Water-yield estimates for critical loadings assessment: comparisons of gauging methods versus an isotopic approach

K.E. Bennett, J.J. Gibson, and P.M. McEachern

Abstract: An isotope mass balance technique is applied to quantify water yield and refine a steady-state critical acid loadings assessment for 49 lakes in hydrologically complex, wetland-rich terrain of northeastern Alberta. The approach uses physical and climatological data combined with site-specific measurements of evaporative isotopic enrichment of ^{2}H and ^{18}O in lake water to measure lake residency and ungauged runoff to lakes. Mean water yields to individual lakes across the region over a 3-year period are estimated to range from 5 to 395 mm·year^{-1}, with a standard deviation of two times the predicted estimates based on interpolation of gauged stream flow from broad-scale watersheds in the area. Comparison of the method with longer-term Water Survey of Canada hydrometric data suggests very similar average water yields for moderate- to large-sized watersheds. However, the isotope-based estimates appear to capture extreme low water yields in flat, disconnected areas and extreme high water yields in other areas thought to be related to stronger connections to regional groundwater flow systems. For aquatic ecosystems of northeastern Alberta, an area expected to be affected by acid deposition from regional oil sands development, continued refinement of the technique is important to accurately assess critical loads for ungauged systems, particularly those in low-yield settings.

Résumé : Une technique de bilan massique isotopique nous permet de quantifier le rendement en eau et de raffiner une évaluation à l'état d'équilibre des charges acides critiques de 49 lacs sur un terrain riche en terres humides et à hydrologie complexe dans le nord-est de l'Alberta. Notre méthodologie utilise des données physiques et climatologiques, de même que des mesures spécifiques au site de l'enrichissement isotopique en ^{2}H et en ^{18}O dans l'eau de lac dû à l'évaporation, afin de mesurer la durée de résidence dans les lacs et le ruissellement non jaugé vers les lacs. Nous estimons que l'apport moyen d'eau aux lacs individuels dans toute la région sur une période de trois ans varie de 5 à 395 mm·an^{-1}, avec un écart type de deux fois les estimations prédites d'après des interpolations des débits jaugés de ruisseaux faites dans des bassins versants à grande échelle de la région. Une comparaison de notre méthode avec les données hydrométriques à plus long terme des Relevés hydrologiques du Canada montre des rendements moyens en eau très semblables pour les bassins versants de taille moyenne à supérieure. Les estimations basées sur les isotopes semblent indiquer des apports d'eau extrêmement faibles pour les régions plates et isolées et des apports extrêmement élevés pour d'autres régions qu'on croit posséder des connections plus importantes avec les systèmes régionaux d'eaux souterraines. Dans le cas des écosystèmes aquatiques du nord-est de l'Alberta, qu'on croit devoir être affectés par les précipitations acides produites par le développement des sables bitumineux de la région, il est important de raffiner la méthodologie afin d'évaluer les charges critiques dans les systèmes non jaugés, particulièrement ceux qui se situent dans des conditions d'apports d'eau faibles.

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Introduction

Previous studies have indicated that lakes and ponds in northeastern Alberta, the hub of oil sands mining and refinery operations in Canada, may be sensitive to acidifying emissions due to the prevalence of acid-sensitive soils and aquatic features common to the region (e.g., Erickson 1987; Schindler 1996). Recent growth in the rate and extent of oil sands development, and commensurate increases in NO_x and SO_x emissions from refinery operations centred near the town of Fort McMurray, are intensifying this concern. Although impacts to aquatic ecosystems are not widely reported at present, there remains a lack of scientific information to evaluate suitable environmental thresholds and ensure that emissions targets are adequately protecting aquatic and terrestrial ecosystems in the long term. Through its NOx SOx Working Group, the Cumulative Environmental Management Association (CEMA), a multi-stakeholder NGO, is currently sponsoring research into the potential sensitivity of the local environment, including assessment of critical loads of acidifying emissions to aquatic ecosystems. Critical loads represent a limit or threshold for atmospherically deposited sulphur and nitrogen that ensure long-term sustainability of the targeted ecosystem. A first approximation of critical acid loads (CL_A) to lakes in the area was undertaken for 449 lakes and ponds in the region using the steady-state water chemistry model (SSWC; Henriksen et al. 1992; Western Resource Solutions (WRS) 2004). The calculated critical loads were exceeded by predicted potential acid input for 17 of the 449 lakes, but with considerable uncertainty due to a number of poorly known factors, primary among them being actual acid deposition and, on the receptor side, water yield. This paper focuses on investigating the hydrological controls at 50 select lake sites, i.e., water-yield factors and how they affect such critical loadings assessments.

Water yield is a difficult parameter to estimate because of the sparsity of the hydrometric network in northern Alberta and, as shown in this paper, the high lake-to-lake variability in runoff, which may reduce the robustness of interpolating between gauging stations. As long-term hydrometric networks were also designed to gauge large-scale runoff in rivers rather than discharge from individual lakes, direct application of discharge data to lakes must be scrutinized cautiously.

Accuracy of the critical acid load estimate by the SSWC model is directly proportional to accurate estimates of water yield (W_Y). Use of in situ isotope measurements provides a sharper focus on water yield than extrapolation from conventional hydrometric monitoring in the area, which can be useful for assessing sensitivity of individual lakes to acid deposition. For a regional subset of the 449 previously studied systems (WRS 2004), an isotope mass balance technique was applied using $\delta^{18}O$ and δ^2H of Gibson et al. (2002), which utilizes the systematic isotopic fractionation that occurs during evaporation to estimate the lake residence time, and the required water yield from the catchment to sustain the observed isotopic balance. Results of the isotopic approach are compared with those from conventional hydrometric techniques to test the implications for critical acid loadings models to illustrate potential errors and limitations in the approaches. This examination also lends insight into scale-dependent landscape features that affect the way in which water is processed and removed from the landscape in boreal forest terrain.

The objectives of this paper are to compare water-yield results obtained from conventional and isotopic methods, to demonstrate their incorporation into a preliminary critical acid loadings assessment, and to highlight the sensitivity of the critical acid loadings model to hydrological controls across a regional domain. This phase of the research does not attempt to use dynamic models to address rapidly fluctuating water balance parameters (for a recent example south of this region, see Smerdon et al. 2007). The results from this preliminary analysis are anticipated to be useful for improving regional perspectives of lake acidification potential, particularly in complex, wetland-rich terrain, and establishing potential for broader incorporation into aquatic ecosystem assessments.

Materials and methods

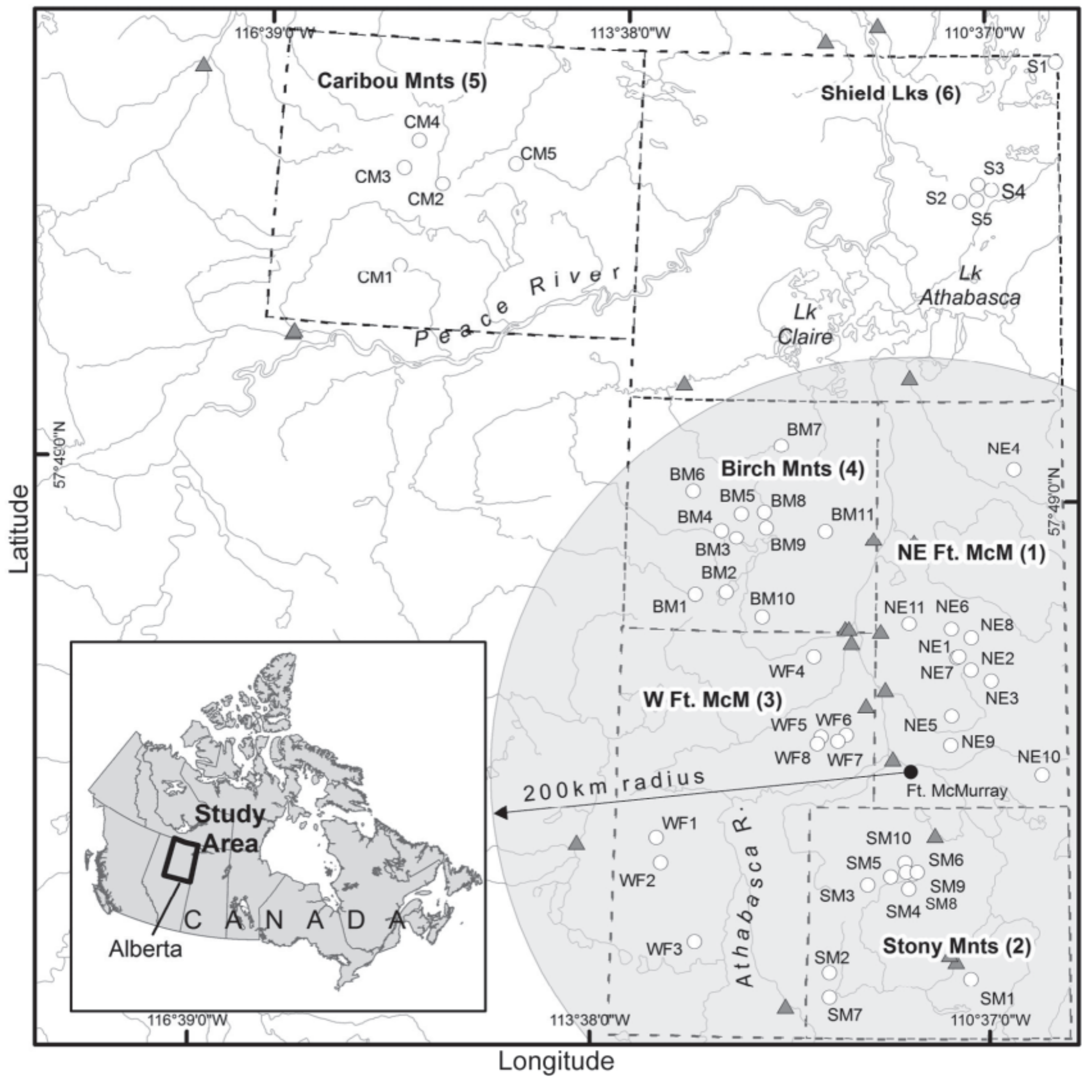
Site description

The lakes under study are located in northeastern Alberta, Canada (55°30′N to 60°N, 30′W; Fig. 1; Table 1). Thirty lakes are situated within 200 km of Fort McMurray and its nearby oil sands developments. Five lakes are found in the Caribou Mountains and four lakes are situated above Lake Athabasca. All are primarily located in headwater catchments and range in size from shallow, small ponds (1 m depth, <0.5 km^2) to large lakes (30 m depth, 43 km^2), with average lake depth and size equal to 4.3 m and 3 km^2, respectively. The lakes were part of an on-going monitoring program of acid-sensitive lakes in Alberta carried out by Alberta Environment and the Regional Aquatics Monitoring Program (RAMP 2004). All lake chemistry data derive from RAMP and a discussion of collection and analysis of water samples for chemistry is reported elsewhere (RAMP 2006). These chemistry data are publicly available from Alberta Environment.

Air temperature normal (1971–2000) at Fort McMurray is 0.7 °C, whereas the average open-water season (May to October) temperature is 11.6 °C. Mean annual precipitation is 456 mm, 69% of which falls as rain during the May to October period (Meteorological Service of Canada 2004). Average annual evaporation is 480 mm (Hamon 1961; New et al. 1999), and evaporation from lakes has been estimated at 578 mm (Bothe and Abraham 1987, 1993). Relative humidity during the open-water period is close to 68%.

Temperature, precipitation, and snowfall for the study years (2001–2004) were calculated based on the October to September water year and compared with the long-term mean values at the Fort McMurray climate station using the R package “seas” (Toews et al. 2007). Study season November through January and midsummer (June and July) daily mean temperatures are, on average, 0.2–3.6 °C warmer, whereas spring and late summer – early fall months (August to October) are generally cooler on average (–2.6 to –0.4 °C) compared with the long-term average (1944–2004) conditions, with the greatest differences observed during the winter (+3.6 °C) and spring (–2.6 °C) seasons (Table 2). Daily total precipitation is less variable than temperature between

Fig. 1. Map of study regions, lakes, Water Survey of Canada gauges, and major rivers. Lake sites are shown as open circles, and WSC gauges are indicated by shaded triangles. The shaded area indicates the 200 km radius, which includes Fort McMurray's (Ft. McM) associated oil sands developments and all lakes that are considered to fall within the area most likely to be impacted by oil sands development. Inset illustrates location of site in Alberta and Canada. Mnts, Mountains; Lks, Lakes.



study years and the long term; the greatest difference in precipitation occurs in the summer season (–25.5 mm; Table 2). Differences in total snowfall are reflective of temperature variations during the study season versus the long-term average, higher mean temperatures in November and December lead to less snow (–10.8 cm).

Long-term (1962–2004) average monthly flow (March to October open-water season) was compared with the study season (2002–2004) average monthly flow at active WSC gauges (13) used in this study. Annual total hydrologic flow is lower on average (10.6 $m^3 \cdot s^{-1}$ vs. 11.6 $m^3 \cdot s^{-1}$) by 1 $m^3 \cdot s^{-1}$, with the exception of the month of October when flows are slightly higher (Fig. 2).

The lakes are grouped within six regional study areas: (1) northeast (NE) Fort McMurray; (2) Stony Mountains; (3) west Fort McMurray; (4) Birch Mountains; (5) Caribou Mountains; and (6) Shield Lakes. Study areas range in elevations from 200 m (region 6) to 1000 m (region 5), with similar average elevations occurring within regions 1 and 3 and regions 2 and 4. Average slopes (based on DEM analysis in a geographic information system) within study catchments are low, ranging from 0.5% in region 3 to 5.4% in region 5, with higher average slopes occurring in the watersheds of regions 5 and 6 and regions 2 and 1. There is a wide range of variation present within the lake sites, including their latitudinal position, morphometry, and the landscapes within which they are situated (Table 1).

Regional surficial materials consist primarily of thick tills (65%), till veneers (21%), with some coarse sands and silts (3%), and minor amounts of sands and gravel, as well as fine silts and clay (Fulton 1996). Soils in regions 1, 2, 3, and 4 are comprised of organics, luvisols, brunisols, and cryosols (region 4), whereas cryosols and regosols are dominant soil types in regions 5 and 6, respectively (Shields et al. 1991; Soil Landscapes of Canada Working Group 2005). Permafrost is sporadic discontinuous (10%–50%), with low ground ice content (<10%) at the Shield and Taiga Plain sites, and in the remainder of the sites, permafrost is either absent or

Table 1. Location, position, and areal extent of study lakes and catchment areas.

Lake no.	Latitude (N)[a]	Longitude (W)[a]	Lake surface area (m^2)	Catchment area (m^2)	Maximum lake depth (m)	Lake volume (m^3)
Region 1: NE Fort McMurray						
NE1	57.15	110.85	652 300	13 111 800	1.83	783 100
NE2	57.09	110.75	336 700	16 987 500	1.83	427 900
NE3	57.96	110.40	1 162 400	15 978 100	1.22	713 500
NE4	57.05	110.59	581 800	6 635 400	2.13	842 500
NE5	56.89	110.90	1 894 900	19 573 200	1.83	1 731 200
NE6	57.27	110.90	372 900	10 682 600	1.39	327 800
NE7	57.15	110.86	111 900	4 073 300	2.00	112 300
NE8	57.23	110.75	114 600	6 470 400	1.22	92 100
NE9	56.77	110.91	3 154 800	20 090 300	1.83	3 517 800
NE10	56.64	110.20	4 188 000	27 669 900	1.50	3 227 700
NE11	57.29	111.24	5 753 200	68 918 300	3.50	7 614 500
Region 2: Stony Mountains						
SM1	55.76	110.76	2 369 500	7 085 700	1.83	1 594 200
SM2	55.79	111.83	1 973 800	24 292 300	1.22	1 126 100
SM3	56.20	111.37	1 861 300	7 677 300	3.05	2 691 700
SM4	56.15	111.23	525 600	11 998 500	1.22	371 100
SM5	56.17	111.55	1 061 000	6 291 900	1.83	1 219 500
SM6	56.22	111.17	699 200	3 393 600	1.52	617 900
SM7	55.68	111.83	1 476 100	5 782 400	3.00	1 885 700
SM8	56.21	111.20	1 912 500	9 719 800	2.50	1 694 600
SM9	56.22	111.25	1 071 400	9 470 800	1.20	608 000
SM10	56.26	111.26	1 352 100	17 390 500	1.22	933 700
Region 3: West Fort McMurray						
WF1	56.35	113.18	3 203 400	24 212 800	1.22	1 874 800
WF2	56.24	113.14	755 100	23 370 200	1.80	707 900
WF3	55.91	112.86	2 163 500	38 142 700	2.00	2 090 700
WF4	57.15	111.98	34 200	1 790 600	1.50	28 600
WF5	56.80	111.92	234 500	6 887 800	1.22	176 700
WF6	56.81	111.72	182 300	5 121 700	1.52	177 500
WF7	56.78	111.79	85 000	1 711 700	1.22	67 500
WF8	56.77	111.95	2 025 000	27 074 100	1.52	1 457 700
Region 4: Birch Mountains						
BM1	57.41	112.93	17 029 700	51 318 200	9.14	98 076 200
BM2	57.42	112.69	43 974 800	119 642 300	27.43	454 190 300
BM3	57.65	112.62	965 600	28 621 000	4.57	1 333 700
BM4	57.69	112.74	4 264 100	34 097 900	1.22	1 828 200
BM5	57.76	112.58	2 636 900	27 892 300	1.22	1 204 300
BM6	57.85	112.97	1 290 200	18 397 900	0.91	639 900
BM7	58.06	112.27	676 900	7 812 200	1.50	446 000
BM8	57.77	112.40	1 215 100	32 684 100	1.83	1 358 900
BM9	57.70	112.38	3 484 800	30 261 500	10.67	11 147 600
BM10	57.31	112.40	393 700	5 094 600	1.50	145 600
BM11	57.69	111.91	55 000	1 478 900	5.00	13 100
Region 5: Caribou Mountains						
CM1	58.77	115.44	1 600 400	23 934 700	8.50	10 332 000
CM2	59.13	115.13	9 550 300	37 926 800	6.00	27 318 000
CM3	59.19	115.46	2 300 100	25 257 900	1.50	4 030 800
CM4	59.31	115.35	2 627 800	35 818 200	16.00	21 733 200
CM5	59.24	114.53	552 300	2 575 500	1.50	865 200
Region 6: Shield Lakes						
S1	59.72	110.02	3 404 900	13 398 600	27.43	22 492 400
S2	59.12	110.83	1 025 200	110 260 700	12.19	3 607 000
S3	59.19	110.68	1 447 900	29 694 400	10.67	4 842 000
S4	59.17	110.57	1 416 300	123 079 400	9.14	5 644 000
S5	59.13	110.69	316 700	4 477 400	8.53	312 800

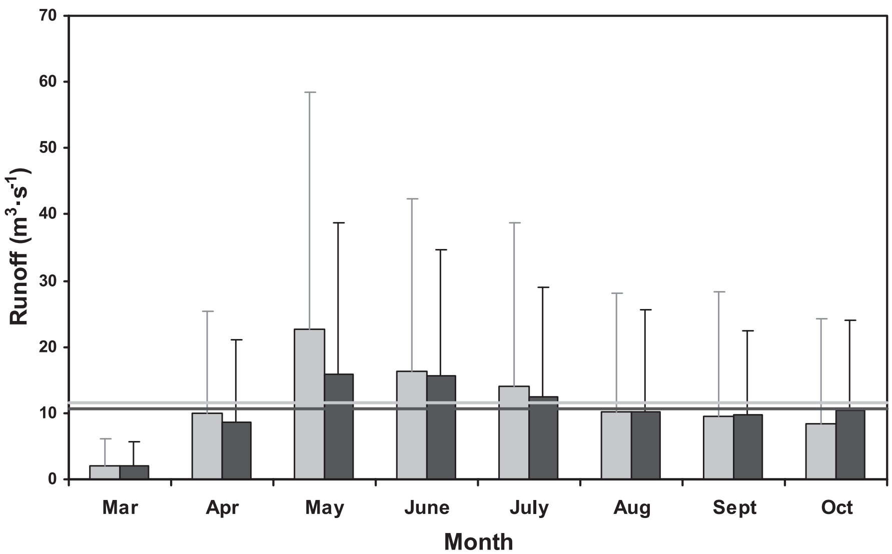
[a]Latitude and longitude are given in decimal degrees.

Table 2. Differences in daily long-term climate (1944–2004) and the study years (2002–2004) at the Fort McMurray climate station.

Month	Season	Minimum temperature (°C)	Mean temperature (°C)	Maximum temperature (°C)	Total precipitation (mm)	Total snow (cm)
December	Winter	3.4	3.6	3.8	–10.3	–10.1
January		2.0	1.4	0.9	0.1	–1.3
February		1.5	1.7	2.0	0.1	1.4
March	Spring	–3.1	–2.6	–2.0	–0.7	–0.6
April		–1.2	–0.9	–0.7	–7.1	–5.1
May		–2.6	–2.4	–2.2	6.7	5.5
June	Summer	–0.9	0.2	1.2	–14.4	0.0
July		0.6	0.8	1.1	6.9	0.0
August		–1.0	–0.7	–0.3	–25.5	0.0
September	Fall	–0.1	–0.4	–0.7	10.4	–1.0
October		–2.0	–1.8	–1.6	7.9	3.0
November		2.7	2.7	2.7	–3.9	–11.5

Note: Snow is the difference between the study years (2001–2004) to account for preseason snowfall.

Fig. 2. Hydrologic range of runoff measured over the long term (1962–2004, light gray bars) and for the three years of study (2002–2004, dark gray bars). Error bars indicate runoff variability +1 SD for both the long term and the study years.



only in isolated patches (0%–10%), with low or low-to-nil ground ice (Brown et al. 1998). The overall study area comprises 13% bogs, 22% fens, and 65% mineral upland. Peatland coverage in specific watersheds varies considerably, but the regional averages are fairly representative of the broader terrain under investigation (see Vitt et al. 1996).

Physical data collection

Water samples were collected in the late summer – early fall during 2002, 2003, and 2004. The 2004 seasonal program (Alberta Environment public water data archives) sampled a subset of 10 lakes and ponds from the 50-lake population and provided support for the hypothesis that lakes in the Wood Buffalo region exhibit annual isotopic highs (peak enrichment) during this time period (see discussion of this issue in Gibson et al. 2002). However, more detailed study of the study lakes in terms of seasonal flux is required. Lake samples were collected from the pontoon of a fixed-wing aircraft, and helicopters were used to access ponds and terrestrial monitoring sites. For lakes greater than 2 m in depth, a composite water sample was collected at the deepest part of the lake by multiple hauls of a polyvinyl chloride tube to the euphotic depth (two times the secchi disk depth) or 1 m above the lake bottom. For lakes less than 2 m deep, a composite sample was created from five 1 L collections at 0.5 m depths from different locations around the lake. Water was transferred from the composite sample to a 30 mL high-density polyethylene bottle, which was tightly sealed and sent to the University of Waterloo (Waterloo, Ontario) for analysis of $\delta^{18}O$ and δ^2H by standard isotope ratio mass spectrometry methods. All δ isotope results are given in per mil (‰) vs. VSMOW (Vienna Standard Mean Ocean Water; see Coplen 1996).

Watershed and lake physical parameters were estimated within a geographic information system (GIS) using 1:10 000 orthophotography and digital elevation models (DEMs) (1:20 000) to digitize lake surface area, drainage basin morphometry, and lake surface elevation. Lake bathymetry was characterized from three to five multiple transects across lake sites

Table 3. Summary of input values for ^{18}O mass balance (IMB).

	Interpolated					Calculated				Measured		Modelled	
Lake no.	P (mm)	E (mm)	T (°C)	h	δ_P (‰)	ε^* (‰)	ε_K (‰)	ε (‰)	m	δ_L (‰)	±1 SD (‰)	δ_A (‰)	δ^* (‰)
Region 1: NE Fort McMurray													
NE01	417	434	12.25	0.67	–18.54	10.45	4.66	15.11	1.97	–15.05	0.78	–23.59	–1.11
NE02	419	434	12.08	0.67	–18.61	10.47	4.66	15.13	1.97	–15.40	0.86	–23.57	–1.07
NE03	379	430	12.61	0.67	–18.51	10.41	4.64	15.06	1.98	–14.44	0.47	–23.89	–1.56
NE04	429	432	12.10	0.67	–18.58	10.46	4.67	15.13	1.97	–13.00	0.11	–23.55	–1.04
NE05	424	436	12.37	0.67	–18.25	10.44	4.68	15.12	1.96	–11.09	0.37	–23.47	–0.93
NE06	409	435	12.24	0.67	–18.54	10.45	4.66	15.11	1.97	–13.94	0.96	–23.64	–1.17
NE07	417	434	12.25	0.67	–18.53	10.45	4.67	15.12	1.97	–16.12	0.74	–23.58	–1.09
NE08	414	434	12.24	0.67	–18.50	10.45	4.66	15.11	1.97	–14.66	0.94	–23.62	–1.16
NE09	436	440	12.47	0.67	–18.17	10.43	4.70	15.12	1.95	–9.24	0.27	–23.41	–0.83
NE10	444	432	12.46	0.67	–18.09	10.43	4.69	15.11	1.96	–9.13	0.86	–23.36	–0.82
NE11	404	437	12.81	0.67	–18.18	10.39	4.67	15.06	1.97	–12.44	0.18	–23.60	–1.19
Region 2: Stony Mountains													
SM01	458	448	12.17	0.67	–17.87	10.46	4.65	15.10	1.98	–8.66	0.54	–23.02	–0.58
SM02	472	457	11.69	0.68	–18.11	10.50	4.58	15.08	2.03	–7.68	1.04	–23.06	–0.82
SM03	458	447	11.78	0.67	–18.36	10.49	4.63	15.13	1.99	–9.79	0.15	–23.23	–0.80
SM04	458	447	11.76	0.67	–18.34	10.50	4.64	15.13	1.99	–11.00	0.89	–23.21	–0.75
SM05	462	449	11.79	0.67	–18.34	10.49	4.62	15.11	2.00	–9.63	0.30	–23.21	–0.83
SM06	457	446	11.85	0.67	–18.36	10.49	4.64	15.13	1.98	–10.47	0.39	–23.23	–0.77
SM07	478	459	11.67	0.68	–18.02	10.51	4.57	15.08	2.03	–8.01	0.74	–23.02	–0.79
SM08	457	447	11.79	0.67	–18.36	10.49	4.64	15.13	1.99	–10.26	0.40	–23.23	–0.78
SM09	457	447	11.74	0.67	–18.37	10.50	4.64	15.14	1.99	–11.51	0.17	–23.24	–0.78
SM10	455	446	11.69	0.67	–18.40	10.50	4.64	15.14	1.99	–12.07	0.24	–23.26	–0.78
Region 3: West Fort McMurray													
WF01	448	457	12.00	0.68	–18.25	10.47	4.48	14.96	2.09	–8.69	0.89	–23.27	–1.45
WF02	448	458	11.94	0.68	–18.23	10.48	4.48	14.96	2.09	–8.19	0.56	–23.23	–1.42
WF03	454	462	12.00	0.68	–17.94	10.47	4.51	14.99	2.07	–9.51	1.20	–23.09	–1.15
WF04	416	447	12.61	0.68	–18.16	10.41	4.61	15.02	2.01	–8.71	0.47	–23.56	–1.36
WF05	427	447	12.45	0.67	–18.29	10.43	4.62	15.05	2.00	–9.37	0.64	–23.43	–1.15
WF06	430	444	12.65	0.67	–18.20	10.41	4.64	15.05	1.98	–11.59	1.37	–23.42	–1.07
WF07	431	447	12.51	0.67	–18.26	10.42	4.63	15.05	1.99	–11.52	1.41	–23.41	–1.10
WF08	430	447	12.39	0.68	–18.26	10.44	4.61	15.05	2.00	–8.32	0.42	–23.42	–1.15
Region 4: Birch Mountains													
BM01	407	451	11.24	0.68	–19.13	10.55	4.48	15.03	2.09	–12.71	0.17	–23.76	–1.86
BM02	408	452	11.47	0.68	–19.00	10.53	4.49	15.02	2.08	–12.31	0.13	–23.75	–1.82
BM03	398	454	11.41	0.68	–19.06	10.53	4.50	15.03	2.08	–14.93	0.68	–23.85	–1.89
BM04	396	453	11.41	0.68	–19.03	10.53	4.49	15.03	2.08	–12.29	0.90	–23.87	–1.93
BM05	393	454	11.36	0.68	–19.10	10.54	4.50	15.04	2.08	–13.19	1.00	–23.90	–1.93
BM06	389	451	11.34	0.68	–19.24	10.54	4.48	15.02	2.09	–15.28	0.64	–23.94	–2.05
BM07	382	447	11.47	0.68	–19.42	10.53	4.52	15.04	2.07	–14.86	0.35	–24.02	–2.01
BM08	392	454	11.35	0.68	–19.07	10.54	4.51	15.05	2.07	–15.03	0.57	–23.91	–1.90
BM09	395	453	11.37	0.68	–19.20	10.54	4.51	15.05	2.07	–13.79	0.49	–23.88	–1.86

Table 3 (*concluded*).

	Interpolated					Calculated				Measured		Modelled	
Lake no.	*P* (mm)	*E* (mm)	*T* (°C)	*h*	δ_P (‰)	ε^* (‰)	ε_K (‰)	ε (‰)	*m*	δ_L (‰)	±1 SD (‰)	δ_A (‰)	δ^* (‰)
BM10	413	451	11.97	0.68	−18.69	10.48	4.54	15.01	2.05	−8.59	0.45	−23.67	−1.64
BM11	390	445	11.58	0.68	−19.28	10.51	4.55	15.07	2.04	−11.54	0.61	−23.86	−1.71
Region 5: Caribou Mountains													
CM01	383	449	10.96	0.68	−19.99	10.58	4.50	15.07	2.08	−16.11	0.19	−24.35	−2.35
CM02	368	437	10.38	0.69	−20.26	10.63	4.42	15.06	2.13	−13.21	0.32	−24.54	−2.73
CM03	364	436	10.41	0.69	−20.28	10.63	4.45	15.08	2.11	−14.39	0.73	−24.56	−2.66
CM04	356	434	10.44	0.69	−20.33	10.63	4.43	15.06	2.13	−16.21	0.26	−24.61	−2.78
CM05	354	433	10.80	0.69	−20.04	10.59	4.40	14.99	2.15	−12.00	0.68	−24.55	−2.89
Region 6: Shield Lakes													
S01	345	391	11.93	0.68	−19.38	10.48	4.53	15.01	2.06	−12.30	0.20	−24.67	−2.68
S02	356	409	12.16	0.68	−19.06	10.46	4.55	15.01	2.04	−15.73	0.14	−24.41	−2.37
S03	356	401	12.12	0.68	−19.11	10.46	4.55	15.01	2.05	−15.04	0.30	−24.44	−2.41
S04	360	401	12.30	0.68	−18.99	10.44	4.56	15.00	2.04	−13.50	0.34	−24.42	−2.38
S05	359	407	12.18	0.68	−19.08	10.46	4.56	15.01	2.04	−12.53	0.12	−24.41	−2.35

Note: *P*, precipitation on the lake; *E*, lake evaporation; *T*, temperature; *h*, relative humidity; δ_P, δ_L, and δ_A, isotopic composition of precipitation, lake water, and the atmosphere, respectively; δ^*, limiting isotopic enrichment; ε, liquid–vapour isotopic separation factor; ε^* and ε_K, the temperature-dependent equilibrium and transfer-mechanism dependent kinetic separations, respectively; *m*, enrichment slope; SD, standard deviation.

using a sounder to record depth at 15-s time intervals and a Garmin handheld global positioning system (GPS) to record position for each transect. Raw data was contoured and converted to lake volume based on the surface area of slices at discrete depth intervals and geometric assumptions for frustral volumes. Lake centroids were used to generate specific latitude and longitude positions for interpolation of variables such as temperature from gridded climate data sets.

Methodology for model parameterization

Runoff and water-yield estimates were generated using an isotope mass balance model (IMB), developed under the assumptions of complete vertical mixing, constant density of water, and steady-state conditions, shown to be a reasonable approximation for typical lakes in the area (Gibson et al. 2002). In hydrologic and isotopic steady state, water and isotope balances are expressed, respectively, as

$$(1)\qquad P + W_Y - Q - E = 0$$

$$(2)\qquad P\delta_P + W_Y\delta_{WY} - Q\delta_Q - E\delta_E = 0$$

where P is precipitation on the lake (m^3), W_Y is catchment water yield, including both surface and groundwater fluxes to the lake (m^3), Q is the lake discharge, including surface and groundwater fluxes from the lake, and E is lake evaporation (m^3). Isotopic variables include δ_P, δ_{WY}, δ_Q, δ_E, the isotopic composition of precipitation, catchment water yield, discharge, and evaporation flux, respectively. The latter is observed to be substantially depleted in heavy isotopes under natural evaporation conditions because of kinetic isotopic fractionation that arises during diffusion of water vapour in air. δ_E was estimated using a simplified version of the one-dimensional Craig–Gordon diffusion model (see Gat 1996), which requires estimates of air temperature, humidity, the isotopic composition of atmospheric moisture δ_A, and the liquid–vapour isotopic separation factors $\varepsilon = \varepsilon^* + \varepsilon_K$, where ε^* and ε_K are the temperature-dependent equilibrium and transfer-mechanism-dependent kinetic separations, respectively, established and widely used from laboratory and wind tunnel experiments (Merlivat and Coantic 1975; Horita and Wesolowski 1994), the latter being representative of boundary-layer conditions for lakes on water budget time scales (Gonfiantini 1986). Several additional simplifications are made to compute the IMB: (*i*) the isotopic composition of catchment water yield is equal to that of precipitation, i.e., $\delta_{WY} = \delta_P$ as would be valid where runoff is locally derived from recent meteoric water that has not undergone substantial isotopic enrichment; (*ii*) the isotopic composition of discharge is adequately characterized by the isotopic signature of lake water δ_L, expected for well-mixed lakes; and (*iii*) lake water is adequately described by the mean isotopic composition of 3 years of late-summer sampling, which has been discussed previously (Gibson et al. 2002).

Rearranging and simplifying eq. 2, substituting $Q = P + W_Y - E$ from eq. 1, $\delta_E = (\delta_L - h\delta_A - \varepsilon)/(h - \varepsilon)$ from Gat (1995), and $\delta_{WY} = \delta_P$, $\delta_Q = \delta_L$ yields an estimate of the fraction of water loss by evaporation ($x = E/(P + W_Y)$) expressed as

$$(3)\qquad x \approx \frac{(\delta_L - \delta_P)}{m(\delta^* - \delta_L)}$$

where $m = (h - \varepsilon)/(1 - h + \varepsilon_K)$ is the enrichment slope, h is the humidity (relative humidity × 100), and $\delta^* = (h\delta_A + \varepsilon)/(h - \varepsilon)$ is the limiting isotopic enrichment.

Data used in the IMB are provided in Table 3. For computing x using eq. 3, atmospheric variables such as temperature, used to calculate the equilibrium separation ε^*, humidity h, the kinetic fractionation ε_K, and hence, m, δ^*, and δ_A were based on long-term climatology weighted according to the monthly evaporative flux to appropriately simulate conditions occurring during the evaporation season when the isotopic enrichment signals are produced (see Gibson 2002). Note that atmospheric moisture is not assumed to be in isotopic equilibrium with precipitation, $\delta_A \neq \delta_P - \varepsilon^*$ but is calculated by coupled scaling of the δ_A–δ_P separation as a common fraction of ε^* for both ^2H and ^{18}O to achieve a best fit to the slope of the regional $\delta^{18}O$–δ^2H evaporative enrichment trend for all lakes. This approach, which accounts for departure from δ_A–δ_P isotopic equilibrium because of seasonality effects (J.J. Gibson, S.J. Birks, and T.W.D. Edwards, unpublished data), serves operationally to constrain δ_A, but sacrifices independent estimates of $\delta^{18}O$ and δ^2H. In this case, residual differences in the outputs from x estimates based on the individual tracers serve to bracket departures from the local evaporative enrichment trend. Importantly, it preserves a description of kinetic isotopic fractionation in the boundary layer that is consistent with established boundary layer theory (see Brutsaert 1982, pp. 91, 97). The isotopic composition of precipitation is estimated using Bowen and Revenaugh (2003), which is based on data from IAEAs Global Network for Isotopes in Precipitation (Birks et al. 2002).

Climate variables were estimated for each site from global gridded data sets (30 years, 1961–1990). Precipitation was estimated from the CRU 0.5 × 0.5 CL1.0 data set (New et al. 1999). E is calculated using a Hamon approach (Hamon 1961; New et al. 1999). Temperature and relative humidity were approximated based on the CRU 10-min climatology (New et al. 2002). The results from gridded climate data analysis indicate that lake surface evaporation (Hamon 1961; Kalnay et al. 1996) ranges from 391 to 462 mm, and precipitation ranges from 345 to 478 mm at study sites across the region. These numbers are in general agreement with other data sources for the region that report evaporation and precipitation numbers between 400 and 500 mm·year^{-1} (Environment Canada 1978). Latitude is also found to be inversely correlated with lake evaporation. For example, differences in evaporation rates are apparent between the southern sites in the Stony Mountains (average 449 mm) and sites in regions 5 and 6 (Caribou Mountains and Shield Lakes, averages 438 and 401 mm, respectively). Evaporation also exceeds precipitation (New et al. 1999) in this region by roughly 7%. Catchment areas for runoff production exceed lake areas by 89% on average. Transpiration is estimated to be 36%–50% of evaporation in this region (Abraham 1999), although landscape runoff presented herein are calculated from the isotope balance rather than using this value. Excluding groundwater inflows or recharge, climatological constraints suggest that water yield should be of the order of 25 to 200 mm·year^{-1} (Environment Canada 1978) across sites in the region, which as we show is less than the IMB-calculated range for the majority of lakes.

Water yield from IMB was calculated for the net catchment area of the 50 lakes using the x output results from eq. 3 and precipitation and evaporation over the lake (m^3) interpolated at each lake site:

$$(4) \qquad W_Y = \frac{E}{x} - P$$

where W_Y is the water yield (in mm·year^{-1}) estimated as W_Y·CA, where CA is net catchment area. Runoff ratio is estimated as the water yield from the catchment area divided by the precipitation volume on the catchment area. Residence time (τ, in years) of lake water was estimated as volume/inflow from the annual throughflow index (x), lake volume (V, m^3), and lake evaporation (E, m^3·year^{-1}), according to the method of Gibson et al. (2002):

$$(5) \qquad \tau = \frac{xV}{E} \quad \text{or} \quad \tau = \frac{V}{I}$$

The Water Survey of Canada (WSC) hydrometric estimates of water yield are based on available long-term average W_Y data (mm·year^{-1}) from 20 hydrometric gauging stations, grouped by representative watershed region (Fig. 3). The stations used in this analysis included both active and discontinued stations (65% and 35%, respectively). Most of the gauges (80%) are seasonally operated (March to October), whereas all of the continuous stations used for this analysis have been deactivated. WSC gauges are located some distance downstream but still within the broad-scale drainage areas of 20 lake sites. For 30 lakes, however, gauges located in adjacent or nearby watersheds were extrapolated to estimate water yield. Study lakes and their catchments in the Stony Mountains are illustrated (Fig. 3). WSC stations 07CD004 and 07CD004 are shown to illustrate the range in size of WSC catchments that may be used to represent water yield from this region. In general, WSC stations range in size from 54 to 14 300 km^2, and 67% of the basins applied in this study to calculate WSC water yield are less than 3000 km^2.

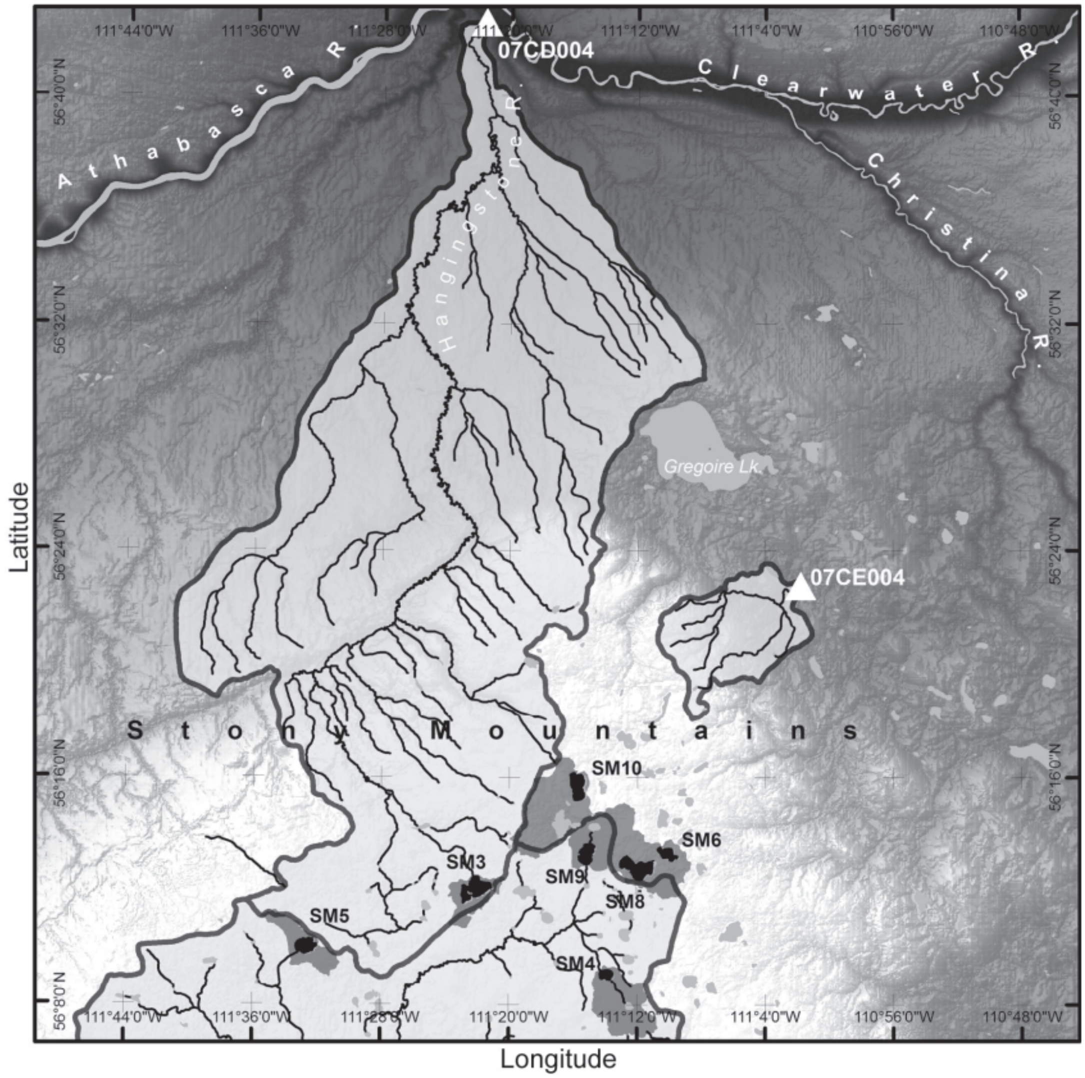
The study lakes are primarily headwater, as these sites are most likely to be sensitive to acid deposition. The location of lakes relatively high in watersheds means that none of the sites contains water survey gauges at its outlets. The lack of any direct measurements of inflow and outflow also preclude the calculation of water balance for comparison with IMB or the WSC water-yield estimates. The WSC hydrometric stations used in this study had an average collection record of 27 years, spanning the years 1962 to 2004. In cases where WSC gauges were operated for short periods of time (<10 years), the data were not considered reliable and were therefore not used.

Critical loadings (kequiv. H^+·ha^{-1}·year^{-1}) were approximated using the estimated W_Y (mm·year^{-1}) to represent the flux (mass × time) of the annual average net catchment runoff, according to (WRS 2004):

$$(6) \qquad CL_A = ([BC]_0 - [ANC_{lim}])\cdot W_Y \cdot 10^{-5}$$

where $[BC]_0$ is the nonmarine flux of base cation concentrations assumed to be equivalent to the sum of base cations in current lake water samples, W_Y equals runoff or water yield (mm·year^{-1}), and ANC_{lim} is the critical acid-neutralizing capacity limit, in this case, corresponding to a pH of 6.0 where

Fig. 3. Example of lake sites in the Stony Mountains and nearby Water Survey of Canada (WSC) gauges used to calculate the WSC water-yield estimate. Note that no lake sites have WSC gauges at their outlets.



biotic effects from acidification have been shown to occur (75 µequiv.$\cdot$L^{-1} for all lakes; WRS 2004). The isotope mass balance model assumes that the lakes are operating at steady state and applies the use of water quality data from the late fall season, which is considered representative of annual average lake water chemistry (Henriksen et al. 1992; RAMP 2006). Bicarbonate is considered the primary buffering source for lakes, and surface runoff from the catchment is the only source of alkalinity (WRS 2004). Note that S4, originally part of the regional subset (n = 50), was not included in the critical acid loading analysis (n = 49) because data for $[BC]_0$ does not yet exist.

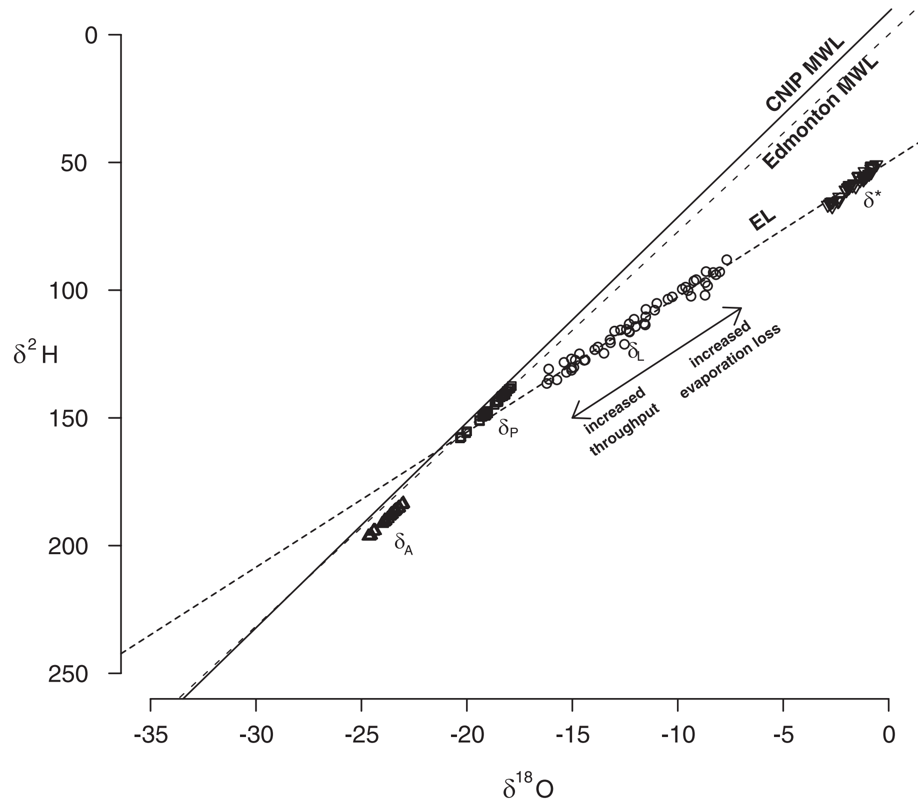
Exceedance occurs when the acid-generating processes are greater than the acid-buffering processes in lake systems. Exceedance is based on a potential acidifying input (PAI) scenario as described in WRS (2004), and the use of an exceedance measure enables us to comparatively examine affected aquatic features occurring within a region. The PAI scenario applied in this analysis uses a baseline assessment undertaken by Alberta Environment (Cheng et al. 1997). When CL_A is smaller than the PAI value, the lake is considered exceeded and therefore at risk of acidifying to a degree harmful to the biological indicator species. It is recognized that PAI values are approximate; however, predicted PAI values remain the primary indicator of acid deposition for accessing exceedance by industry (Imperial Oil 2005). PAI-based acid sensitivity estimates are included in this paper to illustrate the importance of accurate calculation of water yields for input into critical loadings estimates on which exceedance scenarios are built.

Results and discussion

Isotope systematics

As shown in this study (Fig. 4) and described in detail in previous boreal and arctic lakes surveys (Gibson et al. 1993, 2002, 2005), the systematic offset by evaporative isotopic enrichment from the meteoric water line (MWL) serves as a quantitative tracer of lake throughput (x) and, hence, as a flux-weighted measure of hydrological properties of the sur-

Fig. 4. δ^2H–$\delta^{18}O$ plot showing measured and modelled components of the isotope mass balance for the study lakes. MWL, meteoric water line based on Canadian Network for Isotopes in Precipitation ($\delta^2H = 7.8\delta^{18}O + 5.2$, $r^2 = 0.99$; Gibson et al. 2005); EL, evaporation line determined from regression of mean lake water δ_L values; δ_P are interpolated for latitude–longitude coordinates of each lake based on Bowen and Revenaugh (2003), and δ_A and δ^* are determined using a seasonal weighting algorithm described in the text.



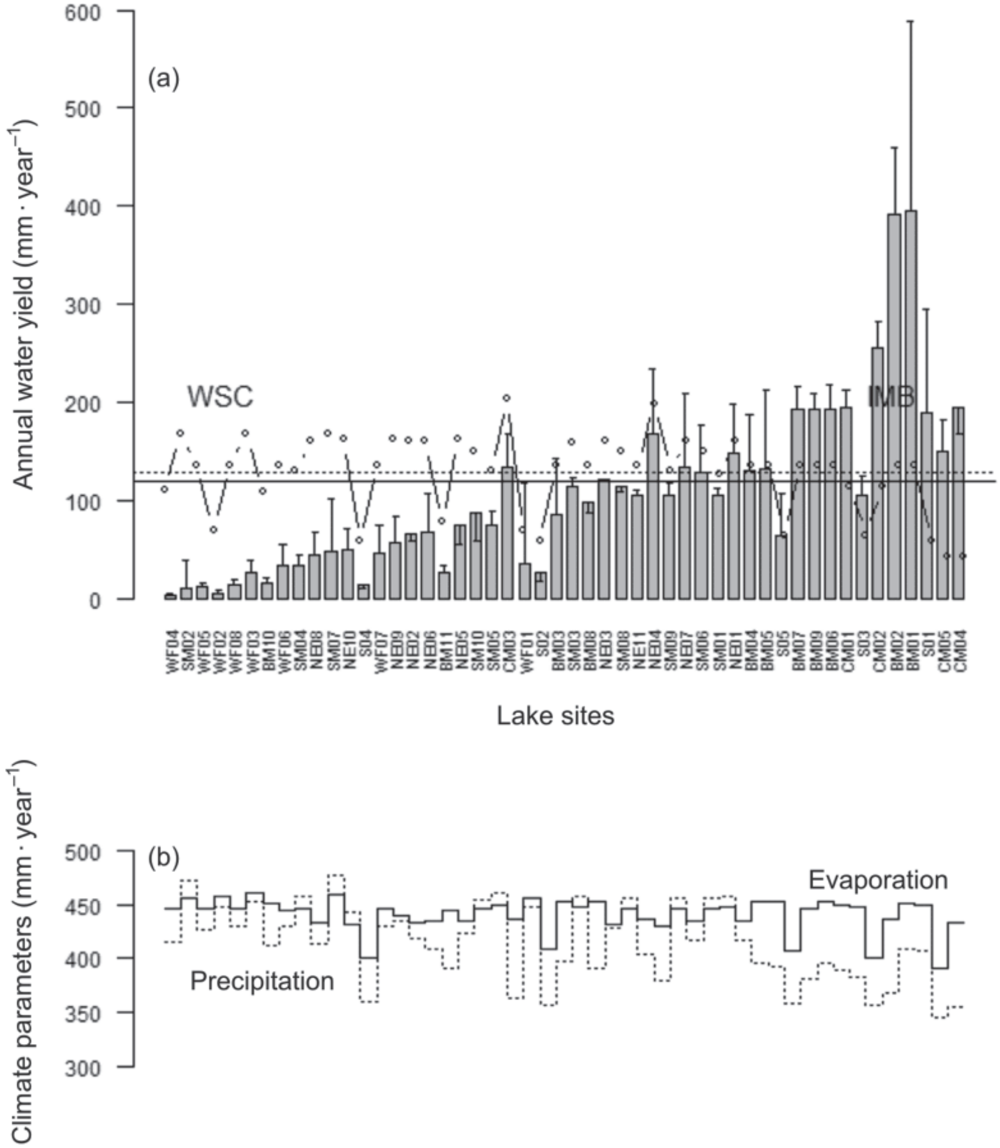
rounding landscape. Both the Canadian Network for Isotopes in Precipitation (CNIP) MWL and the Edmonton CNIP MWL are illustrated; modelled isotopic compositions (δ_P; Bowen and Revenaugh 2003) fall close to the Edmonton CNIP MWL. Lakes that have lower inputs (precipitation + catchment yield) sit furthest away from the MWL towards the limiting isotopic enrichment, whereas lakes with higher input sit closer to the isotopic composition of precipitation. High water yielding lakes (Fig. 5*a*), for example, generally exhibit isotopic lake water signatures δ_L of approximately –14 to –16 $\delta^{18}O$‰ and have increased throughput, whereas low water yield systems exhibit isotopic signatures around the range of –7 to –9 $\delta^{18}O$‰ and have increased evaporation loss (quantitative results and comparisons are presented in Table 4 and illustrated in Figs. 5 and 6).

Hydrologic indicators

The fraction of water loss by evaporation (x, eq. 3) is shown to span the continuum between 8% and 75%, suggesting considerable range in the hydrologic conditions of lakes in the region; lakes with highest x values function as precipitation-fed basins with minor runoff from surrounding areas, whereas those with lowest x values function as nodes in the regional river drainage network, with rapid surface water – groundwater throughput. Residence time (eq. 5) of water in the lakes is also highly variable (~0.2–7 years) and is weakly correlated ($r^2 = 0.24$) with water yield, as residency depends on x and volume, or water yield and volume. Average differences between ^2H and ^{18}O estimates of water yield (eq. 4) are –3% (±3%), which is a useful measure of uncertainty using the best-fit approach as applied with $\delta_P - \delta_A = 0.72\varepsilon^*$ (70% of liquid–vapour equilibrium separation). Year-to-year fluctuations measured in ^{18}O water yield range from 96 to 118 mm·year^{-1}, a difference from the composite water yield (3-year) estimate of –8%, 11%, and –10% in 2002, 2003, and 2004, respectively.

Water yield (W_Y, eq. 4), which is effectively calculated from the IMB by subtracting the influence of direct precipitation falling on the lake, is predicted to be in the range of 4×10^4 to 5×10^6 m^3·year^{-1}. The depth-equivalent IMB W_Y, which accounts for catchment area, ranges from 5–395 mm·year^{-1} compared with 23–196 mm·year^{-1} estimated based on interpolation of stream flow (WSC) data. Differences between the years of study and the long-term climate and hydrology (Table 2) are not anticipated to create large errors in estimate of IMB water yield; even through summers were warmer and drier in general during the study years, only a small difference in runoff was observed. A comparison of the results of IMB and WSC are shown (Fig. 5*a*), where precipitation and evaporation estimates are provided for each lake based on 1961–1990 climate normal (Fig 5*b*). Note that W_Y results are ordered according to the IMB–WSC offset (by percent fraction of IMB) to emphasize the systematic similarities and differences between the two approaches. It is encouraging to note that average water yields of close to 110 mm·year^{-1} (±6 mm·year^{-1}) were obtained for both methods, although median values were 33% lower for IMB, as discussed later in the paper.

Fig. 5. Plot of water yield (W_Y) and interpolated climate fields for various lakes depicting the hydrologic "pulse" of the systems. (*a*) W_Y results for IMB (isotope mass balance model; bars) and WSC (Water Survey of Canada; open circles) are sorted by the fractional differences between the two estimates (IMB – WSC). Error bars illustrate the standard deviations for IMB water yields. The dotted line is average WSC W_Y; the solid line is average IMB W_Y, similar for both methods. (*b*) Climate parameters: precipitation (*P*) is shown as a dotted line; evaporation (*E*) is shown as a solid line. Note that *P* – *E* is typically negative.



Upon closer examination, three distinct populations of lakes can be identified (Fig. 5*a*) comprising lakes in which WSC W_Y estimates were greater than ±50% of IMB and lakes in which the two estimates of water yield were within reasonable bounds (WSC fraction of IMB < 50%, 24 lakes). Lake systems (19) in which WSC W_Y was higher than IMB W_Y (Fig. 5*a*) by 50% tended to have smaller surface areas (60% below that of the data set average) and were located primarily in low-elevation boreal plain environments (regions 1 and 3). Possible errors in the IMB such as non-steady-state conditions within these small lakes or pre-enrichment owing to evaporative waters entering into lakes are likely causes of some, but not all, of the differences between the two methods (Fig 6*b*). At the other end of the spectrum, WSC W_Y is lower than IMB W_Y at seven lakes, four of which are large, deep lake systems (lake surface areas more than 500% greater than the data set average); these lakes are discussed in more detail later in the paper. Removing the effect of the very small and very large systems results in observed values (25th and 75th percentiles) in IMB water yield estimates ranging from 39 to 135 mm·year^{-1}, whereas WSC estimates range from 100 to 150 mm·year^{-1}. The IMB estimate of water yield is directly comparable with known observations (Environment Canada 1978) of runoff for the region, noted earlier in the paper, whereas the WSC fails to capture the low range of water yields. The observed pattern is reasonable considering that WSC W_Y is a large-scale, interpolated estimate, whereas IMB is based on fine-scale, site-specific conditions, which more closely resemble the variability of lake sizes and landscapes present in this complex region (RAMP 2006).

Unfortunately, because of difficulty in gauging lake outflows in the region, it was not possible to directly compare IMB and WSC estimates for identical lake-drainage areas

Table 4. Comparison of hydrologic indices and their potential impact on aquatic loadings and exceedance status.

	Isotope mass balance									Hydrometric			Critical loadings status	
Lake no.	x $\delta^{18}O$ (%)	Diff. x from $\delta^{2}H$ (%)	Residence time (year)	IMB W_Y ($m^3 \cdot year^{-1}$)	IMB W_Y ($mm \cdot year^{-1}$)	IMB 2002 W_Y ($mm \cdot year^{-1}$)	IMB 2003 W_Y ($mm \cdot year^{-1}$)	IMB 2004 W_Y ($mm \cdot year^{-1}$)	IMB runoff ratio	WSC W_Y ($m^3 \cdot year^{-1}$)	WSC W_Y ($mm \cdot year^{-1}$)	WSC runoff ratio	IMB CL_A (kequiv. $H^+ \cdot ha^{-1} \cdot year^{-1}$)	Exceedance condition
NE1	12.7	–0.7	0.35	1 957 900	149	230	166	114	0.36	1 968 600	150	0.36	0.25	Same
NE2	11.4	–1.0	0.33	1 141 000	67	119	64	47	0.16	2 550 500	150	0.36	0.18	Same
NE3	15.9	2.2	0.23	2 700 500	169	200	161	145	0.45	3 061 100	192	0.51	0.56	Same
NE4	23.7	–2.5	0.79	811 300	122	112	135	114	0.29	996 200	150	0.35	0.52	Changed
NE5	36.0	–0.3	0.75	1 491 100	76	61	94	70	0.18	2 987 200	153	0.36	0.49	Same
NE6	18.3	0.8	0.37	735 800	69	106	79	50	0.17	1 603 900	150	0.37	0.25	Same
NE7	8.1	–1.5	0.19	551 000	135	218	122	100	0.32	611 600	150	0.36	0.31	Same
NE8	14.4	–1.0	0.27	298 000	46	75	47	30	0.11	971 500	150	0.36	0.15	Changed
NE9	54.5	–5.9	1.38	1 173 500	58	46	63	60	0.13	3 066 100	153	0.35	0.92	Same
NE10	55.1	–4.9	0.98	1 423 800	51	33	34	65	0.12	4 222 800	153	0.34	0.66	Same
NE11	26.0	0.8	0.79	7 353 000	107	–41	119	96	0.26	8 474 600	123	0.30	2.02	Same
SM1	57.5	–3.7	0.86	758 600	107	73	105	131	0.23	807 800	114	0.25	0.57	Same
SM2	75.0	–4.0	0.94	269 500	11	1	7	23	0.02	3 850 000	158	0.34	0.03	Changed
SM3	47.9	–2.9	1.55	888 400	116	94	126	110	0.25	1 141 900	149	0.32	0.13	Same
SM4	36.1	–2.8	0.57	410 800	34	21	48	35	0.07	1 418 400	118	0.26	0.04	Same
SM5	49.5	–2.6	1.27	473 300	75	74	74	70	0.16	743 800	118	0.26	0.05	Same
SM6	41.0	–1.5	0.81	441 500	130	110	128	143	0.28	474 200	140	0.31	0.35	Same
SM7	68.3	6.6	1.90	285 600	49	8	58	83	0.10	916 400	158	0.33	0.08	Same
SM8	43.0	–1.3	0.85	1 114 700	115	84	115	121	0.25	1 358 100	140	0.31	0.04	Same
SM9	32.2	–3.1	0.41	999 600	106	104	108	103	0.23	1 119 600	118	0.26	0.04	Same
SM10	28.2	–1.3	0.44	1 523 500	88	82	84	87	0.19	2 429 800	140	0.31	0.09	Changed
WF1	63.1	5.6	0.81	883 200	36	4	46	45	0.08	1 269 700	52	0.12	0.23	Same
WF2	70.8	5.3	1.45	150 000	6	1	10	7	0.01	1 225 500	52	0.12	0.00	Same
WF3	48.7	3.9	1.02	1 071 600	28	13	29	44	0.06	6 045 000	158	0.35	0.07	Changed
WF4	64.0	15.4	1.20	9 700	5	5	4	5	0.01	173 800	97	0.23	0.07	Changed
WF5	54.2	7.0	0.91	93 100	14	6	18	13	0.03	855 700	124	0.29	0.09	Changed
WF6	31.6	4.3	0.69	177 700	35	17	53	40	0.08	636 300	124	0.29	0.13	Changed
WF7	32.5	0.8	0.58	80 300	47	25	83	42	0.11	212 700	124	0.29	0.38	Same
WF8	69.2	–3.0	1.11	437 700	16	7	21	17	0.04	3 363 700	124	0.29	0.11	Changed
BM1	28.2	–3.1	3.61	20 250 200	395	345	444	375	0.97	6 367 400	124	0.30	0.60	Same
BM2	30.6	–3.5	7.01	46 862 500	392	345	445	365	0.96	14 844 700	124	0.30	1.61	Same
BM3	15.2	1.6	0.46	2 488 600	87	65	114	69	0.22	3 551 200	124	0.31	0.42	Same
BM4	31.3	1.1	0.30	4 490 100	132	131	182	86	0.33	4 230 700	124	0.31	0.48	Same
BM5	25.3	0.3	0.25	3 700 300	133	117	199	90	0.34	3 460 800	124	0.32	0.65	Same
BM6	14.3	1.2	0.16	3 568 400	194	213	235	142	0.50	2 282 700	124	0.32	0.23	Same
BM7	17.1	–2.3	0.25	1 506 100	193	173	176	205	0.51	969 300	124	0.33	0.03	Same
BM8	14.8	1.2	0.37	3 239 300	99	99	126	76	0.25	4 055 300	124	0.32	0.34	Same
BM9	21.9	–1.4	1.55	5 835 900	193	151	232	194	0.49	3 754 700	124	0.31	0.14	Same
BM10	70.9	6.6	0.58	88 000	17	19	16	14	0.04	486 300	95	0.23	0.17	Same
BM11	38.5	1.9	0.21	42 100	28	20	33	32	0.07	90 200	61	0.16	0.06	Same

Table 4 (*concluded*).

	Isotope mass balance									Hydrometric			Critical loadings status	
Lake no.	x $\delta^{18}O$ (%)	Diff. x from δ^2H (%)	Residence time (year)	IMB W_Y ($m^3 \cdot year^{-1}$)	IMB W_Y ($mm \cdot year^{-1}$)	IMB 2002 W_Y ($mm \cdot year^{-1}$)	IMB 2003 W_Y ($mm \cdot year^{-1}$)	IMB 2004 W_Y ($mm \cdot year^{-1}$)	IMB runoff ratio	WSC W_Y ($m^3 \cdot year^{-1}$)	WSC W_Y ($mm \cdot year^{-1}$)	WSC runoff ratio	IMB CL_A (kequiv. $H^+ \cdot ha^{-1} \cdot year^{-1}$)	Exceedance condition
CM1	13.5	−1.9	1.95	4 693 900	196	178	228	184	0.51	2 382 400	100	0.26	0.75	Same
CM2	31.5	−6.0	2.06	9 722 900	256	260	283	213	0.70	3 775 200	100	0.27	0.93	Same
CM3	23.8	−2.4	0.95	3 385 600	134	163	139	102	0.37	4 955 400	196	0.54	0.03	Same
CM4	14.4	−1.9	2.75	6 978 800	195	195	214	163	0.55	805 800	22	0.06	0.65	Same
CM5	41.1	−5.2	1.49	386 300	150	174	165	106	0.42	57 900	22	0.06	0.26	Same
S1	35.8	−3.9	6.04	2 545 900	190	176	220	163	0.55	533 100	40	0.12	0.8	Same
S2	12.2	1.4	1.05	3 073 600	28	25	30	28	0.08	4 386 900	40	0.11	0.14	Same
S3	15.8	0.9	1.31	3 170 500	107	83	121	105	0.30	1 392 400	47	0.13	0.39	Same
S4	24.2	2.3	2.41	1 835 900	15	12	18	15	0.04	4 896 900	40	0.11	N/A	N/A
S5	31.6	4.3	0.77	295 200	66	60	70	66	0.18	210 000	47	0.13	0.32	Same

Note: See eq. 3 for x; Diff. x from δ^2H, the difference between x calculated from $\delta^{18}O$ and x calculated from δ^2H; W_Y, catchment water yield; IMB, isotope mass balance model; WSC, Water Survey of Canada; CL_A, critical acid loads.

without interpolation. Nor is it possible at the present time to apply IMB directly at the WSC river gauging stations. Without the benefit of a flux-weighted reservoir δ_L, estimation of the isotopic composition of discharge δ_Q in eq. 2 for a river outlet requires a multiyear time-series isotope record, which is currently unavailable at the sites in the area. Error ranges for the IMB and WSC models can be gleaned from ranges in the standard deviations for measured data and the differences in the 2002–2004 modelled water yields (Table 4). Water yield is measured for both IMB and WSC; W_Y from the WSC gauges is measured in the field over a 43-year period, and isotope measurements are sampled at lake sites over a 3-year period. All other parameters used to calculate the IMB and WSC W_Y estimates are applied to both models equally. The IMB W_Y estimates (based on ±1 SD in $\delta^{18}O$ measured at the lakes) range from 94 to 132 $mm \cdot year^{-1}$, whereas the WSC W_Y estimates, calculated as ±1 SD in the gauge runoff, range from 53 to 179 $mm \cdot year^{-1}$. Hence, although the range in the W_Y estimates as provided by IMB was larger than that of the WSC, the variability (as calculated using ±1 SD) across isotopic estimates was lower than that of the gauged runoff.

To determine the range in W_Y estimates obtained over the three study years, water yields were calculated for each individual year. Note that the IMB model estimates provided as comparison to WSC estimates are based on the average signal over the 3-year period of 2002–2004 (Table 4, WSC yearly data not shown). Both estimates of water yield respond, on a relative basis, similarly to average variations in climate; however, the IMB W_Y mirrors the contributions of average precipitation throughout the 3 years. For example, rainfall + snowfall is greatest in 2002 and 2003 and least in 2004, which is reflected in the average IMB results (data not shown). Temperature variations, on the other hand, reflect the WSC estimate; for example, maximum temperatures were greatest in 2003 and lowest in 2002. Further analysis of the combined effects of climate on water yields at more appropriate temporal scales is required to fully understand these relationships.

As noted previously, the median W_Y values were 33% lower for IMB than WSC. This is largely attributed to elevated IMB W_Y for several large, deep lakes (CM2, S1, BM1, and BM2), which were suspected of being connected to regional groundwater flow systems. The uniqueness of these lakes is apparent when examining the average lake area and maximum depth, which are 18.5 km^2 and 17.5 m, respectively, for the four lakes compared with the survey averages of 3 km^2 and 4.3 m, respectively. Similar lakes displaying elevated runoff ratios have been reported in previous isotopic surveys on the boreal plain (Gibson et al. 2005). Because of their increased volume, these lakes also tended to have longer residence times (eq. 5), despite greater water yields. Volumetric runoff ratios ($W_y \cdot P$) were also calculated to evaluate whether the watersheds could plausibly sustain the estimated water yields. Typically, runoff ratios range from 0.1 to 0.5 for precipitation-fed systems in the area, but potentially higher values for groundwater-fed systems, especially fens, might arise (Gibson et al. 2005). For the study lakes in general, runoff ratios were found to range from 0.01 to 0.97 for IMB compared with 0.06 and 0.54 for the WSC approach. The upper limit of the IMB runoff ratio decreases from 0.97

to 0.55 when the large, deep lakes are excluded from the analysis. Although groundwater originating from outside the topographic catchment area is the most likely hypothesis for elevated water yields and runoff ratios in these deep lakes, other uncertainties were also considered. Errors associated with drainage basin area delineation, a problem common in low-relief wetland-rich areas, were judged to be unlikely as the lakes are found in relatively incised terrain. Furthermore, a threefold increase in watershed area would be required in all cases to account for the "excess" water. Chain-of-lake effects (Gat and Bowser 1991) were also considered because the problematic systems are large, non-headwater systems with many contributing lakes feeding into them. However, this effect would in fact result in lower water yields as pre-enrichment of heavy isotopes would accentuate apparent evaporation losses from the system.

As presented, IMB estimates are a first approximation of the water-yield conditions across the 50-lake survey. These estimates should be regarded as guidelines that may be refined over time as monitoring and sampling continue at the sites. Nevertheless, the estimates serve to demonstrate the difference between use of site-specific and regionally interpolated estimates of water yield, a difference that helps to illustrate the potential improvements from incorporation of site-specific IMB into critical loadings assessments.

Critical loadings comparison

Critical loads of acidity CL_A for the study sites are presented for each method (Fig. 6*a*, where the order of lakes from Fig. 5 is preserved), and IMB critical acid loading estimates are also presented (Table 4). Note that the lake number is reduced from 50 to 49 for CL_A calculations as one lake (S4) had insufficient data for calculation of the measure. CL_A is also compared with a preliminary potential acid input (PAI) scenario for the region described in WRS (2004), whereby lakes with CL_A > PAI are considered to be potentially sensitive to acidification (Fig. 6*a*). Despite the first-order nature of the PAI and CL_A models and underlying data sets noted earlier, these provide a practical basis for comparing the propagation of W_Y effects on the assessment. Differences between the IMB and WSC versions are further illustrated (Fig. 6*b*), highlighting lakes for which exceedance status changes when the site-specific IMB results are applied (see also Table 4). In total, exceedance status based on IMB was different in nine of the 49 lakes (18%; Table 4), eight of which were identified as being potentially exceeded as a result of acid inputs and one switched to not-exceeded status. Elevated sensitivity was due to a lower water yield calculated by the IMB method. The one lake (BM07) with reduced sensitivity had elevated water yield calculated by the IMB method and therefore a higher annual loading of base cations (see RAMP (2006) for chemistry data). Differences in CL_A at both extremes of the hydrologic spectrum are nevertheless considerable even for lakes where exceedance status does not change (Figs. 6*a* and 6*b*).

Regionally, changes in exceedance status only appear to affect lakes in the northeast Fort McMurray, Stony Mountains, and west Fort McMurray regions, where PAI is more likely to be close to CL_A, and not in the more distant Birch Mountains, Caribou Mountains, and Shield Lakes regions, despite presence of low-yield systems in all. Improvements in these preliminary assessments will require better characterization of the chemistry of runoff and its variability, as well as improved representation of peatland characteristics.

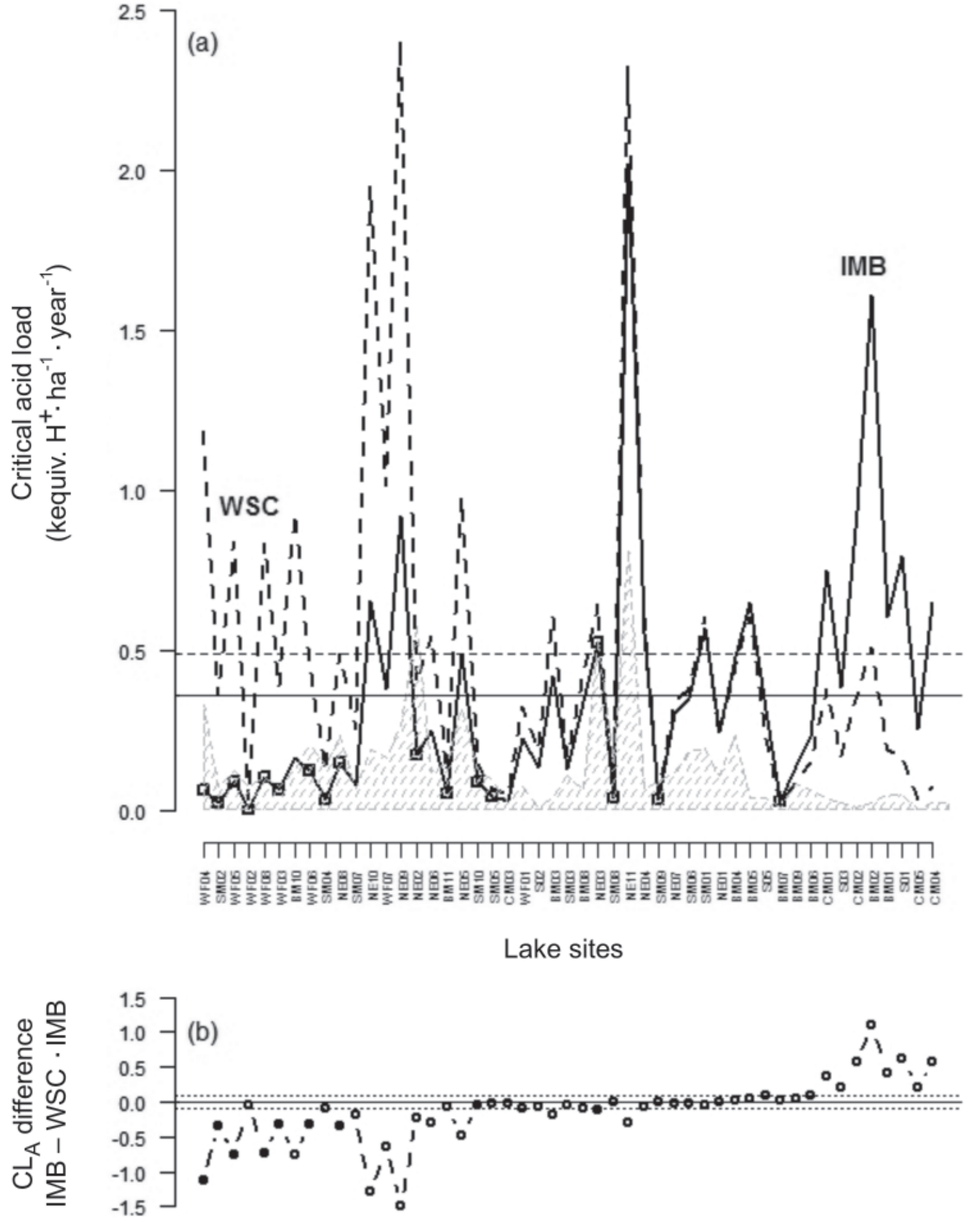
Lake and watershed characteristics

To further understand under what conditions WSC-based water yields were similar to those of IMB, a comparison was made of lake and watershed characteristics for sites with similar W_Y and within the zone of agreement (<50% IMB–WSC, shown in Fig. 5*a*). This coarse-scale analysis sheds some light on landscape controls at work across this region of the boreal forest; however, results would be greatly improved through the application of finer-scale data sets, region by region across the study area. Similarities between the study watersheds and the large WSC basins were evaluated from regression analysis that included factors such as drainage basin area, catchment elevation, slope, and drainage ratio, and vegetation characteristics such as percent coverage of fen, bog, and upland were compared where data permitted. Initial results suggest that differences in WSC and IMB estimates of W_Y are more similar when the slope and elevation of the study watershed are similar to those of the larger WSC watershed, when the slope is higher, and when water residence times in the lakes are comparatively short. Disconnected behaviour of some low- and high-throughput lakes apparently connected to regional groundwater was not captured by the WSC network, which tended to represent mean conditions. Fen area and bog area (at sites where wetlands comprised greater than 50% of the catchment area) were also found to be comparatively important controls on water-yield differences in the systems (r^2 = 0.17 and 0.16, p < 0.05, for fens and bogs, respectively), although the very coarse-scale data sets used to analyse wetlands are not considered sufficient to illustrate this relationship. Additionally, the low water yield regions such as regions 1 and 3 are anticipated to have high percentage wetland and deeper surficial materials (see Smerdon et al. (2007) for a discussion of the influence of depth of surficial materials in a study site slightly further south of these regions), which control water movement across these landscapes; however, relationships could not be found given the existing data. WSC estimates are also improved when IMB lake sites are situated within the broader-scale WSC catchment, illustrating the importance of consistent landscape controls between interpolated sites. Increased density of a gauging network might be one approach to improve hydrologic calculations. Such enhancements seem unlikely considering the movement towards divestment in government-sponsored monitoring in recent years (Shiklomanov et al. 2002).

Research implications

Water yield is often the most unreliable parameter in critical load calculations. Commonly, water yield is based solely on estimates from the available hydrometric network. This study demonstrates an alternative method for estimating site-specific water yield to lakes based on isotope mass balance, applies the approach to calculate water yield and critical acid loadings for 49 lakes in northeastern Alberta, and compares the results with a conventional hydrometric interpolation approach. Importantly, the results suggest that the hydrometric networks fail to capture the scale-dependant

Fig. 6. (*a*) Pulse diagram illustrating a preliminary critical acid loadings (CL_A) scenario for study sites based on isotope mass balance (IMB; solid line) and Water Survey of Canada (WSC; broken line) water yields (W_Y). The shaded hatched background represents the potential acidifying input (PAI) value for each study site. When the PAI value is greater than the critical load, sites are considered acid-sensitive (exceeded systems are illustrated by a square). (*b*) Pulse diagram illustrating difference in predicted critical loads associated with use of in situ IMB W_Y versus interpolated WSC W_Y. Lakes where exceedance conditions depend on W_Y method used are indicated by solid circles.



hydrologic variability present within the boreal landscapes, particularly in some of the most sensitive systems such as the small, evaporative lakes with low runoff. To our knowledge, this is the first time that a critical loadings assessment has been refined using measurements of the stable isotopes of water.

The hydrologic conditions observed (IMB) at study lakes are directly comparable with those of previous studies in the region (Environment Canada 1978; Prepas et al. 2001; Gibson et al. 2002). Four lakes that were found to have high water yields are situated in the Caribou and Birch mountains, zones of enhanced regional groundwater flow, and may reflect deep regional groundwater inputs occurring outside topographically defined local catchments (Toth 1963; Winter et al. 2003). The analysis also reinforces past observations that the boreal plain is in general characterized by a net water deficit (Winter 1989; Ferone and Devito 2004), i.e., evaporation generally exceeds precipitation, so that most lakes depend on runoff from the catchment or groundwater inputs to maintain a long-term hydrologic balance.

The low threshold of evaporative lakes to acidification is important to realize. In Alberta's boreal region of Canada, despite strident controls on emissions, lakes are at high risk to acid deposition because the extent and severity of current impacts is unknown. Small lakes, which comprise a greater percentage of the lake systems of the boreal landscape, are primarily impacted by approaches to calculating sensitive model parameters such as water yield. One promising aspect is that the identification of lakes at risk is possible using the stable isotopes of water, which are easily incorporated into water quality surveys and may help to elucidate aquatic systems at risk at the regional, national, and continental scale.

Collaborative studies are also currently underway to incorporate a refined version of the IMB into a dynamic critical loadings assessment for the region using a model similar to MAGIC (Model of Acidification of Groundwater in Catchments) (see Aherne et al. 2003).

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