nitrogen CL of total (wet + dry) deposition of 3–4 kg N/ha/year is estimated, which current models indicate may be exceeded by 2–3 kg N/ha/year in total deposition (Nanus et al., 2017).

Molar ratios of total nitrogen to phosphorus indicate that Deep Lake is phosphorus limited in June and is co-limited by nitrogen and phosphorus after snowmelt. In a study of sediment cores from two other alpine lakes in the southwestern Wind River Range, Brahney et al., (2015a, 2015b) found that since 1940, human activities and other factors have driven a 50-fold increase in dust transport to alpine areas, driving a two- to threefold increase in lake phosphorus content and a tenfold increase in diatom production, indicating that biotic changes are already underway in the lake.

Levels of pH below 5.5–6.0 can be harmful to sensitive aquatic life, providing an important threshold for concern (Camargo & Alonso, 2006; Doka et al., 2003). In the Colorado Rocky Mountains, native amphibians have been harmed by acidified waters, with increasingly negative effects as pH dropped below 6.0 (Turk & Campbell, 1997). Although pH did not fall in this range during our study period, we observed levels as low as  $6.4 \pm 0.1$ , indicating that episodic acidification could negatively affect the aquatic biota in Deep Lake if nitrate or other acids increase contributions to the system. This is particularly true as the very low ANC in this lake affords little protection against acidification. Because accessing remote alpine lakes during snowmelt is difficult, episodic, short-term acidification has not been a focus of current monitoring programs (Campbell et al., 1995; Grenon et al., 2010; Johannessen & Henriksen, 1978).

While we did not observe lake acidification ( $\text{ANC} < 0 \mu\text{eq/L}$ ) during our study, June ANC at Deep Lake's outlet steadily declined through snowmelt (Fig. 2) and reached a low of  $35 \pm 10 \mu\text{eq/L}$  on 17 June, the day before our sampling concluded. Based on the observed trend, it is possible that the lake did acidify at the end of snowmelt but after we concluded sampling. ANC levels at the lake epilimnion never exceed  $100 \pm 10 \mu\text{eq/L}$ , indicating that the lake was sensitive to nitrogen input throughout the year and was extremely vulnerable to acidification in the later stages of snowmelt when values were below  $50 \pm 10 \mu\text{eq/L}$  (Williams & Tonnessen, 2000).

Studies of seasonal variation in alpine lakes of the Rocky Mountains show a similar trend of peak nitrate concentrations during snowmelt, indicating that if atmospheric deposition of nitrogen continues to increase, episodic acidification will likely affect the entire Rocky Mountain region (Baron et al., 2000; Brooks et al., 1999; Burns, 2004; Campbell et al., 1995; Ingersoll et al., 2016; Reuss et al., 1995; Wolfe et al., 2001). However, in a Long-term Ecological Research site 30 km from the city of Boulder in the Colorado Rocky Mountains, total nitrogen concentrations peaked in summer (Mladenov et al., 2012), suggesting that the trend could vary spatially and the pattern should be investigated further. This geographic variation emphasizes the importance of lake monitoring programs, and the need to account for large-scale spatial and temporal variation.

#### 4.4 Monitoring Implications

Many long-term lake monitoring programs only sample lakes once per year, or even more infrequently, as with the US EPA Western Lakes Survey which collected single samples from 69 lakes in 1985 (Landers et al., 1987), and later compared those to samples collected in 1999 (Clow et al., 2003). However, there is limited understanding of the variation in alpine lake chemistry with time of day, day-to-day, following storms, between seasons, and location, which is essential to providing context to the variation in lake chemistry over longer time periods. Our findings indicate that within-day and day-to-day variations were minimal, storms were of little importance, but the difference between the snowmelt and snow-free season mattered greatly.

Total nitrogen was nearly three times greater in June than that in August at the lake outlet,  $\text{NO}_3^-$ -N was an order of magnitude greater during June than that during August, and  $\text{NH}_4^+$ -N was twice as great in June compared to that in August. Measured pH was also lower in June compared to that in August, as was ANC. While pH, ANC, and the concentrations of strong base cations and strong acid anions did decline significantly over time in June as snowmelt progressed, total nitrogen and total phosphorus were not significantly influenced by date as snowmelt progressed. Our findings imply that, when possible, lakes should be sampled during the snowmelt window if episodic acidification is of concern. Later

dates in this window had the lowest levels of ANC when researchers may find easier access to lakes and reveal key indicators of vulnerability to acidification by targeting late snowmelt. Under the current lake monitoring program for the Bridger-Teton National Forest, Season 1 samples are collected after the ice on the lake surface begins to break up (Grenon et al., 2010). Our findings of extremely low ANC values while the lake was still iced over suggest that the current Season 1 sampling window may need to be moved to earlier in the season if possible to capture potential episodic acidification events.

Likewise, researchers may be able to capture representative peak values of total nitrogen and total phosphorus later in the snowmelt window at a time when access may be easier, and equally representative of potential maximums. Unfortunately, our study did not include samples from the period immediately post-ice off to compare, but this time period merits further investigation to determine when the major shifts between June and August occurred, with a particular focus on the time of overturn.

Flexibility in sampling may be gained in a reduction of sampling locations. In August (the only period when both inlet and mid-lake samples were collected), we found inlet samples to differ significantly (for all metrics aside from pH) between the inlet and the mid-lake or outlet, but that the outlet and mid-lake samples were not statistically different. This is consistent with Clow et al. (2003) who compared chemistry for outlets and mid-lake epilimnia at 14 lakes in US National Parks and found no significant difference in measures of nitrate, phosphorus, ANC, pH, strong base cations, and strong acid anions. We found that inlet samples were higher in total nitrogen, total phosphorus, titrated ANC, strong base cations, and strong acid anions than mid-lake or outlet samples. This suggests that water enters the lake with higher chemical concentrations and becomes altered through chemical, physical, and biological processes (Table 1; Fig. 4). Thus, effort could be reduced by not sampling at both the mid-lake and outlet as such samples are essentially duplicates. Because mid-lake samples are typically retrieved from a small raft, such a protocol could reduce risk in the field for researchers. Outlet samples can be collected more efficiently and are less likely to be missed due to high winds and building

lightning storms, providing a more consistent time series in the alpine with the same estimates of epilimnion chemistry.

The time of sampling (morning versus evening) played no significant role in lake chemistry with the exception of pH in August and may also provide some flexibility in sampling protocols for both peak snowmelt and in summer. We did find that pH was lower in the morning relative to the evening for August only ( $p=0.01$ ; Table 2; Online Resource S3). However, because the lake had a circumneutral pH, these pH changes are probably not of concern for episodic acidification, nor impacting native species, as those effects begin near a pH of 6.0 (Turk & Campbell, 1997). A single daily sample should suffice, which may reduce total time required to sample sites that require a long hike to access. Likewise, precipitation, wind, and cloud cover during and between sampling events generally did not have a meaningful influence on lake chemistry, contrary to our expectation that they could. Cloud cover had no effect on lake chemistry metrics. Precipitation did have a weakly positive effect ( $p=0.03$ ) on pH in June, and wind speed had a weakly positive effect on titrated ANC ( $p=0.05$ ) in August, but given the number of models evaluated, such results could be type I error. This indicates that meteorologic factors likely did not impact lake chemistry via direct or indirect pathways, or the effects were too small to matter. Collectively, this suggests that researchers can choose to sample in the best weather window, without concern that samples chemistry may be altered by active or recent storms.

## 5 Conclusion

Our findings suggest that the winter snowpack stores atmospheric deposition until spring, when an increase in water flow due to snowmelt causes a dilution of ANC, decrease in pH, and increase in total nitrogen, putting the Deep Lake at high risk for episodic acidification. The diatom community in adjacent lakes of the Wind River Range suggests that biotic changes to the lakes in the region are already underway as a result of changes to nutrient inputs (Brahney et al., 2015a, 2015b). Researchers and monitoring programs concerned about episodic acidification and nitrification of alpine lakes should focus on collecting

samples from the snowmelt window when peak seasonal input was shown to occur and when the lake is most sensitive, as similarly was found by Johannessen and Henriksen (1978), Campbell et al. (1995), and Reuss et al. (1995). To gain flexibility in monitoring effort, inlet and outlet samples should be prioritized over mid-lake epilimnion samples which are effective duplicates of outlet samples. Time of day and local weather conditions are of minimal importance in understanding the variation in the lake. Nitrogen enrichment is a problem impacting lakes across the Northern Hemisphere (Bergström & Jansson, 2006), and given the land use history of the area, it is likely that increasing loads of nitrogen deposition will continue broadly—the problem of nitrogen pollution is identified by Sala et al. (2000) as the third largest driver of global change in the twenty-first century. The extent of atmospheric deposition and resulting ecological impacts must be better monitored to understand and mitigate this threat in a changing world.

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**Data Availability** The data are available at <https://doi.org/10.5061/dryad.8pk0p2nn1> through the Dryad digital repository.

**Code Availability** All statistical analyses were performed in program R.

## Declarations

**Conflict of Interest** The authors declare no competing interests.

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