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Regional trends in evaporation loss and water yield based on stable isotope mass balance of lakes: The Ontario Precambrian Shield surveys

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ABSTRACT

Stable isotopes of water, oxygen-18 and deuterium, were measured in water samples collected from a network of 300 lakes sampled in six ~100 km^2 blocks (centred at 49.72°N, 91.46°W; 48.49°N, 91.58°W; 50.25°N, 86.62°W; 49.78°N, 83.98°W; 48.24°N, 85.49°W; 47.73, 84.52°W) within Precambrian shield drainages in the vicinity of Lake Superior, northern Ontario, Canada. Additional sampling was also conducted within the Turkey Lakes watershed (47.03°N, 84.38°W), a research basin situated in the Algoma region located 50 km north of Sault Saint Marie, Ontario. The studies were undertaken to gain a better understanding of hydrology and geochemistry of watersheds in the region in order to better predict acid sensitivity of lakes. The main objective of this paper is to describe the hydrologic variations observed based on stable isotope results. Evaporative isotopic enrichment of lake water was found to be systematic across the region, and its deviation from the isotopic composition of precipitation was used to estimate the evaporation/inflow to the lakes as well as runoff (or water yield) based on a simple isotope mass balance model. The analysis illustrates significant variability in the water yield to lakes and reveals a pattern of positively skewed distributions in all six widely spaced blocks, suggesting that a high proportion of lakes have relatively limited runoff whereas relatively few have greater runoff. Such basic information on the drainage structure of an area can be valuable for site-specific hydrologic assessments but also has significant implications for critical loads assessment, as low runoff systems tend to be less buffered and therefore are more sensitive to acidification. Importantly, the Turkey Lakes sampling program also suggests that isotope-based water yield is comparable in magnitude to hydrometric gauging estimates, and also establishes that uncertainty related to stratification can be as high as ±20% or more for individual lakes, although it likely has only a minor influence on regional survey results. While further analysis in gauged lake watersheds would be beneficial to constraining the accuracy of the method or calibrating it for operational use, it is nevertheless a powerful tool in its present form for lake-to-lake and regional runoff inter-comparisons.

1. Introduction

Lake hydrology in Canada has proven difficult to monitor due to the sheer number of lakes and vast areas that are remote and ungauged. Canada has an estimated 2 million lakes, covering roughly 7.6% (758,000 km^2) of Canada's total land area (Canada, Natural Resources Canada, 2016). This corresponds to 28% of the total lake area worldwide based on the area estimates of Tamrazyan (1974; 2.7 × 10^6 km^2). A more recent global lake area estimate was provided by Downing et al. (2006; 4.2 × 10^6 km^2) who used global models at enhanced spatial resolution to demonstrate that lakes smaller than 1 km^2 form a dominant proportion of lakes, and these have not been included in the traditional inventories. Including these smaller lakes, the projected number of lakes in Canada is undoubtedly much higher. Clearly there is a need for improved hydrologic characterization of lakes and surface waters in Canada, but also for basic information on the extent and distribution of surface water resources.

Use of conventional hydrometric methods for monitoring of lakes has been spatially limited as national networks in Canada have tended to focus on flowing waters (rivers) and mostly larger lakes due to the relative importance of these water bodies, and

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given limited resources. While some methods such as radar altimetry techniques have shown promise for remote hydrologic characterization of lakes, these methods remain immature (e.g. Smith and Pavelsky, 2009) and are therefore not a substitute for field-based assessment at the present time. The need for site-specific or regional hydrologic information to plan for hydroelectric or mining development, or to support research on water or climatic impacts, is still a pressing need. One promising approach that has been demonstrated for obtaining site-specific information in local and regional surveys is stable isotope mass balance. Previous studies have applied the stable isotopes of water for establishing hydrologic control in sustainable forest management studies (Prepas et al., 2001; Gibson et al., 2002), for mine-site evaporation and water-balance investigations (Douglas et al., 2000; Gibson et al., 1996, 1998; Gibson and Reid, 2010, 2014), for examining flood history of delta lakes (Yi et al., 2008; Brock et al., 2009; Wolfe et al., 2012), and for regional assessment of climate- or catchment-driven gradients (Gibson and Edwards, 2002; Turner et al., 2010; Brooks et al., 2014; Gibson et al., 2015a). A recent review of isotope mass balance and its application in various climatic regions is given by Gibson et al. (2015b). Several previous studies have also used isotope mass balance for estimating water yield as a component of critical loads assessments (Bennett et al., 2008; Jeffries et al., 2010; Scott et al. 2010; Gibson et al., 2010a,b). These studies have demonstrated regional patterns in water balance for areas of British Columbia, Alberta, Saskatchewan and Manitoba.

Here we provide an additional case study from application of isotope mass balance in Ontario, which contains approximately 18% of Canada's lake area (Canada, Statistics Canada, 2005). The study, designed to provide water yield estimates for a regional critical loads assessment carried out as part of Canada's National Acid Rain Program, demonstrates typical hydrologic characteristics of lakes in six blocks situated north of Lake Superior, in Canadian Shield watersheds with limited soil cover. As part of this analysis, a sub-study was also conducted at an acid rain research site, the Turkey Lakes watershed (see Jeffries et al., 1988), where the isotope method was similarly applied to estimate water balance for a variety of lakes which had well-defined stratification status. The objective of this paper is to describe the water balance results to illustrate hydrologic variability of lakes in the region, and to test assumptions in selected lakes about use of well-mixed isotope balance models, as information on thermal stratification is not always available for regional surveys. Influence of sampling date, stratification status and sampling strategy were also evaluated and are also discussed.

1.1. Study area

300 lakes, ranging in size from <1 to >5000 ha, were sampled in six different sampling blocks (L, M, N, O, P, and Q) during 2008 (Fig. 1a). Sampling blocks are 100 km × 100 km areas selected for intensive sampling. Rationale for selection of sampling blocks as part of Canada's national acid sensitivity program has been described previously by Jeffries et al. (2010). The northern blocks: L, N, O and P are characterized by boreal shield vegetation (dominated by white spruce, black spruce, balsam fir, and poplar) with mean annual temperature of between 1.5 and 3.0 °C and annual precipitation of between 670 and 740 mm based on interpolation from the North American Regional Reanalysis dataset (Mesinger et al., 2006). The southern blocks, M and Q, are situated near the northern margin of the Great Lakes-St. Lawrence forest type with old growth hardwood dominated by sugar maple and yellow birch. Mean annual temperature is 3.0–4.0 °C (Mesinger et al., 2006) with similar precipitation to the more northerly blocks. Blocks P and Q are situated on the north shore of Lake Superior and so are expected to have a somewhat cooler and wetter climate. Vegetation in the Turkey Lakes watershed is similar to that described for blocks M and Q.

1.2. Field methods

Within each selected block a stratified-random lake selection methodology was employed, as outlined in Jeffries et al. (2010). The method involves random selection of lakes within eight defined size classes (>1–2 ha, >2–5 ha, >5–10 ha, >10–50 ha, >50–100 ha, >100–500 ha, >500–5000 ha, and > 5000 ha). 5 lakes in the Turkey Lakes watershed (Fig. 1b), as described in detail by Jeffries et al. (1988, 2002), were also sampled and temperature stratification was measured at the time of sampling. Water samples for the block survey lakes were 2-L grab samples taken from a helicopter using a dipper at 1-m depth in a mid-lake location. Block sampling was carried out in early October 2008. At the conclusion of the flight, a portion of the samples were transferred to 30-mL high-density polyethylene (HDPE) bottles for isotopic analysis, with the majority of the sample being used for various geochemical analyses. The Turkey Lakes were sampled the subsequent year, between 14 October and 30 November 2009 using grab sampling, which involved collection in 2-L bottles, as well as integrated sampling of the epilimnion, metalimnion, hypolimnion, and bulk sampling (of the whole water column). Both integrated and bulk samples were collected using an Arnott tube sampler. Water was then transferred to 30 mL HDPE bottles. Temperature profiles were measured in the Turkey Lakes for several minutes at the time of sampling using a thermistor string, to identify if lakes were stratified or turned over.

1.3. Laboratory analysis

All isotope results were analyzed at the Alberta Innovates Technology Futures (AITF) lab in Victoria using a Thermo Scientific Delta V Advantage Dual Inlet/HDevice system. Results are reported in δ notation in permil (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW) and normalized to the SMOW-SLAP scale, where SLAP is Standard Light Arctic Precipitation (see Coplen, 1996). Analytical uncertainty is estimated as the standard deviation of repeat measurements, which was ±0.06‰ for $\delta^{18}O$ and ±0.60‰ for $\delta^{2}H$ for 2008 and ±0.1‰ for $\delta^{18}O$ and ±0.44‰ for $\delta^{2}H$ for 2009. This was equal to or better than routine uncertainty of ±0.1‰ and ±1‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively reported by AITF and many other labs.

1.4. Theory

Site-specific hydrology was characterized using an isotope mass balance (IMB) model developed under the assumption of a well-mixed water body and steady-state conditions, which has been demonstrated previously for shallow lakes in northern Canada (Gibson et al., 2002, 2010a,b, 2015a; Bennett et al., 2008). The IMB is used to estimate evaporation/inflow based on the isotopic offset between the evaporatively enriched lake water compared to precipitation input. Then precipitation and evaporation estimates for the site are used to constrain the ungauged inflow to the lake and resulting outflows. The theoretical basis of this method has been described in detail by Gibson et al. (2015b) and a brief overview is presented below.

The annual water balance and isotope balance for a well-mixed lake or reservoir in isotopic and hydrologic steady state can be written, respectively as:

$$I = Q + E \quad (\mathrm{m^3 \cdot yr^{-1}}) \tag{1}$$

$$I\delta_I = Q\delta_Q + E\delta_E \quad (‰ \cdot \mathrm{m^3 \cdot yr^{-1}}) \tag{2}$$

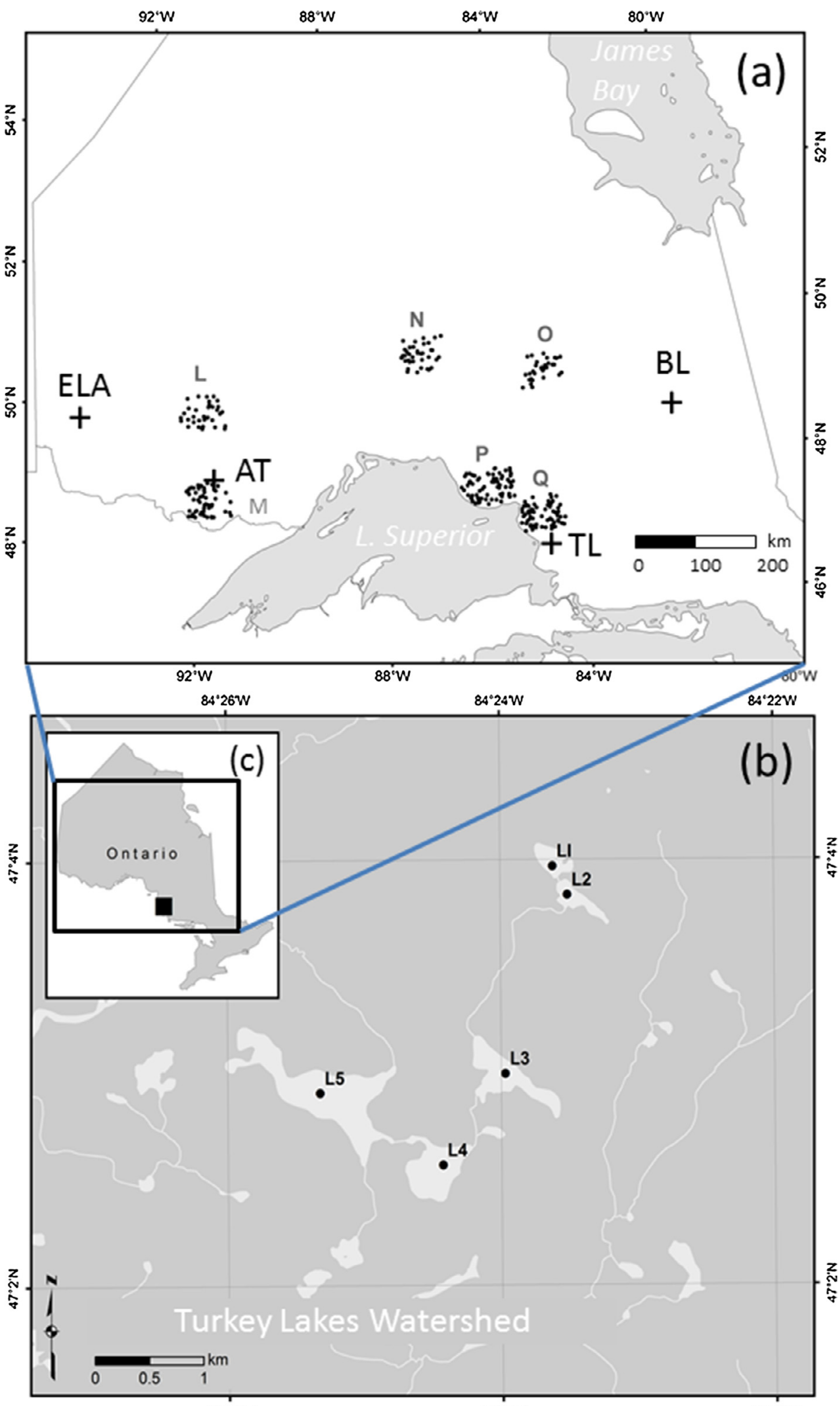

Fig. 1. (a) Location of sampling blocks in Ontario, Canada during 2008 and (b) location of lakes sampled in the Turkey Lakes watershed (TL), Fall 2009. L1 Batchawana L. (north), L2 Batchawana L. (south), L3 Wishart L., L4 Little Turkey Lake, and L5 Turkey Lake. (c) Map of the Province of Ontario showing location of the Turkey Lakes watershed relative to the sampling blocks. Also shown are GNIP stations at Experimental Lakes Area (ELA), Atikokan (AT) and Bonner Lake (BT).

where I, Q and E are lake inflow, discharge and evaporation rates ($m^3 \cdot yr^{-1}$), and δ_I, δ_Q and δ_E are the isotopic compositions of inflow, discharge and evaporation fluxes (‰), respectively. Rearranging Eq. (2), and substituting $Q = I - E$ from Eq. (1) yields:

$$E/I = (\delta_I - \delta_Q)/(\delta_E - \delta_Q) \quad \text{(dimensionless)} \tag{3}$$

where E/I is the evaporation to inflow ratio. For well-mixed lakes we assume $\delta_Q \approx \delta_L$ where δ_L is the isotopic composition of lakewater. For headwater lakes the isotope composition of inflow is often closely approximated by that of precipitation, i.e. $\delta_I \approx \delta_P$, whereas the isotopic composition of evaporate δ_E can be estimated using the Craig and Gordon (1965) linear resistance model:

$$\delta_E = ((\delta_L - \varepsilon^+)/\alpha^+ - h\delta_A - \varepsilon_K)/(1 - h + 10^{-3}\cdot\varepsilon_K)\ (‰) \tag{4}$$

where h is the relative humidity (decimal fraction), δ_A is the isotopic composition of atmospheric moisture (‰), ε^+ is the equilibrium isotopic separation (‰; see Horita and Wesolowski, 1994), α^+ is the equilibrium isotopic fractionation, where $\varepsilon^+ = \alpha^+ - 1$, and ε_K is the kinetic isotopic separation (‰; see Horita et al., 2008). Substitution of δ_E into Eq. (3) yields:

$$x = E/I = (\delta_L - \delta_I)/(m(\delta^* - \delta_L)) \quad (\text{dimensionless}) \tag{5}$$

where

$$m = (h - 10^{-3}\cdot(\varepsilon_K + \varepsilon^+/\alpha^+))/(1 - h + 10^{-3}\cdot\varepsilon_K) \quad (\text{dimensionless}) \tag{6}$$

and

$$\delta^* = (h\delta_A + \varepsilon_K + \varepsilon^+/\alpha^+)/(h - 10^{-3}\cdot(\varepsilon_K + \varepsilon^+/\alpha^+))\ (‰) \tag{7}$$

As the inflow to a lake is comprised of precipitation on the lake surface, P, as well as ungauged inflow, R, i.e. $I = P + R$, we can estimate R for headwater lakes by substitution of Eq. (5):

$$R = E/x - P \quad (\mathrm{m}^3\cdot\mathrm{yr}^{-1}) \tag{8}$$

where $E = e\cdot LA$ and $P = p\cdot LA$; e and p are the annual depth-equivalent of evaporation and precipitation ($\mathrm{m}\cdot\mathrm{yr}^{-1}$), and LA is the lake area (m^2). Water yield, or the depth-equivalent runoff, can then be estimated as

$$Wy = R/WA\cdot 1000 \quad (\mathrm{mm}\cdot\mathrm{yr}^{-1}) \tag{9}$$

where WA is the watershed area. Note that for non-headwater lakes, which may receive some isotopically enriched water from upstream lakes, the water yield may therefore be slightly underestimated and needs to be regarded as a lower limit. Further discussion of chain of lakes isotopic enrichment effects is provided by Gibson and Reid (2014).

Isotopic composition of atmospheric moisture δ_A is estimated by fitting predicted enrichment to the observed local evaporation line based on a partial equilibrium approach (see Gibson et al., 2015b). This approach accounts for seasonality observed in evaporation losses to the atmosphere.

1.5. Watershed parameters

Application of the IMB model requires delineation of the watershed areas, lake areas, and lake elevations for each of the study lakes. Using the coordinates (latitude-longitude) for each lake, watershed area, lake area, and lake elevation were obtained using digital elevation data in raster format from 1:50,000 Canada National Topographic Series (NTS) map sheets. Canadian National Hydro Network data in vector format were obtained from the GeoBase portal (www.geobase.ca). Terrain preprocessing to incorporate the vector hydrographic network and to fill small sinks was required before the Digital Elevation Model (DEM) could be used for efficient watershed delineation (see Jeffries et al., 2010).

Individual watersheds were delineated in the ArcGIS program using the ArcHydro tools where each watershed was delineated upstream of a lake outlet. Hydrographic and elevation datasets were used to depict the lake outlet locations. In some cases two or more partial watersheds had to be merged together to create a final watershed polygon feature. The planimetric area of both the lake and watershed polygons was calculated in the ArcGIS program based on the equal area projection.

1.6. Climate parameters

Climate parameters were obtained from the North American Regional Reanalysis (NARR) dataset (Mesinger et al., 2006). Monthly climatologies (based on data from 1979 to 2003) were extracted for the grid cells corresponding to the location of each of the study lakes. The parameters extracted were (i) surface total precipitation ($\mathrm{mm\ yr}^{-1}$), (ii) 2-m relative humidity (%), (iii) surface evaporation ($\mathrm{mm\ yr}^{-1}$), and (iv) 2-m temperature (K). The evaporation flux-weighting approach (see Gibson et al., 2015b) was used to flux-weight estimates of relative humidity and temperature so that the water balance calculations are representative of the open water season.

1.7. Isotopic parameters

Monthly precipitation $\delta^{18}O$ estimates were obtained for each lake location based on empirically derived global relationships between latitude and elevation (Bowen and Wilkinson, 2002) fitted to regional precipitation data from the Canadian Network for Isotopes in Precipitation (see Birks and Gibson, 2009). The δ^2H composition of monthly precipitation was calculated assuming that precipitation would follow the relationship defined by the Global Meteoric Water Line (GMWL; Craig, 1961). Comparable results would be obtained if the Local Meteoric Water Line (LMWL) for Atikokan, Ontario or Bonner Lake, Ontario were to be used instead (see Fig. 2). Annual averages of $\delta^{18}O$ and δ^2H in precipitation were amount-weighted using monthly precipitation depths obtained from the NARR dataset. Note that calculations were performed using long-term climatologies of the parameters.

2. Results and discussion

2.1. Isotope characteristics

Isotopic data for Blocks L through Q are provided in the Supplementary Material. A summary of the isotopic characteristics of each block are provided in Table 1, and plotted in δ^2H versus $\delta^{18}O$ space in Fig. 2.

In general, isotopic results from the surveys are characterized by systematic offset below the GMWL, and indicate variable evaporative enrichment in the lakes. LMWLs for the region are expected to be similar to that shown for Atikokan (Fig. 2) although higher deuterium excess in precipitation has been noted for areas in the prevailing downwind areas of the Great Lakes (Gat et al., 1994). This may be the case for Blocks P and Q where several lakes were also found to plot above the GMWL. The local evaporation lines (LEL) for different blocks differ slightly in their slopes (equations for LEL shown in Fig. 2) with the lowest slope for Block L (3.8) and the highest slope for Block N (4.8). Similarly, data from Block L also show the highest scatter ($r^2 = 0.71$), whereas Block N has the least scatter ($r^2 = 0.95$). The isotopic data were found to be normally distributed (Fig. 3).

Isotopic composition of precipitation has been measured at three stations in the region (Experimental Lakes Area, Atikokan and Bonner Lake) as part of the Canadian Network for Isotopes in Precipitation (CNIP) (see Jasechko et al., 2014). Similar results for the lake blocks are obtained by interpolation using the Bowen and Wilkinson (2002) model, with values ranging between −13.21‰ and −13.84‰ for $\delta^{18}O$ and −95.7‰ and −100.8‰ for δ^2H. For all blocks, these values are depleted relative to the intercept of the GMWL and LELs (Table 2).

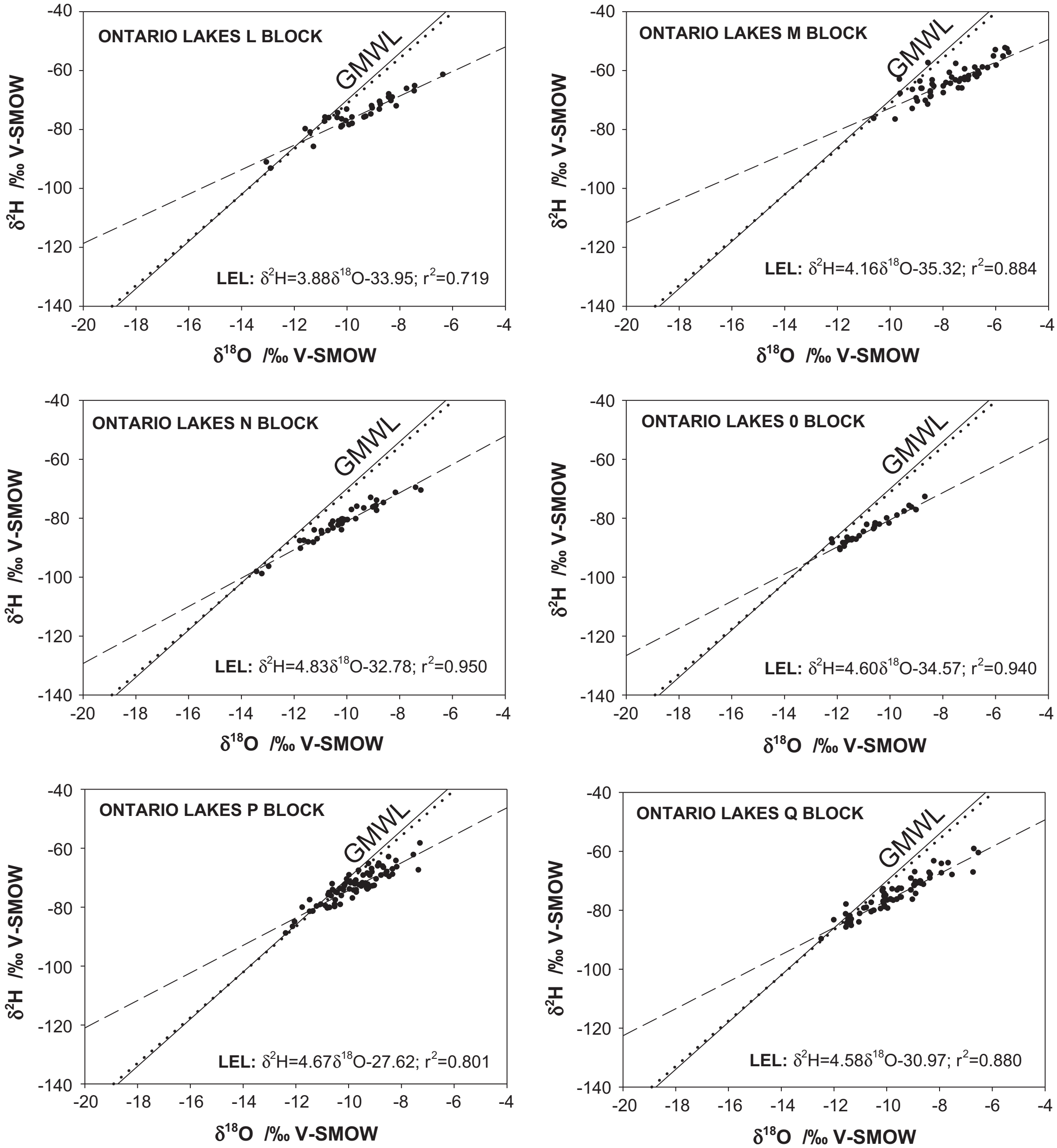

Fig. 2. δ^2H-δ^{18}O plots of lakes in different blocks of Ontario surveyed during 2008. LEL denotes the apparent slope of the local evaporation line based on linear regression of lake values for each block. Solid line is Global Meteoric Water Line of Craig (1961); dotted line is Local Meteoric Water Line (LMWL) of Atikokan, Ontario., $\delta^2H = 7.84\ \delta^{18}O + 7.5$. Similar LMWLs are noted for Bonner Lake ($\delta^2H = 7.70\ \delta^{18}O + 5.1$) and Experimental Lakes Area ($\delta^2H = 7.75\ \delta^{18}O + 5.0$).

Table 1
Summary of isotopic characteristics of lakes by block.

Block	N	Mean		Min		Max		LEL		
		δ^{18}O	δ^2H	δ^{18}O	δ^2H	δ^{18}O	δ^2H	Slope	Intercept	r^2
L	35	−9.57	−75.2	−13.02	−93.5	−6.33	−61.7	3.88	−33.95	0.719
M	53	−7.67	−63.7	−10.59	−76.8	−5.47	−52.6	4.16	−35.32	0.884
N	69	−10.48	−83.1	−13.39	−99.2	−7.16	−69.89	4.83	−32.78	0.950
O	31	−10.82	−84.4	−12.18	−91.0	−8.64	−73.0	4.60	−34.57	0.940
P	78	−9.74	−73.1	−12.35	−89.1	−7.26	−58.6	4.67	−27.62	0.801
Q	65	−9.66	−75.2	−12.45	−90.0	−6.49	−59.5	4.58	−30.97	0.880

2.2. Evaporation/inflow ratios

Evaporation/inflow (x) was estimated for the study lakes based on Eq. (5). Two scenarios were run: (i) using modelled precipitation as the isotopic composition of inflow, and (ii) using the GMWL-LEL intercept as the isotopic composition of inflow. The runs using modelled precipitation were found to have fewer negative values for water yield as values were always more depleted than lake

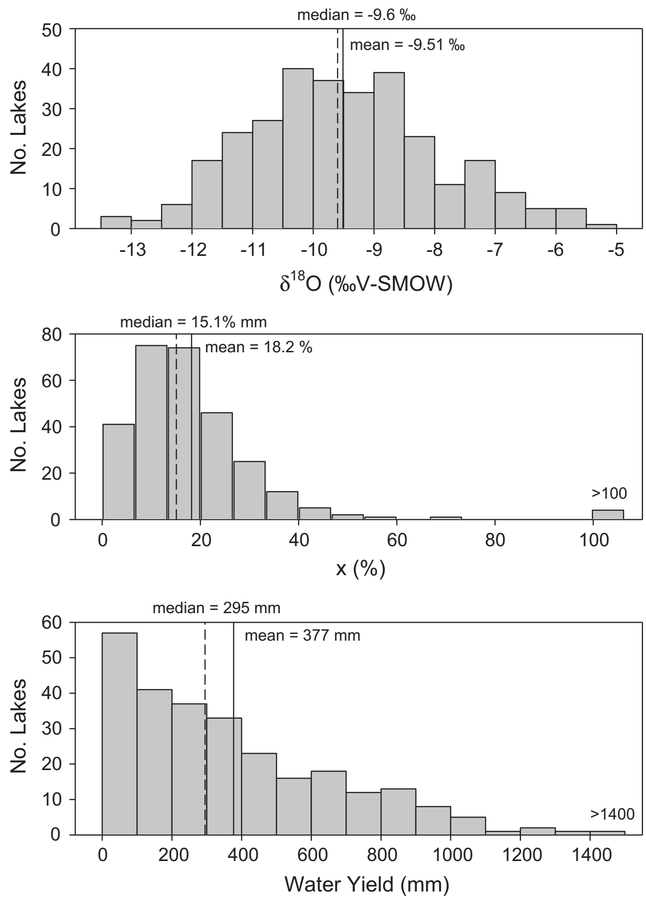

Fig. 3. Overall distribution of $\delta^{18}O$, evaporation/inflow (x), and water yield to lakes for Blocks L through P.

water, however, simulation of the slope of the evaporation trend was more realistic using the intercept approach. Results from the two scenarios, although similar in terms of capturing variability, were averaged to calculate the final water yields used for each lake. Negative water yield values, obtained mainly where simulated input was enriched relative to lake water, were considered to be outliers and were therefore excluded from the statistical summaries.

Based on mean results of the two run scenarios, evaporation losses from the lakes were found to average close to 18%, with values of between 8 and 28% for individual blocks. Highest values were noted for lakes in Block M (farthest south) and lowest values for lakes in Block O (second most northerly) (Table 3). Highest variability was noted for lakes in Blocks P and Q, which are possibly influenced more by the lake effect, i.e. lake moisture feedback to the atmosphere. Evaporation/inflow was found to be positively skewed (Fig. 3) as noted in previous surveys (Gibson et al. 2010a,b), and is a reflection of the non-linear relationship between isotopic enrichment and evaporation loss (see Eq. (5)).

2.3. Water yield

Water yield estimated from Eq. (9), and based on the average of the two run scenarios, was found to range from less than 100 mm to >2000 mm for individual lakes (see Supplementary Material). Water yield results are also summarized by block in Table 2. While the average water yield obtained using IMB of 377 mm is similar to the average runoff interpolated for all blocks based on Bemrose et al. (2009) or the Hydrological Atlas of Canada (Canada, Fisheries and Oceans Canada, 1978), and the range is similar (285–490 mm for IMB versus 250–425 mm to both Bemrose et al. (2009) and the Hydrological Atlas), the correlation between the two methods is found to be low ($r^2 = 0.35$). The correlation improves considerably if Block L is excluded ($r^2 = 0.66$). Overall, water yield is found to have a positively-skewed distribution (Fig. 3), comparable to previous surveys in western Canada (Gibson et al., 2010a,b). Skewness is also systematic among all blocks (Fig. 4) and clearly suggests that lakes with low water yield are more common than lakes with high water yield. Variation in water yield within sampling blocks was found to be more pronounced than inter-block variations, as expected for a region where large-scale climate is fairly similar but local, lake-specific physiographic and hydrologic controls are more prevalent. Lake-to-lake variability within each block is found to be upwards of an order of magnitude larger than variability in precipitation or evaporation rates estimated based on the NARR dataset. The distributions have significant implications for critical loads assessment as low water yield lakes tend to be less buffered by runoff containing base cations from their catchment areas, and therefore more lakes are expected to be acid sensitive.

2.4. Regional patterns and limitations of the approach

Few comprehensive assessments of regional variations in lake water balance have been conducted based on direct observations from multiple lakes, mainly due to logistical constraints in applying conventional water balance or energy balance approaches. In regional comparisons, one or more important process such as evaporation are often not measured (e.g. Sacks et al., 1998). More frequently, regional studies have supplemented observational data with remote-sensing data or modelling (e.g. Biskop et al., 2016) or by regionalizing point data to predict spatial water balance variations (e.g. Reeves, 2010). While these approaches are useful and often informative, they are subject to varying levels of uncertainty (Winter, 1981). Surveys of the stable isotopes of water have also been used to infer spatial patterns in water balance based on vari-

Table 2
Isotopic characteristics of modelled precipitation, GMWL-LEL intercept by block. Amount-weighted precipitation for nearby CNIP stations is also shown.

Block/Station	Precipitation		GMWL intercept	
	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H
L	−13.84	−100.8	−10.66	−75.3
M	−13.48	−97.9	−11.80	−84.4
N	−13.82	−100.6	−13.49	−98.0
O	−13.53	−98.3	−13.10	−94.9
P	−13.29	−96.3	−11.30	−80.4
Q	−13.21	−95.7	−11.98	−85.8
Atikokan	−12.61	−91.62		
Bonner Lake	−13.82	−100.7		
ELA	−12.33	−90.3		

Table 3
Summary of E/I, water yield and interpolated runoff. Precipitation and evaporation are based on NARR data; Runoff is based on Canada, Fisheries and Oceans Canada (1978).

Block	N	E/I		Precipitation		Evaporation		Water yield			Runoff
		Mean	1σ	Mean	1σ			Mean	Median	1σ	
L	35	0.17	0.08	668	40	650	45	490	361	485	250
M	53	0.28	0.08	614	90	484	60	285	250	192	250
N	69	0.15	0.08	690	60	591	100	365	272	328	330
O	31	0.09	0.05	738	60	601	120	395	338	340	350
P	78	0.13	0.15	700	74	559	92	393	322	273	425
Q	65	0.16	0.18	691	53	618	64	382	274	322	450

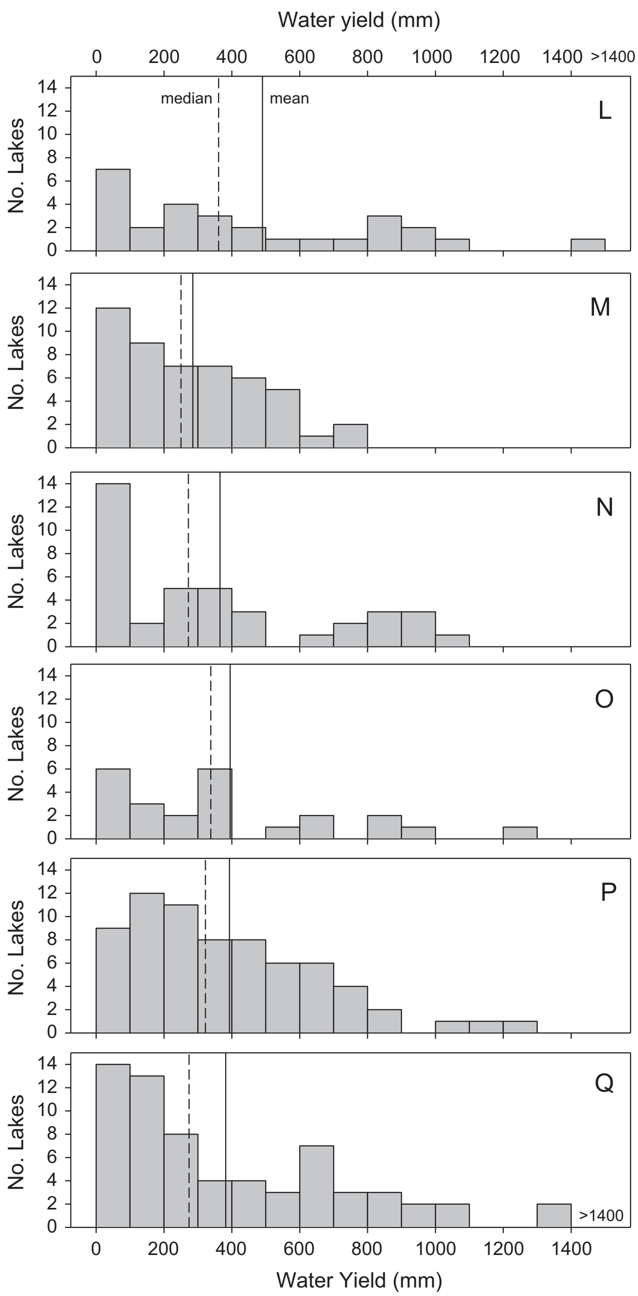

Fig. 4. Distribution of water yield to lakes by block in Ontario during 2008. Note that both x-axis and y-axis scales are identical for all sampling blocks.

ation in isotope mass balance parameters (e.g. Sacks, 2002; Gibson et al., 1993, 2015a; Gibson and Edwards, 2002). Past isotopic surveys have revealed pronounced variability in the isotopic composition of lakes, commonly interpreted to be a reflection of variations in water loss by evaporation (e.g. Gibson et al., 1993; Gibson and Edwards, 2002; Ichiyanagi et al., 2003; Leng and Anderson, 2003; Yi et al., 2008; Brock et al., 2009; Turner et al., 2010; Tondu et al., 2013; Anderson et al., 2013). Several studies have also demonstrated that isotopic variations may reflect variations in water yield (i.e. runoff) to lakes (Bennett et al., 2008; Gibson et al., 2010a,b, 2015a). The strength of the isotopic approach is commonly regarded as the ability to compare water balance across a number of lakes, rather than absolute quantification (Gibson et al., 2015b).

In general, stratified-randomly selected lake surveys across Canada have revealed negatively-skewed to normal distributions of $\delta^{18}O$ and $\delta^{2}H$, but commonly with positively-skewed distributions of evaporation/inflow and water yield (Gibson et al., 2010a, 2015a). Brooks et al. (2014) show negatively skewed $\delta^{18}O$ and $\delta^{2}H$ and positively skewed E/I for lakes sampled across the contiguous United States. Positively-skewed water-yield distributions, observed in all six blocks observed in this study, appear to reflect the predominance of lakes with lower than average runoff, but this property may possibly be regionally dependent on drainage configuration including topographic variations and lake order (Sherry and Soranno, 2006). Contributing areas may also determine the local characteristics of runoff to lakes (see Pomeroy et al., 2005). Similarity of the sampling blocks in our study may reflect a common configuration for Precambrian Shield terrain in the region. We can expect that regional drainage in lake-rich shield terrain may include corridors where lakes have higher lake-to-lake or lake-to-stream throughput and therefore may contribute more significantly to regional runoff. Other areas may be flatter and/or poorly connected to adjacent lakes or streams and therefore may be less connected to regional runoff. The role of landscape position and lake order/configuration in determining water balance in the study region warrants further research.

Further assessment of the effect of headwater versus non-headwater lakes is also required to improve upon site-specific estimates of water balance using isotope techniques. In non-headwater situations, the isotopic composition of average inflow may be underestimated due to isotopic enrichment occurring in upstream lakes or wetlands. This, in turn would lead to overestimation of the evaporation/inflow and underestimation of the water yield. However, as enriched lakes or wetlands tend to have reduced outflow due to mass balance considerations, we suggest that the headwater effect may only have a limited influence on the resulting estimates of water yield in many systems. Gibson and Reid (2014) suggest that evaporation loss may be overestimated by as much as 30% in some circumstances using headwater models, and water yield underestimated by a similar amount, although the average effect is likely less than half that value. While it is likely that non-headwater effects also enhance skewness somewhat, positively-skewed distributions have also been found for headwater lake surveys, as shown for lakes in the oil sands region of Alberta (Gibson et al., 2015a). We emphasize that the assessment presented should be regarded as a regional first-approximation but may have led to underestimation of the apparent runoff in some lakes due to use of a headwater lake model. We recognize this as a fundamental limitation of the current work, but one that could be overcome by sampling inflows or upstream lakes in future surveys.

2.5. Turkey Lakes watershed

To better understand the potential influence of stratification on the water yield estimation, we applied the isotopic method to a dataset collected in 2009 from the Turkey Lakes watershed, a well-known acidification research basin where significant previous work on critical loads and hydrology has been conducted. As shown in δ^2H-δ^{18}O space (Fig. 5), the 2009 samples from the 5 Turkey Lakes fall along an evaporation line (LEL) with a slope of 4.9, plotting below and offset from the GMWL. The observed slope is similar to that noted nearby for Block Q based on a larger number of lakes (see Fig. 2, Table 1). Lakes exhibit differing degrees of offset along the LEL. Batchawana L. (north) is found to have the most enriched isotopic signature and highest evaporation/inflow, while Little Turkey Lake has the most depleted isotopic signature and the lowest evaporation/inflow. Temporal shifts in isotopic composition of the lakes, which tend to be relatively subdued, but do confirm minor seasonal variations in water budget, are also noted.

To evaluate potential uncertainty in the water yield model using different sampling strategies (grab, bulk, stratified), and to assess the effect of sampling at different times during fall when the lake may be in various stages of turnover, we ran the model for all situations listed in Tables 4 and 5. Note that the model was run for each lake with identical parameters, with the exception of the isotopic composition of water. Also, for the purposes of this test, stratified samples were treated as whole lake samples. We realize that a better estimate of water yield would be obtained for Turkey Lake as a whole by using an IMB with multiple water layers of specified volume, accounting for liquid diffusion between layers, but this was considered to be beyond the scope of this analysis.

Mean water yield estimates for the lakes in 2009 ranged from 458 to 501 mm for Turkey Lakes, Little Turkey Lake, Wishart lake and Batchawana Lake (south), while Batchawana Lake (north) was found to be significantly higher at 840 mm. For comparison, gauged water yield (discharge/area) for the Turkey Lakes watershed ranged from 390 to 760 mm during 1982–1996 (Mitchell et al., 2011), and for 2005–2009 ranged from 411 to 604 mm, averaging 481 mm based on Water Survey of Canada records for the

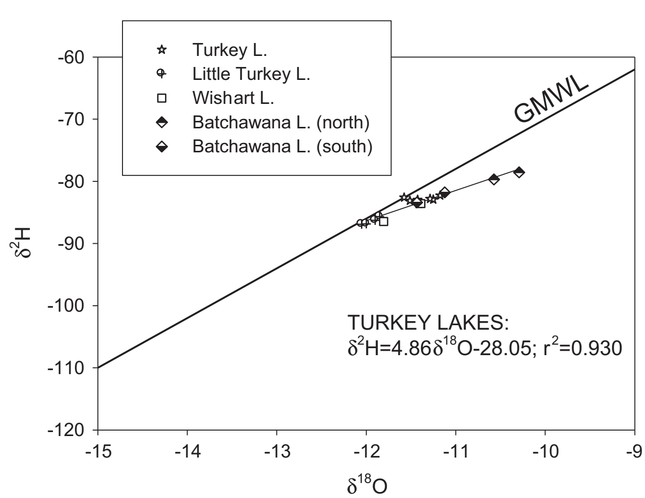

Fig. 5. δ^2H-δ^{18}O plots of lakes in Turkey Lakes watershed, Ontario. GMWL denotes the Global Meteoric Water Line of Craig (1961).

same years. Water yield estimates also varied somewhat for each lake depending on the time and type of sampling used.

A general trend is noted towards depletion in isotopic composition and higher apparent water yields as fall progressed. Excluding Wishart L., the observed temporal shift (depletion) in bulk samples during the sampling period ranged from 0.15‰ to 0.31‰ in δ^{18}O and 0.30 to 1.61‰ in δ^2H, which are meaningful in comparison to a conservative estimate of analytical uncertainty (2σ) of ±0.2‰ and ±0.88‰, respectively, for this dataset. The observed depletion is expected in fall due to increase in inflow and increased humidity, and commonly due to more depleted isotope composition of atmospheric moisture associated with colder temperatures. The more extreme shift in Wishart L. (0.42‰, 2.89‰) is unexpected and may possibly reflect undetected stratification or incomplete mixing in the lake on the first sampling date.

Stratified samples from Turkey L. (Table 4) illustrate a systematic decrease in isotopic composition from epilimnion to metalimnion to hypolimnion, due to the evaporative enrichment of surface waters and presumably due to enhanced groundwater recharge in the hypolimnion. Subtle differences in the hypolimnion signature, plotting on the GMWL rather than the evaporation line, also supports the greater significance of groundwater, but further work would be required to separately quantify groundwater as a contributor to the integrated water yield. Overall the isotopic data are systematic and behave expectedly. For example, a bulk sample of lake water from Turkey Lake is found to be intermediate in isotope composition compared to its various stratified layers, and is slightly biased towards epilimnion values due to larger volume of this layer. One metre-depth grab samples in both Turkey Lake and Little Turkey Lake are also more enriched than bulk samples of the water column due to similar stratification effects.

Using the basic water yield model, we conclude the following about sampling methods:

- Grab sampling led to underestimation of the water yield in Turkey Lake (a deep lake) by 18% relative to bulk sampling. For Little Turkey Lake (a shallower lake) grab sampling underestimated by 6%.
- Bulk sampling of Turkey Lake was within 11% of an unweighted average of 3 stratified samples.

Our test also suggested the following about effect of sampling at different times in fall:

- Bulk sampling of Turkey Lake at 3 times between Oct 27 and Nov 30, 2009 was consistent to within ±20% (2σ).
- Drift in water yield (towards higher values in all cases) was 11% for Batchawana Lake (south), 16% for Little Turkey Lake, 18% for Batchawana Lake (north) and Turkey Lake, and 38% for Wishart Lake. Based on the observed isotopic shift, the latter is not easily explained unless incomplete mixing occurred at the time of first sampling but was not characterized.

Overall, the observed isotopic changes were systematic, and estimated water yield followed expected patterns. Our assessment suggests that margin of uncertainty of ±20% is adequate to capture errors related to sampling and stratification. Grab samples at the 1-m depth and near-bottom may be one strategy to further limit uncertainty, but this approach remains to be tested. It is important to note that this uncertainty is likely smaller than uncertainty related to extrapolation of gauge or climate data over short distances, and the observed uncertainty does not negate the usefulness of the method for site-specific assessment. Yet it is important to note that the strength of the isotope method resides in the ability to characterize relative differences in water balance between lakes, and as we show, for statistical analysis of many lakes.

Table 4
Summary of isotope data, modelled evaporation/inflow (x) and water yield, and selected statistical results for (a) Turkey Lake and (b) Little Turkey Lake based on multiple sampling events in 2009.

Sampling Event ID	Status	Date	Type	Depth (m)	$\delta^{18}O$ (‰)	δ^2H (‰)	x (%)	Water yield (mm)	Error (%)
Turkey Lake									
1.	Stratified	14 Oct 09	Grab	1	−11.17	−82.26	7.9	384	–
2a.	Stratified	27 Oct 09	Epilimnion	0–12.5	−11.25	−82.91	7.4	409	–
2b.	Stratified	27 Oct 09	Metalimnion	12.5–17.3	−11.42	−83.65	6.6	469	–
2c.	Stratified	27 Oct 09	Hypolimnion	17.3–32	−11.58	−82.58	5.7	542	–
2d.	Stratified	27 Oct 09	Bulk	0–32	−11.29	−82.81	6.5	420	–
3.	Stratified	23 Nov 09	Bulk	0–32	−11.43	−82.94	6.1	473	–
4.	90–95% turned over	30 Nov 09	Bulk	0–32	−11.51	−83.11	6.5	510	–
5.	Mean of above							458	–
6.	Mean of 2a, 2b, 2c (stratified average 27 Oct 2009)							473	–
7.	Mean of 2d, 3, 4 (bulk samples)							468	–
8.	Difference of 2d and 6 (single bulk vs. multiple stratified samples)							53	11%
9.	Difference of 2d and 4 (temporal shift, bulk samples)							85	18%
10.	1 standard deviation of 2d, 3, 4 (bulk samples)							45	10%
11.	Difference of 1 and 7 (grab vs bulk sample)							84	18%
Little Turkey Lake									
1.	Stratified	14 Oct 09	Grab	1	−11.85	−85.7	4.5	407	
2.	Turned over	16 Oct 09	Bulk	Unknown	−11.90	−86.3	4.2	430	
3a.	Turned over	27 Oct 09	Bulk	Unknown	−12.05	−86.9	3.6	514	
3b.	Turned over	27 Oct 09	Grab	1	−12.00	−86.9	3.8	483	
4.	Mean of above							459	–
5.	Mean of 2, 3a, 3b (after turn over)							476	–
6.	Mean of 1, 3b (grab samples, 1-m depth)							445	–
7.	Mean of 2, 3a (bulk samples)							472	–
8.	Difference of 6 and 7 (grab samples vs. bulk samples)							27	6%
9.	Difference of 1 and 3b (temporal shift, grab samples)							76	16%
10.	Difference of 2 and 3a (temporal shift, bulk samples)							84	16%

Table 5
Summary of isotope data, modelled evaporation/inflow (x) and water yield, and selected statistical results for (a) Wishart Lake, (b) Batchawana Lake (North) and Batchawana Lake (South) based on two sampling events in 2009.

Sampling Event ID	Lake status	Date	Type of sample	Depth (m)	$\delta^{18}O$ (‰)	δ^2H (‰)	E/I (%)	Water yield (mm)	Difference (%)
Wishart Lake									
1.	Turned over	14 Oct 09	Bulk	0–4	−11.39	−83.6	6.9	375	–
2.	Turned over	28 Oct 09	Bulk	0–4	−11.81	−86.5	4.8	552	–
3.	Mean of above							464	
4.	Difference of above (temporal shift, bulk samples)							177	38%
Batchawana Lake (North)									
1.	Turned over	14 Oct 09	Bulk	0–10	−10.29	−78.6	16.0	759	–
2.	Turned over	28 Oct 09	Bulk	0–10	−10.57	−79.7	13.6	921	–
3.	Mean of above							840	–
4.	Difference of above (temporal shift, bulk samples)							162	18%
Batchawana Lake (South)									
1.	Turned over	14 Oct 09	Bulk	0–4	−11.12	−81.79	9.7	441	
2.	Turned over	28 Oct 09	Bulk	Unknown	−11.43	−83.40	7.9	560	
3.	Mean of above							501	–
4.	Difference of above (temporal shift, bulk samples)							59	11%

3. Implications

Use of site-specific water yield based on isotopes was introduced in critical loads studies (Gibson et al., 2010a,b; Jeffries et al., 2010; Scott et al., 2010) and is used here as a potential improvement for regional surveys that previously relied on site-specific geochemistry but regional hydrometric gauging or climate-based indicators of runoff potential such as river gauging or estimates of water availability based on the precipitation minus evapotranspiration (P-ET) deficit. Due to complexity and heterogeneity of runoff behaviour on the large scale (see Sivapalan, 2003) conventional approaches may be less suitable for interpolating, especially in lake rich regions. While the isotope-based approach remains to be tested in a wider array of gauged basins, these opportunities are rare. The results presented here indicate reasonable agreement with a long-term study basin and suggest that the method is useful for lake-to-lake comparisons and regional-scale applications such as critical loads assessment. One of the direct implications of the isotope-based assessment presented here is evident from the positively skewed water yield distributions; that is, there is a higher proportion of low water yield lakes that are likely more sensitive to acidification due to weaker buffering from base cations flushing from their catchment areas. A complete critical loads assessment using this water yield dataset is currently in preparation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2016.11.016.

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