The hydrochemistry of high-elevation lakes in the Georgia Basin, British Columbia

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ABSTRACT

High-elevation lakes are sensitive to acidification from atmospheric deposition owing to their generally small catchment areas, thin soils and low bedrock weathering rates. The Georgia Basin, southwest British Columbia, Canada, receives atmospheric inputs from emissions originating in Vancouver, Victoria, and from marine traffic in the Strait of Georgia. There is growing concern on the influence of this air pollution on high-elevation systems in the region. Water chemistry and catchment characteristics were used to assess the sensitivity of 72 lakes in the Georgia Basin to acidic deposition. Twenty percent of the study lakes had pH levels less than 6, and acid neutralising capacity (ANC) concentrations below 20 µeq L^{-1}, which are key thresholds for biological sustainability. Base cation and trace metal concentrations were low, typical of the dilute nature of high-elevation lakes (median conductivity = 7.0 µS cm^{-1}). Nonetheless, concentrations of trace metals (such as lead) decreased with distance from major cities. The primary factors influencing the pH and ANC of surface waters were investigated using multiple linear regression; both ANC and pH were related to longitude and the proportion of the catchment dominated by ice and glaciers. Increasing sulphur deposition resulted in decreasing pH. The median critical load of acidity (sulphur) for the study lakes was approximately 70 meq m^{-2} y^{-1}; 18% of the lakes received sulphur deposition (range: 6-81 meq m^{-2} y^{-1} for the period 2005-2006) in excess of their critical load.

Key words: acidification, sulphur and nitrogen deposition, long-range transboundary air pollution, acid neutralising capacity, critical loads, Canada

1. INTRODUCTION

High-elevation catchments are characterized by dilute surface waters, small terrestrial areas, limited vegetative cover, thin soils and low bedrock weathering rates (Psenner 1989; Drever & Zobrist 1992). As such, they are sensitive to surface water acidification and eutrophication owing to atmospheric acid (Psenner 1989; Mosello *et al.* 1995) and nitrogen (N) deposition respectively (Williams *et al.* 1996a; Campbell *et al.* 2000). Accordingly, high-elevation lakes are considered early warning systems to the impacts of long-range air pollution. Synoptic water chemistry surveys have played an integral role in identifying the major factors influencing surface water chemistry and in assessing lake sensitivity (Baron 1992; Marchetto *et al.* 1994; Jeffries *et al.* 2010, this issue; Scott *et al.* 2010, this issue). Acid neutralising capacity (ANC) and its relation to catchment characteristics have been commonly used to assess sensitivity to acidic atmospheric deposition (Sullivan *et al.* 2007; Nanus *et al.* 2009).

The Georgia Basin, located in the southwest corner in British Columbia (BC), Canada, encompasses the major cities of Vancouver and Victoria (Fig. 1). There is growing concern on the influence of atmospheric deposition (specifically sulphur (S) and N) on the high-elevation catchments that dominate this mountainous region. Continental-scale model simulations indicate that the Georgia Basin receives high levels of S and N deposition (Moran *et al.* 2008). The response of high-elevation systems to these pollutants has been studied in many regions in the world. Lake surveys in the Italian Alps found that the major acidifying agents were S and N deposited from the atmosphere (Mosello *et al.* 1990; Marchetto *et al.* 1995). Similarly, lake surveys in the Tatra Mountains, Slovakia, indicated that during peak acid deposition, the pH of high-elevation lakes decreased substantially to a median pH of 5.3 (Stuchlik *et al.* 2006). High surface water nitrate (NO_3^-) concentrations were related to atmospheric N deposition (Stuchlik *et al.* 2006), a trend also observed in lakes in the Rocky Mountains of Colorado (Williams *et al.* 1996a; Clow *et al.* 2002).

The sensitivity of surface waters to acid deposition has been widely assessed using the effects-based critical load approach, defined as "a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Nilsson & Grennfelt 1988). Lakes in the Georgia Basin have long been suspected as highly sensitive to acid deposition because the region is dominated by acidic rocks with poor weathering capacity (Weins 1987). Few studies have assessed the sensitivity of lakes in the Georgia Basin to long-range air pollution (Sullivan & Samis 1988; Swain *et al.* 1985). Moreover, lake
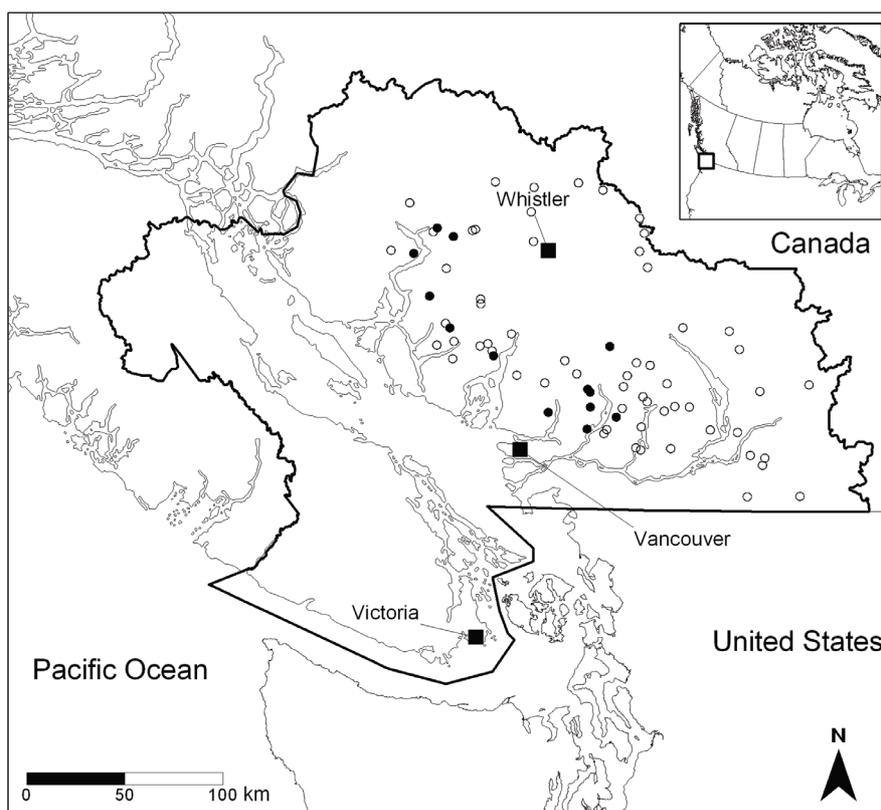
Fig. 1. Location of the Georgia Basin, British Columbia, Canada (delineated by bold black line). The study lakes are denoted by circles (filled circles indicate lakes that receive sulphur deposition in excess of their critical load) while major cities are denoted by filled squares.

surveys conducted in the mid-1980s focussed on readily accessible or large (insensitive) water bodies.

During October 2008, a survey of high-elevation lakes (n = 72) was carried out within the Georgia Basin. The objectives of this study were to: (a) describe the hydrochemistry of high-elevation lakes, (b) assess their acid sensitivity by investigating the primary factors influencing chemical composition, and (c) determine the critical load and exceedance of acidity (S) for the study lakes.

2. METHODS

2.1. Study area

The Georgia Basin encompasses 48,000 km² and is surrounded by four mountain ranges; the Olympic Mountains, Vancouver Island Ranges, the Coast Ranges and the Cascades. The area receives high levels of precipitation especially along the coastal regions as a result of orographic precipitation. Moreover, due to the variable topography, air masses and their associated pollutants can be trapped leading to potentially high atmospheric deposition. The major emitters of S and N within the basin include the marine, transportation and industrial sectors (Environment Canada 2004). The basin encompasses seven biogeoclimatic zones (regions characterized as having specific climates, soils and vegetation communities): coastal Douglas fir (CDF), coastal west-

ern hemlock, mountain hemlock, interior Douglas fir, montane spruce, Engelmann spruce-subalpine fir and the alpine tundra (AT) zones (Meidinger & Pojar 1991). Temperatures within these zones vary greatly, with mean annual temperatures ranging from 10.5 °C in the low elevation CDF zone to -4.0 °C in the high altitude AT zone (Meidinger & Pojar 1991).

2.2. Field sampling and laboratory analysis

In October 2008, 72 high-elevation lakes were sampled within the Georgia Basin (Fig. 1). The lakes were chosen based on lithology; the majority of the lake catchments being dominated by the rock types of granodiorite and quartz diorite, both characterized by low buffering capacity and low weathering rates. The elevation of the study lakes ranged between 90 and 2005 m a.s.l. with 65% of lakes ≥1000 m a.s.l. (Tab. 1).

Water collections were made centre-lake from a float-equipped Bell 206 helicopter. Water depths were measured using an Eagle Cuda168™ depth sounder with a float-mounted transducer and the position was logged using a Garmin 76S™ global positioning unit. Surface water conductivity, pH and temperature were measured *in situ* using a Yellow Springs Instrument Model 6600 sonde. Near-surface water samples were collected using pre-cleaned plastic bottles. Samples were dispensed into individual analytical bottles and

Tab. 1. Summary statistics for the study lakes (n = 72) including both chemical and morphological characteristics (P25 refers to the 25th percentile while P75 refers to the 75th percentile). [§]: DOC = dissolved organic carbon.

Variable	Mean	Min	P25	Median	P75	Max
Elevation (m)	1145	90	880	1174	1442	2005
Lake area (ha)	43	4	8	16	41	629
Watershed area (ha)	731	26	135	261	390	16892
Alpine/Barren (%)	50.7	0.0	21.1	56.1	78.3	100.0
Forested (%)	33.4	0.0	0.7	29.1	61.0	100.0
Ice and glacier (%)	3.7	0.0	0.0	0.0	0.3	62.4
Precipitation (mm y^{-1})	3218	1627	2488	3184	3829	4974
S deposition (kg ha^{-1} y^{-1})	3.75	1.01	2.13	3.55	4.38	11.71
N deposition (kg ha^{-1} y^{-1})	8.65	2.07	4.56	6.98	10.60	37.23
Conductivity (μS cm^{-1})	9.43	2.00	4.00	7.00	10.50	43.00
Alkalinity (μeq L^{-1})	78.2	19.0	38.3	61.3	101	287
pH	6.44	5.44	6.13	6.42	6.85	7.32
Ca^{2+} (μeq L^{-1})	57.9	3.19	20.0	43.8	63.40	346.82
Mg^{2+} (μeq L^{-1})	9.21	1.23	3.50	5.68	10.9	49.9
K^+ (μeq L^{-1})	3.87	0.69	1.66	2.66	3.87	20.1
Na^+ (μeq L^{-1})	16.8	4.18	11.1	13.9	19.8	53.9
Cl^- (μeq L^{-1})	5.46	1.41	1.41	4.23	6.53	36.20
SO_4^{2-} (μeq L^{-1})	17.5	2.08	5.52	8.54	15.3	169
NO_3^- (μeq L^{-1})	1.73	0.18	0.18	0.78	2.35	9.71
NH_4^+ (μeq L^{-1})	0.24	0.18	0.18	0.18	0.18	1.10
ANC (μeq L^{-1})	63.0	5.95	21.8	60.7	78.8	246
DOC (mg L^{-1})§	1.12	0.15	0.42	0.74	1.60	7.22
Organic anion (μeq L^{-1})	7.80	1.01	2.93	5.29	11.4	45.8

kept cool for shipment to laboratories (within approximately 24 hours).

Water samples were analyzed for pH, total alkalinity by titration, major anions by ion chromatography, ammonium and total phosphate by colourimetry, and dissolved organic carbon (DOC) by combustion following 0.45 μm membrane filtration and metals by ICP and ICP-MS. External quality assurance involved blind submission of blanks and sample duplicates. Further, the quality of the analytical data was checked by ion balance. Organic anion concentrations were calculated from DOC and pH following Oliver *et al.* (1983); ANC was estimated as the difference between the sum of base cations and sum of acid anions in μeq L^{-1}.

2.3. Catchment data

Catchment boundaries for the study lakes were delineated from a digital elevation model (DEM: 1:20,000 BC Ministry of Environment) using a geographic information system (GIS). Lake areas were obtained from the BC National Topographic Series (1:50,000) maps. Land-use data for each catchment were delineated from the 1:250,000 Baseline Thematic Mapping (version 2 BC Ministry of Environment), which was compiled from Landsat 7 imagery from 1999 onwards. Catchment lithology was delineated from the digital geology map of BC (1:250,000 BC Ministry of Energy, Mines and Petroleum Resources). Rock types were grouped into four buffering or weathering categories from Nanus *et al.* (2009) and the weathering sequence developed by Goldich (1938): (a) low buffering (e.g., gneiss, granite, diorite), (b) medium buffering (e.g., basalt, amphibolite), (c) high buffering (e.g., horneblende, olivine), and (d) unknown buffering (e.g., some sedimentary rocks). Precipitation data was extracted from the Parameter Elevation Regressions on Independent Slopes (PRISM: Daly *et al.* 1994) model, at a 4 km by 4 km grid resolution. Annual average total (wet and dry) S and N deposition for the period 2005-2006 was obtained from the Community Multiscale Air Quality (CMAQ: Di Cenzo & Lepage 2003) model at a 4 km by 4 km grid resolution. Evaluations of the CMAQ model by Eder and Yu (2006) indicated good agreement between measured and modelled sulphate (SO_4^{2-}) and ammonium (NH_4^+) deposition levels and markedly improved NO_3^- prediction compared to earlier CMAQ versions.

2.4. Statistical analysis

All statistical analyses were conducted using STATISTICA 7.0 and Kyplot 2.0; alpha values were set at 0.05. The non-parametric Spearman rank-order correlation was conducted on all chemical and catchment characteristics as the majority of the data were not normally distributed (Kolmogorov-Smirnov, $p < 0.05$). Only correlation results that were significant and pertinent to the objectives of the study are reported in detail. Explanatory models were developed using stepwise forward regression. The number of model variables was based on both model parsimony (minimizing explanatory variables) and model performance (ability to predict ANC and pH). Models were limited to a maximum of four explanatory variables. All data were log$_{10}$ transformed in the analysis of pH, whereas only those that were not normally distributed were transformed for analysis of ANC determinants.
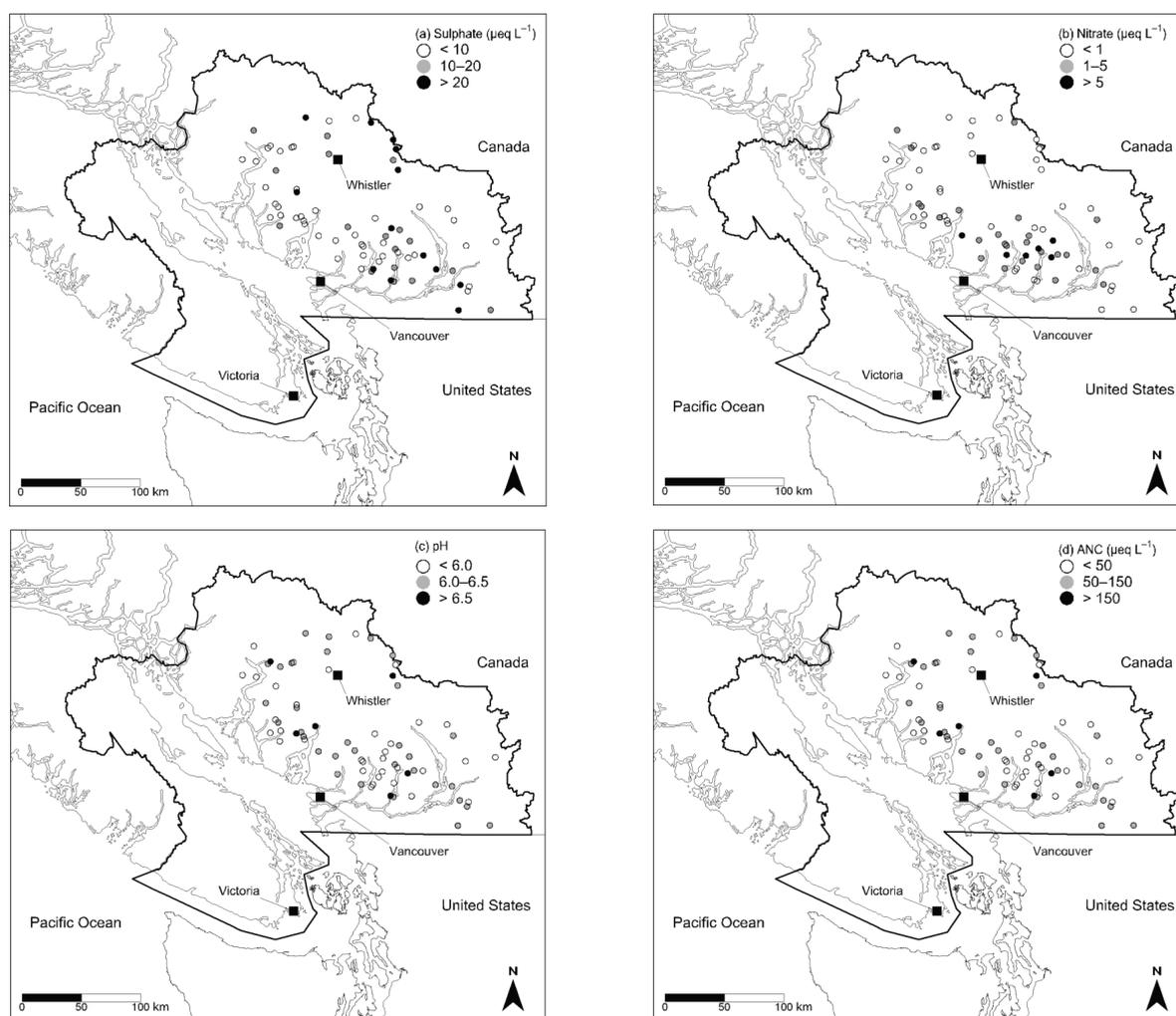
Fig. 2. Distribution of (**a**) sulphate, (**b**) nitrate, (**c**) pH and (**d**) ANC concentrations in the Georgia Basin.

2.5. Critical loads

The steady-state water chemistry (SSWC) model (Aherne *et al.* 2002; UBA 2004) was used to estimate the critical load of acidity [CL(*A*)] for the study lakes. The model incorporates a critical chemical limit (ANC$_{limit}$) to protect a selected biological indicator from significant harmful effects. A value of 20 µeq L^{-1} is commonly used to protect fish species (Lien *et al.* 1996); however, ANC is highly influenced by natural organic acids. The current study incorporated a lake-specific ANC$_{limit}$ based on DOC (mg L^{-1}) following Lydersen *et al.* (2004):

$$ANC_{limit} = 10 + (10.2/3) \times DOC \quad (1$$

The present exceedance of critical load [Ex(A)] was calculated as anthropogenic sulphate deposition (Sdep) plus present N leaching flux (N$_{leach}$) minus CL(*A*). Nitrogen is largely retained in terrestrial catchments, as such N deposition cannot be used directly to estimate exceedance. The current study included the acidifying impact of N deposition at present rates of N retention in the catchment (i.e., at present N leaching).

In addition to surface water acidification, N deposition can potentially cause terrestrial and aquatic eutrophication. Most plants are adapted to nutrient-poor conditions, and can only survive or compete successfully under low N availability. The nutrient impact of N deposition was evaluated using empirical critical loads (derived from field studies and experiments). Empirical critical loads in the range of 5-15 kg N ha^{-1} y^{-1} have been recommended for alpine terrestrial ecosystems (Achermann & Bobbink 2003; UBA 2004). Furthermore, critical loads derived from changes in diatom assemblages in lakes in the Loch Vale catchment in Rocky Mountain National Park, Colorado have been proposed at 1.5 kg N ha^{-1} y^{-1} (Baron 2006).

3. RESULTS AND DISCUSSION

3.1. Acidity, acid neutralising capacity and alkalinity

The pH values for the 72 study lakes ranged from 5.44 to 7.32 (Tab. 1). Almost 20% of the lakes had pH values less than 6.0 (Fig. 2c), the level at which biological impacts are expected to occur (Jeffries 1997). There were no lakes, however, experiencing severe
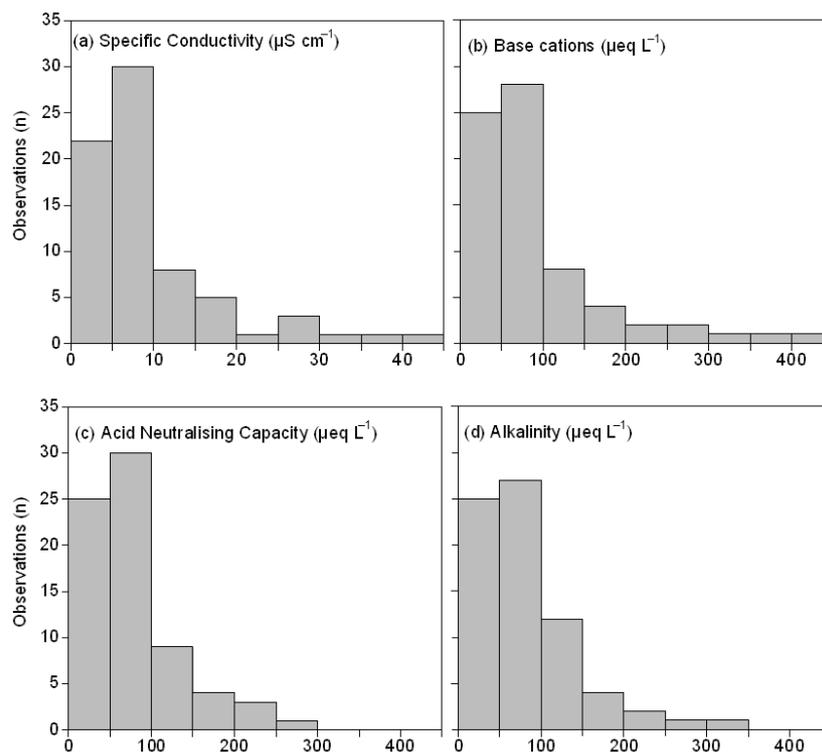
Fig. 3. Frequency distributions of (**a**) specific conductivity, (**b**) sum of base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+), (**c**) acid neutralising capacity (ANC) and (**d**) alkalinity for the study lakes (n = 72).

acidification (pH $\leq$5.0) causing the mobilization of toxic forms of aluminium (Baker & Schofield 1982). The pH values reported for the Georgia Basin, are comparable to those reported from mountainous regions of Europe, including the central and eastern Alps (Marchetto *et al.* 1995; Psenner 1989) and the Swiss Alps (Drever & Zobrist 1992).

Most study lakes had low conductivities (Fig. 3a) and low alkalinity (Fig. 3d). Fifty-two (70%) of the 72 lakes had specific conductivities less than 10 µS cm^{-1}. The mean conductivity ($\approx$10.0 µS cm^{-1}) is noticeably lower than remote lakes in many parts of the world (see Rogora *et al.* 2008). Alkalinity was also low, with the majority (74%) of lakes having concentrations less than 100 µeq L^{-1} (Fig. 3d). Acid neutralising capacity levels varied greatly between the lakes (between 5.95 and 246 µeq L^{-1}) with 21% having levels less than 20 µeq L^{-1}. Acid neutralizing capacity thresholds are commonly used to evaluate the acid sensitivity of lakes. Using ANC thresholds suggested by Herlihy *et al.* (1993) and Sullivan *et al.* (2004), 34 of the study lakes within the Georgia Basin were sensitive to atmospheric deposition (ANC $\leq$50 µeq L^{-1}), 6 lakes were insensitive (ANC $\geq$150 µeq L^{-1}) and 32 lakes were moderately sensitive (Figs 2d and 3c).

Significant negative correlations were observed between pH and both S deposition ($r_s = -0.351$, $p = 0.03$) and precipitation ($r_s = -0.572$, $p <0.001$), indicating that increases in either is reflected by decreased pH levels in surface waters. Decreases in pH as a result of the at-

mospheric deposition of S containing compounds has been documented in many aquatic systems worldwide and has been identified as a principal driver of acidification in freshwater systems (Schindler 1988; Aherne *et al.* 2002). Within the Georgia Basin, estimated S deposition ranged between approximately 1 and 12 kg ha^{-1} y^{-1} (Tab. 1). Those lakes receiving the greatest S deposition also had the lowest pH values.

Increased precipitation in mountainous regions typically results in greater deposition loads of atmospheric pollutants compared with the surrounding low lying areas (Williams & Tonnessen 2000). In the current study, lakes receiving precipitation amounts between 3500 and 5000 mm y^{-1} had S deposition rates as high as 11 kg ha^{-1} y^{-1}. Furthermore, 9 of the 14 lakes with pH <6.0 were observed within this precipitation range. As expected, in concert with pH, ANC and alkalinity were found to decrease significantly with increasing precipitation amounts ($r_s = -0.558$, $p <0.001$ and $r_s = -0.603$, $p <0.001$, respectively).

In the majority of mountainous regions studied, pH decreases with increasing elevation, a feature attributed to the lower bedrock weathering rates at higher elevations (Drever & Zobrist 1992). In the Georgia Basin, the opposite trend was true and pH increased with elevation ($r_s = 0.252$, $p = 0.03$). Lake catchments between 1000 and 1500 m a.s.l. received an average of 3510 mm y^{-1}, while those above 1500 m a.s.l. received an average of 2577 mm y^{-1}. These higher elevation lakes therefore have pH levels that are not as influenced by atmospheric

inputs compared to lakes at lower elevations. In addition, organic anions have been shown to contribute to the acidification of freshwaters (Oliver *et al.* 1983; Kahl *et al.* 1989), especially in dilute lakes where small amounts of organic anions can result in substantial pH depression (Kahl *et al.* 1989). Organic anion concentrations in our study lakes ranged from 1.01 to 45.8 µeq L^{-1} (Tab. 1); and decreased significantly with increased elevation (r_s= -0.643, *p* <0.001), owing to decreased vegetative land cover and increased barren lands at high altitudes.

3.2. Base cations, sulphate and nitrate

Surface water base cations originate from a variety of sources including weathering of catchment soils and bedrock and the atmospheric deposition of terrestrial dust and sea salts (Aherne *et al.* 2002). Calcium (Ca^{2+}) was the dominant base cation in the study lakes with a mean concentration of 57.9 µeq L^{-1} (Tab. 1). Eighty-five percent of the lakes had concentrations less than 100 µeq L^{-1}. Sodium (Na^+) was the next dominant base cation with a mean concentration of 16.8 µeq L^{-1}, followed by magnesium (Mg^{2+}: mean = 9.21 µeq L^{-1}) and potassium (K^+: mean = 3.87 µeq L^{-1}; see Tab. 1). Sixty-six of the 72 study lakes had total base cation concentrations less than 200 µeq L^{-1} (Fig. 3b), thereby classifying them as low base cation lakes (Sullivan *et al.* 1988).

Sulphate and NO_3^- are the most common acid anions affecting surface waters, with SO_4^{2-} generally considered the most influential in acidification (Aherne *et al.* 2002). Sulphate concentrations in the study lakes range from 2.08 to 169 µeq L^{-1}, with a mean concentration of 17.5 µeq L^{-1} (Tab. 1). Of the 72 study lakes, 18% had SO_4^{2-} concentrations greater than 20 µeq L^{-1} (Fig. 2a). Typically, dilute lakes with concentrations greater than 20 µeq L^{-1} are considered to be impacted by S deposition (Aherne *et al.* 2002).

The role of N in the acidification of surface waters has gained increased interest (Williams & Tonnessen 2000). Nitrogen emissions resulting from the combustion of fossil fuels and agriculture have altered the global cycling of N (Vitousek *et al.* 1997). In particular, NO_3^- has been shown to influence the acidity of alpine lakes during spring, when strong acid pulses result from rapid snow melt (Schindler 1988; Williams *et al.* 1993). Nitrate levels within the study lakes were generally much lower than SO_4^{2-} ranging between 0.18 µeq L^{-1} and 9.71 µeq L^{-1} (mean = 1.73 µeq L^{-1}: Tab. 1 & Fig. 2b).

Base cation concentrations showed significant increases with increased SO_4^{2-} concentrations. This may indicate that the leaching of soil base cations is occurring within these catchments as a result of acid deposition. Sodium increased with increased sulphur deposition, however not significantly (r_s = 0.209, *p* = 0.078). With the exception of K^+, all base cations decreased with increasing proportion of barren surfaces (areas al-

most completely devoid of vegetation) in the catchment, however the relationship was only statistically significant for Na^+ and Mg^{2+} (r_s = -0.652, *p* <0.001 and r_s = -0.337, *p* = 0.004, respectively). Potassium concentrations increased in response to increased barren surfaces within the catchments (r_s = 0.103, *p* = 0.391). Barren landscapes were characterized by greater proportions of granodiorite and alkali feldspar lithologies, both of which contain significant amounts of K^+. Further, barren surfaces do not support internal cycle of K^+, typically associated with forested catchments. Sodium concentrations show a clear maritime influence, with levels decreasing significantly with increasing distance from the coastal areas of the Georgia Basin, (r_s = -0.403, *p* <0.001). Concentrations of NO_3^- and SO_4^{2-} decreased significantly with increased distance from the major cities of Vancouver and Victoria (r_s = -0.401, *p* <0.001 and r_s = -0.339, *p* = 0.004, respectively). As would be expected, this indicates that greater amounts of deposition occurred in closer proximity to the major urban emission sources. The decrease in SO_4^{2-} concentrations from the coastal regions may also indicate that SO_4^{2-} derived naturally from the ocean is a significant source of SO_4^{2-} in high-elevation surface waters close to the coastal regions of the Georgia Basin. Geological sources of SO_4^{2-}, such as the oxidation and weathering of sulphide and pyrites, may also contribute to surface water concentrations.

3.3. Trace metals

Metals in lake waters are derived from regional geological sources and from atmospheric deposition (Lydersen *et al.* 2002). In areas affected by acidic deposition, the mobility of metals from terrestrial sources increases, resulting in elevated concentrations in surface waters (Lydersen *et al.* 2002). At pH greater than 7, trace metals are typically insoluble in water and complex with other particles (such as DOC: Schindler 1988). In the study lakes, trace metal concentrations were extremely low, with many lakes containing concentrations below detection limits.

With increasing acidification, aluminium (Al) concentrations commonly increase in surface waters (Lydersen *et al.* 2002). The toxicity of Al to aquatic biota is well-known (Baker & Schofield 1982; Hutchinson *et al.* 1989) and typically occurs at pH levels <5.0 (Baker & Schofield 1982). Mean total Al concentration in the study lakes was 113 µg L^{-1}; however, none of the lakes had pH <5.0, suggesting that toxic effects to aquatic organisms are not occurring. The positive correlation between Al and organic anions (r_s = 0.591, *p* <0.001) further supports this inference as Al commonly becomes complexed with organic materials resulting in minor effects on aquatic biota (Lydersen *et al.* 2002). A significant negative correlation, however, was observed between Al and pH (r_s = -0.325, *p* = 0.005). This may indicate that if the pH of lakes decrease further, Al may become increasingly mobile in surface waters.

The deposition of lead has been attributed to emissions from transportation and mining industries (Bashkin 2002). Lead concentrations correlate with long range atmospheric deposition (Steinnes & Henricksen 1993). Concentrations were very low in all the study lakes; ranging from below detection limits to 0.66 µg L^{-1} and concentrations decreased significantly with distance from major cities (r_s = -0.435, p <0.001).

Manganese (Mn^{2+}) concentrations in surface waters are typically not attributed to the direct influence of atmospheric deposition (Eisenreich 1980); however, Mn^{2+} concentrations have been found to increase in lakes experiencing low pH levels (Borg 1983). In the Georgia Basin, Mn^{2+} concentrations ranged from 0.43 to 68.1 µg L^{-1} (mean = 3.24 µg L^{-1}). Manganese was positively correlated with SO_4^{2-} concentrations (r_s = 0.419, p <0.001), a trend also observed in Norwegian lakes by Steinnes & Henriksen (1993). They attributed this increase in Mn^{2+} with SO_4^{2-} to the leaching of Mn^{2+} from soils as a result of acidic precipitation. While the positive correlation between Mn^{2+} and S and N deposition supports this possibility, the relationships were not statistically significant.

3.4. *Factors influencing acidity and acid neutralising capacity*

Multiple linear regression was utilized to explore the relationship between catchment characteristics and the pH and ANC of the study lakes. Several studies have found relationships between lake ANC, pH and catchment land cover, geology, elevation and atmospheric deposition (Drever & Zobrist 1992; Nanus *et al.* 2009; Marchetto *et al.* 1995). Accordingly, the current study included elevation, latitude and longitude, modelled S and N deposition, precipitation, land cover and geology.

Lake pH was primarily attributed to longitude, S deposition, precipitation and the amount of ice and glacier influencing the catchment. Similarly ANC was also related to longitude, precipitation and the proportion of ice and glacier within the catchment; however, bedrock type also significantly influenced lake ANC.

$$pH = 186 - 36.8 \times longitude - 0.23 \times S\ deposition -$$
$$- 0.34 \times precipitation + 0.10 \times ice/glacier \quad (2$$
$$r^2 = 0.585$$

$$ANC = 2656 - 20.6 \times longitude - 0.02 \times$$
$$\times\ precipitation + 10.7 \times ice/glacier + 34.4 \times rock \quad (3$$
$$r^2 = 0.582$$

In the regressions, longitude represents distance from emission sources; lakes closer to the primary emission sources (Victoria and Vancouver) had lower pH and ANC values. Acid neutralising capacity and pH were also explained by precipitation. As precipitation increased, both ANC and pH decreased; increased precipitation is associated with higher loading of atmospheric pollutants in mountainous regions (Williams *et al.* 1996b). Acid neutralising capacity increased as the proportion of the catchment containing unknown buffering rocks (rocks that were unable to be classified into weathering and acid-buffering categories) increased (r_s = 0.333, p = 0.004) indicating that these are rock types with substantial acid buffering capabilities. Several studies (Berg *et al.* 2005; Nanus *et al.* 2009) have shown that the buffering capacity of rocks are significantly related to the ANC of surface waters, and that catchments containing rock types such as quartzite and granite are associated with ANC levels <50 µeq L^{-1} (Nanus *et al.* 2009).

The pH and the ANC of the study lakes was influenced by the proportion of ice and glacier cover in the catchment. Although not significant, pH increased with increased glacier and ice cover (r_s = 0.115, p = 0.333). This could be the result of the composition of glacial melt waters. Lakes fed by glacial melt waters receive greater loads of suspended sediments as a result of the production of glacial flour (Sommaruga *et al.* 1999). Moreover, depending on the nature of the bedrock, glacial melt waters have been shown to be high in base cation concentrations, especially Ca^{2+} and K^+ (Anderson *et al.* 1997). Glacial melt waters are also typically low in DOC (Sammaruga *et al.* 1999); therefore the influence of acidic organic anions is negligible.

The multiple regression analysis indicated that S deposition was a primary factor influencing the pH of high-elevation lakes in the Georgia Basin. Acidic deposition occurs when sulphur dioxide (SO_2) is oxidised in the atmosphere forming sulphuric acid (Ahrens 2003). The major source of SO_2 emissions within the Georgia Basin is the burning of fossil fuels, especially from the marine sector (Environment Canada 2004). The lakes receiving the highest S deposition were characterized by low pH and ANC levels.

3.5. *Critical loads of acidity and nutrient nitrogen*

The mean CL(A) for the study lakes was 90.1 meq m^{-2} y^{-1} (median: 68.5. meq m^{-2} y^{-1}, Fig. 4), which is similar to lakes in acid sensitive regions in eastern Canada (Henriksen *et al.* 2002). In contrast, mean S deposition was approximately half (23.2 meq m^{-2} y^{-1}). Approximately 18% (n = 13) of the study lakes received S deposition above their CL(A) (Fig. 4). All lakes are protected if acid deposition is below the minimum CL(A). However, to discard outliers, account for uncertainties, and ensure that a sufficient percentage of lakes are protected, a 95% protection limit for the CL(A) is commonly used. The pentile CL(A) for the study region was approximately 10 meq m^{-2} y^{-1}.

Modelled S and N deposition to the study sites were highly correlated (r_s = 0.855, p = <0.001); however, N deposition was more than twice that of S (mean: 8.65 kg ha^{-1} y^{-1}, Tab. 1). Along with surface water acidification, increases in the N deposition has been linked to terrestrial ecological changes, including soil biogeochemistry and plant community diversity. In contrast,
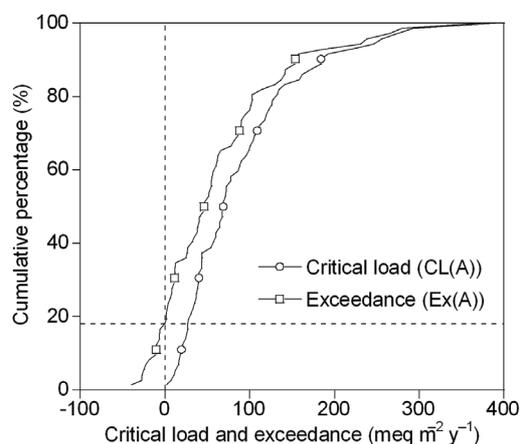
Fig. 4. Cumulative distribution functions (% of lakes) for critical load of acidity [CL(*A*)] and exceedance [Ex(A)] for study lakes (n = 72). Note: for presentational purposes the sign on exceedance has been reversed, i.e., negative values indicate exceedance of critical load. Approximately 18% of the lakes received sulphate deposition in excess of the CL(*A*).
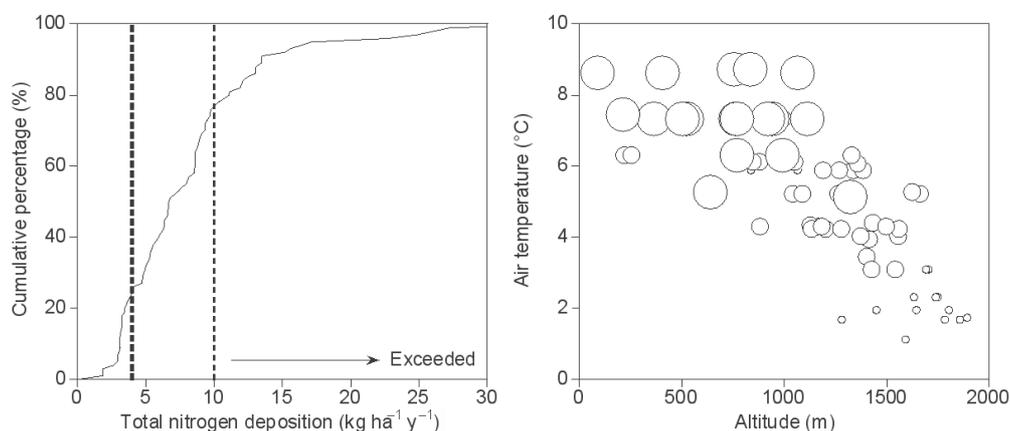

Fig. 5. Left panel: cumulative distribution of total nitrogen deposition to the study lakes for the period 2005–2006. Dashed vertical lines indicate the empirical critical loads for nutrient nitrogen of 4.0 (heavy dashed) and 10.0 (lighted dashed) kg ha^{-1} y^{-1}. Right panel: relationship between air temperature, altitude and nitrogen deposition. Small open circles denote lakes receiving <4 kg ha^{-1} y^{-1}, medium circles denote lakes receiving between 4 and 10 kg ha^{-1} y^{-1} and large circles denote lakes receiving >10 kg ha^{-1} y^{-1} (1 kg N ha^{-1} = 7.14 meq m^{-2}).

primary production in almost all surface waters is phosphorus-limited however, increased N loading to N-limited surface waters can result in changes in phytoplankton communities, increased biomass and eutrophication (Bergstrom & Jansson 2006). Approximately 27% of the study catchments receive N deposition above the empirical critical load of 10 kg N ha^{-1} y^{-1} (range of 5-15 kg N ha^{-1} y^{-1}) for alpine terrestrial ecosystems. Bowman *et al.* (2006) similarly found an empirical N critical load of 10 kg N ha^{-1} y^{-1} for changes in alpine plant community composition, but recommend a lower critical load of 4 kg N ha^{-1} y^{-1} to protect against changes in individual alpine species. Although 77% of the study lakes exceeded this critical load (Fig. 5), the highest elevation sites with shorter growing seasons received the lowest deposition loads (Fig. 5). Furthermore, all study lakes received N-deposition in excess of the critical load of 1.5 kg ha^{-1} y^{-1} for the eutrophication of aquatic ecosystems outlined by Baron (2006).

3.6 Overall acid sensitivity

High-elevation lakes in the Georgia Basin are sensitive to atmospheric acid deposition. Approximately 47% of the study lakes had ANC concentrations less than 50 µeq L^{-1}, suggesting that almost half are unable to counteract the effects of current or increased deposition loads (Sullivan *et al.* 2004). The low base cation concentrations observed in the study lakes are indicative of low weathering rates. Typically, weathering rates in alpine regions are low and decrease with increasing elevation (Drever & Zobrist 1992). Mongeon *et al.* (2010, this issue) estimated weathering rates at 19 sites in the Georgia Basin using the PROFILE model (Warvinge & Sverdrup 1992); the lowest rates were found at high-elevation alpine sites.

Land cover and geology undoubtedly influence the acid sensitivity of high-elevation catchments. In the

southern Appalachian mountains, acid-sensitive lakes were predicted to occur in regions underlain by base-poor bedrock (Sullivan *et al.* 2007). Similarly, in the US Rocky Mountains, acid-sensitivity was related to bedrock geology (Nanus *et al.* 2009). The dominant geology of the Georgia Basin primarily consists of bedrock with low buffering capacities. Moreover, the primary land cover in the study catchments consisted of barren, exposed bedrock. In general, high-elevation catchments within the Georgia Basin are unable to efficiently buffer incoming acidic deposition.

Sulphur deposition is the primary anthropogenic pollutant affecting the high-elevation lakes in the Georgia Basin; 18% of the study lakes received S deposition in excess of their CL(*A*). Emissions of SO_2 are expected to increase owing to the anticipated growth of Vancouver and Victoria. The Greater Vancouver Regional District (GVRD 2003) has forecasted that the emissions of SO_2 will increase by 23% by the year 2020. The role of N deposition in the acidification of surface waters has gained increased interest (Vitousek 1997). Nitrogen deposition leading to episodic acidification of surface waters during snow melt has been reported in the catchments of the Colorado Front Range (Baron 1992; Williams *et al.* 1996a), the Adirondack Mountains (Sullivan *et al.* 1996) and in high-elevation basins in the Sierra Nevada Mountains in California (Williams *et al.* 1993). These symptoms have been observed in alpine catchments with deposition rates as low as 3 kg ha^{-1} y^{-1} (Campbell *et al.* 2000). Emissions of N oxides (NO_x) within the Georgia Basin are also expected to increase in the coming years.

4. CONCLUSIONS

This study suggests that high-elevation regions within the Georgia Basin are sensitive to acidification from long-range atmospheric deposition from both local and distant sources. Moreover, surface water chemistry suggests that acidification has occurred under current emission levels and a significant number of catchments currently receive S deposition in excess of their CL(*A*). These regions are unable to efficiently buffer acidic inputs owing to the dominance of low buffering bedrock in their catchments and lack of vegetative land cover. In contrast, lakes at higher elevations show the unusual trend of having increased pH levels. This is most likely attributed to the decreased influence of organic anions and the abundance of glacial land cover contributing sediment rich melt waters to the catchments.

Increased monitoring of surface water chemistry and atmospheric deposition is imperative in further assessing the impacts on these catchments. Although S deposition has been considered the primary pollutant in acidification of surface waters, the role of N should not be ignored and research should be conducted to further understand the complex biogeochemical processes that lead to the acidification and eutrophication of high-elevation catchments and surface waters as a result of N deposition.

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