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# Stable isotope fingerprint of open-water evaporation losses and effective drainage area fluctuations in a subarctic shield watershed

## J.J. Gibson<sup>a,\*</sup>, R. Reid<sup>b,1</sup>

<sup>a</sup> Alberta Research Council and University of Victoria, 3 – 4476 Markham St., Victoria, BC, Canada V8Z 7X8 <sup>b</sup> Water Resources Division, Indian and Northern Affairs Canada, 3rd Floor, Bellanca Building, P.O. Box 1500, Yellowknife, Northwest Territories, Canada X1A 2R3

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## Introduction

## SUMMARY

Stable isotopes of water, oxygen-18 and deuterium, were measured at biweekly to monthly intervals during the open-water season in a small, headwater lake (Pocket Lake, 4.8 ha) near Yellowknife Northwest Territories, and concurrently in a nearby string-of-lakes watershed (Baker Creek, 137 km<sup>2</sup>) situated in the subarctic Precambrian Shield region. As measured in water samples collected over a 12 year period (1997–2008), the levels of evaporative isotopic enrichment in both lake and watershed outflow were differentially offset, and seasonal variations were found in both to be driven by variations in open-water evaporation. Systematic differences measured in the magnitude of the offset between the lake and watershed outflow are interpreted as being caused by changes in the effective drainage area contributing to runoff. Based on the observed and extremely consistent relationship between isotopic compositions of lake water and watershed outflow ( $r^2 = 0.849$ , p < 0.001) we extend the analysis of open-water evaporation losses and effective drainage areas back to 1991 when less-frequent water sampling at the sites commenced. This 18-year record serves to demonstrate for the first time the expected variability in the evaporation and transpiration partitioning, upper limits on the effective drainage area, and isotopic signals transferred downstream in a typical shield drainage system within the Mackenzie Basin.

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String-of-lakes drainages are common features of the subarctic Canadian Shield region. They are important hydrologic regulators of river discharge, particularly in the eastern portion of the Mackenzie River Basin (Rouse, 2000), and have been shown to have a measurable influence on the geochemistry (Reeder et al., 1972; Millot et al., 2002) and stable isotopic composition of river discharge (Hitchon and Krouse, 1972; Yi et al., accepted for publication). The hydrology of string-of-lakes drainages has been described in detail at the small scale in a few areas (e.g. Spence and Woo, 2002, 2003; Spence and Rouse, 2002; Woo and Mielko, 2008). Formed as water flows across undulating crystalline bedrock, string-of-lakes drainages are characterized by highly variable or intermittent runoff. This variability is driven by fluctuations in storage, and expansion and contraction of contributing areas as lakes, low-lying wetlands and soil filled valleys respond to snowmelt, rainfall and evaporative demand. This 'fill-and-spill' mechanism (Spence and Woo, 2003), while also relevant to humid

regions, is one of the most challenging runoff processes to model and upscale in seasonally-arid subarctic regions, as flow linkages are more frequently severed (Woo and Mielko, 2008). Low runoff and abundant surface water is also expected to heighten sensitivity to climate warming, due to potential for accelerated evaporation efficiency in areas with abundant surface water (Rouse et al., 2008).

The stable isotope composition of string-of-lakes drainages has been previously measured in spatial surveys across the subarctic region (Gibson and Edwards, 2002), revealing significant variation in heavy isotope enrichment due to evaporation from open-water, estimated to account for up to 60% of water losses from subarctic boreal forest terrain near Yellowknife (Gibson and Edwards, 2002). String-of-lakes evaporative enrichment has been modelled as a special case of heavy isotope enrichment in a coupled evaporative system (see Gat and Bowser, 1991), which has shown that cumulative heavy isotope enrichment signals down a string-oflakes can be quantitatively interpreted particularly when humidity exceeds 50%. Broad areal surveys of lakes have shown that imprint of evaporation is widespread across boreal, subarctic and low arctic regions of Canada (Gibson et al., 2005). The purpose of this paper is to examine and interpret the controls on temporal isotopic signals associated with evaporation loss in lake and watershed discharge, and to demonstrate and critically evaluate a transferable





<sup>\*</sup> Corresponding author. Tel.: +1 250 721 7341; fax: +1 250 483 1989.

E-mail addresses: jjgibson@uvic.ca (J.J. Gibson), Bob.Reid@inac-ainc.gc.ca (R. Reid).

<sup>&</sup>lt;sup>1</sup> Tel.: +1 867 669 2661.

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quantitative method for estimating vapour partitioning and effective drainage area for shield string-of-lakes hydrologic systems. Implications regarding propagation of isotopic signals down the drainage network to larger rivers are discussed.

## Theory

Heavy isotope enrichment of water exposed to evaporation arises from mass-dependent differences in the equilibrium vapour pressures and gas-phase molecular diffusivities among the naturally occurring water isotopomers, including common water containing <sup>1</sup>H and <sup>16</sup>O only (<sup>1</sup>H<sup>1</sup>H<sup>16</sup>O) and the heavy isotopic species containing <sup>18</sup>O and <sup>2</sup>H (<sup>1</sup>H<sup>1</sup>H<sup>18</sup>O and <sup>1</sup>H<sup>2</sup>H<sup>16</sup>O). This produces a vapour depleted in the heavy species (more negative  $\delta$  values<sup>2</sup>) and a residual water which is enriched in the heavy isotopic species (more positive  $\delta$  values). The relationship between liquid and vapour in an evaporating system, is commonly approximated using a simplified version of the Craig and Gordon (1965) model assuming no resistance to mixing in the liquid phase given by (Gat, 1995):

$$\delta_E = \frac{\alpha^* \delta_L - h \delta_A - \varepsilon}{1 - h + 10^{-3} \cdot \varepsilon_K} (\%) \tag{1}$$

where  $\alpha^*$  is the equilibrium liquid–vapour isotope fractionation ( $\alpha^* = 1 + \varepsilon^*$ ), *h* is the atmospheric relative humidity (ranging from 0 to 1) normalized to the saturation vapour pressure at the temperature of the air–water interface,  $\delta_A$  is the isotopic composition of ambient moisture, and

$$\varepsilon = \varepsilon^* + \varepsilon_K(\%) \tag{2}$$

where  $\varepsilon$  is the total isotopic separation factor including both equilibrium  $\varepsilon^*$  and kinetic  $\varepsilon_K$  components<sup>3</sup>. The equilibrium separations can be evaluated using the empirical equations determined experimentally by Majoube (1971) or Horita and Wesolowski (1994), the latter given for oxygen-18 by

$$\begin{aligned} \varepsilon^{*18} &\approx 10^3 \cdot \ln \alpha (^{18}\text{O}) \\ &= -7.685 + 6.7123(10^3/T) - 1.6664(10^6/T^2) \\ &+ 0.35041(10^9/T^3)(\%) \end{aligned} \tag{3}$$

and for deuterium by

$$\begin{split} \epsilon^{*2} &\approx 10^3 \cdot \ln \alpha (^2H) \\ &= 1158.8(T^3/10^9) - 1620.1(T^2/10^6) + 794.84(T/10^3) \\ &- 161.04 + 2.9992(10^9/T^3)(\%) \end{split} \tag{4}$$

where *T* is the interface temperature (K).

Kinetic enrichment factors  $\varepsilon_K$  are dependent on both the boundary layer conditions and the humidity deficit evaluated according to

$$\varepsilon_{K} = C_{K}(1-h)(\%) \tag{5}$$

where the kinetic fractionation constant,  $C_K$ , is set at 14.2‰ for oxygen and 12.5‰ for hydrogen, as established from laboratory and experimental testing to be representative of typical lake evaporation conditions (Gonfiantini, 1986; Araguas-Araguas et al., 2000).

For a well-mixed lake with inflow and exposure to open-water evaporation, the water-mass and isotope mass balances for hydrologic and isotopic steady-state conditions are given, respectively, by:

$$I_L = Q_L + E_L(\mathbf{m}^3) \tag{6}$$

$$I_L \delta_I = \mathbf{Q}_L \delta_0 + E_L \delta_E(\mathbf{m}^3 \%) \tag{7}$$

where  $I_L$  is inflow to the lake (surface and subsurface),  $Q_L$  is outflow (surface and subsurface),  $E_L$  is evaporation, and  $\delta_I$ ,  $\delta_Q$  and  $\delta_E$  are the isotopic compositions of inflow, outflow, and the evaporation flux, respectively. Note that if we assume constant density of water then water masses can be substituted for volumes in Eqs. (6) and (7).

Combining Eqs. (2) and (3), substituting  $\delta_E$  from (1), and noting that for a well-mixed lake that the isotopic composition of the lake  $\delta_L$  is close to the isotopic composition of discharge  $\delta_Q$ , i.e.  $\delta_L \approx \delta_Q$ , we obtain an expression for the fraction of water loss by evaporation ( $x_L$ ) (Gibson et al., 2002):

$$x_L = \frac{E_L}{I_L} = \frac{(\delta_L - \delta_I)}{m(\delta^* - \delta_L)} \quad (\text{dimensionless})$$
(8)

where  $m = (h - \varepsilon)/(1 - h + \varepsilon_K/1000)$ , which is the enrichment slope as defined previously (Welhan and Fritz, 1977; Allison and Leaney, 1982), and  $\delta^* = (h\delta_A + \varepsilon)/(h - \varepsilon/1000)$  is the limiting isotopic enrichment, which is atmospherically controlled (Gat and Levy, 1978; Gat, 1981).

This steady-state approximation can be used assuming  $\delta_I = \delta_P$ , where  $\delta_P$  is the isotopic composition of precipitation, to solve for the water budget of a headwater lake, where  $I_L = P_L + Wy$ ,  $P_L$  being the precipitation volume on the lake, and Wy being the water yield (runoff volume) from the lake catchment.

For the case of a watershed containing numerous lakes and receiving only precipitation input, we propose to characterize the cumulative catchment evaporation losses in the watershed discharge  $x_{C}$  using:

$$x_{C} = \frac{E_{C}}{P_{C}} = \frac{(\delta_{C} - \delta_{P})}{m(\delta^{*} - \delta_{C})} \quad (\text{dimensionless})$$
(9)

where  $E_c$  and  $P_c$  are the total open-water evaporation and precipitation, respectively, subscript c referring to the watershed. Note that the transpiration flux  $T_c$  is biologically mediated and is therefore not expected to be isotopically fractionating (Gat, 1995).

The fraction of water loss by evaporation from a watershed is expected to depend, to a first-approximation, on

$$x_C \approx \frac{e}{p} \cdot \frac{L_E}{C_E}$$
 (dimensionless) (10)

where *e* and *p* are the depth of open-water evaporation and precipitation, respectively (m/year), for the watershed, and  $L_E$  and  $C_E$  are the effective area of lakes and effective watershed area, respectively. Note that for a watershed that is fully-connected (i.e. all areas are contributing to flow), these effective areas are equal to the topographically delineated areas, *L* and *C*, respectively. For a partially-contributing watershed (i.e. with temporally variable source areas) the effective areas are commonly smaller. Partitioning of the evapotranspiration (*ET*) fluxes in the effective drainage basin would then be possible to evaluate using

$$\frac{E_C}{E_C + T_C} = \frac{x_c P_C}{P_C - WY_C} \left( \approx \frac{e}{p - wy} \cdot \frac{L_E}{C_E} \right) \quad (\text{dimensionless}) \tag{11}$$

where  $WY_C$  is the total catchment runoff (m<sup>3</sup>) and wy is the depth of runoff estimated for the topographic catchment area (in mm). The advantage of using the  $x_C$  term in Eq. (11) is that the contributing area need not be assumed.

Two specific cases of partial contributing areas in shield terrain can be considered: (i) a string-of-lakes in which both effective lake area and catchment area vary over time, and (ii) a string-of-lakes in which effective lake area remains constant and equal to the topographically delineated area, while effective catchment areas vary over time. The latter case, while less realistic, provides an upper

<sup>&</sup>lt;sup>2</sup>  $\delta$  values express isotopic ratios as deviations in per mil (‰) from the Vienna-SMOW (Standard Mean Ocean Water), such that  $\delta_{\text{sample}} = 1000((R_{\text{sample}}/R_{\text{smow}}) - 1)$ , where *R* is <sup>18</sup>O/<sup>16</sup>O or <sup>2</sup>H/<sup>1</sup>H.

<sup>&</sup>lt;sup>3</sup>  $\varepsilon$  values represent instantaneous isotopic separations in per mil between coexisting liquid and vapour, such that  $\varepsilon_{liquid-vapour} = 1000((R_{liquid}/R_{vapour}) - 1) \approx (\delta_{liquid} - \delta_{vapour}).$ 

limit on the effective drainage area  $C_E^{ul}$  of the watershed. We use this indicator, given by

$$C_E^{ul} \approx \frac{eL}{px_c} (\mathrm{km}^2) \tag{12}$$

based on the isotopic signals in Baker Creek discharge,  $x_c$ , to illustrate how variations in the degree of connectivity of the watershed are likely occurring. Such variations are shown to contribute to maintenance of an isotopic signal which is more evaporatively enriched (i.e. more "lakey") than would be expected if the contributing area of the watershed was equal to the topographic area.

Application of Eqs. (9)–(12) to watersheds assumes that evaporation is occurring from open-water, and that evaporation from bare soil is minor. While bare soil evaporation can be locally important, significant contributions to isotopic enrichment by this mechanism in the present setting are not expected (see also Gibson, 2001). Nor are such signals observed in some large dryland river systems (Gibson et al., 2008a).

## Study area

Yellowknife is situated in a subarctic continental climate, dominated by Arctic Air masses in winter and spring, and strong westerly air flows from the Pacific Ocean during summer and fall (Wolfe, 1998, p.8). The region is characterized by short cool summers and long cold winters, with mean monthly temperatures ranging from 16.8 °C in July to -26.8 °C in January. Mean annual precipitation is 281 mm (1971–2000), about 40% falling as snow (Environment Canada, Climate Normals Online). Average daily temperatures generally remain below zero from late September through to late April.

The Baker Creek watershed is situated near Yellowknife, Northwest Territories (Fig. 1), and is typical of lake-dominated drainage regimes in the Precambrian Shield areas of the northeastern Mackenzie Basin. Watershed relief is subdued, ranging from 112 m.a.s.l. near Great Slave Lake to 268 m.a.s.l. at the basin headwaters. About 85% of the watershed is underlain by Archaean granodiorite, diorite, and allied intrusive rocks, while the remainder consists mainly of mafic volcanic rocks (Wight, 1973). The watershed lies within what has been called the driftless zone (Park, 1979, p.33) as surficial deposits are absent over approximately 50% of the watershed area. Where it occurs, drift is mainly restricted to numerous depressions and to open fractures and joints in upland areas.

Four land cover types dominate the watershed, namely bare Precambrian bedrock (27%), open black spruce forest (24%), surface water (21%) and peatland (15%, including bogs, fens, palsen) (Spence, 2006). There are 349 perennial lakes in the watershed with a median area of 5400  $m^2$ , eight lakes having areas larger than 1 km<sup>2</sup>, but the vast majority of lakes (97%) having areas less than  $0.5 \text{ km}^2$ . Martin Lake, situated near the mouth of the watershed and immediately upstream of the gauging station has an area of 3 km<sup>2</sup> (Fig. 1). While permafrost is widespread and discontinuous in the region, it tends to be associated with peat deposits, and is generally absent in areas of exposed bedrock, under watercourses, and in well-drained sandy overburden (Wolfe, 1998). Bedrock topography combined with low regional gradients has promoted drainage into localized depressions, many of which have no surface outlet and contribute to Baker Creek drainage intermittently when they overflow (Park, 1979). Depression storage is very significant and in some years may nearly completely negate runoff.

The West Bay fault (Fig. 1), evident as a shallow linear depression about 50–100-m wide and dividing the watershed roughly in half from northwest to southeast, plays a dominant role in controlling the drainage pattern of Baker Creek. Surface runoff tends to

flow towards the West Bay fault zone from the northeast and southwest and then alters course to move along the fault zone towards Great Slave Lake to the southeast. Movement of water along the West Bay fault zone is mainly by interflow, as slow seepage through organic terrain (Park, 1979). The exception is during high flow episodes such as spring melt and fall when surface connections between lakes may be maintained for variable periods of time.

## Methods

A program of physical monitoring and isotope-based measurements began in 1991 at the Pocket Lake site (Fig. 1). The site was selected due to its proximity to a local tailings reservoir and its appropriateness as a natural analog for a high-closure tailings pond. Early work at the site focused on comparing evaporation estimates between the Penman combination method, a meteorological technique involving measurement of energy and aerodynamic properties over the lake, and an isotope balance approach based on measurement of heavy isotope enrichment of water (Gibson et al., 1998). By 1997 the study evolved to include monitoring of the discharge of nearby Baker Creek. A series of unpublished hydrogeological investigations were also conducted at the Giant Mine, which included analysis of the Baker Creek watershed (see Fracflow and Gibson, 1998). More recent work by Spence (2006) has also included a detailed nested watershed study of runoff response along the string-of-lakes watercourse which runs along the West Bay fault zone traversing the watershed (Fig. 1).

Water samples for isotopic analysis were collected in 30 mL high-density polyethylene bottles with minimal headspace and tightly sealed lids to minimize potential for evaporation. Five to ten near-surface grab samples were collected per year from Pocket Lake in the littoral zone and from Baker Creek at centre, mid-depth in the channel during the ice-free period, and were subsequently submitted to the Environmental Isotope Laboratory, University of Waterloo for analysis of <sup>18</sup>O/<sup>16</sup>O and <sup>2</sup>H/<sup>1</sup>H by standard isotope ratio mass spectrometry methods.  $\delta^{18}$ O and  $\delta^{2}$ H values are reported relative to SMOW and normalized to SMOW-SLAP (Standard Light Arctic Precipitation). (See Coplen, 1996). Analytical uncertainty is estimated to be better than 0.2% for  $\delta^{18}$ O and 2% for  $\delta^{2}$ H. A class-A pan and micrometeorological tower have been operated at Pocket Lake since 1993. Details of the setup, and estimates of evaporation based on the Penman method (Reid and Faria, 2004) and an isotope mass balance method (Gibson et al., 1998) have been presented elsewhere.

## **Results and discussion**

Isotopic data collected during the study are presented in Figs. 2 and 3, discharge-isotope relations are shown in Fig. 4, and an interannual summary of results, including isotope-based estimates of evaporation loss (x), evaporation/evapotranspiration (E/ET) and effective drainage area are given in Fig. 5 and Table 1. Note that partitioning calculations in Table 1 are based upon average isotopic compositions measured during the open-water period. Evaporation/inflow  $(x_L)$  for Pocket Lake is estimated using Eq. (8),  $x_C$  for Baker Creek is estimated from Eq. (9), and watershed-weighted E, T, and E/ET are estimated using Eq. (11). The upper limit on effective contributing area,  $C_E^{ul}$ , is estimated from Eq. (12) assuming that the areal distribution of lakes is the topographically delineated lake area L. Note also that the average 180 values for Baker Creek for the 1992-1996 interval are only approximated (not measured), but this was considered to be useful and warranted based on the strength of the regression in Fig. 3b ( $r^2 = 0.849$ , p < 0.001).  $\delta^2$ H values for Baker Creek for these years were estimated as a function of



**Fig. 1.** Map of the Baker Creek watershed near Yellowknife, Northwest Territories, showing location of the West Bay fault, Pocket Lake, and the Giant Mine. The watershed headwaters lie close to Duckfish Lake from where water flows generally southward along a complex string-of-lakes to the mouth of Baker Creek at Yellowknife Bay on Great Slave Lake. General surface flow directions are depicted with black arrows. The Water Survey of Canada gauging station (G) is located at the outlet of Lower Martin Lake. Solid and dashed grey lines depict the gauged and ungauged areas, respectively, of the watershed (modified from Fracflow and Gibson, 1998).



Fig. 2. Time series of oxygen-18 in Baker Creek and Pocket Lake waters sampled during the open-water period, 1997–2008. Both undergo systematic seasonal enrichment in response to changes in evaporation/inflow, although the isotopic separation between them is variable from year to year.

 $\delta^{18}$ O using the Baker Creek evaporation line (regression line 2, Fig. 3a). These approximations are included to provide a continu-

ous representation of watershed response for an 18-year period from 1991 to 2008.



**Fig. 3.** (a)  $\delta^2 H - \delta^{18} O$  plot showing isotopic composition of Baker Creek discharge, Pocket Lake water, and precipitation waters (rainfall, snow). Analytical uncertainties are smaller than the symbols shown. Correlations and significance (*p*-value) for each water type are shown; (b) cross-plot showing systematic correlation between Baker Creek and Pocket Lake water sampled during 1991 and 1997–2008. Note that Baker Creek and Pocket Lake were identical at the time of sampling in summer 2000.



**Fig. 4.** Plot of  $\delta^{18}$ O versus discharge for Baker Creek. Correlations with significance (*p*-value) are also shown. Observed relationships suggest snowmelt-driven system but with a diverse range of pathways and runoff times in all seasons.

Seasonal  $\delta^{18}$ O variations in both Pocket Lake and Baker Creek are shown to be typically of the order of 2–3‰ with minimum enrichment in the early ice-free open-water period, and peak enrichment occurring in late summer (Fig. 2). Similar trends are observed for  $\delta^2$ H (not shown). For Pocket Lake, the mean isotopic enrichment above that measured in precipitation is controlled by the overall water balance (evaporation/inflow), with short-term rates of isotopic enrichment being strongly correlated with rate

of evaporation (see Gibson et al., 1998). Similar patterns in Baker Creek are likewise attributed to evaporative enrichment under arid summertime atmospheric conditions. Both Pocket Lake and Baker Creek become depleted in heavy isotopes during the late summer/early fall due largely to increased amounts and more depleted isotopic composition of precipitation, as well as reactivation of severed runoff pathways from upland areas.

On a  $\delta^2 H - \delta^{18}O$  plot (Fig. 3a), both Pocket Lake and Baker Creek plot on similar evaporation lines with slopes close to 5 and are systematically offset from local precipitation (rain/snow regressions, Fig. 3a) The intersection of the meteoric water line and the local evaporation lines (approx. -21.5% for  $\delta^{18}O$ , -168.0% for  $\delta^{2}H$ ) is significantly more depleted, i.e. by roughly five times the analytical uncertainty for both tracers, than an estimate of the isotopic composition of annual precipitation from monthly sampling at the nearby Yellowknife airport in the 1980s (-20.5% for  $\delta^{18}O$ , -157% for  $\delta^{2}H$ , see Birks et al., 2002). The evaporation line slopes for both Baker Creek and Pocket Lake are not significantly different as tested using a slope/intercept equality test.

Correlation between Pocket Lake and Baker Creek in time (Fig. 3b), indicates a systematic, but variable offset between the lake and watershed signals. From both the time-series observations (Figs. 2 and 5) and cross-plot (Fig. 3b) it is evident that convergence of the isotopic signals in Pocket Lake and Baker Creek occurs when runoff declines to near zero, and divergence occurs when Baker Creek is better connected to upstream lakes and land areas. Similar isotopic signals in Baker Creek and Pocket Lake observed on 21 July 2000, one of the driest months on record during the study, suggests complete disconnection of Baker Creek above Martin Lake. The most depleted isotopic signal was measured on 5 April 2006, one of the wettest months during the study, at which time Baker Creek was about 3% depleted in  $\delta^{18}$ O relative to Pocket Lake. This qualitatively suggests more complete connectivity between non-evaporated water sources such as soil filled valleys and uplands within the Baker Creek drainage.

The negative correlation ( $r^2 = 0.143$ , p < 0.001) between discharge and <sup>18</sup>O in Baker Creek (Fig. 4) confirms that periods of low flow are also characterized by heavy isotope enrichment. For individual seasons, the pattern is similar but more complex (see



**Fig. 5.** Interannual water balance summary showing: (a) mean  $\delta^{18}$ O in Baker Creek and Pocket Lake, error bars denoting two times analytical uncertainty, (b) mean isotope balance estimates of evaporation/inflow ratios, with errors estimated from differences between  $\delta^{18}$ O and  $\delta^{2}$ H mass balance, (c) annual Penman evaporation estimated from meteorological measurements at Pocket Lake (mm), dotted line showing study period average, (d) annual precipitation and Baker Creek annual runoff with errors (mm), (e) evaporation/evapotranspiration ratios based on isotope partitioning, dotted line showing study period average, and evaporation/evapotranspiration estimated from water balance only, assuming a fully connected watershed, and (f) mean isotope-based estimate of effective drainage area upper limit, dotted lines showing approximate upper and lower limits. Note that errors associated with isotopic estimates in (b), (e) and (f) vary from year to year increasing mainly during periods of high evaporative enrichment or lower relative humidity. Selected data and calculations are also plotted in Table 1.

Fig. 4). In general, spring is a time of higher discharge and lower  $\delta^{18}$ O associated with snowmelt, summer is typified by reduced flow and higher  $\delta^{18}$ O associated with evaporative enrichment, and late summer/fall marks a return to higher flows and lower  $\delta^{18}$ O due to enhanced precipitation and reduced evaporation. The considerable scatter in discharge-isotope relationships suggests a

diverse range of pathways and residence times for water runoff. As noted by previous workers (Spence and Woo, 2002, 2003, 2006; Spence, 2006), 'fill and spill' runoff systems are typified by spatially and temporally variable storage capacities in bedrock depressions, soil filled valleys, and surface water bodies, connected by saturated overland or shallow subsurface flow. As these systems

#### Table 1

Summary of annual water and isotope balance. Physical monitoring data were collected at Yellowknife airport, except runoff which was measured at the Water Survey gauging station, and evaporation estimated at Pocket Lake (see Fig. 1). Isotope data include mean  $\delta^{18}$ O and  $\delta^{2}$ H. Partitioning data include mean E/I based on Eqs. (8) and (9) for Pocket Lake and Baker Creek, respectively, and E/I error, estimated as absolute value of differences between E/I for individual tracers. Note that the watershed-weighted vapour partition and effective drainage area are based on Eqs. (11) and (12) applying mean E/I values.

Date	Physical monitoring data					Isotope data and partitioning											
	Relative humidity	Air temp. (°C)	Precip. (mm)	Runoff (mm)	Evaporation mm)	Pocket L				Baker Creek				Watershed-weighted vapour partition			Effective DBA
						$\delta^{18} 0$	$\delta^2 H$	E/I		$\delta^{18} O$	$\delta^2 H$	E/I		Ε	Т	E/ET	(km²)
						(‰)	(‰)	Mean	Error	(%)	(‰)	Mean	Error	(mm)	(mm)		
1991	0.57	18.0	358	138	392	-11.12	-118.4	1.42	0.22	-14.72	-131.0	0.49	0.09	174	46	0.79	77
1992	0.62	16.0	258	94	339	-11.39	-119.2	1.16	0.06	-13.46	-127.9	0.61	0.00	158	7	0.96	74
1993	0.77	10.8	279	46	363	-10.83	-116.2	1.24	0.03	-12.45	-123.1	0.76	0.03	211	22	0.90	59
1994	0.66	13.2	214	18	460	-10.31	-113.4	1.65	0.16	-11.51	-118.7	1.08	0.07	231	n.d	1.18	68
1995	0.66	14.6	225	7	445	-10.74	-117.6	1.33	0.09	-12.29	-122.3	0.86	0.04	194	24	0.89	79
1996	0.72	13.9	261	11	414	-11.26	-122.1	1.20	0.36	-13.22	-126.8	0.70	0.01	182	68	0.73	78
1997	0.68	13.9	298	19	376	-11.67	-122.9	0.92	0.18	-12.00	-121.0	0.93	0.05	278	1	1.00	46
1998	0.70	14.4	311	37	436	-10.40	-111.5	1.89	0.68	-11.62	-117.1	1.18	0.30	366	n.d	1.38	41
1999	0.65	13.0	246	44	402	-11.10	-117.2	1.22	0.05	-12.45	-120.1	0.89	0.20	219	n.d	1.09	63
2000	0.68	12.5	316	11	435	-10.53	-117.4	1.31	0.24	-11.53	-121.4	0.96	0.15	303	2	0.99	49
2001	0.72	13.5	350	125	386	-10.58	-117.2	1.35	0.16	-13.45	-128.0	0.58	0.03	204	21	0.91	65
2002	0.73	12.7	308	101	361	-11.74	-119.2	1.01	0.08	-14.68	-132.4	0.41	0.01	127	80	0.61	97
2003	0.70	13.4	251	70	425	-11.88	-121.3	1.32	0.01	-14.38	-110.0	0.53	0.05	140	41	0.77	104
2004	0.67	15.8	181	30	337	-11.17	-119.3	1.46	0.04	-13.44	-130.1	0.62	0.11	111	40	0.74	104
2005	0.68	15.6	389	111	372	-11.64	-122.9	1.12	0.21	-13.90	-132.2	0.52	0.11	204	73	0.74	63
2006	0.66	17.5	304	106	431	-12.40	-124.0	0.98	0.03	-14.87	-135.1	0.41	0.05	125	73	0.63	118
2007	0.66	15.8	311	54	397	-11.89	-123.0	1.07	0.10	-14.17	-132.7	0.49	0.08	154	104	0.60	88
2008	0.66	13.4	398	98	379	-11.85	-121.2	0.94	0.02	-13.78	-129.2	0.53	0.02	211	88	0.71	61
Mean	0.68	14.3	292	62	397	-11.25	-119.1	1.25	0.15	-13.22	-125.5	0.70	0.08	200	38	0.83 <sup>a</sup>	74

*Note*: Shaded values are estimated based on measured Pocket Lake isotope data and correlation shown in Fig. 3b; n.d. – value is negative, indicating that steady-state model may not be appropriate due to substantial storage reduction.

<sup>a</sup> For estimating the mean E/ET, values greater than 1 were assumed to be equal to 1.

depend on hydrological processes within each element as well as degree of connectivity with upstream and downstream elements they can produce dissimilar runoff responses. Isotopic signals contributed by each element may also vary due to differing residence times, and differing exposure times to evaporation and transpiration. Collectively, the 'fill and spill' architecture tends to regulate flow and isotopic composition, but it also promotes mixing and interaction between a diverse network of soilwater and surface water storages leading to a more distributed isotopic response. The presence of localized permafrost, seasonally frozen ground and arid conditions, the latter of which can selectively sever drainage pathways, also contributes to overall variability in residence times and runoff pathways.

#### Water balance estimates and partitioning

A series of simple calculations provide an isotopic perspective of changes in annual water balance conditions in the Baker Creek watershed during 1991-2008 (Fig. 5, Table 1). To compare inter-annual patterns, we apply a steady-state isotope mass balance model based on Eqs. (8) and (9) for Pocket Lake and Baker Creek, respectively, to interpret the measured isotopic trends (Fig 5a). Use of a non-steady-state model was not attempted, owing to limitations in available data on watershed storage volumes and changes over time, and complex residence time and mixing effects that may contribute to uncertainty in the timing and isotopic signature of runoff. As we show, the steady-state model illustrates basic differences in magnitude of E/I (Fig. 5b) and water-loss mechanisms (Fig. 5e) between the lake and watershed. For comparative purposes, an identical value for isotopic composition of atmospheric moisture,  $\delta_A$ , was used in Eq. (1) for both Pocket Lake and Baker Creek ( $\delta^{18}O = -29.5$ ;  $\delta^{2}H = -223$ ). This value is obtained by a best-fit method that minimizes average differences between E/I based on  $\delta^{18}$ O and  $\delta^{2}$ H, while preserving a match between the predicted and observed evaporation line slopes (see Bennett et al., 2008). Although sacrificing independent application of the two tracers, this approach serves to constrain an important yet difficult to measure unknown. Values used for  $\delta_A$  are in close agreement with previous estimates for Yellowknife, Northwest Territories calculated using a seasonally-weighted Global Network for Isotopes in Precipitation dataset ( $\delta^{18}$ O = -28.7;  $\delta^2$ H = -219; Gibson et al., 2008b). To illustrate model uncertainty and goodness of fit in each year, *E*/*I* differences between the two tracers are provided in Table 1 (as *E*/*I* error).

Note that E/I = 1 is an important theoretical balance point for a constant volume reservoir, marking the limit where liquid outflow stops. E/I > 1 indicates volumetric reduction up to the atmospherically controlled limit of  $\delta^*$ , approached as a water body evaporates toward dryness. E/I estimated for Pocket Lake averaged greater than one (1.25), with a maximum of 1.89 in 1998 and a minimum of 0.92 in 1997. E/I values greater than one imply that Pocket Lake had no liquid outflow, and furthermore, was in a temporary declining condition. This is consistent with observations. In fact, the lake is known to have undergone significant seasonal variations in water level, typically drawing down over the course of the summer by up to 10 cm. Summer lake level observations made at times over the past four decades, while anecdotal, advise that the lake volume was significantly lower during the 1990s than in 1967, 1970 and 1971 when the lake was observed to have "slight" outflow (ungauged) during the freshet period in April and May (Wight, 1973). For 2002, and during 2005–2008, *E/I* values were found to average ~1.02 while at the same time intermittent surface outflows to Baker Creek were again observed via a small ungauged surface channel. We suggest that the 1990-2001 period was relatively dry but that the post-2001 period is more similar in terms of water balance conditions to the late 1960s and early 1970s when outflow occurred in some years (see Wight, 1973, p. 200).

Similar patterns for E/I are recognized for the Baker Creek watershed (Fig. 5b), but with lower overall E/I ratios averaging close to 0.7 during the study period. This is typical of a reservoir with

a balance between evaporation and outflow. Maximum values of 1.18 are found for 1998, indicating drying conditions and near zero outflow, while minimum values of 0.41 are found in 2002 and 2006, indicating higher runoff than evaporation. The *E*/*I* estimates are also compared with the meteorological lake evaporation records for Pocket Lake (Fig. 5c) and the precipitation and runoff record for Baker Creek (Fig. 5d).

For the Baker Creek watershed, evaporation/evapotranspiration (E/ET) is estimated both from the isotope partitioning method based on Eq. (11) and from the 'water balance only' perspective (Fig. 5e). The latter uses no isotopic partitioning information but instead assumes that evaporation occurs only from lakes, that lakes account for a fixed 21% of the watershed area, that lake evaporation records from Pocket Lake are representative of all lakes in the watershed, and that the watershed is fully contributing at all times. The most striking feature of this comparison is the pronounced disagreement between these two methods, particularly during most of the 1990s. While the latter scenario is somewhat unrealistic, it is intentionally included in Fig. 5 to illustrate limitations in the 'water balance only' perspective for tracking the vapour partitioning. The isotopic perspective, on the other hand is naturally weighted over the source area of its signal, although this effective area is not easily determined based on isotopic information alone.

Essentially, we find that the isotopic signal in Baker Creek is more enriched than would be expected if the entire watershed were contributing to the discharge. Reconciliation of the E/ET signals using Eq. (12) provides one approach to calculate the upper limit of the effective drainage area (Fig. 5f). For this we assume that the effective drainage area would contain a higher fraction of lakes, as would be expected if wetter areas of the watershed remained connected whereas drier areas, particularly uplands, became intermittently disconnected. Annual changes predicted in effective drainage area, ranging from about 25% to 85% of the topographic drainage area, are likely averages of much more variable connectivity conditions, as observed first hand in the Baker Creek watershed by Spence (2006). Based on physical observations, he identified that contributing area of the watershed varied at times between 4% and 100% during May to September 2003 and 2004, although no time- or flow-weighted connectivity average is calculated which makes it difficult to compare directly to the isotope balance results presented here. Our isotope balance results suggests an effective drainage area of 104 km<sup>2</sup> or close to 76% of the topographic drainage area during the time period of his study, which is about 20% larger than the 1991-2008 average.

Overall, the Baker Creek dataset reveals at least two distinct climate-water balance periods during the study. A period of relatively dry conditions with high evaporation/inflow, lower runoff, and higher *E/ET* between 1991 and 2000, followed by a period of wetter conditions between 2001 and 2008 with lower evaporation/inflow and lower *E/ET*. According to the Climate Trends and Variations Bulletin of Canada 2008 (Environment Canada, 2009), annual precipitation was higher than the 62-year normal in Mackenzie District in 6 of 9 years during the observed wet period (1991–2000), and was below normal in 6 of 9 years during the dry period (2001–2008). Interestingly, the shift from drier to wetter conditions was evidently accompanied by an increase in the proportion of water lost to non-fractionating outflow (both transpiration and runoff) as effective drainage area expanded.

The strong correlation we observe between isotopic enrichment by evaporation in an index lake and in a nearby watershed may offer a simplified approach for monitoring of E/ET partitioning and effective drainage area changes, as we have demonstrated. However, the method remains to be tested under a wider range of hydrologic settings in both shield and plains watersheds. In particular, sensitivity of the Craig and Gordon model (i.e. Eq. (1)) to choice of atmospheric moisture and relative humidity also warrants further field-based experiments including direct sampling and partitioning of evaporation and transpiration fluxes in the near surface boundary layer.

## Implications for regional runoff

Runoff from Precambrian Shield watersheds carries the isotopic signal of open-water evaporation loss and this signal can vary significantly as we have shown, both seasonally and interannually in response to degree of connectivity and vapour loss mechanisms in a typical subarctic watershed. Flux-weighted isotopic composition of Baker Creek during the study period was found to be -14.4% in  $\delta^{18}$ O and -114.5% in  $\delta^2$ H at a mean instantaneous discharge of 0.41  $m^3/s,$  which is enriched by roughly 7.1% and 54%, respectively from annual precipitation. We suggest that the Baker Creek watershed is a good example of the source of evaporative isotopic enrichment signals known to be propagated from headwater systems downstream along the Mackenzie River to the Arctic Ocean. (see Gibson et al., in press). Ongoing research continues to explore the application of these distinct isotopic signals to trace contributions of flow derived from wetland and lake sources during extreme high-flow events in the Mackenzie River system (Yi et al., accepted for publication).

## Conclusions

This analysis has revealed systematic seasonal and inter-annual patterns in the isotopic offset between lake and watershed outflows in a Precambrian Shield watershed. This 18-year record serves to demonstrate for the first time the expected variability in the evaporation and transpiration partitioning, upper limits on the effective drainage area, and isotopic signals transferred downstream in a typical shield drainage system within the Mackenzie Basin. Despite being in a snowmelt-driven region, flow-weighted discharge from the watershed is found to be distinctly isotopically labeled by the evaporative enrichment process. This provides an example of the origin of evaporative isotopic signals known to be propagated downstream along the Mackenzie River to the Arctic Ocean.

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