Recently surveyed lakes in northern Manitoba and Saskatchewan, Canada: characteristics and critical loads of acidity

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ABSTRACT

Based on minimal information, lakes in the western Canadian provinces of Manitoba (MB) and Saskatchewan (SK) have long been considered unaffected by acid rain. However, emissions of acidifying pollutants from MB smelters and oil sand processing in Alberta (AB) may pose a developing threat. Surveys of 347 lakes located on geologically sensitive terrain in northern MB and SK were conducted to assess their acidification sensitivity and status. The survey domain (~193,000 km²) contained 81,494 lakes ≥1 ha in area. Small lakes dominated the inventory in terms of numbers, and large lakes dominated in terms of area. Survey lakes were selected using a stratified-random sampling design in 10 sampling blocks within the overall survey domain. Few lakes had pH <6, and only three (all in SK) were acidic, i.e., Gran Alkalinity (Alk) <0 μeq L⁻¹. A broad range in lake sensitivity was apparent, and very sensitive lakes (low specific conductance, base cations and Alk) were present in all sampling blocks. Dissolved organic carbon (DOC) was an important constituent of many lakes. Critical loads (CL) of acidity calculated using the Steady-State Water Chemistry model (SSWC) revealed extremely low 5th percentile values for every block (range 1.9 to 52.7 eq ha⁻¹ y⁻¹). Block CL exceedances calculated using estimated S and N deposition for 2002 ranged from 54.5 to 909 eq ha⁻¹ y⁻¹. The largest exceedances were for sampling blocks located near smelter sources or downwind of the oil sands. Lake chemistry revealed by our surveys was compared to others conducted both nearby and outside Canada.

Key words: regional lake survey, lake chemistry, acid sensitivity, acidification status, critical loads and exceedances

1. INTRODUCTION

Chemical and biological aquatic effects of acid rain occur where geologically sensitive terrain coincides with elevated levels of sulphur (S) and nitrogen (N) deposition. In Canada, enormous regions of sensitive terrain are associated with an east-west arc of Precambrian geological formations collectively known as the Canadian Shield (Environment Canada 1988). Igneous and metamorphic silicate bedrock overlain by glacially-derived deposits of variable thickness typifies Shield geology.

Until recently, the region of concern for acid rain effects in Canada was restricted to the central and southern parts of the provinces of Ontario and Quebec, plus New Brunswick, Nova Scotia and Newfoundland (Jeffries et al. 2003). This was because anthropogenic sources of acidifying emissions (SO₂ and NOₓ) in western Canada were either too small or too distant from sensitive terrain to be considered a problem. However, ongoing SO₂ emissions from base metal smelters at Thompson and Flin Flon in MB and increasing SO₂ and NOₓ emissions from oil sand operations near Fort McMurray, AB (Fig. 1) suggest that sensitive terrain located on the Shield in the northern parts of MB and Saskatchewan (SK) may now be at risk.

In the most recent national assessment of acid rain science in Canada, Jeffries et al. (2005) concluded that the information available for evaluating the regional acidification status of lakes in many parts of western Canada was too old, too sparse or too unrepresentative to permit a meaningful analysis. Conducting new and representative lake surveys was recommended. Our purpose here is to present results from lake surveys conducted on the Canadian Shield in MB and SK in 2006 and 2007 that enable evaluation of regional acid sensitivity and acidification status in potentially acid sensitive regions through calculation of critical loads (CL) and exceedances (Henriksen et al. 2002; Jeffries & Ouimet 2005). In addition, the results will be compared to those from other nearby or overlapping surveys conducted by Hudson Bay Mining and Smelting Ltd. and Vale Inco Ltd. in 2005 and 2006 (UMA 2007a, b) and the Saskatchewan Ministry of Environment in 2007 and 2008 (Scott et al. 2010, this issue).

2. METHODS

2.1 Study location

We used the national acid sensitivity map based on bedrock and soil characteristics (Environment Canada 1988) to guide selection of survey domains. Accordingly, a domain in northwestern MB bounded by 55° to 60° north latitude and 100° to 102° west longitude was defined for a survey in 2006, and a domain in north-central SK bounded by the Canadian Shield margin to
the south and 58º latitude to the north was defined for a survey in 2007 (Fig. 1). These domains cover a very large (~193,000 km²) and very remote geographical area which necessitated the use of helicopters and fixed-wing aircraft to access the lakes. In order to minimize the logistical costs, 11 sampling blocks (blocks labelled A, B, etc. in Fig. 1) were defined assuming that they were representative of the overall domains. In the end, study budget constraints prevented sampling of the most northerly block (E) in MB.

2.2. Lake inventories and sample lake selection

A comprehensive, preferably digital inventory of lakes within the survey domains was needed to select a representative subset of sample lakes. Unfortunately, no such inventory existed for this part of MB or SK and we were obliged to create one. This was accomplished using GIS technology applied to the digital National Topographic Database (NTDB) at the 1:50,000 scale. The 1:50,000 topographic maps were stitched together into a single contiguous map and the boundaries inspected to identify and correct the minor discontinuities that arise during this process. Water body centroid coordinates, area (not including islands), plus other NTDB identifiers and polygon attributes were extracted for the entire survey domain and placed in separate databases and GIS shape-files. A unique random identification number was assigned to every database record, i.e. lake, using a Microsoft Access utility. Water bodies having centroid coordinates falling outside the geographic boundaries of the overall survey domains were not included in the inventories even though parts of them were within the boundaries. On 1:50,000 maps, water bodies with an area greater than ~500 m² (~0.05 ha) should be identifiable, and approximately half of the inventory records represented these extremely small lakes. Physically accessing such small water bodies, even by helicopter, can be problematic, however. We therefore decided to limit our target population (i.e., the one used to select sample lakes) to lakes ≥1 ha.

The sampling blocks shown in figure 1 were composed of two adjacent 1:50,000 NTDB map units in MB and four adjacent map units in SK. The lake inventory information applicable to each of them was screened from the overall domain inventory by identifying all water bodies that had centroid coordinates within the block boundaries.

The scale of the sampling effort was very much constrained by the financial resources available for the field surveys such that we were able to visit 152 lakes in MB and 295 lakes in SK.

A stratified-random lake selection methodology similar to that of Henriksen et al. (1996) was used. The lake inventory records were screened into the eight size classes (strata) shown in table 1, and each one sorted according to their unique random identifier thereby providing a randomized list of lakes for each strata in each sampling block. Given the constraints on the total num-
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2.3. Sample collection, processing and chemical analysis

We visited the lakes in mid to late September in expectation that fall overturn would have occurred thereby yielding mixed water-column samples. In reality, this was a little early since a few lakes were still thermally stratified. However, most lakes were shallow and well-mixed, and it is unlikely that the limited number of stratified cases significantly affect the acidification evaluation presented here.

At a visually defined, mid-lake position selected during helicopter approach, physical measurements (water depth, Secchi depth, and a thermal profile) were recorded, and a two litre bulk sample collected from one meter below the surface. After returning to a field laboratory, pH and specific conductance were measured and the bulk sample was sub-divided and processed (i.e., filtered, preserved, etc. as required for the chemical analyses to be conducted on that sub-sample) into aliquots for major ion, nutrient and metal analyses. The aliquots were express shipped on ice to the water chemistry laboratory at the Great Lakes Forestry Centre (GLFC) in Sault Ste Marie, Ontario where chemical analyses were performed as soon as possible (immediately for perishable nutrient parameters). The GLFC laboratory uses standard methods for all chemical parameters and participates in national QA-QC programs to assure production of high quality chemical analyses. We also use charge balance calculations to independently verify the data quality.

2.4. Critical load and exceedance calculations

The Steady-State Water Chemistry Model (SSWC) was used to calculate CL of acidity (expressed as eq ha⁻¹ y⁻¹) for the survey lakes (Henriksen et al. 2002; UNECE 2004). The SSWC employs an alkalinity threshold called ANClimit to define the onset of significant harmful effects, most commonly loss of fish populations. Values for ANClimit have ranged from 20 µeq L⁻¹ (Lien et al. 1996) through 40 µeq L⁻¹ (Henriksen et al. 2002) to 75 µeq L⁻¹ (WRS 2004). The SSWC as originally formulated did not explicitly consider the influence of natural organic acids when calculating CL; however, this will be important for our DOC-rich sample population (see discussion). Lydersen et al. (2004) showed that the fit between Norwegian fish status and ANC improved when an organic acid adjusted ANC was used. This led UNECE (2004) to recommend that the Lydersen et al. (2004) relationship be used to estimate ANClimit on a lake-by-lake basis in waters with higher DOC levels. Here we have used ANClimit = 10 + (10.2/3) × DOC where DOC is in mg L⁻¹ (J. Aherne, pers. comm.).

In addition to lake water chemistry and the ANClimit, the SSWC requires a value for two other variables. First, runoff is needed to convert concentrations into chemical fluxes. Here we used lake specific runoff values estimated by Gibson et al. (2010, this issue) using the Isotope Mass Balance Model (IMB). Second, the

<table>
<thead>
<tr>
<th>Overall</th>
<th>Size Class</th>
<th>Overall area</th>
</tr>
</thead>
<tbody>
<tr>
<td>n. of lakes</td>
<td>&gt;5000 (ha)</td>
<td>&gt;500 to 5000 (ha)</td>
</tr>
<tr>
<td>A (MB)</td>
<td>362</td>
<td>1</td>
</tr>
<tr>
<td>B (MB)</td>
<td>786</td>
<td>2</td>
</tr>
<tr>
<td>C (MB)</td>
<td>853</td>
<td>4</td>
</tr>
<tr>
<td>D (MB)</td>
<td>362</td>
<td>1</td>
</tr>
<tr>
<td>E (MB)</td>
<td>280</td>
<td>1</td>
</tr>
<tr>
<td>F (SK)</td>
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<td>0</td>
</tr>
<tr>
<td>G (SK)</td>
<td>1509</td>
<td>2</td>
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<td>H (SK)</td>
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<td>1405</td>
<td>0</td>
</tr>
<tr>
<td>J (SK)</td>
<td>2109</td>
<td>2</td>
</tr>
<tr>
<td>K (SK)</td>
<td>1557</td>
<td>3</td>
</tr>
</tbody>
</table>

Tab. 1. Overall number of lakes ≥1 ha and number in eight size classes identified in the survey domain and in 11 sampling blocks (see Fig. 1; block E was never sampled however). The cumulative lake area (km², excluding islands) is shown also.
value for the so-called $F$-factor (which relates the present-day excess production of base cations (Cb) from catchment soils to the long-term changes in inputs of non-marine acid anions) was estimated using the equation suggested by Brakke et al. (1990).

The CL exceedance is calculated as acidifying deposition minus the CL and can be either positive or negative. A negative exceedance value implies that the lake is not presently being harmed by acidic deposition within the confines of the ANClimit used to calculate the exceedance. A negative exceedance value for the so-called Steady-state exceedance:

\[
\text{Steady-state exceedance} = \text{Total S deposition} + \text{Total N deposition} - \text{CL} \quad (2)
\]

First, the present-day contribution of N deposition to the exceedance is reflected in the $\text{NO}_3^–$ flux leaving a lake. Hence:

\[
\text{N-leaching exceedance} = \text{Total S deposition} + \text{NO}_3^– \text{leached} - \text{CL} \quad (1)
\]

The $\text{NO}_3^–$ leached is estimated as the product of the lake $\text{NO}_3^–$ concentration and runoff. Second, if all N deposition becomes acidifying then an estimate of total N deposition can be used directly to calculate the so-called Steady-state exceedance:

\[
\text{Steady-state exceedance} = \text{Total S deposition} + \text{Total N deposition} - \text{CL} \quad (2)
\]

3. RESULTS

3.1. Water chemistry

The distribution of the number of lakes among the eight size classes for the overall (MB + SK) survey domain and the individual sampling blocks is given in table 1. The overall domain contains 81,494 lakes ≥1 ha in area corresponding to a landscape lake density of 0.42 lakes per km² and a total lake area of 45,285 km². The lakes in our inventory cover >23% of the domain surface area, and this does not count the area associated with rivers. As expected, small lakes dominate the inventory in terms of numbers; 62% of the lakes are <10 ha in area. Large lakes (>5000 ha) are few in number (just 76 which includes Reindeer Lake on the MB-SK border – a quasi "Great Lake" shown on figure 1 with an area of 565,800 ha), but they constitute 29% of the overall lake area.

Among the sample blocks, lake density ranged from 0.17 lakes per km² (Block B) to 0.78 lakes per km² (Block G) which accounts for the block-to-block differences in the number of selected sample lakes (Tab. 2). In the MB survey domain, lake density tends to be greater in the north compared to the south. The central part of the SK survey domain (represented by Block G) contains the highest lake density.

Selected measurements made during the lake visit or shortly thereafter in the field laboratory are summarized in table 2. There was no opportunity to survey the lakes’ bathymetries, so we can only use the depth measured at the mid-lake sampling point as an indicator of lake depth. The broad range in mid-lake depth observed in all blocks reflects the broad range in the size of sample lakes, i.e. larger lakes tend to be deeper although note that the largest lake was also the deepest in only one Block (B), and in Block D, the deepest lake was only 37 ha in area. Overall, the sample lakes tended to be shallow which probably explains why so few of them were thermally stratified even though surface water temperatures were usually >4 °C, i.e., they are routinely mixed by wind. Mean mid-lake depth ranged from 3.1 to 9.0 m with Blocks J and K (the most southerly Blocks in the SK domain) having the greatest mean depth.
Water transparency as reflected in the Secchi Depth measurements (Tab. 2) is variable as shown by the broad ranges, but on average is very limited. Mean Secchi depths ranged from 1.6 to 2.9 m across the sampling blocks. The poor light penetration occurring in these lakes is most likely due to substantial DOC concentrations (see discussion).

An indicator of lake sensitivity is the specific conductance statistics presented in table 2. Situated within the sparingly soluble silicate geology that characterizes much of the Canadian Shield, the lakes have relatively low dissolved ion concentrations that are reflected in their specific conductance values. In particular, the statistics for Blocks C through H in table 2 show that some of their sample lakes have very low specific conductance, e.g., minimum values <10 µS cm\(^{-1}\). These lakes should be very sensitive to atmospheric inputs of strong acids and they will probably greatly influence the critical loads determined for those blocks.

Similar statistics are provided for three other recent surveys in the same general region (see text). *: Vale Inco Ltd. 2006/07 surveys (UMA 2007a, 2008); 2 anomalous Total N values excluded; †: Hudson Bay Mining and Smelting Co. Ltd. 2006 survey (UMA 2007b); 1 Total Al excluded; ‡: Saskatchewan Ministry of Environment 2007 and 2008 surveys (Scott et al. 2010, this issue).
Cumulative frequency distributions for $\text{Cb}$ ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) are presented in figure 2a. Lakes from all blocks were grouped by province to produce these distributions. Base cations present in a lake originate from either mineral weathering in the terrestrial catchment or atmospheric deposition. High Cb concentrations generally reflect rapid weathering, and therefore little sensitivity to acidic deposition (weathering is an acid consuming process). Such lakes have high CL values. The minimum Cb concentrations reported in table 3 show sensitive lakes in all the sampling blocks, although as suggested by the mean concentrations, Blocks C through H have the highest proportions of such lakes. A Cb concentration $<400$ µeq L$^{-1}$ has traditionally been used as an indicator of acid sensitivity (Jeffries et al. 2005). Figure 2a suggests that ~75% of our MB and SK sample lakes may be considered sensitive to acidification.

Both table 3 and figure 2 contain information from three other recent surveys conducted in the same region. In 2006, Vale Inco Ltd. (VI) who operates a nickel smelter at Thompson, MB (see Fig. 1) commissioned UMA Engineering Ltd. to conduct a survey of 50 lakes within roughly a 300 km radius of Thompson (UMA 2007a). Ten lakes further south were added the following year (UMA 2008). The sampling protocol involved access using fixed wing aircraft meaning that only lakes greater than 75 to 100 ha in area could be sampled. Hudson Bay Mining and Smelting Ltd. (HBMS) who operates a copper smelter at Flin Flon, MB also commissioned UMA Engineering Ltd. in 2006 to conduct a similar survey of 50 lakes surrounding its smelter (UMA 2007b). The third survey of 250 lakes was conducted in 2007 and 2008 by the SK Ministry of Environment (SK ENV; Scott et al. 2010, this issue) in the west central part of the province downwind of the rapidly expanding emissions produced by oil sand processing in the Fort McMurray area of AB. Sample lakes were selected randomly from alternating segments of a 300 km radial grid centred on Fort McMurray. Part of the radial grid, notably those segments closest to Fort McMurray, was off the Canadian Shield. Lake access was achieved by helicopter so that a broad range of lake sizes was sampled.

Mean Cb concentrations measured by the VI and HBMS surveys (1028 and 1635 µeq L$^{-1}$ respectively) are much higher than ours (minimum values are comparable) although the data for Blocks A, B and K where some survey overlaps occurred do show our highest Cb concentrations in table 3. The difference between the VI-HBMS Cb data and ours is due to two factors: first, VI-HBMS sampling was focused in the somewhat less sensitive terrain that surrounds the smelters, and second, small lakes were excluded. The cumulative frequency distribution for Cb (Fig. 2a) clearly shows how much the VI and HBMS survey results differed from ours, i.e. <40% of their sample
populations are sensitive to acidification compared to 75% of ours. Conversely, the SK ENV survey which had a large degree of spatial overlap with Blocks H, I and to a lesser extent G showed Cb statistics (Tab. 3) and a cumulative frequency distribution (Fig. 2a) that are very similar to ours, lending credence to the results of both surveys. The higher maximum Cb concentration found by the SK ENV survey is due to the off-Shield sampling that occurred near the SK-AB border.

Gran Alkalinity statistics (Tab. 3) and cumulative frequency distribution (Fig. 2b) provide the same information as Cb. Note that negative values for Alk were recorded in Blocks G and J and by the SK ENV survey. Negative Alk defines a lake as acidic. It was caused here by the occurrence of natural organic acidity in combination with extremely low Cb. Values for the calculated variable ANC were always higher than our Alk values because they do not include the influence of organic acidity.

Sulphate and Cl$^-$ are minor anions compared to Alk although there is evidence of some regional differences. For example, mean SO$_4^{2-}$ concentrations are higher in the blocks nearer the smelters, and the four SK blocks located nearest the Shield boundary (H to K) had slightly higher mean and substantially higher maximum Cl$^-$ levels, most likely due to the higher evaporative concentration that arises from the lower annual precipitation and runoff occurring to the west and south.

Dissolved organic carbon (a surrogate for natural organic acidity) was an important source of anions in many of our survey lakes. Organic anions constitute an important component of our chemical charge balance, on average 40% and 37% of the anion sum for the MB and SK lakes respectively. While there are some very clear, low DOC lakes as evidenced by the minimum values in table 3, the mean and maximum DOC values show that many lakes have substantial and sometimes very high concentrations. The cumulative frequency distribution (Fig. 2c) shows this well. More than 50% of the lakes in all the surveys (except the SK ENV survey) have more than 10 mg L$^{-1}$ DOC. This is approximately double the median DOC concentration reported for all the eastern provinces by Jeffries et al. (2005).

There is a decreasing, east-to-west gradient in regional DOC concentrations across our study area. Vale Inco conducted the most eastern survey of the five shown in figure 2c, and it clearly exhibited the highest DOC concentrations in its cumulative frequency distribution. The HBMS survey which had a greater spatial communality with our survey blocks showed a DOC distribution very similar to our MB survey. To the west, the DOC distribution from our SK survey is shifted to lower concentrations, and finally, the DOC distribution for the SK ENV survey, which focused its sampling even further west, exhibits an even greater shift to lower concentrations. Note however that this is where the spatial trend stops. Lakes that are yet further west, i.e., near Fort McMurray (Fig. 1) and off the Shield, have much higher DOC concentrations (Jeffries et al. 2005). The existence of this DOC gradient across north-central MB and SK is probably related to a combination of terrain and climatic factors, i.e. more prevalent lowland/wetland terrain and somewhat greater annual precipitation to the east.

Ecosystem acidification mobilizes Al from drainage basin soils and bedrock thereby increasing lake water concentrations. This is important because labile, ionic Al species are toxic to fish (Poléo et al. 1997). We could not quantify labile Al within our sampling and analytical protocol; however, mean Total Al concentrations (Tab. 3) were <100 µg L$^{-1}$ for all sampling blocks except Block J – the same block that showed the lowest pH and Alk concentrations. Significant positive relationships ($p < 0.001$) existed between Total Al and DOC for both of the MB and SK data sets. Binding of ionic Al species to organic anions reduce their toxicity, so it is unlikely that Al toxicity is important in our survey lakes.

Other metals (Cd, Cu, Ni, Pb and Zn) were also measured but not shown in table 3. Most values for all metals except Zn were below analytical detection limits. Mean Zn concentrations were 54 and 65 µg L$^{-1}$ for the MB and SK data sets respectively. Blocks A and K were located closest to a smelter (the HBMS facility at Flin Flon, Fig. 1), but their metal concentrations were no higher than those measured in other, more distant blocks.

The mean Total P concentrations of our remote survey lakes were higher than expected and would result in a mesotrophic classification. On the other hand, soluble reactive P concentrations (measured only in the 2007 SK survey; mean 7.5 µg L$^{-1}$) were much lower suggesting that a significant component of the Total P was organic P. This was also the case for Total N. The inorganic forms of N (NO$_3^-$ and NH$_4^+$) were almost always undetectable in our survey samples, and hence, almost all the Total N existed in organic forms.

### 3.2. Critical loads and exceedances

Having been included as recommended methodology by UNECE (2004), the SSWC has been used extensively and successfully to calculate CL and influence emission reduction policy in Europe. This has also been the case in Canada (e.g., Henriksen et al. 2002; WRS 2004; Dupont et al. 2005; Jeffries & Ouimet 2005). However, we have employed two modifications that distinguish its use here from those previous applications, namely consideration of the influence of DOC through the use of the Lydersen et al. (2004) equation to calculate ANC$_{limat}$ and substitution of lake-by-lake values for runoff derived using the IMB Model (Gibson et al. 2010, this issue) for long-term regional runoff values. This runoff substitution applied to both our survey lakes and those of SK ENV.
Table 4 includes the 5th percentile value for each of our sampling blocks. The 95th percentile N-leaching and Steady-state exceedances were calculated using modelled S and N deposition for 2002 (see text). *: the 5th percentile is taken as the CL for regional data set (Jeffries & Ouimet 2005). **: Vale Inco Ltd. 2006 and 2007 surveys (UMA 2007a, 2007b). †: Hudson Bay Mining and Smelting Co. Ltd. 2006 survey (UMA 2007b). ₹: Saskatchewan Ministry of Environment 2007 and 2008 surveys (Scott et al. 2010, this volume).

<table>
<thead>
<tr>
<th>Sampling Block</th>
<th>Critical Load (eq ha⁻¹ y⁻¹)</th>
<th>95th Percentile Exceedance (eq ha⁻¹ y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>A</td>
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<td>B</td>
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<td>1370</td>
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<td>2170</td>
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<tr>
<td>E</td>
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<td>F</td>
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</tr>
<tr>
<td>H</td>
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</tr>
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<td>I</td>
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</tr>
<tr>
<td>J</td>
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<tr>
<td>K</td>
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<td>4330</td>
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<tr>
<td>VI*</td>
<td>171</td>
<td>10100</td>
</tr>
<tr>
<td>HB†</td>
<td>7.0</td>
<td>3380</td>
</tr>
</tbody>
</table>

The Lydersen et al. (2004) ANCᵢₕᵢₚ values ranged from 14.4 μeq L⁻¹ for a very clear, sensitive lake in SK (DOC = 1.3 mg L⁻¹; Cb = 162 μeq L⁻¹) to 145 μeq L⁻¹ for an extremely brown, insensitive lake, also in SK (DOC = 39.7 mg L⁻¹; Cb = 2660 μeq L⁻¹). The mean ANCᵢₕᵢₚ was 41 μeq L⁻¹ in SK (very close to the value of 40 used by Henriksen et al. 2002; Dupont et al. 2005; and Jeffries & Ouimet 2005); and 65 μeq L⁻¹ in MB, which was slightly less than the value of 75 used by WRS (2004) for high DOC lakes in AB.

The influence of substituting IMB runoff values for long-term regional values has been evaluated by Gibson et al. (2010, this issue). The IMB values tend to be lower and more variable than the regional values, causing the SSWC to yield lower and more variable CL.

SSWC CL results are presented in table 4. Minimum CL values for the sampling blocks are very close to zero (and even negative in one of the two cases that had negative Alk) implying that the most sensitive lakes in our survey are unable to accommodate any level of anthropogenic acidifying input. However, the range is much higher CL determined for the VI and HBMS surveys (see discussion in Jeffries & Ouimet 2005). The mean CL (176 to 400 eq ha⁻¹ y⁻¹) are similar to the Ontario and Quebec provincial CL determined by Jeffries & Ouimet (2005).

In Canada it has been customary to adopt the 5th percentile CL value from a regional dataset in order to provide protection for 95% of the threatened ecosystems. Table 4 includes the 5th percentile value for each of our sampling blocks. The sensitive (low Cb) component of our survey lakes results in very low 5th percentile CL values for all of our sampling blocks (range 1.9 to 52.7 eq ha⁻¹ y⁻¹), particularly the most northerly Blocks C through H and Block J (range 1.9 to 8.5 eq ha⁻¹ y⁻¹). Blocks I and K near the Shield margin in SK had the highest CL among the 10 Blocks. The CL value for the SK ENV survey (Tab. 4) falls within the range of values for Blocks G, H and I where the surveys overlapped. The much higher CL determined for the VI and HBMS surveys are due to the higher Cb levels in their sample lakes.

The AURAMS model estimates wet and dry deposition on a 42 km grid for a number of atmospheric S and N species. For our survey lakes, AURAMS estimates of total S deposition varied from 67 to 1320 eq ha⁻¹ y⁻¹ and total N deposition varied from 40 to 140 eq ha⁻¹ y⁻¹. Minimum estimated deposition (both species) occurred for lakes in Blocks C and D in MB blocks while maximum estimated S deposition occurred in Block A that is nearest the smelter SO₂ source at Flin Flon (Fig. 1). Maximum N deposition was estimated for a lake in Block H, the block closest to the large NOₓ emissions associated with oil sand processing near Fort McMurray, AB. AURAMS estimated even greater deposition for some of the lakes in the other surveys, i.e., total S estimated for a lake near Thompson, MB from the VI survey was 3300 eq ha⁻¹ y⁻¹ and total N deposition for a lake near the AB border in the SK ENV survey was 230 eq ha⁻¹ y⁻¹.

Using the same protection rationale that defined regional CL values, 95th percentile exceedences for our survey blocks and the three other surveys are shown in table 4. All of our sampling blocks and the SK ENV survey have positive exceedences, both in the current situation (the N-leaching exceedance) and in the case where the lakes ecosystems become N saturated (the Steady-state exceedence). Since NO₃⁻ concentrations in our survey lakes are almost always below the analytical
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limit of detection (i.e., <2.9 µeq L⁻¹), the N-based component of the N-leaching exceedance is very small. Hence, for these MB and SK lakes, the N-leaching exceedance is almost completely a S-based value, and the difference between the N-leaching and Steady-state values reflects a possible future contribution to the exceedance by the current level of N deposition should it continue until an ecosystem steady-state is obtained.

Since exceedance is the difference between acidifying deposition and the CL, positive values can occur either because the deposition is high or the CL is low. Here the positive exceedances are primarily due to the latter. For higher CL (as was the case for the VI and HBMS data sets), the current exceedance is negative.

4. DISCUSSION

Prior to the surveys reported here, most chemical data available for assessing lake sensitivity and acidification status in northern and central MB and SK were very old (often collected in the 1980s or earlier), limited in number and geographical coverage, focused on large lakes, or collected for other reasons, e.g., evaluating the quality of drinking water supplies. Therefore, they were unrepresentative of the lake populations in western Canada that are likely to be affected by acidifying emissions. Our surveys, conducted using stratified-random sampling designs, now provide chemical data representative of 81,494 lakes located within the survey domain. Note however, that for logistical reasons we did not include in our target population the approximately equal number of lakes <1 ha in area. The acidification sensitivity and status of these extremely small lakes has not been assessed.

An inventory of lakes ≥1 ha for our survey domain has not existed in a quantitative, digital form until now. This lack of fundamental water resource information has a historical parallel. At the beginning of the acid rain research and monitoring program in eastern Canada in the 1970s, there was also no digital lake inventory until one was developed by Hélie et al. (1993). Lakes in a broad range of sizes and regional densities are an important landscape feature in central and northern MB and SK. On average, the lakes are not very deep which presumably reflects the rather low relief of this part of Canada. Like other locations on the Canadian Shield in eastern Canada, small lakes are a particularly important component of the inventory in terms of numbers; 19% of the lakes in our survey domain are 1 to 2 ha in area. Although not a significant proportion of the lake resource by area, such small water bodies are important habitat for migratory waterfowl. Conversely, the large lakes (>500 ha) in the survey domain are renowned for recreational angling.

All the indicators of acid sensitivity (Specific Conductance, Cb and Gran Alkalinity) showed a wide range with distinct regional patterns that are related both to the type of silicate bedrock and the quantity and nature of the glacial overburden [cf. the criteria used to develop the terrain sensitivity map in Environment Canada (1988)]. With the exception of Block K, every one of our sampling blocks contained some lakes with pH <6, the generally accepted pH threshold that defines the onset of biological damage (Baker et al. 1990), and little capacity to neutralize additional acid inputs; hence, the very low regional (5th percentile) CL determined by the SSWC.

Dissolved organic carbon is a very important constituent in many of the lakes. Leaching of humic and fulvic acids as water moves through organic soils yields the brown coloration and very shallow Secchi depths observed in many lakes. Drainage from the low relief, sometimes swampy terrain surrounding many of our sample lakes, yielded many highly coloured, high DOC samples (Tab. 3). DOC tended to be higher in small lakes, but there were cases of high DOC in all size classes. The combination of high DOC and high Cb and Alk is unusual in eastern Canada, but it is common in our surveys here and also in AB lakes to the west (WRS 2004). Natural organic compounds are generally amphoteric, that is, they can act as either acids (proton donors) at higher pH or bases (proton acceptors) at lower pH. In high DOC waters, this amphoteric behaviour contributes both to a lower pH than would otherwise be the case (if DOC was absent), and to greater buffering against strong acid inputs. Use of the Lydersen et al. (2004) equation for ANCnon is the way the SSWC compensates for this behaviour when calculating CL. If and how the high DOC lakes acidify will depend on the DOC-acidity interaction.

Lake surveys with statistically-based sampling designs have been conducted for the purpose of acidification assessment in northeastern and upper Midwest regions of the USA (Brakke et al. 1988; Eilers et al. 1988), in various countries and regions of northern Europe (Henriksen et al. 1998) and regions of southwestern Quebec (Dupont 1992). It is instructive to compare results from these surveys with ours. Average regional chemistry was reported as medians in the US and Europe and as means in Quebec. Denmark was one of the countries included in the northern Europe survey, and because its lakes are largely situated in calcareous terrain, the Danish data will be excluded from the comparisons that follow. The range in average block Cb concentrations for our survey (189–681 µeq L⁻¹) was similar to the range in regional averages reported for the northeastern US (246–671 µeq L⁻¹), lower than that observed in the upper Midwest US (205–949 µeq L⁻¹), and greater than that in Europe (79–240 µeq L⁻¹) and Quebec (98–340 µeq L⁻¹, Ca²⁺ + Mg²⁺ only). The ranges of our block average Alk and ANC concentrations (126–467 and 163–608 µeq L⁻¹ respectively) were higher than the range of regional averages for all the other surveys except those reported for the upper Midwest US. The high end of the range for the upper Mid-
west (802 μeq L⁻¹) was attributed to ANC concentrations in the Upper Great Lakes area—a region known to contain some calcareous bedrock and glacial tills. The range in our block average SO₄²⁻ concentrations (14–60 μeq L⁻¹) was lower than those reported for all the other surveys (northeastern US, 75–159 μeq L⁻¹; upper Midwest US, 50–78 μeq L⁻¹; Europe, 26–82 μeq L⁻¹; and Quebec, 40–117 μeq L⁻¹). The range in block average DOC concentrations (6.8–20.6 mg L⁻¹) in MB and SK was much higher than those reported in all the other surveys (northeastern US, 3.8–5.2 mg L⁻¹; upper Midwest US, 4.6–9.2 mg L⁻¹; Europe, 1.9–8.6 mg L⁻¹; and Quebec, 5.3–8.0 mg L⁻¹). Note that the US and Quebec surveys occurred more than two decades ago, and the European survey more than one decade ago. Interpretation of the above comparisons must be tempered by the fact that lake chemistry in these regions has been changing as acidic deposition levels decline (Stoddard et al. 1999; Monteith et al. 2007).

The current level of S and N deposition in our survey domain is low relative to southeastern Canada except in the vicinity of the point sources at Thompson, Flin Flon and Fort McMurray. Sulphate concentrations in the lakes tend to reflect relative proximity to these sources. Nitrate levels are uniformly low (usually below analytical detection limits) suggesting that the boreal forest in their catchments is N limited. The low deposition levels and even lower CL values result in positive but generally small S-based exceedances for all of our sampling blocks (the Block A exceedance might be considered an exception). This new information for western Canada has only come to light because our survey design captured the sensitive component of the lake population, i.e., the lakes with low Cb that were absent from the assessment databases available to Jeffries et al. (2005). The recent VI and HBMS surveys contained few low Cb lakes as well, probably because their selection criteria had a minimum size restriction (~100 ha), and they sampled the less sensitive parts of MB and SK that surround the smelters. In any case, the positive exceedances signal a challenge to the current emission control strategy in Canada which is based on reducing deposition to CL levels.

HBMS has recently announced that it intends to cease smelting operations at Flin Flon in 2010. It remains to be seen whether or not this closure is permanent. The largest long-term acidification threat to the MB and particularly SK lakes is the expansion of oil sand processing in AB. Not far downwind are some of Canada’s most sensitive lakes. Lakes in SK north of our domain boundary (58° N latitude) may also be vulnerable to oil sands emissions, and a survey of this area is being conducted in 2009.

5. CONCLUSIONS

Recent surveys of lakes designed to obtain a representative sample of the lake population in northwestern MB and north-central SK have shown that a very sensitive component of the population is threatened by current levels of S and N deposition. However, at present there is only a small number of lakes with pH <6. Aquatic effects may be alleviated to some degree by the announced closure of the smaller smelter source at Flin Flon, MB, but additional acidifying emissions from the expansion of oil sand processing just west of SK (or even in SK) may increase the threat to a large population of very sensitive lakes in the west-central part of that province. Very high DOC levels in many lakes may yield acidification responses that differ from those observed in eastern Canada. A small subset of lakes should be selected for ongoing chemical and biological monitoring to quantify inter-annual variability and temporal trends.

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