Chemical characteristics and acid sensitivity of boreal headwater lakes in northwest Saskatchewan

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ABSTRACT

Boreal ecosystems in northwest Saskatchewan may be threatened by acidification as this area is downwind of atmospheric emissions sources from regional oil sands mining operations. To evaluate the status of lakes in this region, a survey of 259 headwater lakes was conducted during 2007–2008 within ~300 km of Fort McMurray, Alberta. Acid sensitivity by ecoregion increased from Mid-Boreal Upland to Churchill River Upland to Athabasca Plain, with 60% of lakes classified as sensitive (50–200 μeq L^{-1} acid neutralizing capacity (ANC)), and 8% as very sensitive (<50 μeq L^{-1} ANC) to acid deposition. Organic anions dominated the acidity balance in most lakes, but non-marine sulphate varied positively with lake elevation and % upland cover (r^2 = 0.24). Base cation concentrations (Ca, Mg, K, Na) were correlated with % deciduous forest in the catchment area (r^2 = 0.33), while dissolved organic carbon (DOC) was related most strongly to % bog and lake flushing variables (r^2 = 0.53). Variation in runoff coefficients derived by isotope mass balance corresponded with catchment area attributes that proxy controls on evaporation, infiltration and storage, and showed some ecoregional differences. The findings have implications for assignment of runoff values required to calculate critical loads of acidity. Although acidification appears not to be significantly advanced, many dilute oligotrophic lakes with pH 6.0 to pH 6.5 are vulnerable to acid deposition.

Key words: acidification, lake chemistry, land cover, critical load, SSWC model, Canada

1. INTRODUCTION

Ecosystem acidification has been a phenomenon in eastern Canada and elsewhere for many decades (Environment Canada 2005). More recently, awareness of regional acidification liabilities in areas of western Canada has been increasing, particularly in relation to the rapid growth of the energy sector (Shewchuk *et al.* 1981; Hazewinkel *et al.* 2008). Acidification occurs when deposition of strong acid precursors (primarily sulphur (S) and nitrogen (N) oxides) in wet and dry forms exceed the base cation (BC) supply rate to the ecosystem from geological weathering and deposition. Ultimately, the chemical responses include a decline in pH of soils and surface waters, metal mobilization and toxic metal speciation, nutrient limitation, and increased UV radiation exposure in lakes due to declines in water colour (Mushak 1985; Gilmour & Henry 1991; Scully & Lean 1994; Schindler *et al.* 1996; Driscoll *et al.* 2003). Biological effects are adverse, as loss of aquatic biological diversity is common below pH of 6 and may result in complete loss of all higher trophic levels.

Acid neutralizing capacity (ANC) is a widely used index of the extent of surface water acidification and sensitivity to acidification, as it correlates with the direct biological stressors of pH and toxic aluminium species (Sullivan *et al.* 1989; Lydersen *et al.* 2004). The ANC of surface water is assumed to be governed by the size of the exchangeable BC reservoir in catchment area soils (Houle *et al.* 2006), modified by a variety of controls (Watmough *et al.* 2005). The hydrological coupling between lakes and ombrotrophic-minerotrophic wetlands (bogs and fens) is important, as wetlands tend to be significant sources of organic acids (Urban *et al.* 1989; Hemond 1990; Halsey *et al.* 1997; Prepas *et al.* 2001; Laudon *et al.* 2004; Keller *et al.* 2008), and redox sinks for S and N (Hem 1960; Rudd *et al.* 1990). Observed relationships between biological effects and acid-base chemistry have formed the basis for critical limits of ANC (ANC$_{limit}$), or pH limits required to minimize biological damage from acid deposition (Henriksen *et al.* 1995; Lien *et al.* 1996; Holt *et al.* 2003; Lydersen *et al.* 2004; Hesthagen *et al.* 2008). Critical load of acidity [CL(*A*)] models have been developed on the principles of steady-state acid-base mass-balance, and provide a practical method to link levels of acid deposition to biologically protective criteria (Henriksen & Brakke 1988; Curtis *et al.* 2001; Henriksen & Posch 2001).

There has been few extensive lake surveys carried out in northern Saskatchewan (Liaw & Atton 1981; Shewchuk 1983; UMA 2007; Jeffries *et al.* 2010, this issue). Jurisdictional monitoring in this region has
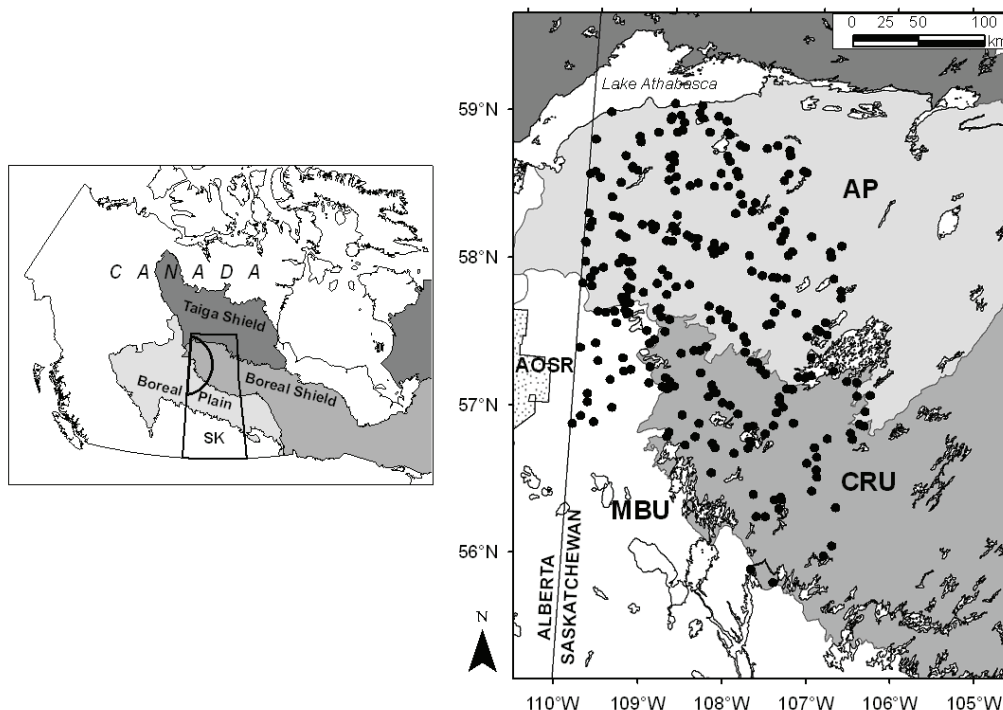
Fig. 1. Sampling domain and locations of 259 study lakes in Saskatchewan, showing their distribution across three ecoregions (AP = Athabasca Plain; CRU = Churchill River Upland [AP & CRU = Boreal Shield]; MBU = Mid-Boreal Upland [Boreal Plain]; AOSR = Athabasca Oil Sands Region - portion of approximate active mining area is shown).

tended to be of large lakes with relatively high ANC, that are unrepresentative of smaller and more numerous low order lakes. This study was motivated by the general lack of regional (and current) information and the need to develop an aquatic monitoring network. In this study, exposition of general relationships between lake chemistry and drainage basin attributes may contribute to the refinement of lake classification and prediction with respect to acid sensitivity and response regimes (c.f. Berg *et al*. 2005). This paper reports physical-chemical results from a survey of 259 headwater lakes assessed between 2007 and 2008, with an emphasis on measures pertinent to acidification. Ecoregional comparisons, and relationships between lake chemistry and drainage basin characteristics are discussed. Finally, CL(*A*) based on the Steady-State Water Chemistry (SSWC) model (Henriksen & Brakke 1988; Henriksen & Posch 2001) are compared using regional runoff versus site-specific runoff values to assess any systematic divergences with respect to landscape setting and catchment area characteristics.

2. STUDY AREA

The sampling domain intersected three ecoregions, ranked by proportion of the study area as Athabasca Plain (AP) > Churchill River Upland (CRU) > Mid-Boreal Upland (MBU) (Fig. 1). AP and CRU are physiographic divisions of the Boreal Shield ecozone. There are 15 defined landscape areas nested within the three ecoregions (not shown). The AP differs from the CRU

by having an overlay of younger sandstones, less basement rock exposure, and a mantle of thicker glacial deposits. The moraine is very sandy, so both deep and shallow groundwater linkages to lakes are expected to feature commonly across much of the AP and elsewhere according to soil porosity and ground moraine depths. The CRU has thinner veneers of glacial till, glaciofluvial, and glaciolacustrine deposits over crystalline Precambrian bedrock. However, the CRU and MBU within the study area retain similarities to the AP as a result of sandy morainal drifts transitioning from the AP. Well-drained upland positions are dominated by Brunisolic soils, with Luvisolic soils on silty and clayey glaciolacustrine deposits. In areas where dunes are active, Regosolic soils dominate, and especially feature in the Athabasca Sand Dunes area of the AP (Abouguendia 1981). Organic-Gleysols and local Cryosols dominate wetland areas, which vary from extensive plains found in the northwestern part of the AP to numerous local situations. The landscape varies from flat to strongly rolling, with distinctive upland areas. Localized relief can be as much as 90 m but is generally less that 60 m. Eskers and drumlin slopes are common features in some areas, where greater relief and incised lake settings occur. The elevation (for the study lakes) ranges from 210 m a.s.l. to 554 m a.s.l. Jackpine (*Pinus banksiana*)/lichen forest with variable canopy closure predominates on well-drained sand plains and till ridges throughout the area, and extensively on the AP. Black spruce (*Picea mariana*) forest with lesser frequencies of

mixedwood and hardwood forest (primarily jackpine /black spruce/white birch (*Betula papyrifera*)/trembling aspen (*Populus tremuloides*)) occur along intermediate moisture gradients and finer soils. Here, an increasing diversity of various tall and short shrubs and herbs are supported. Black Spruce dominates treed bogs, with lesser occurrences of Tamarack (*Larix laricina*) in fens. The climate is subarctic, presenting a latitudinal gradient. Mean annual, July, and January temperatures are ~2.3 °C, 16 °C, and –24 °C, respectively. Mean annual precipitation is in the order of 450 mm to 530 mm, with 288 mm to 318 mm falling as rain between May and September, with the lower values to the north. The prevailing wind is from the W-NW (Shewchuk *et al*. 1981; Acton *et al*. 1998).

3. METHODS

3.1. Lake selection

The study domain (56° to 59° latitude; −107° to −110° longitude) was defined by a 300 km radius extending into Saskatchewan from the estimated centroid of the active Athabasca Oil Sands Region (AOSR), north of Fort McMurray, Alberta, divided by 10 degree azimuth angle increments, and intersected at 25 km radial intervals. The final sampling grid was a subset of alternating distance-direction segments. Stream arc and lake polygon layers were obtained from a networked version of 1:50,000 scale Canadian National Topographic Series hydrography (Saskatchewan Ministry of Environment, v2) for the Athabasca and Upper Churchill basins. Connected polygons were stratified using Shreve link ≤5 of the terminal lake-path arcs to define a subset of headwater lakes. Random selections of ≤10 candidate lakes per segment of 10 to 400 ha were made, to include backup lakes. Several larger headwater (11), smaller headwater (6) and non-headwater lakes (3) were selected manually for special interest reasons, as backup lakes, and at the remote refuelling locations. In 2008, when 114 new lakes were sampled, those situated closest to optimized flight paths established in 2007 were prioritized. Candidate sites <1 m depth, or showing extensive macrophyte cover from the air were rejected. Non-headwaters were excluded from this analysis. By ecoregion, the number of lakes reported is: AP = 166, CRU = 70, MBU = 23.

3.2. Lake sampling and water chemistry

Lakes were sampled by helicopter during the lake circulation period in late September (148 lakes in 2007, and 200 lakes in 2008 of which 86 were repeats from 2007). Sampling locations were near the lake center, with repeated lakes informed by depth data recorded during the 2007 sampling. Lake water was collected at 1 m, coincident with water temperature, pH and conductivity (COND). Field preparation of samples occurred daily: filtrate was obtained using pre-rinsed, disposable syringe-filter assembly (pore size = 0.7 μm). For nitrate

(NO_3) and ammonium (NH_4), 20 mL of filtrate was acidified with 30 μL ultra-pure sulphuric acid and analyzed within 14 days. For cations, 50 mL of filtrate was acidified with 30 μL nitric acid. Un-acidified filtrate was stored refrigerated for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), silica (Si), sulphate (SO_4), chloride (Cl), colour (COL) and absorbance at 350 nm (ABS350). Total alkalinity (ALK) was measured by titration to pH 4.5 and Gran titration if <10 mg L^{-1} in 2007, and by both methods in 2008. Analytical quality control included blind submission of sample duplicates, blanks and certified reference standards. Chemical analyses were carried out by the Biogeochemical Analytical Laboratory, University of Alberta, Edmonton.

3.3. Drainage basin attributes and hydrology

Delineation of topographic drainage basin areas (DBA), and calculation of the lake-specific isotope mass balance (IMB) runoff (Q_{IMB}) and regional grid-based runoff (Q_{GRID}, 35 km × 35 km) are described by Gibson *et al*. (2010, this issue). Runoff coefficients were derived from Q_{IMB} normalized to 30-year climate-normal precipitation (1961–1990). Lake surface area (LA) excluded islands and was calculated from the hydrographic dataset. Lake water residence times (RT, years) were estimated as:

$$RT = (Z_{mean} \times LA)/[I - (E_L + P_L)] \quad (1$$

where Z_{mean} is the mean lake depth (m), I is the runoff volume ($Q_{IMB} \times$ [DBA - LA], m³ y^{-1}) and E_L and P_L are the lake surface evaporative loss (set to zero here) and direct precipitation to the lake (m³ y^{-1}), respectively. In the absence of complete bathymetry, Z_{mean} was assumed to equal $Z_{max} \times 0.5$ (approximated from Wetzel 2001). Depths were logged under a slowly moving helicopter on floats for 4 to 10 minutes using a recording sonar and global positioning system. In some lakes, recordings were made at more than one location.

DBA and catchment area (CA = DBA − LA) slope rasters were generated from the NASA Shuttle Topography Radar Digital Elevation Model (STRM DEM, 90 m horizontal resolution) using the slope tool in ESRI's Spatial Analyst extension. Mean percent slope (SLOPE) was calculated as the average cell slope value for each DBA and CA. Lake elevation (ELEV) was extracted from the STRM DEM. Additional CA attributes were derived from the Northern Digital Land Cover (NDLC) (Hall *et al*. 2002). The NDLC is based on a combination of Landsat 5 Thematic Mapper data representing *ca* 2000 conditions. Existing classifications for hardwood (HW), mixedwood (MW), jackpine (JP), spruce (SPR) (where JP + SPR = softwood) were supplemented with derived classes as coniferous (CONIF = softwood + mixedwood × 0.5), broadleaf deciduous (DECID = hardwood + mixedwood × 0.5), wetland (WETL = treed and open BOG + FEN), CA surface water area (CSW), and upland (UPLAND = CA − WETL − CSW) for each

CA. Fire history requires elaboration for further analysis, but a variable combining recent (*ca* 2000) and regenerating burn areas was included (BURN).

3.4. Critical loads of acidity

CL(*A*) calculations used the formulation of SSWC model described by Henriksen & Posch (2001). Lake BC and SO_4 were sea-salt corrected (signified as *) assuming all Cl comes from marine sources. Common "default" model values, as applied in eastern Canada were used. The model calculates a long-term (time-invariant) annual acidity flux protective of a chosen ANC_{limit} for a sensitive indicator organism, as:

$$CL(A) = Q \times ([BC^*]_0 - [ANC]_{limit}) \qquad (2$$

where Q is the mean annual watershed runoff (m y^{-1}), and $[BC^*]_0$ is the pre-acidification BC concentration. Lake-specific ANC_{limit} (Henriksen *et al*. 1995) was set at 10 µeq L^{-1}, scaled to account for organic acidity: $[ANC]_{limit} = (10 + 10.3/3 \times [DOC])$, where 10.3 represents a generalized charge density per unit mass of DOC (Lydersen *et al*. 2004). $[BC^*]_0$ is estimated from the present day base cations, $[BC^*]_t$, using the so-called *F* factor, as:

$$F = \sin\left(\frac{\frac{\pi}{2} \times Q \times [BC^*]_t}{S}\right) \qquad (3$$

where S is the base cation flux at which $F = 1$. The value of S has been estimated to be 400 meq m^{-2} y^{-1} from studies in Norway, and this value has been been applied in eastern Canada (Henriksen *et al*. 2002; Watmough *et al*. 2005; Watmough & Aherne 2008), and was used in this study. Pre-industrial sulphate $[SO_4^*]_0$ was estimated as:

$$[SO_4^*]_0 = 8.0 + 0.16 \times [BC^*]_t \qquad (4$$

Different coefficients have been estimated for Eqn 4 (Henriksen & Posch 2001). However, since Eqn 4 was constrained so that $[SO_4^*]_0$ could not be greater than the observed SO_4^*, CL(*A*) was not very sensitive to moderation of these coefficients.

3.5. Data screening and analysis

In summary, the dataset analyzed here consisted of 16 chemical variables: Ca, Mg, Na, K, NH_4, aluminium [Al], SO_4, NO_3, Cl, organic anions [OA], ALK, DIC, DOC, COL, pH, COND, and 15 environmental variables (LAT, ELEV, SLOPE, LA, CA, Z_{max}, RT, Q_{IMB}, %CSW, %BOG, %FEN, %CONIF, %DECID, %UPLAND, %BURN). For 86 lakes that were sampled over two years, the average of the variable was used. (Time is not treated here, but COND, ANC, Ca, Mg, K, and SO_4 were not statistically different between the two years. Average DOC statistically increased in 2008 [6.2 *vs* 6.7 mg L^{-1}], and average Na statistically decreased

[1.15 *vs* 1.03 mg L^{-1}]). Free OA concentration was estimated according the pH-equilibrium model of Oliver *et al*. (1983), modified to a charge density of 7.5 µeq mg^{-1} DOC, as determined from electro-neutrality optimization of all samples from the study sites. To maintain independence of charge components from partial pressure of CO_2, organic adjusted ANC was calculated according to Lydersen *et al*. (2004): $ANC_{oa} = ([Ca] + [Mg] + [K] + [Na]) - ([SO_4] + [NO_3] + [Cl] + 3.43 \times [DOC])$, where DOC is in mass units. To meet normality assumptions for parametric tests, univariate distributions were tested for skewness and kurtosis and $\log_{10}$, arcsine-power (% landcover classes only) or power (SLOPE only) transformed, except pH, ELEV and LAT. Pearson least-squares correlation matrices were generated to assess the strength and significance of relationships between the environmental and DBA variables (Bonferroni-adjusted significance probabilities, $0.05 \geq p \leq 0.01$). Student's *T*-tests for significant differences were based on permutation procedures (999 randomizations) using untransformed data. Multiple regression models were derived using a forward stepwise procedure. Analyses were conducted with Statistica v6 (StatSoft Inc. 2001).

4. RESULTS AND DISCUSSION

4.1. Lake chemistry and ecoregional comparisons

The percentile distributions for BC and ANC_{oa} indicate a high degree of acid sensitivity among the lakes: 60% were sensitive (50–200 µeq L^{-1} ANC_{oa}), and a further 8% highly sensitive (<50 µeq L^{-1} ANC_{oa}) to acid deposition (Tab. 1). The remaining 32% of lakes were well buffered to acid deposition (>200 µeq L^{-1} ANC_{oa}). For all lakes, the average percent of BC (as equivalents) was Ca (41%), Mg (27%), Na (26%), and K (4%). Ca and Mg were strongly correlated ($r = 0.91$, $p <0.01$). Na and K were correlated with each other ($r = 0.71$, $p <0.01$), and with hardness [HARD = Ca + Mg] ($r = 0.77$ and 0.71, respectively, $p <0.01$). COND (range, 6–282 µS cm^{-1}, median 18 µS cm^{-1}) was highly correlated with ANC_{oa} ($r = 0.98$, $p <0.01$).

The major ion data indicated that OA was the dominant acidifying ion, being typically more than double the SO_4 equivalents (Tab. 1). DOC distributions were skewed towards a low/intermediate quartile range, with an overall mean of 6.7 mg L^{-1}. DOC was considerably lower than typical averages described from surveys of Boreal Plain lakes in northern Alberta or Northwest Territories (e.g., Moser *et al*. 1998; McEachern *et al*. 2000; Prepas *et al*. 2001; Rühland *et al*. 2003; WRS 2004). Chloride was low in most lakes (75th percentile <10 µeq L^{-1}). However, in 7 lakes (6 of 41 lakes within the Carswell Plain area of AP) high Cl resulted in negative SO_4^*. These lakes were in the 95th percentile of Cl concentrations (Tab. 1), with Na/Cl ratios 0.2 to 0.7, and high average Ca and Mg concentrations (625 µeq L^{-1} and 627 µeq L^{-1}, respectively). Collectively, these ratios

Tab. 1. Characteristics of the 259 headwater study lakes: (**a**) lake chemistry; (**b**) drainage basin characteristics. ANC_{oa}, organic acid adjusted Acid Neutralizing Capacity; SO_4^*, +ve non-marine sulphate (n = 252); OA, organic anions; LA, lake area; Z, sampling location depth; R, catchment area/LA ratio; CONIF, coniferous forest; DECID, deciduous forest; CSW, catchment area surface water; †, grid based runoff (Q_{GRID}) & isotope mass balance runoff (Q_{IMB}) from Gibson *et al.* (2010).

(a)	pH	Alk	ANC_{oa}	Na	K	Ca	Mg	Al	NH_4	Cl	NO_3	SO_4	SO_4^*	OA	DOC
							(μeq L^{-1})								(mg L^{-1})
Minimum	5.4	6	10	25	1	10	10	0.1	0.2	1	0.0	2.3	0.0	10	1.3
10th percentile	6.3	47	57	33	4	51	22	0.1	0.8	3	0.0	8.3	7.8	18	2.5
25th percentile	6.6	81	90	39	6	54	32	0.2	1.1	4	0.1	11.9	11.3	27	3.7
Median	6.9	127	136	50	8	79	48	0.5	1.6	6	0.1	17.1	16.2	41	5.7
75th percentile	7.1	239	238	65	12	127	96	1.6	2.3	10	0.3	24.2	23.0	62	8.7
90th percentile	7.3	468	440	85	21	235	167	4.2	5.0	32	0.8	34.6	33.0	94	13.0
Maximum	8.3	2608	2290	167	35	1166	1312	14.0	72.1	573	12.0	67.7	67.6	186	25.3

(b)	LA	Z	R	Slope	BOG	FEN	CONIF	DECID	CSW	UPLAND	Q_{GRID} †	Q_{IMB} †	Elevation
	(ha)	(m)					(%)				(mm)	(mm)	(m asl)
Minimum	3	1.0	1.2	0.2	0.0	0.0	0.5	0.0	0.0	13.5	84	4	210
10th percentile	18	1.5	2.4	1.2	0.3	0.0	33.4	0.0	0.0	65.1	98	33	317
25th percentile	34	1.9	4.3	1.8	2.5	0.1	51.0	0.3	0.0	75.8	102	64	423
Median	69	4.4	7.4	3.1	7.4	0.1	66.8	1.6	1.7	84.6	109	123	485
75th percentile	142	9.1	16.6	4.4	16.2	2.3	79.2	4.4	5.6	94.5	115	204	511
90th percentile	257	15.8	36.6	6.5	26.1	9.3	86.5	10.5	11.1	97.8	119	331	530
Maximum	3160	49.2	369	10.1	88.1	42.3	98.3	65.9	22.7	100.0	120	697	575

suggest reverse softening processes involving halite and dolomite weathering. Excluding these cases, the assumption that all Cl is from marine sources appears valid. Should geological Cl be included, correcting to non-marine fractions would result in a more conservative estimate of SO_4^*, while its effect on the BC* would lower CL(*A*). However, since cases of high Cl were associated with high BC the practical implications (for exceedance) would be small and have minor effect on percentile distributions of CL(*A*) in a large dataset dominated by low Cl. SO_4^* concentrations were relatively low but upper values were more than double the 75th percentile (Tab. 1). NO_3 and NH_4 concentrations were very low in most lakes and contributed little to the ANC, indicating that most N deposition is currently retained (refractory storage) or lost (e.g., fire, denitrification) from the drainage basins. Total dissolved Al concentrations were low, consistent with most lakes having pH >6.0 (Sullivan *et al.* 1989). Al was correlated with DOC ($r = 0.67$, $p < 0.01$) and covariates, COL and ABS350 ($r = 0.8$, $r = 0.75$, respectively, $p < 0.01$), consistent with organic complexation. The higher correlation between Al (assumed to be transported in runoff) and COL suggest that the internal-external source balances for DOC affects the COL/DOC ratio. This is discussed further below with respect to CA characteristics, and is consistent with studies that suggest autochthonous lake DOC may diverge in humic acid content relative to allochthonous DOC generated in wetlands (and upland soils), with higher proportion of fulvic acids and contrasting acidic properties (Kahl *et al.* 1989; Wilkinson *et al.* 1992; Siegel *et al.* 2006). Indeed, COL had a higher correlation with pH than did DOC ($r = -0.36$ and $r = -0.17$, respectively, $p < 0.01$), suggesting that COL may resolve some of the variability in DOC charge den-

sity and functional group dissociation. The correlation between COL and DOC ($r = 0.77$, $p < 0.01$) was higher than found by Prepas *et al.* (2001) for Boreal Plain lakes in Alberta ($r = 0.69$), but lower than McEachern *et al.* (2000) ($r = 0.94$) on peatland dominated lakes in northern Alberta. In this study, higher variability among CA settings with respect to bogs, fens, upland areas, and other morpho-hydrological attributes are likely to control the variation.

Only 7 lakes had pH <6.0 (Tab. 1, Fig. 2). These lakes were shallow (<3.8 m) and very dilute (6–13 μS cm^{-1}), where OA accounted for 50 to 80% of the anions, while SO_4^* accounted for 5 to 32% of the anions.
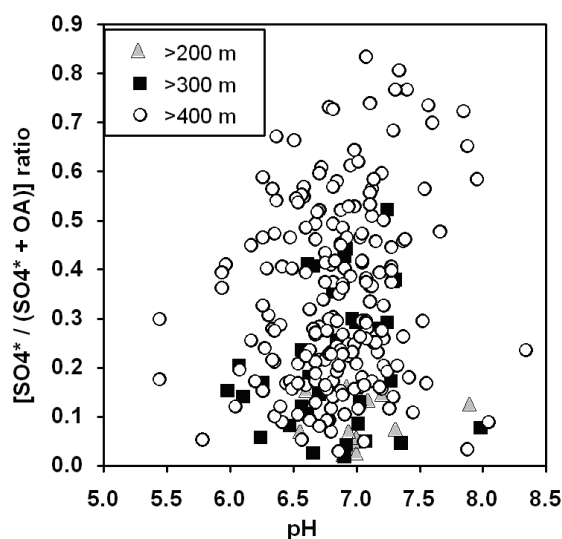

Fig. 2. Distribution of non-marine sulphate [SO_4^*] to organic anion [OA] ratio *vs* pH, categorized by elevation of the study lakes (m a.s.l.; n = 252).

These lakes are not acidified, but represent a vulnerable class of very dilute, low ANC lakes in the dataset, with variable DOC and pH <6.5 (16% of lakes). The ratios of mineral to organic acidity were highly variable across the observed pH range, however lakes situated at the highest elevations had a higher average proportion of SO_4* relative to OA ($r = 0.44$, $p <0.01$) (Fig. 2). This is discussed below with respect to DBA attributes.

Tab. 2. Comparison of significant differences (two-tailed *T*-test results, 999 permutations) of selected variables across the three ecoregions intersected by the study domain (Athabasca Plain [AP], Churchill River Upland [CRU], Mid-Boreal Upland [MBU]). +: significant at $p \leq 0.05$; ++: significant at $p \leq 0.01$. Blank cells indicate no significant difference. (CA, lake catchment area; RT, lake flushing rate; other abbreviations as given in table 1).

	CRU *vs* MBU	AP *vs* MBU	AP *vs* CRU
pH	+	++	++
Conductivity	++	+	
ANC_{oa}	++	++	
Alkalinity	++	+	
DIC	++		
ABS350		+	+
COL			
DOC			++
Cations (µeq L^{-1})			
NH_4			+
Al	+	+	
Ca	++	+	
Mg	+		
Na		++	++
K		++	++
Fe			
Mn			
Anions (µeq L^{-1})			
HCO_3	++	+	
OA			++
NO_3			
Cl			++
SO_4		+	
(SO_4*)		++	
(SO_4* / SO_4* + OA)			
Morphology and Hydrology			
LK AREA	+	+	
DEPTH			++
DEPTH/LK AREA			
LK ELEVATION		++	++
CA			
CA/LK AREA			+
Q_{GRID}	++		++
Q_{IMB}	++	+	
$Q_{GRID} - Q_{IMB}$	++	+	
RT (years)			+
% SLOPE	++		++
Catchment Area Landcover			
% BOG	++	+	++
% BURN	++	++	
% CONIF		++	++
% DECID			++
% FEN	+		++
% CSW		++	+
% ROCK			++
% UPLAND	++		++

Statistical difference tests by permutation for both lake chemistry and DBA variables are summarized in table 2. The ANC-ALK-DIC cluster and covariables COND and HARD, showed consistent differentiation: Boreal Shield (AP and CRU) lakes were statistically different (lower) than Boreal Plain lakes. Conversely, Na and K were different between the AP (lower) and CRU, but not between CRU and MBU, consistent with lesser influence of igneous rock types in the AP (Acton *et al.* 1998). MBU lakes had higher average and median hardness (435 µeq L^{-1} and 306 µeq L^{-1}, respectively), compared to Boreal Shield lakes (198 µeq L^{-1} and 129 µeq L^{-1}, respectively) (Fig. 3). Spatially restricted maxima for hardness were evident in Boreal Shield areas (notably, Carswell Plain, Pinehouse Plain and Frobisher Plain – not shown), where younger Ordovician and Silurian carbonate rocks become evident. For all lakes, the average Ca/Mg ratio was 1.6 (range 0.3 to 3.4, median 1.6) and average Ca/Na ratio was 2.0 (range 0.2 to 11.4, median 1.7) (Fig. 4). Only 31 lakes had Ca/Mg ratio <1 (24 in AP and 7 in CRU, none in the MBU). Therefore, the significantly higher average hardness observed for MBU lakes is prevalently calcite derived. Several Shield lakes with higher hardness had Ca/Mg ratios close to 1, indicative of localized dolomite (notably Carswell Plain) (Fig. 4a). In addition, all these higher hardness lakes had Ca/Na ratios >4, consistent with carbonate weathering (Drever & Hurcomb 1985). Ca/Na ratios were much lower in most Shield lakes (10th and 90th percentile, 0.76, 2.87; median, 1.63), indicative of silicate weathering (Fig. 4b). Most lakes (97%) had Ca/SO_4 ratio >1 (range 0.3 to 336, median 4.8). DOC and OA were significantly different between AP (lower) and CRU only, reflecting regional variability in DBA characteristics discussed below. Both SO_4 and SO_4* were statistically different between the AP (lower) and MBU only, indicating a latitudinal difference (discussed further below). The [SO_4*/(OA+SO_4*)] ratio was not statistically different among the ecoregions, since on average these ion concentrations were directionally similar (Tab. 2).

For drainage basin attributes (Tabs 1b and 2), the average lake elevations sampled on the AP were statistically different (lower) than those of the CRU and MBU, reflecting the elevation gradient of the study area being lower to the north. This is important since a number of DBA and lake chemical attributes were related to ELEV, as discussed below. As a result of the ecoregion sample sizes and variable densities of candidate lakes, average LA was statistically different between Boreal Shield lakes and those on the MBU for both the random population (10 to 400 ha) and the full dataset. CA and DEPTH/LA ratios were not significantly different among the ecoregions.

However, CA/LA ratios were statistically different between the CRU (lower) and AP, with steeper average SLOPE and a higher average %ROCK (Tab. 2).
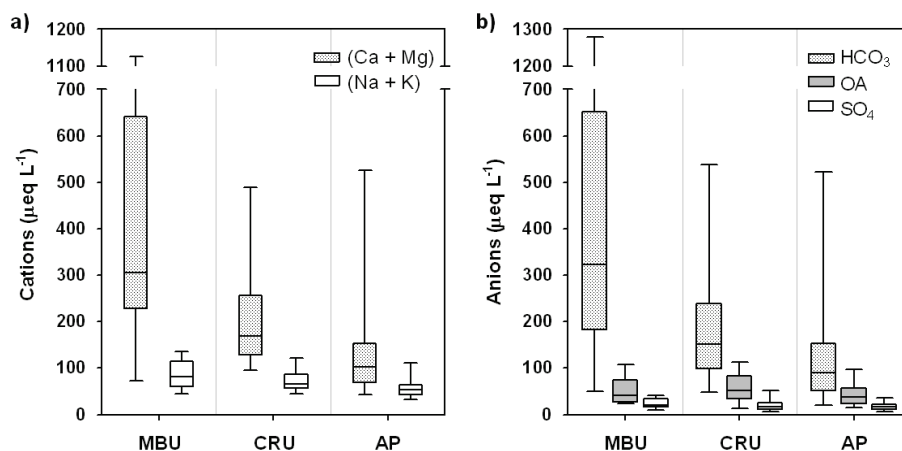
Fig. 3. Chemical distributions for the 259 survey lakes: (**a**) major cations; (**b**) anions (nitrate not shown as concentrations were negligible); categorized by ecoregion: MBU = Mid-Boreal Upland, n = 23; CRU = Churchill River Upland, n = 70; AP = Athabasca Plain, n = 166. OA = organic anions. (Box: upper and lower quartiles; Whisker: 5th and 95th percentiles; Line: median).
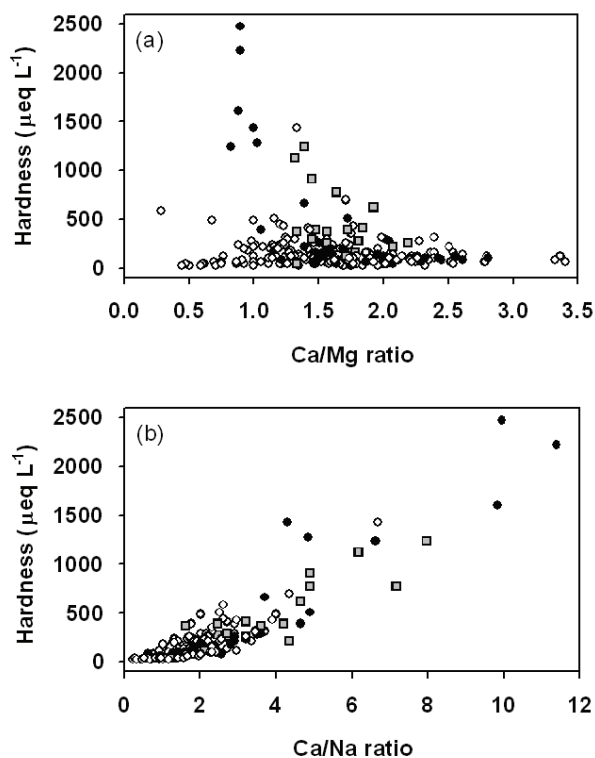

Fig. 4. Variation in hardness [Ca+Mg] in relation to (**a**) Ca/Mg ratio and (**b**) Ca/Na ratio, for the study lakes (n = 259). Distinctions are made to emphasize changes in cation ratios in two areas with high hardness lakes (solid circles: Boreal Plain lakes; filled squares: Carswell Plain area of Boreal Shield; open circles: all other Boreal Shield lakes).

In those cases, there would a tendency for flashier runoff responses to precipitation (i.e. less infiltration, higher runoff coefficients). Similarly, the CRU had steeper average SLOPE than the MBU (Tab. 2). Several upland areas on the AP had higher median and maximum SLOPE than the CRU (data not shown), but

the higher sample size and representation on extensive low relief plains on the AP lowered average SLOPE. With higher SLOPE came a tendency for smaller CA/LA ratios ($r = -0.26$, $p < 0.01$, n = 259).

4.2. DBA attributes and relationships to DOC

For all lakes, DOC was most related to %BOG and DEPTH ($r = 0.6$ and $r = -0.51$, respectively, $p < 0.01$). DOC had weaker positive correlations with %DECID, and %FEN ($r = 0.31$, $r = 0.21$, respectively, $p < 0.01$), and negative correlations with %UPLAND, %BURN, %CONIF, %CSW, ELEV, and SLOPE ($r = -0.46$, $r = -0.23$, $r = -0.22$, $r = -0.26$, $r = -0.31$, and $r = -0.22$, respectively, $p < 0.01$). For hydrology, RT retained sufficient independence with DEPTH to be included in a multiple regression model, which explained 53% of the variation in DOC (Eqn 5).

$$\log(DOC) = 0.74 + 0.47 \times \arcsin(\%BOG^{0.33}) - 0.74 \times \log(DEPTH) + 0.45 \times \log(RT) \quad (5$$
$$r^2 = 0.53$$

Consistent with other studies on Boreal Plain and Boreal Shield lakes (D'Arcy & Carnigan 1997; Prepas *et al*. 2001) and elsewhere, the data indicate that bogs and to lesser extent fens are external sources of DOC to these lakes. Some of the model error likely relates to lack of both spatial and temporal resolution for hydrological connectivity to external DOC generating environments, which may range from zero to highly influential and proximate sources, as well as cryptic wetlands (Creed *et al*. 2003). The negative relationship between DOC and DEPTH is consistent with DOC being subject to in-lake transformation and loss processes (Rasmussen *et al*. 1989), as well as potential for diminished autochthonous production by depth-related nutrient dynamics (Vollenweider 1975). Eqn 5 shows that the partial effect of RT independent of DEPTH (although small at 6%) became positive for

DOC. This partial effect of RT may relate to evapo-concentration and reduced outflow losses. Keller *et al.* (2008) concluded that pH changes in 12 Shield lakes in Ontario were related to variation of DOC and temperature, and that weather affected DOC production and net export from catchment area sources. Therefore, climate change will have implications for acidity balances in these lakes. An improved wetland classification would be useful for the study area to better differentiate ombrotrophic-minerotrophic types. With these factors in mind, and based on the unexplained portion of DOC variability, upland dominated lakes are likely to have proportionately more internally generated DOC. The negative relationship of DOC with SLOPE was directionally consistent with Prepas *et al.* (2001) ($r = -0.4$) for Boreal Plain lakes, and with D'Arcy & Carnigan (1997) for Boreal Shield lakes ($r = -0.63$).

4.3. DBA attributes and relationships to sulphate

For all lakes, SO_4* was correlated positively with ELEV, SLOPE, DEPTH, Q_{IMB} and %UPLAND ($r = 0.43$, $r = 0.31$, $r = 0.26$, $r = 0.26$, $r = 0.26$, respectively, $p < 0.01$, n = 252), and negatively with LAT, %BOG and CA/LV ($r = -0.28$, $r = -0.22$, -0.24, respectively, $p < 0.01$). ELEV and %UPLAND were statistically independent for the full dataset ($r = 0.01$). %BOG had only a weak negative relationship with ELEV ($r = -0.15$, $p < 0.05$), whereas SLOPE was more related to a decline in %BOG ($r = -0.33$, $p < 0.01$). SLOPE and DEPTH tended to increase with ELEV ($r = 0.35$, $r = 0.32$, respectively, $p < 0.01$). ELEV and %UPLAND explained 24% of the variability in SO_4* (Eqn 6).

$$\log(SO_4\text{*}) = 0.22 + 0.41 \times \text{ELEV} + \\ + 0.22 \times \arcsin(\text{\%UPLAND}) \quad\quad (6 \\ r^2 = 0.24$$

By ecoregion, the strongest comparative two-variable models for AP, CRU and MBU lakes included: ELEV and %UPLAND ($r^2 = 0.32$), CA/LV and ELEV ($r^2 = 0.23$), and LAT and %BOG ($r^2 = 0.37$), respectively. Therefore, Eqn 6 is influenced most strongly by the AP lakes, which are situated at higher average latitude and differing geology. In the model for MBU lakes, LAT was a better predictor than ELEV by ~15%, but is probably spurious. CRU had the highest average runoff coefficients (discussed below) among the ecoregions, but also the highest average depths and RT. The relationship between CA/LV and SO_4* for CRU lakes ($r = -0.43$, $p < 0.01$) may involve higher in-lake evapo-concentration in larger volume, higher RT lakes. Lower productivity in deep lakes might also diminish in-lake S reduction.

Overall, a lack of independence of ELEV from LAT ($r = -0.6$, $p < 0.01$) makes it difficult to assert a spatial relationship between lake SO_4* concentration and S emissions from the AOSR. LAT and distance from the AOSR explained 10% of the variability in SO_4* (com-

pared to 18% by ELEV). Deposition of pollutant S may be expected to occur on a concentration-distance gradient, broadly constrained by westerly prevailing wind direction. However, SO_4* concentrations were not statistically different between MBU and CRU (mean, 23.3 µeq L^{-1} and 20.4 µeq L^{-1}, respectively). There was a statistically significant difference between SO_4* concentrations on MBU (higher) and AP (mean 17.3 µeq L^{-1}). While this could hypothetically construe a latitudinal gradient of pollutant S deposition, geological S (Eqn 4) and differences pertaining to DBA attributes and annual precipitation cannot be discounted. Also, the effect of evaporation from Lake Athabasca has potential to influence the ionic characteristics of precipitation in that area (Fig. 5). Questions pertaining to impacts would be better informed by paleolimnological investigations and monitoring.

The within ecoregion variability of ELEV was highest for AP lakes, but similar between MBU and CRU lakes (CV = 20.5%, 6.8%, 6.3%, respectively). Variability of (log) SO_4* was also slightly higher for the AP compared to CRU and MBU (CV = 25.6%, 20.5% and 20.9%, respectively). Thus, the larger range of lake elevation sampled on AP probably subsumes more of the variability of mechanisms influencing delivery and storage/attenuation of S compared to the other ecoregions. %UPLAND is inversely related to the sum of wet landscape classes, so these tend to lack statistical independence. Inclusion of multiple landcover classes would over fit the regression models, but the mechanistic ambiguity between upland and lowland in Eqn 6 is exemplified by the importance of %BOG for MBU lakes. Upland dominated catchment areas with higher slopes and lower percentages of wetland may have lower net immobilization of SO_4 (as sulphide) within low-redox environments upstream of lakes (Hem 1960). Alkalinity generation by SO_4 reduction may be up to 10^3 higher at the sediment surface relative to the water column (Wetzel 2001), so unaccounted variability in related factors within catchment areas are likely to be a significant source of model error in Eqn 6. Seasonality of sulphur exports to the lakes relative to flushing rates, and spatio-temporal variability of water table heights affecting oxidation and mobilization of reduced S are obvious sources of variability in lake SO_4 concentrations.

4.4. DBA attributes and relationships to base cations

For all lakes, Ca, Mg, Na, K and total BC were positively related to %DECID ($r = 0.54$ and $r = 0.59$, $r = 0.49$, $r = 0.43$, $r = 0.57$, respectively, $p < 0.01$). Conversely, Ca, Mg, Na, K and total BC were negatively related to %CONIF ($r = -0.17$, $r = -0.19$, $r = -0.15$ [$p < 0.05$], $r = -0.17$, $r = -0.18$, respectively, $p < 0.01$) and ELEV ($r = -0.16$ [$p < 0.05$], $r = -0.27$, $r = -0.32$, $r = -0.29$, $r = -0.25$, respectively, $p < 0.01$). The simple rela-
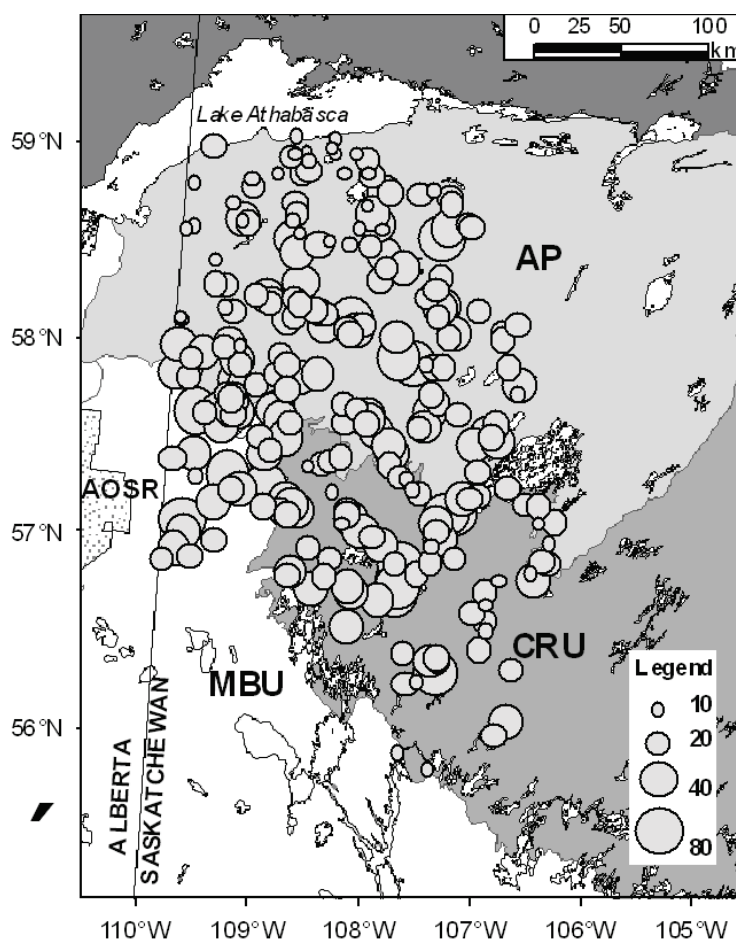
Fig. 5. Spatial distribution of positive non-marine sulphate concentration (μeq L^{-1}) for the study lakes (n = 252), representing 2007–2008 conditions. (AP = Athabasca Plain; CRU = Churchill River Upland [AP & CRU = Boreal Shield]; MBU = Mid-Boreal Upland [Boreal Plain]; AOSR = Athabasca Oil Sands Region – portion of approximate active mining area is shown).

tionship with %DECID explained up to 33% of the variability in HARD and BC (Eqn 7 and 8):

$$\log(HARD) = 1.69 + 0.57 \times \arcsin(\%DECID^{0.25}) \quad (7$$
$$r^2 = 0.32$$

$$\log(BC) = 2.0 + 0.58 \times \arcsin(\%DECID^{0.25}) \quad (8$$
$$r^2 = 0.33$$

Inclusion of up to 3 additional terms (ELEV [–], DEPTH [+] and CA/LA [+]) for both models provided increments of independent explanation of 2–3% each up to a final r^2 of 0.41 for BC (not shown). By ecoregion, %DECID remained the strongest single predictor of HARD (followed by ELEV) for both the MBU ($r = 0.64$, $p < 0.01$) and the AP ($r = 0.55$, $p < 0.01$). Both of these ecoregions contained some lakes influenced by carbonate weathering, as previously discussed. When carbonate influenced lakes on the Carswell Plain landscape area were removed from the AP, a much smaller (but still dominant) correlation between %DECID and HARD remained ($r = 0.28$, $p < 0.01$). For CRU lakes, ELEV was the strongest correlate of BC and HARD ($r = 0.61$ and $r = 0.58$, respectively, $p < 0.01$), whereas

%DECID was less correlated ($r = 0.40$ and $r = 0.38$, respectively, $p < 0.01$). This suggests that for the CRU (and elsewhere), catchment areas of higher elevation lakes probably have smaller BC reservoirs because of thinner (or leached) soils. Thus, the practical utility of Eqn 7 and 8 may only be as a qualitative rank of BC potential. In large part, mixedwood boreal forest reflects stand age, successional state, and fire history, and is subject to degrees of transience. Serotinous jackpine forest dominating the CONIF class on thin and sandy soils within the study area are deemed a more stable forest type. Overall, the association of deciduous dominated stand types and lake BC concentrations may reflect finer and possibly deeper soils having more optimal moisture gradients, with propensity for higher BC weathering and soil cation exchange capacities, but also potential shifts from silicate to carbonate mineralogy at the extremes of the relationship. Houle *et al.* (2006) showed by direct measurement that soil exchangeable Ca and Mg reservoir sizes were strongly related to lake concentrations (and ANC) in 21 Shield headwater lakes in Québec. Thus, inferring high %DECID to reflect soil properties conducive to larger

Tab. 3. Summary critical loads of acidity (meq m^{-2} y^{-1}) for the 259 headwater lakes, calculated by ecoregion, using two different estimates of runoff [Q_{GRID}, grid-based runoff method; Q_{IMB}, isotope mass balance method (Gibson *et al.* 2010)].

| | Q_{GRID} method | | | | Q_{IMB} method | | | | Difference |
	Athabasca Plain	Churchill River Upland	Mid-Boreal Upland	All	Athabasca Plain	Churchill River Upland	Mid-Boreal Upland	All	($Q_{IMB} - Q_{GRID}$) All
Minimum	2.7	6.9	7.6	2.8	0.7	4.5	2.3	0.7	−2.1
5th percentile	5.0	9.8	8.9	5.7	1.9	7.5	3.4	2.6	−3.1
25th percentile	8.7	15.6	24.3	10.4	5.0	16.6	8.9	7.4	−3
Median	12.4	19.4	40.8	15.5	12.5	28.3	21.5	18.2	2.7
75th percentile	17.6	30.9	79.7	25.2	31.1	55.9	66.9	38.8	13.6
95th percentile	57.5	60.7	110.2	88.4	80.6	142.1	136.1	120.1	31.7
Maximum	222.9	142.3	130.8	222.9	337.9	171.2	150.4	337.9	115
Mean	19.8	25.9	50.9	24.2	26.4	44.3	40.2	32.5	8.3

exchangeable BC reservoirs would be a reasonable hypothesis. In addition to soil reservoir size, Houle *et al.* (2006) found that elevation increased the predictability of lake K, and hypothesized this reflected a positive relationship with increasing deciduous forest. So, in addition to the size of exchangeable BC reservoirs in soils, surface water concentrations may be enhanced by differences in biological cycling of BC in deciduous *vs* coniferous forest (Duschesne *et al.* 2001). Concentration of BC in soil solution by higher evapo-transpiration in deciduous forest may increase runoff concentrations. The extent to which soil cation exchange with H$^+$ and Al^{3+} may be involved in elevating lake BC concentrations is the study lakes is not known (c.f. Aherne 2008).

4.5. Critical loads of acidity and runoff

Percentile distributions of CL(*A*) calculated by the SSWC model for the study sites are summarized in table 3. CL(*A*) using Q_{GRID} provides a reference from which divergence among the lake-specific Q_{IMB} can be assessed. For all lakes, 46 % of CL(*A*) decreased using Q_{IMB}. The average magnitude of CL(*A*) differences for all lakes using Q_{IMB} (±meq m^{-2} y^{-1}) were: decrease (-3), increase (+28), and overall change (+8.3). Q_{IMB} resulted in a 14% increase in the number of lakes having CL(*A*) <20 meq m^{-2} y^{-1}, which can be regarded as a vulnerability threshold of priority interest for this region. For Boreal Shield lakes, the greatest increases (proportion of lakes and magnitude) in CL(*A*) occurred on the CRU using Q_{IMB} (more runoff) compared to the AP. This is directionally consistent with differences in SLOPE and %ROCK between study lakes in the two ecoregions described above, and likely to increase runoff coefficients. Conversely, 52% of AP lakes had lower CL(*A*) using Q_{IMB} (less runoff), compared to only 21% of CRU lakes. Again, the general trend is consistent with a greater infiltration opportunity in the deeper sandy moraines of the AP. Interestingly, 78% of MBU lakes had lower CL(*A*) using Q_{IMB} (less runoff), and this is also consistent with reduced yields from flatter topography.

CA and %FEN collectively explained 23% of variation in the runoff coefficients for Q_{IMB} (based on climate normal precipitation). With CA excluded from the model, underlying mechanistic factors and directions of influence were exemplified (%CSW [–], SLOPE [+], %FEN [+], %DECID [–], r = 0.43), representing the interaction of evaporation and transpiration, infiltration and transport, and depressional storage. The positive coefficient for %FEN might reflect short RT (less unit evaporation) relative to that of CSW (i.e. upstream lakes), and proportionately less upland cover for transpiration. Alternatively, net groundwater support to some fens could be involved. This analysis has been limited by the resolution of the DEM, use of climate normal precipitation values relative to site-specific resolution of Q_{IMB}, and the fact that soil variables are missing. However, comparing ecoregions, the average runoff coefficients demonstrate the general differences discussed for CL(*A*) (CRU = 0.36; AP = 0.31; MBU = 0.21). The overall average runoff coefficient for Q_{GRID} was 0.26. Interpretation may be improved by examining the extent to which Q_{IMB} based a single autumn water sample corresponds with seasonal samples, and relationships with empirical precipitation data. As time series accrue for these lakes by monitoring, an empirical assessment of temporal variation in the F factor will be possible, and the role of chemical *vs* site-specific runoff variation can be quantified.

5. CONCLUSIONS

Many headwater lakes situated on the Boreal Shield in northwest Saskatchewan are characterized by a high degree of acid sensitivity. Potential for exceedance of steady-state critical loads is high. Continued monitoring in the region is required to support effective policy development for present and future air emissions arising from regional economic development opportunities. On the basis of ANC and pH distributions, acidification of lakes is not advanced across the study region, but results indicate that low Ca is a prevalent state. Among other negative effects, Ca stress may increase susceptibility of biota to UV (Hessen & Rukke 2000), while Kratz *et al.* (1997) suggested that low-order lakes already low in calcium and magnesium may express drought and longer-term climate change by decreases in these cations, compared to high-order lakes that may increase through greater evapo-concentration. Therefore, many of the headwater lakes assessed in this survey could

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