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Synoptic and time-series stable isotope surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003 to 2006

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SUMMARY

We report oxygen and hydrogen isotopic composition of river discharges in the main stem and tributaries in Mackenzie River system, Canada, based upon a synoptic survey and a time-series monitoring program undertaken between 2003 and 2006. The water isotope signals in the Mackenzie River system exhibit distinct geographic variations. Isotopic results from the comprehensive synoptic survey offset from meteoric water lines in $\delta^{18}O$–$\delta^{2}H$ space, and suggest a snowmelt-driven discharge regime with mixing between heavy-isotope depleted discharge from Liard River and Mackenzie Mountains, and evaporatively-enriched water from Great Slave Lake catchment. Based upon these isotopic data in river discharge, we propose an evaporative-mixing line for the Mackenzie River system ($\delta^{2}H = 6.0 \times \delta^{18}O - 40.8$), which highlights the integrated effects of the two most important hydrologic processes (i.e., evaporation and mixing). Time-series investigation of water isotope signatures and river discharge at three key hydrometric stations demonstrates the isotopic response to the strong seasonality of river discharge in northern Canada. In general, isotopic compositions in river discharge tend to be negatively correlated with discharge amount, which is a typical snowmelt-driven isotope-discharge pattern. However, low flow conditions are found to be noisy with a wide range of isotopic variability. More importantly, we also observe that extreme high flow events, especially in the Liard River, appear to be unexpectedly enriched in heavy isotopes, which indicate contributions from evaporated water that are probably derived from wetland surface storage. This is a situation, which produces a reversal in the isotope-discharge pattern and marks important episodes that may impact chemical and riverine/estuarine biotic processes at times of extremely high runoff.

Introduction

Rivers are important links between terrestrial landscapes and oceanic ecosystems. On a global scale, rivers transport $\sim 38.3 \times 10^{3}$ km^{3} of water from the land to the ocean annually, including $\sim 3.3 \times 10^{3}$ km^{3} to the Arctic Ocean (Perry et al., 1996; Fekete et al., 2002; Dai and Trenberth, 2002; Trenberth et al., 2007). This freshwater input to the Arctic Ocean is believed to have a profound effect on North Atlantic Deep Water (NADW) formation and Atlantic Thermohaline Circulation (THC), which subsequently affect the climate system on this planet (Rahmstorf, 1995; Broecker, 1997). However, our understanding of hydrological fluxes and storages in pan-Arctic drainages, and its effect and response to climate variability are surprisingly limited (Shiklomanov et al., 2002). Consequently, studies of water cycling processes in large northern river basins have remained a virtual scientific frontier over the past decades (GCIP, 1998; Rouse, 2000; Peterson et al., 2002; McClelland et al., 2008).

While coordinated efforts to study the Mackenzie River system in northern Canada have been undertaken (e.g. Reeder et al., 1972; Rouse, 2000; Woo and Thorne, 2003; Gibson et al., 2005), detailed understanding of the mechanisms controlling the quantity and the seasonality of freshwater flow, especially extreme events, remains inadequate, largely due to a lack of high-frequency measurements/observations in the field (Kane et al., 1992; Kane, 2005). Stable isotopes have been applied as an alternative technique for gaining quantitative hydrological information in remote areas (Gibson et al., 2002; Gibson and Edwards, 2002; Vitvar et al., 2007). Early surveys of isotope composition of river discharge across the Mackenzie Basin have revealed a great potential to delineate precipitation, runoff and evaporation processes, but most of the

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surveys were unfortunately limited to measurements of $\delta^{18}O$ only (Hitchon and Krouse, 1972; Telang et al., 1982). Other surveys that included both tracers were spatially patchy (Gibson and Prowse, 2002).

This study reports on data collected through systematic sampling and measurement of oxygen and hydrogen isotopes in river discharge (including main flow and tributary flow) from 2003 to 2006. Key hydrological processes within the Mackenzie River system that control isotopic variability in discharge are identified and described. Discharge records are combined with isotopic data at selected hydrometric stations to understand the isotopic effect of the Liard River and Great Slave Lake on the main channel of the Mackenzie River. Overall, this paper presents data from isotope analyses that are used to characterize temporal and spatial variability of hydrological processes in a large northern river basin. Such data may also be a useful diagnostic tool for the development of more realistic hydrological models.

Methods

Study area

The Mackenzie River is the largest source of freshwater to the Arctic Ocean on the North American continent (Fig. 1), and extends over 1500 km from Great Slave Lake to Tsiigehtchic, just north of the Mackenzie River Delta. The river system drains 1.8 million km^2, about one-fifth of Canada, with an average annual discharge of 9700 m^3s^{-1} at the mouth to Beaufort Sea. The drainage basin is comprised of three major physiographic regions, (1) the North American Cordillera to the west, (2) the Canadian Shield to the east, and (3) the Interior Plain in the middle. The elevation is greatest on the western edge of the basin along the Cordillera mountain ranges and decreases eastward across the Interior Plain. The Precambrian Shield, which is characterized by highly weathered crystalline metamorphosed sedimentary and volcanic rocks, experienced extensive glaciation during the Pleistocene. The characteristic topography combined with the unique geological history produced several great lakes of Northern Canada following the retreat of the glaciers. The lakes include Great Bear Lake (3.13×10^4 km^2), Great Slave Lake (2.86×10^4 km^2) and Lake Athabasca (0.79×10^4 km^2) (Smith, 1994). Intensive fluvial processes within the drainage formed three major deltas (i.e., Peace-Athabasca Delta, Slave River Delta and Mackenzie River Delta), which are of hydrological and ecological interest. Gauging stations measuring water flow in river channels are mainly situated in the low elevation communities along the rivers main stem and major tributary outlets.

The physical character of the main channel of the Mackenzie River changes along its course in response to physiography, and can be divided into three distinct reaches (Fig. 2a). The upper reach of river, from the outlet of Great Slave Lake to Fort Simpson near the confluence with the Liard River, is generally flat with swift currents. In addition to the outflow from Great Slave Lake, the landscape contributing runoff into this section of the river is characterized by a myriad of lakes, wetlands and boreal forest. Along the middle reach, from Fort Simpson to Fort Norman, the river flows fast between steep banks with inflow from numerous mountainous streams and creeks. Below Fort Norman, the third reach of the river flows through rolling terrain with moderate relief until it meets with the Arctic Red River at Tsiigehtchic. Beyond Point Separation near Tsiigehtchic, water flows into the Mackenzie River Delta where the landscape has evolved into a maze of interconnecting channels, numerous cutoff lakes, circular ponds and wetlands. The last major tributary of the Mackenzie River system, the Peel River, flows into the delta to the west of Point Separation. The Mackenzie River does not have a well-defined main channel as it traverses the delta. Distribution and movement of water within the delta is known to be extremely complicated. As a result, the sampling and discussions in this paper will focus on the three reaches, from Great Slave Lake to Tsiigehtchic. Discharge at the latter site is commonly used to represent the mouth of the Mackenzie River, although it is sometimes combined with discharge in the Peel River to approximate the total discharge from the Mackenzie Basin to the Beaufort Sea.

Water sampling and isotopic analysis

Over the past 7 years, two collaborative sampling campaigns were undertaken for studies of isotope hydrology in the Mackenzie River Drainage System. A synoptic sampling excursion was completed along the Mackenzie River main channel in the summer of 2003 (August 5 to September 8) from Tsiigehtchic to Great Slave Lake. Waters along the main stem and at the mouth of major tributaries (a few hundred meters above the confluence) were sampled for analysis of stable isotopes ($\delta^{18}O$ and $\delta^{2}H$), trace elements and water chemistry. Samples were collected 12–15 cm below the surface on launches from the Canadian Coast Guard vessels "Dumit" and "Ekaluk". At the Mackenzie-Liard confluence, where water-color was prominently darker in the Liard portion of the channel than the other, duplicate samples were taken in different sections of a channel transect to investigate the effectiveness of lateral mixing. Sampling sites are shown in Fig. 1.

In addition, a time-series sampling campaign at key hydrometric stations was launched in 2002 by the Water Survey of Canada (WSC) as a contribution to an IAEA CRP initiative (International Atomic Energy Agency Coordinated Research Project). The Mackenzie River at Strong Point (above the confluence with Liard River), Liard River at the mouth, and Mackenzie River at Tsiigehtchic are three key hydrological nodes with long-term river discharge measurements by the WSC (Fig. 1). From 2004 to 2006, water samples were collected approximately every month at the time of visits by WSC personnel. In 2002, 2003 and 2007, only sporadic sampling was carried out. River discharge records were obtained through the National Hydrometric Program WSC (Environment Canada, 2005) for the same day that isotopic samples were collected. Discharge measurements were mainly generated by a discharge-stage model.

All water samples were sealed in 30 mL high-density polyethylene bottles and returned to the University of Waterloo – Environmental Isotope Laboratory for analysis. $\delta^{2}H$ in water was determined on a CF-IRMS system, by reduction of water to H_2 gas using chromium metal as active reducing agent (Morrison et al., 2001); $\delta^{18}O$ in water was measured on a dual-inlet VG-Micromass 903 mass spectrometer by applying a CO_2 equilibration method (Epstein and Mayeda, 1953). Results are reported in δ values, expressed in per mil (‰) vs. the international reference V-SMOW (Coplen, 1996). Analytical uncertainties are ±0.05‰ for $\delta^{18}O$ and ±0.3‰ for $\delta^{2}H$.

Results and discussions

Isotopic characteristics of synoptic sampling

Oxygen isotope values from the main channel of the Mackenzie River are presented in Fig. 2a. It is apparent that the water isotope composition is closely associated with physiographic characteristics of the river channel. Water in the upper reach is the most heavy-isotope enriched (i.e., isotopically enriched) with an averaged $\delta^{18}O$ value of -17.04 ± 0.17‰, while water in the lower reach is the most heavy-isotope depleted (i.e., isotopically depleted) with

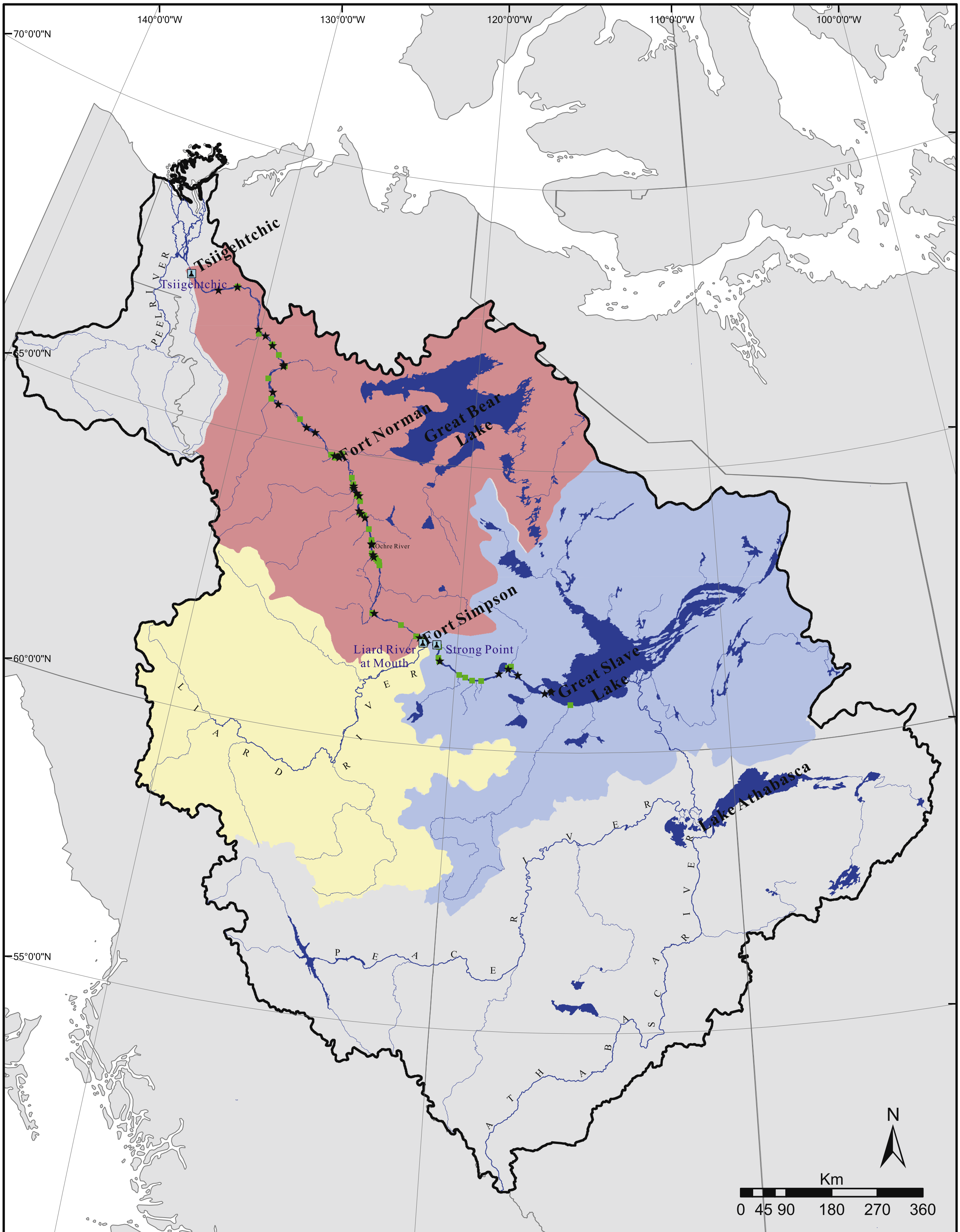

Fig. 1. The drainage basin for Mackenzie River system. Solid lines outline the boundary for the Mackenzie River drainage basin in northern Canada. Colors highlight three out of six sub-basins (i.e., coral for Great Bear Lake sub-basin; blue for Great Slave Lake sub-basin; yellow for Liard River sub-basin) that are examined in this study. Black stars (Å) indicate the sampling locations of main flow, while green squares (■) indicate the sampling sites of tributary flow. *i* shows the location of three hydrometric stations conducting time-series sampling. Major tributaries in the drainage basin and the Ochre River are labelled. Locations, where three sections of main channel are divided, are also indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

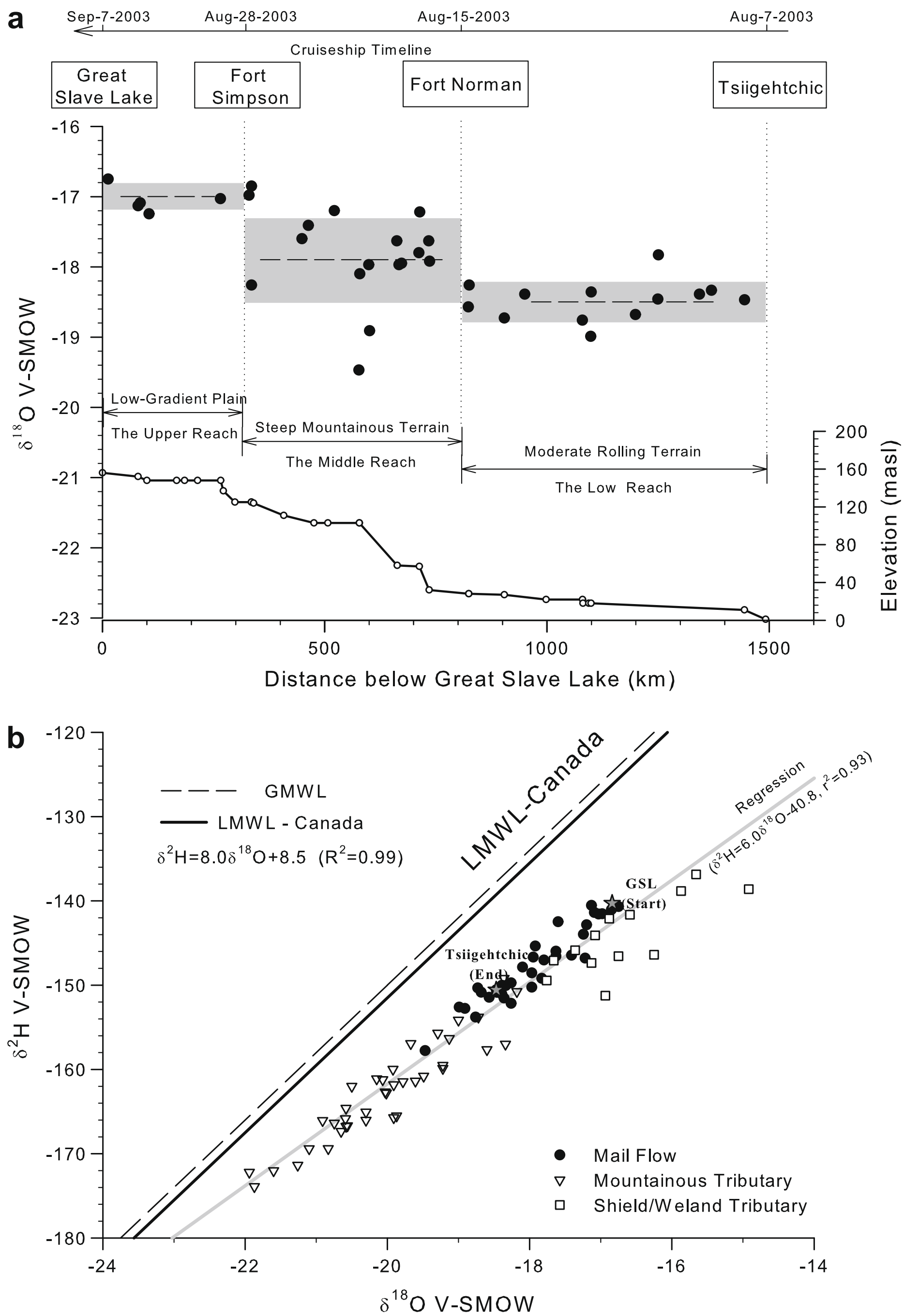

Fig. 2. Isotopic results of the synoptic sampling in 2003. (a) Main flow δ^{18}O values vs. downstream distance from the outlet of Great Slave Lake (0 km) to Tsiigehtchic (1444 km), demonstrating step-wise heavy-isotope depletion in three sections of main channel of the Mackenzie River. Dash lines indicate mean δ^{18}O values for each section and gray bars indicate the standard deviation. (b) δ^{18}O and δ^{2}H results of main flow (solid circles) and tributary flow (triangles for mountainous tributaries and squares for shield/wetland tributaries), demonstrating the coherent isotopic pattern in main channel and tributaries in δ^{18}O–δ^{2}H space. Stars emphasize the isotopic composition of main flow at headwater (Great Slave Lake) and mouth (Tsiigehtchic) respectively, which again illustrates the progressive depletion of isotopic signals along the main channel.

an average δ^{18}O value of −18.47 ± 0.31‰. Both the upper and lower reaches demonstrate low variability in river water isotope compositions, as indicated by standard deviation (Fig. 2a). In the middle reach, the isotopic compositions of river water are generally intermediate (mean: −17.91 ± 0.65‰) with high variability (ranging from −16.85‰ to −19.47‰). Duplicate samples below the Mackenzie-Liard confluence (near Fort Simpson) show distinct δ^{18}O signatures (−16.85‰ vs. −18.26‰). Main flow δ^{18}O values from sites 2 km apart (i.e., above vs. below confluence with Ochre River) are substantially different (−17.97‰ and −18.91‰), while the oxygen isotope composition in tributary flows (i.e., Ochre River), is −20.15‰. Applying a two-member mixing calculation showed that a contribution of ∼44.9% was needed from the Ochre River to produce the isotopic signature in the sampled downstream flow. However, the Ochre River is a small tributary with an average discharge rate of ∼16.5 m^3/s in August, which is three magnitudes less than the discharge rate in Mackenzie River main channel. Such a significant variation in river water isotope values over a short distance are probably an artifact of insufficient lateral mixing between upstream water and incoming tributary flow.

Previous studies, based on water chemistry and stable isotope investigations, indicate that within ~300 km downstream of the confluence of the Liard River and the Mackenzie River, the waters are not fully mixed laterally (MacKay, 1970; Krouse and MacKay, 1971). This synoptic survey confirms the phenomena of incomplete lateral mixing in the main channel of the Mackenzie River. Furthermore, the survey suggests that the middle reach (between Fort Simpson and Fort Norman) is the poorly-mixed zone (Fig. 2a), which probably is caused by rapid flow as a result of the steep elevation gradient in this section of the river. By contrast, the upper and lower reaches with a gradual elevation gradient exhibit more complete mixing of upstream water with contributing tributaries. Based upon these observations, we recommend that flow-weighted sampling strategy (Raymond et al., 2007; Cooper et al., 2008) should be applied in future sampling efforts along the middle reach of Mackenzie River, whereas cost effective grab samples from upper and lower reaches would be representative for water chemistry and biogeochemical investigations.

Despite the difficulty in sampling water across a large river basin, there have been several studies that have characterized the isotopic profiles of great rivers of the world, including the Amazon River in South America, Ganges River in Asia, and St. Lawrence and Missouri Rivers in North America (Longinelli and Edmond, 1983; Ramesh and Sarin, 1992; Yang et al., 1996; Winston and Criss, 2003). Most of these studies, with the exception of the St. Lawrence River, reported progressive increases of the $\delta^{18}O$ values in river water with distance downstream, demonstrating the cumulative effects of evaporation as water flows toward the mouth. However, the synoptic survey of Mackenzie River revealed a unique stepwise depletion in oxygen isotope composition with increasing distance from its headwaters (Fig. 2a), which is opposite to the anticipated isotopic enrichment due to evaporation.

Furthermore, in $\delta^{18}O$–$\delta^{2}H$ space, the main flow along the Mackenzie River demonstrated a strong linear correlation between $\delta^{18}O$ and $\delta^{2}H$ values. This correlation is graphically compared with Global Meteoric Water Line (GMWL) and Local Meteoric Water Line for Canada (LMWL-Canada) in Fig. 2b. The GMWL is generally considered as a good reference to indicate effects of evaporation based upon the deviation from the line (Rozanski et al., 1993). The LMWL-Canada (Gibson et al., 2005) is also presented in Fig. 2b if GMWL is debatable to be representative for the Mackenzie River Basin. Note that St. Amour et al. (2005) proposed a LMWL for lower Liard River Basin, which is very close to GMWL. For the clarity and simplicity of the graph, the basin-specific LMWL proposed by St. Amour et al. is not included in Fig. 2b. Nonetheless, isotopic compositions in the main channel flow deviate significantly from meteoric water lines on a shallower slope, thus indicating the importance of evaporation. Main flow along the Mackenzie River is characterized by isotopically enriched headwaters (i.e. at the outlet of Great Slave Lake) on the upper-right side and isotopically depleted water at the mouth (i.e., at Tsiigehtchic) on the lower-left side. The total heavy-isotope depletion from the headwaters to mouth is 1.59‰ in $\delta^{18}O$ (9.4‰ in $\delta^{2}H$). To explain this progressive depletion, it is necessary to consider hydrological processes other than evaporation.

Fortunately, 52 tributaries were sampled for stable water isotope analysis in this synoptic survey. Plotting tributary flow in the same $\delta^{18}O$–$\delta^{2}H$ space (Fig. 2b) provided additional insight into hydrological processes in the Mackenzie River Basin. According to catchment characteristics, tributaries can be classified as mountain- or shield/wetland-dominated. As for those mountain-dominated tributaries, contributions of snowmelt (or glacier melt) and runoff originating from high-altitude regions lead to depletion in water isotope composition, with values ranging from −21.94‰ to −18.18‰ for $\delta^{18}O$ (−172.2‰ to −150.8‰ for $\delta^{2}H$). By contrast, the high isotopic values in shield/wetland tributaries, ranging from −13.91‰ to −17.76‰ for $\delta^{18}O$ and from −128.2‰ to −149.4‰ for $\delta^{2}H$, are attributed to substantial open-water evaporation due to long water residency in surface storage. More importantly, main flows and tributary flows form a coherent linear trend in $\delta^{18}O$–$\delta^{2}H$ space. Mountainous tributaries are found to plot diagonally-below the main flows in $\delta^{18}O$–$\delta^{2}H$ space, whereas shield/wetland-dominated tributaries are similar or slightly enriched in isotopic signatures compared to main flows (Fig. 2b). Also note that a substantial proportion of sampled tributaries (~73%) are mountainous, which are believed to contribute a significant amount of water into the main flow (Woo and Thorne, 2003). Multiple lines of evidence suggest that it is probably the mixing of main flow and tributary flows (especially mountainous tributaries) that leads to the progressive depletion of isotopic signals along the Mackenzie River. Latitudinal isotope gradients in *in situ* precipitation (~4‰) may also contribute to the trend of isotopic depletion downstream as the river flows northward. Currently, there is no sophisticated way to separate and quantify these two potential effects. However, given the limited contribution of direct precipitation to the overall Mackenzie River flow (Louie et al., 2002; Woo and Thorne, 2003) and the strong linear coherence between main flow and tributary flow in $\delta^{18}O$–$\delta^{2}H$ space, mixing with isotopically depleted tributaries is more likely to be the leading cause of progressive depletion in the main channel. Well-thought experimental design and sophisticated modeling efforts are needed to further interrogate this hypothesis.

Overall, the $\delta^{18}O$–$\delta^{2}H$ signals from both main flows and tributary flows suggest strong evidence of evaporative effects on river discharges in both main channel and tributaries. Superimposing on the evaporation, the contribution of isotopically depleted water such as mountainous tributary flows is another important process for the Mackenzie River. As such, we propose that the linear regression ($\delta^{2}H = 6.0 \times \delta^{18}O - 40.8$, $R^2 = 0.93$) in Fig. 2b represents an evaporative-mixing line for the Mackenzie River Basin. Slightly different from the concept of evaporation line in stagnant surface water bodies, the evaporative-mixing line is not only a result of evaporation, but also the mixing of waters experiencing varying degrees of evaporation under similar climate condition. The relative position of an individual sample along the evaporative-mixing line indicates the contribution of multiple water sources under a common evaporation regime. Both evaporation and mixing are important in the Mackenzie River system and isotopic investigation holds the potential to quantify two processes separately.

Isotopic characteristics of the time-series sampling

The synoptic survey, a snapshot over a 1500-km reach, revealed a distinct evolution of isotopic signatures along the Mackenzie River. However, little is known about the temporal variation of the isotopic systematics within the drainage basin, especially in the main channel. Do the spatial characteristics observed in the synoptic survey during summer hold through time? How does the isotopic signal respond to strong seasonality in northern Canada? The time-series sampling at hydrometric stations provides insight into the temporal dynamics of the isotopic characteristics.

Isotopic compositions of discharge collected at three key hydrometric stations (Fig. 1) are presented in Fig. 3, including Mackenzie River at Strong Point (above the confluence with Liard River and near Fort Simpson), Mackenzie River at Tsiigehtchic and Liard River near the mouth (above the confluence of Mackenzie River). Note that Strong Point is regarded as representative of outflow from Great Slave Lake and its contributing area. Water sampled at the mouth of the Liard River represents inputs from the Liard Basin into the main channel, while the main flow at Tsiigehtchic integrates signals from all tributaries including the Liard River basin. Comparison among three sampling nodes is expected to reveal

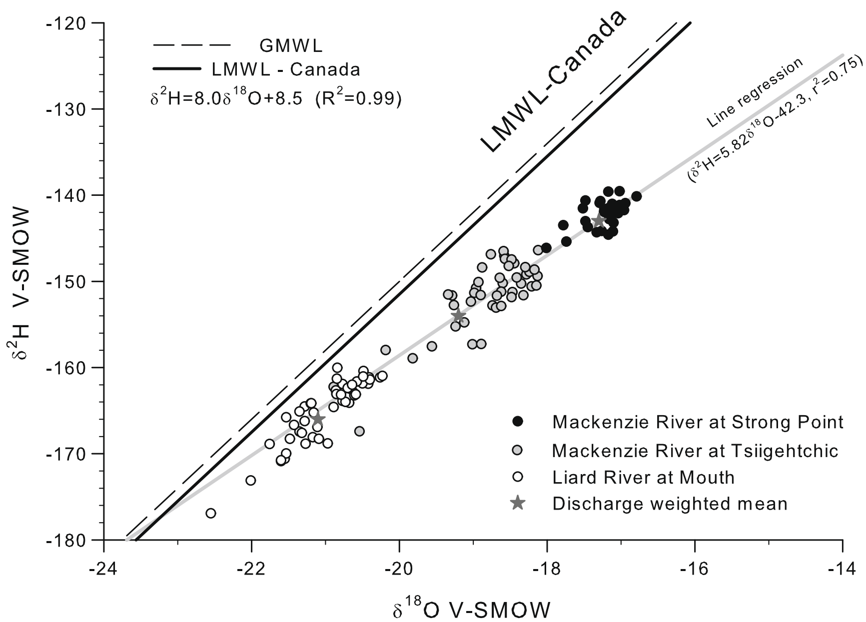

Fig. 3. δ^{18}O and δ^{2}H results of time-series sampling between 2004 and 2006 at three hydrometric stations e.g. Mackenzie River at Strong Point (solid circles), Mackenzie River at Tsiigehtchic (grey circles) and Liard River at Mouth (open circles). Stars (Å) designate flow weighted values for three stations respectively. The distribution pattern of isotopic signature in the three stations illustrates the mixing relationship between evaporated river discharges from Liard River and Great Slave Lake.

the temporal influence of the Liard River, the biggest tributary in the system, on the Mackenzie River.

Similar to the synoptic survey, the stationary survey was also found to deviate from meteoric water lines in δ^{18}O–δ^{2}H space, demonstrating the effect of evaporation (Fig. 3). Moreover, water samples from each individual station appear to form their own cluster, which is isotopically distinct from others. For instance, isotopic values of main flow at Strong Point ranged from −16.79‰ to −18.01‰ in δ^{18}O (−139.5‰ to −146.1‰ in δ^{2}H); values of tributary flow at Liard River ranged from −20.23‰ to −22.55‰ in δ^{18}O (−160.0‰ to −176.9‰ in δ^{2}H); while main flow at Tsiigehtchic presented intermediate isotopic values, ranging from −18.12‰ to −20.89‰ in δ^{18}O (−146.4‰ to −167.4‰ in δ^{2}H). A linear regression through this data set yields a mixing line ($\delta^{2}H = 5.8 \times \delta^{18}O - 42.3$, $R^2 = 0.75$) which is very similar to the evaporative-mixing line from the synoptic survey, indicating that the spatial pattern observed in the synoptic survey holds through time to a large extent. Although the Liard River is not the only input into the middle reach of the Mackenzie River, it is isotopically representative of mountainous tributaries. The isotopic variability of the Liard River in Fig. 3 is comparable to that of mountainous tributaries (between −21.94‰ and −18.18‰ for δ^{18}O) in Fig. 2b. In addition, the Liard River is the biggest tributary, contributing ~27% of the total Mackenzie River discharge into the Arctic Ocean (Woo and Thorne, 2003). Stationary isotopic data from the time-series sampling campaign, as shown in Fig. 3, again strongly suggests that the mixing between isotopically enriched water from Great Slave Lake (including its contributing watershed) and isotopically depleted water from Mackenzie Mountains (such as discharge from Liard River) produces the fundamental isotopic (probably geochemical as well) signature at Tsiigehtchic. However, it is not the only factor affecting water composition in main channel of the Mackenzie River. We confirm that Great Slave Lake and the Liard River are the two most important hydrologic nodes from which to monitor future changes of water quality and quantity in the Mackenzie River system.

Because the separation of the isotopically enriched source (i.e., Great Slave Lake) from the isotopically depleted source (represented by Liard River discharge) is prominent and well-defined, we made a further attempt to estimate the relative contribution of Great Slave Lake to the main flow based on data presented in Fig. 3. The average δ^{18}O signature from Great Slave Lake is −17.23‰ with standard deviation of 0.25‰ ($n = 35$). The average δ^{18}O signature from Liard River is −21.00‰ with standard deviation of 0.48‰ ($n = 49$). Considering these two as end-members, a simple two-member mixing model yields a contribution of 55.7% from Great Slave Lake to produce the isotopic signature at the Tsiigehtchic (average δ^{18}O values is equal to −18.90‰ with standard deviation of 0.71‰). Within the uncertainty of one standard deviation, the contribution of Great Slave Lake can vary from 45.8% to 64.5%. Similarly, the δ^{2}H-based estimation is comparable and suggests that the contribution from Great Slave Lake is ~56.3% with a range of 44.2–66.4%. Our δ^{18}O- and δ^{2}H- derived estimates are consistent in magnitude with previous data (Woo and Thorne, 2003). This isotope-based partitioning is simplified and did not consider other potential contributors. However, the quantitative potential of the isotopic investigation in multiple sources partitioning can not be understated, especially when other potential sources such as mountainous tributaries, groundwater and wetland waters can be constrained in δ^{18}O–δ^{2}H space. We believe that future efforts should consider characterization of other end-members to further constrain hydrometric partitioning.

As mentioned above, river discharge at three stations was also monitored (Environment Canada, 2005). Therefore, it is intriguing to evaluate the relationship between discharge and isotopic composition of river water. Time-series of discharge and isotopic signals during the sampling period are presented in Fig. 4. The water isotope compositions (δ^{18}O and δ^{2}H) at the Liard River mouth and Tsiigehtchic are found to be negatively correlated with instantaneous discharge rate. More specifically, an increase in river discharge during spring freshet is generally accompanied by a decrease of δ^{18}O and δ^{2}H values. A similar pattern of changes in isotopic composition and streamflow has been reported in small streams in northern Canada (St. Amour et al., 2005). The depletion in isotopic composition of water is attributed to the contribution of snowmelt, which is isotopically depleted (St. Amour et al., 2005; Stadnyk et al., 2005; Woo and Thorne, 2003). The general correlation between isotopic values and discharge for the Liard River and

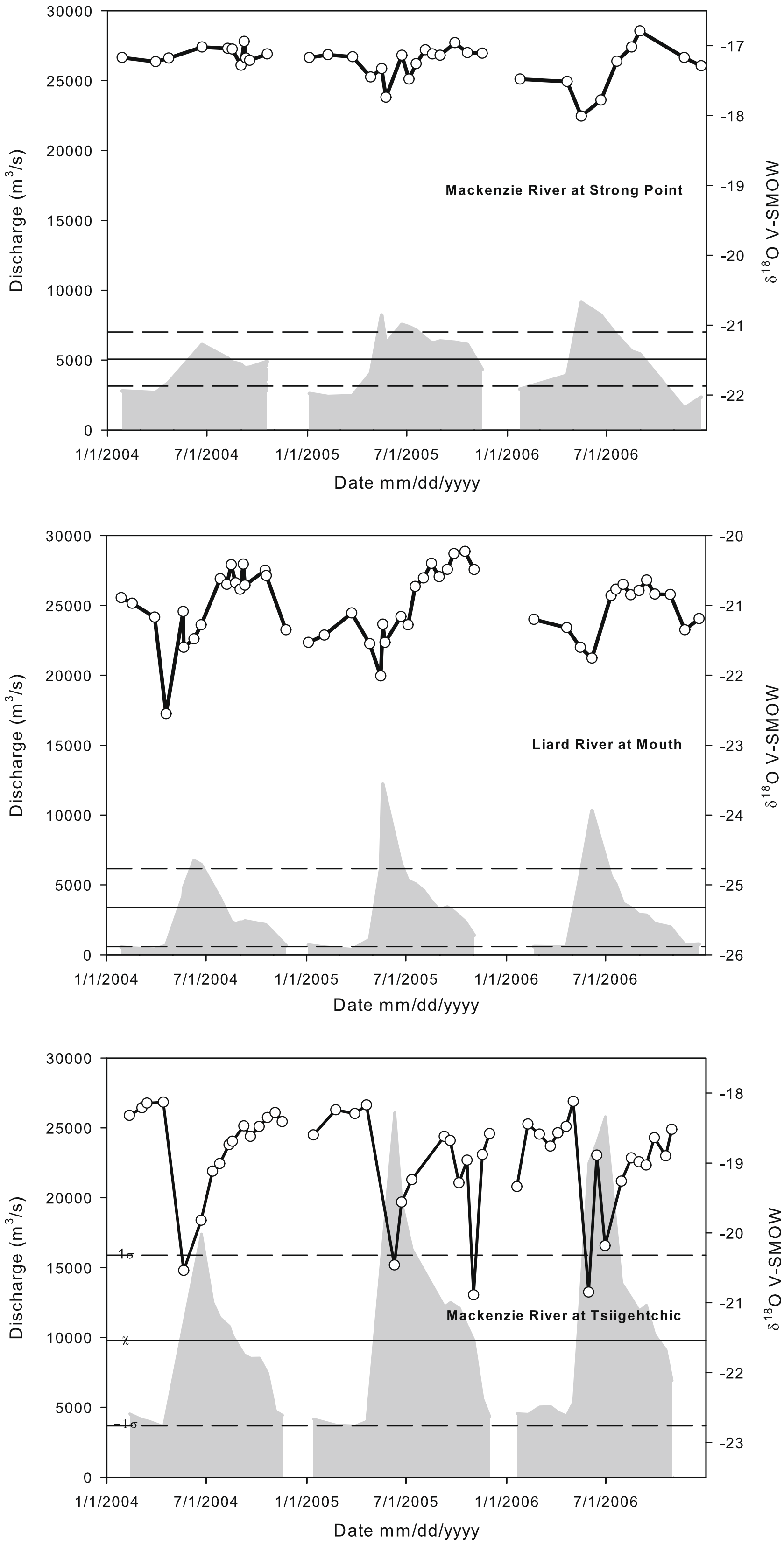

Fig. 4. Time series records of discharge (m^3/s) and δ^{18}O values (‰) at each hydrometric station during sampling campaign between 2004 and 2006. The solid line indicates the mean discharge values (χ) over the study period, and dash lines indicate the value for standard deviation (±1σ). The temporal variation of isotopic compositions at Liard River mouth and Tsiigehtchic are in phase with the rise and fall of hydrograph through the season, while the isotopic, as well as hydrological, variation at Great Slave Lake station is dwindled, probably because of the buffering capacity of the Great Slave Lake.

Tsiigehtchic emphasizes the hydrological and isotopic influence of snowmelt runoff to both rivers. By contrast, the discharge-isotope relationship at Strong Point is not as pronounced as those observed at the other two sites. Isotopic variation at Strong Point was small

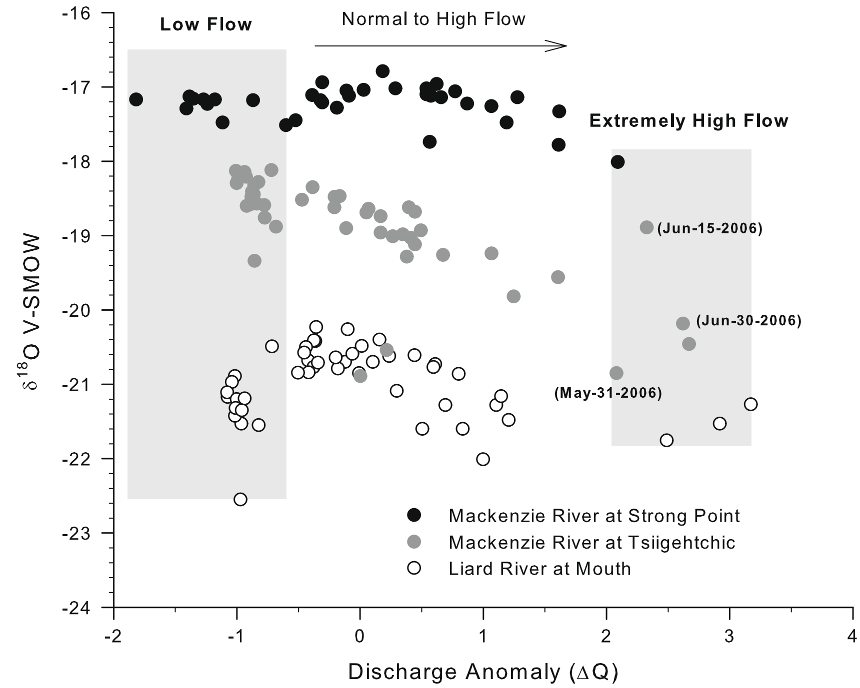

Fig. 5. A crossplot δ^{18}O vs. discharge anomaly (ΔQ).

(<0.8‰ in δ^{18}O) in 2004 and 2005, as were the variations of discharge which reflect the regulatory role of Great Slave Lake. Interestingly, in 2006 there was a relatively large variation in discharge and isotope composition (~1.22‰ in δ^{18}O) at Strong Point. The pattern of variation in 2006 was similar to Liard River and Mackenzie River at Tsiigehtchic, suggesting that water with depleted isotopic signatures may flush into the upper reach of the Mackenzie River.

Discharge measurements were also normalized to their mean and standard deviation and presented as discharge anomaly in Fig. 5. Discharge anomaly (ΔQ)[1] measures the difference between instantaneous discharge and mean values recorded over the 2004 to 2006 period. Regardless of varying specific discharges at each hydrometric station, ΔQ is a good relative indicator of river flow intensity among multiple sites, because the difference is normalized to its standard deviation. In other words, the further ΔQ is away from 0, the more extreme is the flow condition. Also note that similar ΔQ values for two stations indicate similar flow intensities, although specific discharge can be significantly different. In this paper, for the convenience of discussion, river flow with a ΔQ of −0.5 to +0.5 is considered as normal intensity. River flows ranging from −0.5 to −2.0 are regarded as low flow conditions, and flows ranging from +0.5 to +2.0 are considered to be high flows. ΔQ values >+2.0 (or <2.0) imply extremely high flows (or low flows). While somewhat arbitrarily defined, these categories are established to illustrate an interesting point. The isotopic patterns in the low flow, normal-to-high flow and extremely high flow zones (Fig. 5) suggest systematic differences in the source water relationships at three stations.

The most prominent pattern observed at normal-to-high flows is a negative correlation between δ^{18}O and discharge anomaly, particularly for the Liard at mouth and Mackenzie at Tsiigehtchic. This is the evidence of isotopically depleted snowmelt, which drives spring freshet. The coherence at the two sites strongly suggests that the isotopic impact of spring freshet in the Liard River basin is inherited into the main flow of Mackenzie River. On the other hand, the pattern is muted at Strong Point due to the dominant regulatory effect of Great Slave Lake which effectively dampens seasonal variability in flow and isotopic composition along the upper reach of the Mackenzie River. Unlike other stations, the δ^{18}O–ΔQ trend at Strong Point appears to reverse in the range of $-0.5 < \Delta Q < 0$, possibly due to higher proportions of local tributary flow compared to Great Slave Lake outflow when flow intensity is below normal.

More interestingly, the isotopic compositions during extremely high flow conditions did not follow the trajectory projected by the normal-to-high flow scenarios. Instead, the isotopic compositions in both rivers during an extremely high flow event revealed slightly more enriched δ^{18}O values than would be expected from a snowmelt driven mechanism. Liard River is particularly striking in this pattern, where extremely high flows in two consecutive years (2005 and 2006) exhibit more enriched isotopic values than that would be projected from the normal-to-high flow scenario. But Mackenzie River at Tsiigehtchic is somewhat obscured with zigzag variations of isotopic compositions within one month (between May-31-2006 and June-30-2006 as indicated in Fig. 5). There maybe more complicated isotope-discharge response in Mackenzie River than in the Liard River. Clearly, more data during extremely high flow conditions are needed to achieve a comprehensive interpretation. Nonetheless, from an isotopic perspective, this observation suggests that, in addition to snowmelt, these infrequent high-intensity runoff events are partially sustained by water bearing an enriched isotopic signature, especially in the Liard River. In consideration of landscape characteristics, we hypothesize that the additional source of water is most likely from lakes and wetlands, which are a dominant feature of the landscape in lowland areas bordering the Liard and upper Mackenzie Valley, and are known to acquire significantly enriched isotopic signatures (St. Amour et al., 2005; Gibson et al., 1993).

At low flow, the Liard River ranges from −20.49‰ to −22.55‰ in δ^{18}O, the Mackenzie River at Tsiigehtchic ranges from −18.12‰ to −19.34‰ in δ^{18}O, and Mackenzie River at Strong Point ranges from −17.11‰ to −17.52‰. Apart from Strong Point, which is apparently buffered by the regulatory effect of Great Slave Lake, variability in isotope composition at times of low flow reflects a

[1] $\Delta Q = \frac{Q-\chi}{\sigma}$, where Q is the instantaneous discharge; χ and σ are the mean value of discharge and the standard deviation, respectively, for the study period as indicated in Fig. 4.

wide range of potential water sources. Low flow conditions (see lower dashed line in Fig. 4) occurred mostly in winter and fall when water sources are expected to be groundwater influenced (Gibson and Prowse, 2002). But, the depleted isotope signatures also suggest inputs from early melting of snow, especially from southerly tributaries. Multiple potential sources to sustain the low flow probably result in the wide range of isotopic variations in discharge at Tsiigehtchic and Liard River mouth.

In summary, time-series measurements of isotopic composition in discharge at three hydrometric stations provide insights into the temporal dynamics of isotopic systematics in the Mackenzie River system. Great Slave Lake is an important hydrological regulator of isotopic composition in the upper reach of the Mackenzie River, while the Liard River has a significant impact on both flow and isotopic composition in the middle and lower reaches of the Mackenzie River. The isotopic contrast between Liard River and Great Slave Lake discharges is significant and maintained through time. A simple two end-member mixing model based on isotopic signatures suggests that ~50% of the flow at Tsiigehtchic is contributed by Great Slave Lake. This estimation can still be improved with better constraints on other potential water sources The contribution of snowmelt during the freshet period from the Liard River basin and other mountainous areas has a clear isotopic imprint on the discharge at the mouth of the Liard River and at Tsiigehtchic. Snowmelt is the dominant process enhancing discharge at normal-to-high flows. However, extremely high flows are found at times to have enriched isotopic signatures that may indicate a significant component of water displaced from wetlands and small lakes. With the exception of the upper reach which is buffered to a great degree by Great Slave Lake, isotopic signals during low flows demonstrate noticeable variability in the context of a small range of discharge variations. This is attributed to subtle changes in the amount and proportion of groundwater, surface water and snowmelt in fall and over-winter discharge.

Concluding remarks

This paper systematically reports both oxygen and hydrogen isotope compositions of the main channel, and its tributaries, in the Mackenzie River system for the first time. The isotopic character of main flow in the Mackenzie River exhibits large geographic variations, while isotopic compositions of tributary flow are strongly associated with their catchment characteristics. A zone of poor mixing is generally identified along the high gradient reach of the river below the confluence of Liard River and the main channel. In addition to evaporation, mixing of isotopically enriched Great Slave Lake discharge with isotopically depleted mountainous runoff (such as Liard River discharge) is another important hydrological process revealed by the synoptic survey of $\delta^{18}O$ and $\delta^{2}H$ values in the main and tributary flows. As a result, we propose an evaporative-mixing line ($\delta^2H = 6.0 \times \delta^{18}O - 40.8$) for the Mackenzie River system, which can be an important reference line for future research. The concept of the evaporative-mixing line is further supported by documentation of water isotope time-series (in three consecutive years) at three key hydrometric stations. Great Slave Lake and Liard River are demonstrated to be two important hydrologic components for monitoring future change of water quantity and quality in the Mackenzie River system. Further investigation of both isotopic signals and discharge in time-series samplings suggests that in normal- to high- flow conditions, the contribution of snowmelt to Liard River discharge, and subsequently to the main channel, is remarkably important. However, snowmelt may not be the only contributor to extremely high flows. Heavy-isotope enriched discharge during extremely high flows suggests that wetland-stored water may contribute significant quantities of water, especially in the Liard River Basin.

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