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Hydrology using isotope tracers has advanced in Canada.

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Abstract:

Precipitation networks, hydrograph separation and groundwater investigations, river basin hydrology, lake and catchment water balance, and isotope palaeohydrology from lake sediment records comprise an overview of recent Canadian contributions to isotope hydrology research. Since they are an excellent complement to physical and chemical methods, tracer-based techniques, which predominantly use naturally occurring environmental isotopes, have been incorporated into a variety of hydrological and biogeochemical research programmes The Mackenzie River watershed has been a prominent geographic focus of Canadian isotope hydrology research, contributing to projects like the Global Energy and Water Cycle Experiment. International projects like the International Atomic Energy Agency's (IAEA) Coordinated Research Study on Large River Basins and the World Network for Isotopes in Precipitation have both benefited significantly from Canadian research. In order to better characterise the regional and temporal variations in isotope signatures and their underlying causes, consistent long-term monitoring of precipitation and river discharge is one key trend in Canadian research. One key finding from earlier research conducted in Canada is that using 18O and 2H together allows for the separation of precipitation variability and evaporation effects, offering important advantages over using the individual tracers alone. One new area of study that results from the capacity to incorporate isotope monitoring into both water quality and water quantity surveys is the study of hydrological controls on water chemistry. Authorized by John Wiley & Sons, Ltd., 2005.

INTRODUCTION

Stable- and radio-isotope tracers have been widely applied in Earth systems studies, including hydrological and climatological research, for their ability to provide a sharper focus on some of the underlying processes that control chemical and physical behaviour of elements and compounds in the natural environment. The ability to study widespread effects has generally made naturally occurring tracers more useful and more environmentally accepted than artificially introduced tracers, as well as more transferable to a broader range of biogeochemical problems. Isotopes of particular interest for hydrological studies include the stable isotopes of water (^{18}O, ^{2}H), which are incorporated within the water molecule ($H_2{}^{18}O$, $^{1}H^{2}H^{16}O$), and exhibit systematic spatial and temporal variations as a result of isotope fractionations that accompany water-cycle phase changes and diffusion. Isotope fractionation produces a natural labelling effect within the global water cycle that has been applied to study a wide range of hydrological and climatic processes at the local, regional, and global scales. Anthropogenic nuclides, such as tritium (^{3}H), another isotope incorporated in the water molecule ($^{1}H^{3}H^{16}O$),

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have also proven useful for studying the dynamics of hydrological systems owing to the capability for tracing precipitation and recharge in the post-1960s era (e.g. Rank *et al.*, 1998). Other radioactive isotopes, such as ^{14}C, are used for dating groundwater and other relatively old water sources. Solute isotope systems (e.g. carbon, nitrogen, strontium, boron, sulphur, chloride) also provide capability for labelling solute and pollution sources and, in general, for the study of hydrological and biogeochemical processes that control water quality (e.g. Hooper and Kelly, 2001). An extensive review of the application of isotope tracers to hydrological studies was recently published by Mook (2000). Herein, we focus on reviewing applications of the stable water isotopes (^{1}H, ^{2}H, ^{16}O, ^{18}O), which are the most universal tracers in hydrological research, and among the most commonly applied in recent studies in Canada.

The use of stable oxygen and hydrogen isotopes as tracers in hydrologic studies has expanded over the past five decades following the initial description of systematic variations in world precipitation (Craig, 1961; Dansgaard, 1964), development of theory describing isotopic fractionation during evaporation (Craig and Gordon, 1965), and testing and validation under a range of field conditions (e.g. Fritz and Fontes, 1980; Gat and Gonfiantini, 1981; Gat, 1996; Clark and Fritz, 1997; Kendall and McDonnell, 1998; see also Gibson and Prowse (2000)).

Isotopic compositions are expressed conventionally as υ values, representing deviation in per mil (‰) from the isotopic composition of a specified standard, such that υ^2H or υ^{18}O 1000 $[(R_{\text{sample}}/R_{\text{standard}})$ 1], where R refers to the ^{2}H/^{1}H or ^{18}O/^{16}O ratios in both sample and standard. The most widely used standard in hydrological applications is the Vienna standard mean ocean water (V-SMOW), which approximates the bulk isotopic composition of the present-day global ocean reservoir, and hence has υ^2H and υ^{18}O values both defined to be exactly 0‰. This is a logical datum for hydroclimate studies, since evaporation from the oceans is the fundamental source of global atmospheric moisture, which provides the precipitation input for continental water cycling, and the isotopic composition of the oceans is more-or-less invariant on human time scales. Use of the υ scale referenced to V-SMOW also implies that most precipitation and continental waterswill have negative values, indicating a lower heavy isotope content compared with the world oceans.

Isotope variations in precipitation are generally characterized by strong linear correlations between ^{18}O and ^{2}H that reflect mass-dependent partitioning of the water isotopes in the hydrological cycle. This coupling is exemplified by the global meteoric water line (MWL; Craig, 1961), defined as υ^2H 8 υ^{18}O 10, which closely approximates the observed relation between υ^{18}O and υ^2H in mean annual amount-weighted precipitation world-wide (Figure 1). Variations in the isotopic composition of precipitation reflect climatic processes, including (i) meteorological conditions in the oceanic source area, (ii) rainout mechanisms (i.e. fraction of precipitable water and continental recycling), (iii) air mass mixing and interaction, and (iv) second- order kinetic effects, such as those occurring during snow formation and during evaporation from raindrops (Araguás-Araguás *et al.*, 2000). The existence of the MWL is consistent with a conceptual model where global atmospheric moisture arises primarily from a well-mixed source (i.e. the subtropical ocean surface) and undergoes progressive rain-out of mass and heavy isotopes during subsequent poleward atmospheric transport (Edwards *et al.*, 2004). These effects produce a general shift towards lower heavy isotope content from coastal to inland areas and with increasing latitude. Strong coupling of air-mass vapour content and isotope depletion, often described as a multistep Rayleigh-type open-system distillation process, is well illustrated by comparison of the global fields of precipitable moisture and precipitation υ values (e.g. see Birks *et al.* (2002: Figure 2)), and is also reflected indirectly in the spatial relations that are observed between precipitation υ values and air temperatures at mid to high latitudes (Rozanski *et al.*, 1993). The stability of the MWL, which is essentially a long-term isotope climate normal, is confirmed by the fact that it has changed little despite extensive augmentation of the dataset over the past 40 years, including significant contributions from Canadian networks that expanded spatially in the 1980s (Figure 1). From a monitoring perspective, the most notable Canadian contributions include operation of one of the longest continuous time-series records of ^{18}O, ^{2}H and ^{3}H in precipitation (Ottawa), and expansion of networks to the Arctic in the 1990s, which has extended the range of isotope climate observations to the northern high latitudes.

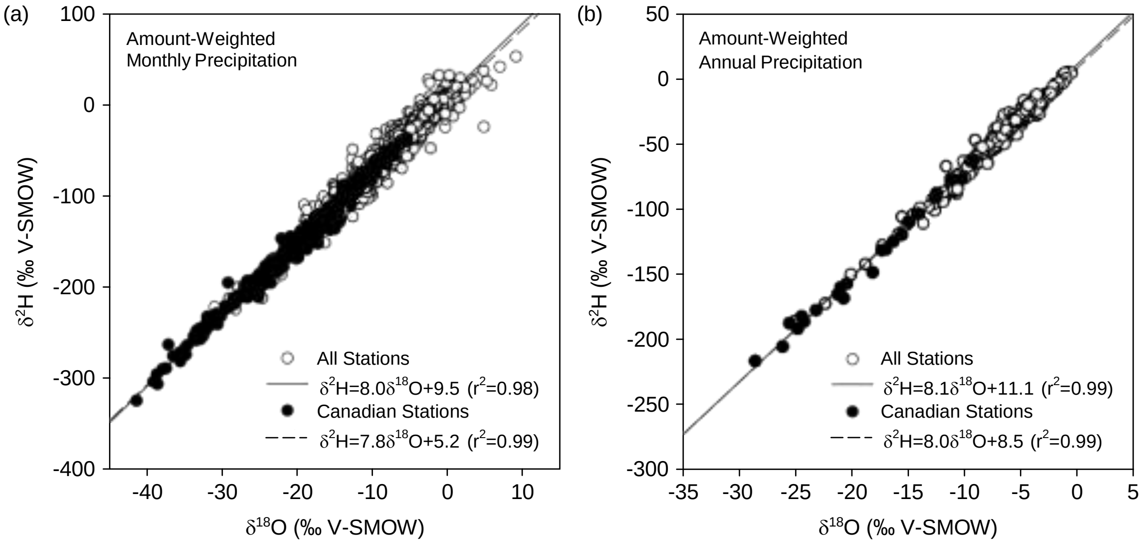

Figure 1. Cross-plots of ^{18}O and ^{2}H composition of precipitation and related regressions based on data archived within the IAEA/WMO Global Network for Isotopes in Precipitation (GNIP) during 1961–97. The Canadian contribution to this dataset is highlighted: (a) monthly amount-weighted precipitation, (b) annual amount-weighted precipitation. Note that the regressions are a close approximation of the global MWL of Craig (1961), and illustrate the systematic co-variance of ^{18}O and ^{2}H in precipitation input to hydrological systems

Amount-weighted υ^{2}H and υ^{18}O values of monthly precipitation received over the year at individual sites also commonly plot in strongly linear clusters in υ^{2}H–υ^{18}O space close to the MWL, and best-fit local MWLs drawn through these clusters can provide isotopic input functions for local hydrological studies. Substantial seasonal variability is typical, especially in cold regions, with winter precipitation generally strongly depleted and more variable in heavy-isotope content compared with that received during the summer season (Figure 2). Seasonal changes typically produce shifts along the MWL, which accounts for the extended range of isotope compositions observed in monthly versus annual υ values (Figure 1).

Groundwaters generally reflect the isotopic signature of precipitation in the zone of recharge, although individual reservoirs may acquire signatures reflecting their mean residence time and seasonal timing of inputs, as modified by mixing between other sources, such as river water or artificial recharge. Although transpiration does not generally fractionate the heavy-isotope signature of groundwater, evaporation from bare soil may produce isotopic enrichment of groundwater, leading to offset below the MWL (see Gat (1996)). Evaporation from surface detention storage prior to recharge may likewise produce minor evaporative enrichment. Mixing of recharge with the *in situ* groundwater pool tends to mute seasonal variations in the latter, particularly in deep, well-connected systems, and often enables distinct labelling of individual rainfall events. This labelling effect has been extensively applied to partition streamflow hydrographs into event and pre-event contributions using isotope hydrograph separation. For large river basins, the lag and the degree of damping of seasonal isotope signals in river discharge can be useful indicators of the mean residence time and the effective groundwater reservoir volumes respectively (Gibson *et al*., 2002a). Isotopes have also been important tools for the study of glacial and pro-glacial systems (see Stichler and Schotterer (2000)), and a wider range of water-cycle processes (Gibson and Prowse, 2000; see also Gat and Gonfiantini (1981)).

See Figure 3, which deviate from the MWL (slope ¾8) along slopes that

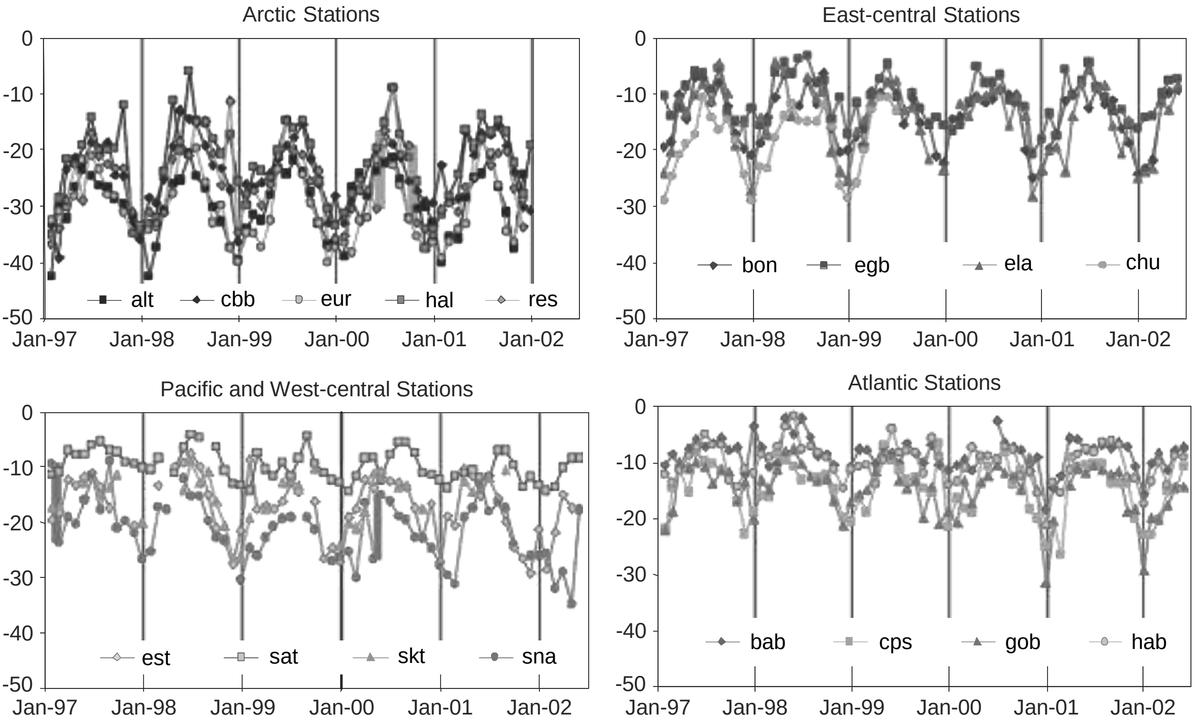

Figure 2. Time series of monthly υ^{18}O in precipitation from stations in the active Canadian Network for Isotopes in Precipitation (CNIP) network (above) illustrating clear regional differences in the annual cycle, as well as in their response to interannual variations in climate. Note, for example, very depleted winter υ^{18}O for the Atlantic stations during the winter of 2000–01, which accompanied a period of greater-than-normal southerly penetration of cold Arctic air. υ^{2}H and *d*-excess trends are also available from CNIP (not shown)

usually range between 4 and 7, depending on local atmospheric conditions during the evaporation season, primarily relative humidity, temperature, and the isotopic composition of ambient moisture. Studies conducted across northern areas of Canada have also shown a systematic steepening of LELs associated with climate shifts and enhanced seasonality towards higher latitudes, although more northerly areas also tend to have lower maximum offsets (Figure 3). Intersection of the LEL with the MWL often provides a useful empirical approximation of the weighted-mean isotopic composition of input waters to a catchment, and displacement of a given lake water along the LEL provides an index of water balance, which can be quantified in terms of evaporation : inflow ratio (*E*/*I*) via isotope mass balance considerations, as discussed in the section Lake and Catchment Water Balance.

PRECIPITATION NETWORKS

Collection and analysis of precipitation isotope data in Canada, a long-standing contribution to the IAEA/WMO GNIP database, has shown that the distribution of amount-weighted isotope fields across Canada reflect differences in the dominant meteorological regimes (Pacific, Arctic and/or Gulf Stream) associated with each region (Fritz *et al.*, 1987, Moorman *et al.*, 1996). Although these efforts were fundamental in providing local hydrological input functions and calibration for palaeoclimate archives, there was growing awareness of the

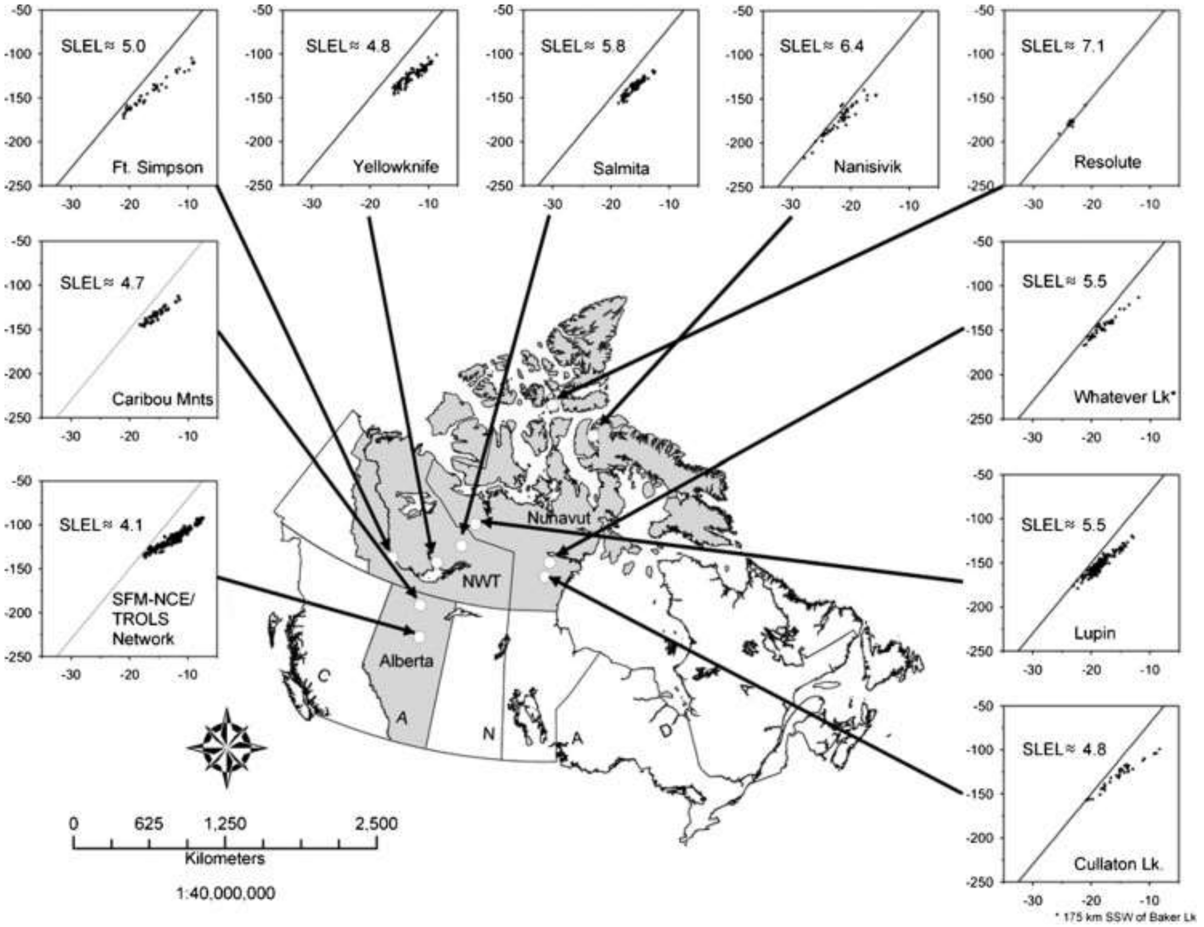

Figure 3. Map of research sites and associated cross-plots of ^{18}O versus ^{2}H for lakes and shallow wetlands sampled in areas of Alberta, Northwest Territories and Nunavut, Canada. Note that LELs fall below the MWL (solid lines). As shown, the slope of LELs (S_{LEL}) tends to steepen with latitude, and the total displacement from the MWL tends to diminish. Data are compiled from Gibson (1996; Gibson *et al*., 1998, 2002b)

The network consists of 18 stations (Figure 4) distributed across Canada (spanning almost 40° of latitude and 70° of longitude) collecting weighted monthly precipitation samples for υ^{18}O and υ^{2}H analyses. This marks the first time that both the southern and northern regions of the country have been sampled simultaneously. Sampling of the southern stations was initiated in 1997 to supplement an existing informal arctic network (now formally incorporated in CNIP) resulting in a 5 year dataset for the entire country (Figure 3), encompassing a complete El Niño – southern oscillation (ENSO) cycle. The arctic subset of the data includes over a decade of sampling and, consequently, is suitable for evaluating the isotopic expression of the Arctic oscillation (AO).

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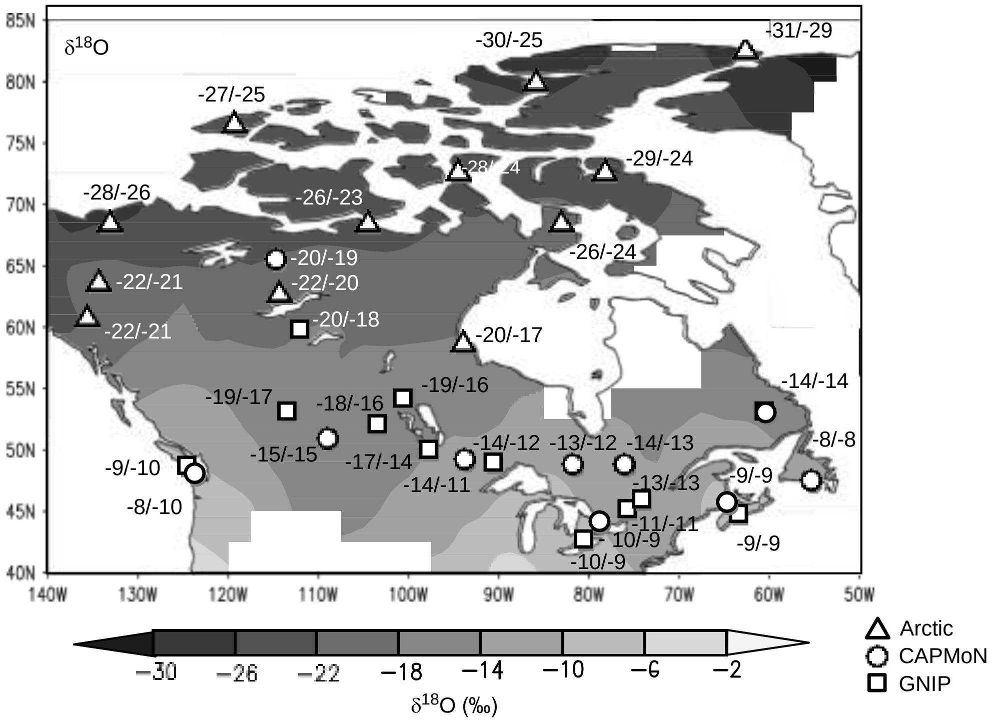


Figure 4. Map of long-term amount-weighted υ^{18}O in precipitation across Canada based on the GNIP and CNIP. CNIP incorporates both the Arctic and Canadian Air and Precipitation Monitoring (CAPMon) networks

The sensitivity of isotope– climate signals to modes of interannual variability such as ENSO and AO is of interest because the latter are a primary cause of interannual climate variability. The effects of ENSO are felt not only near the source in the equatorial Pacific Ocean, but also at higher latitudes; however, the strength, location and timing of climate variations in extratropical areas are less predictable, since they are the result of oceanic and atmospheric teleconnections. Time series of monthly υ^{18}O (Figure 2), υ^{2}H and *d*-excess (not shown) collected between 1997 and 2001 as part of the CNIP network show clear regional differences in both the magnitude of the annual cycle and in the response to interannual variations in climate. Across Canada, the annual cycle of υ^{18}O varies with latitude and continentality, with the largest annual ranges found at arctic and continental interior stations, and more subdued annual cycles at coastal stations (Figure 2). The strongest climate anomalies are typically found during the winter following the 1997 El Niño event, consistent with a strengthening of the Pacific North American pattern (Shabbar and Khandekar, 1996; Shabbar *et al.*, 1997; The *d*-excess time series for the east-coast stations also includes an apparent longer term trend of increasing *d*-excess values over the 1997– 2001 period. A review of the associated isotope anomalies in precipitation in the interior of Canada is presented by Birks (2003).

Regional networks are also under development in Canada. Building on the initiatives of the CNIP, the recently established Manitoba Network for Isotopes in Precipitation (MNIP) enlists a network of Manitoba schools to collect precipitation. During phase 1 of MNIP, which began in January 2003, 20 schools have been issued precipitation collection devices and a number of other locations are being considered to expand the network in the near future (phase 2). Manitoba, situated in the heart of North America, is an ideal place to study the influence of air masses on the isotopic composition of precipitation. The province is affected by a wide variety of air masses and, importantly, is subject to considerable short- and long-term atmospheric circulation variability. For example, a particular month can be dominated by deep upper level troughing in one year (often associated with colder than normal temperatures), but the same month in the following year can be dominated by pronounced upper level ridging (usually associated with warmer than normal temperatures). Thus, analogues for a wide variety of circulation anomaly scenarios of interest to climatologists, and others, are observed in Manitoba. The dense distribution of MNIP precipitation collection sites supports the spatial resolution (2▯8° longitude) necessary to test atmospheric global circulation models and higher resolution regional climate models that incorporate precipitation isotope data. With a dense network of stations from across the province of Manitoba, MNIP will be in a position to investigate the influence of atmospheric anomalies (e.g. height and flow anomalies) on the isotopic composition of precipitation. A successful MNIP programme is expected to foster development of similar precipitation isotope networks in other parts of Canada.

HYDROGRAPH SEPARATION AND GROUNDWATER STUDIES

Two- and three-component isotope hydrograph separations are commonly applied in small-scale catchment studies, particularly during rainfall or storm events, to identify the origin, timing, and pathways of surface and subsurface runoff, with the primary objective of evaluating streamflow generation mechanisms. Often, isotope tracers are applied in conjunction with geochemical tracers (major ions, trace elements, dissolved organic carbon, etc.) to provide capability for labelling interactions with specific substrate materials such as bedrock or organic layers. One of the earliest applications of stable isotopes to define the pre-event and event water components of watershed runoff was carried out by Fritz *et al.* (1976), with subsequent applications in various physiographic regions of Canada (e.g. Sklash *et al.*, 1976; Krouse *et al.*, 1978; Sklash, 1978, 1979; Sklash and Farvolden, 1980, 1982; Bottomley *et al.*, 1985, 1986; Obradovic and Sklash, 1986; Blowes and Gillham, 1988; Moore, 1989; Buttle and Sami, 1990, 1992; Wels *et al.*, 1990, 1991a,b; Gibson *et al.*, 1993a; Waddington *et al.*, 1993; Allan and Roulet, 1994; Hinton *et al.*, 1994; Buttle *et al.*, 1995; Maclean *et al.*, 1995; Peters *et al.*, 1995). Comprehensive overviews of methodology and field applications have been presented elsewhere (e.g. Buttle, 1994; Kendall and McDonnell, 1998). The large majority of past studies have established that stormflow in small, forested or wetland headwater catchments in Canada is dominated (>60%) by water stored in the basin prior to a runoff event. A number of recent studies in Canada, conducted in a wide range of hydroclimatic settings, have reaffirmed these findings (e.g. Laudon and Slaymaker, 1997; Buttle and Peters, 1997; Cey *et al.*, 1998; Brassard *et al.*, 2000; Gibson *et al.*, 2000; Metcalfe and Buttle, 2001; Fitzgerald *et al.*, 2003).

In general, isotope hydrograph separation, applied in conjunction with physical monitoring, has been helpful for establishing or redefining conceptual models of water delivery on the hillslope or small catchment scale. Buttle and Peters (1997) found that simultaneous monitoring of conservative and non-conservative tracers in streamflow offers additional insight on the age and flow paths of water reaching the basin outlet. The study of Metcalfe and Buttle (2001) also highlighted the need to carry out multi-event or multiyear hydrometric measurements and water sampling in a poorly drained boreal landscape dominated by wetlands, because they found that the dominance of source waters (old versus new water) and flow pathways (surface water versus deep groundwaters) varied from year to year depending on the intensity of the snowmelt period, the amount of premelt storage of water, and the extent of soil thawing. For instance, a frost table close to the surface and large premelt storage in surface depression will lead to high flows primarily of meltwater routed over wetland.

A modelling study of a headwater wetland in Oak Ridges Moraine in southern Ontario by Brassard *et al*. (2000) revealed that groundwater– surface water mixing during rainstorm events could explain the majority of isotopic signature in the stream and could also be used to measure the extent of potential secondary runoff mechanisms, such as pipeflow. A study of the interaction between groundwater and surface water was also undertaken in a small agricultural watershed in southern Ontario (Cey *et al*., 1998). Hydrograph separations were conducted using υ^{18}O and electrical conductivity on two large rainfall events with different antecedent moisture conditions in the catchment. Both events showed that pre-event water (groundwater) dominated streamflow and flow in tile drains, with 64– 80% of the total discharge contributed by pre-event water. An innovative study by Spoelstra *et al*. (2001) also applied isotopes of nitrogen and oxygen to distinguish between two sources of nitrate in surface waters and groundwaters in two forested catchments within the Turkey Lake watersheds, Ontario. Waddington and Devito (2001) presented a novel approach to hydrograph separation using an inexpensive irrigation device for artificial application of environmental tracers in hillslope and wetland runoff studies.

In a steep bog– forest watershed in north coastal British Columbia, a three-component hydrograph separation analysis using υ^{18}O and υ^{2}H showed that shallow hillslope groundwater dominated bog and event water as runoff generation sources in a hyper-maritime bog– forest catchment (Gibson *et al*., 2000). Importantly, this study also showed that the deuterium excess parameter, defined as d Dυ^{2}H Đ 8υ^{18}O (see Froehlich *et al*. (2002)), which varies seasonally in west coast precipitation, has the potential to label water sources (e.g. bogs, shallow and deep groundwater) according to their residence times. Observations at a nearby coastal headwater swamp revealed that the groundwater regime is dominated by rapid infiltration and short, emergent flow paths. With relatively short turnover time, potential disturbances to the system by harvesting of upslope areas can be expected to occur rapidly (Fitzgerald *et al*., 2003). At higher elevation sites in the Coast Mountains of British Columbia, isotope hydrograph separation predicted consistent high prestorm water contribution from subalpline and alpine basin outlets (Laudon and Slaymaker, 1997). The authors suggested that pressure propagation from the macropore (fractured bedrock) system could generate the rapid efflux of stored water to the stream channel, and rainfall was believed to runoff as overland flow due to the steep slopes in combination with hydrophobic soils until it can enter the subsurface environment.

A study by McEachern (2004) also shows the application of isotope techniques for defining the range in response of northern boreal forest basins to storm events where topographic characteristics and variable proportions of peatlands, and thus antecedent moisture conditions, give rise to highly variable local runoff responses. Combined with geochemical tracers, isotope signatures were used to highlight the importance of rapid response through organic soil pathways, where low topographic slope and discontinuous permafrost create relatively shallow aquitards, when compared with more steeply sloped catchments, where infiltration was unrestricted and piston flow of older water dominated stream discharge. McEachern (2004) further shows that lowland basins in areas underlain by discontinuous permafrost may be more sensitive to disturbances, such as timber harvesting or forest fire, because water tables are more likely to intersect organic soils. Increased export of nitrogen, phosphorus and carbon in lowland versus upland basins was attributed to enhancement of water storage in these areas due to reduction in evapotranspiration following the disturbance (McEachern, 2004).

Recent advances have also been made in understanding the process of isotope fractionation during snowmelt. Although the majority of this work has been conducted outside Canada, the findings have significant implications for application of hydrograph separation during spring freshet in the Canadian environment. Detailed laboratory experiments and modelling have shown that a 1– 4‰ enrichment in υ^{18}O of meltwater can arise under a plausible range of conditions due to isotopic exchange between liquid and ice as meltwater percolates down through the snow column (Feng *et al*., 2002; Taylor *et al*., 2002). In field studies of deep, slow-melting snowpacks, such changes in the isotopic signature of meltwater have also been verified (e.g. Unnikrisha *et al*., 2002). The main implication of this work is that the bulk snow composition measured prior to melt may not be adequately characterized as a static end-member for hydrograph separation analysis, although the magnitude of this effect remains to be measured under a wider range of field conditions, including conditions commonly observed in non-alpine, northern regions of Canada (i.e. lighter snowpacks and rapid melt). Importantly, Laudon *et al*. (2002) present a simple method that greatly improves the separation of event and pre-event water during snowmelt by accounting for both spatial and temporal change in snowmelt isotopic signal and the temporary storage of meltwater in the catchment.

Groundwater studies have increasingly relied on isotope tracers for labelling water sources and interactions in the subsurface. Examples of these applications include the study of groundwater– surface water interaction in a coastal area of the Great Lakes (Huddart *et al*., 1999) and in fractured bedrock terrain (Oxtobee and Novakowski, 2002), mine and mineral deposit hydrogeology (Douglas *et al*., 2000; Harrison *et al*., 2000; Sie and Frape, 2002; Aravena *et al*., 2003), and groundwater as a climate archive (Remenda *et al*., 1994; Remenda and Birks, 1999; Birks *et al*., 2000). Numerous studies have also addressed contaminant tracing (Killey *et al*., 1998), although an exhaustive review of this topic is beyond the scope of this article.

RIVER BASIN HYDROLOGY

In addition to small-scale catchment studies, the stable isotopes of water have the capability for application in large river basin studies for partitioning relative contributions of flow derived from uniquely labelled geographical sources or distributed components, such as direct precipitation runoff, shallow and deep groundwater, and surface waters including lakes and wetlands. Isotopic responses are often complex in large rivers, reflecting the cumulative influence of hydrological processes from precipitation to discharge and including the influence of groundwater, melting glaciers, dams, lakes, karst terrain, evaporation, snowmelt events, and tributary mixing. Recent global initiatives, such as the IAEAs Coordinated Research Project 'Isotope tracing of hydrological processes in large river basins', have shown that river discharge signatures provide insight into the basin-integrated hydroclimate forcings on water cycling, such as precipitation variability (e.g. changes in condensation temperature, latitude/altitude of precipitation, air mass mixing and recycling, distance from ocean source, and seasonality) and evaporation from the river or contributing sources (Gibson *et al*., 2002a). The IAEA network, which includes river basins in arctic, temperate and tropical areas, the arid zone, and lowland and alpine drainages, is poised to monitor monthly isotope signals in runoff over the next 5 years from 22% of the continental land surface, accounting for approximately 33% of the global river discharge. The Canadian contribution to this programme includes water sampling at 22 stations in the Mackenzie basin (Figure 5) and three stations in the Ottawa– St Lawrence river system, and has stimulated interest in development of similar networks in the South Saskatchewan and Coppermine River basins. In addition to collectively improving global capability for isotope hydrology studies and closing the continental isotope mass balance, researchers involved in the project are seeking to improve understanding of linkages between water and nutrient cycling, pollution sources, salinity controls and other water quality issues, as well as hydrological model validation and climate and environmental change detection, particularly where long-term datasets are available.

Sustained Canadian research efforts to study hydrological processes in large river basins have focused mainly on the Mackenzie River basin within programmes such as the Mackenzie GEWEX study and more recently the IAEA project, although significant hydrological and biogeochemical tracing studies have also been undertaken on the lower Great Lakes drainage basin (Gat *et al*., 1994; Machavaran and Krishnamurthy, 1995; Yang *et al*., 1996; Hélie *et al*., 2002), the Ottawa River (Telmer and Veizer, 2000), the Frazer River (Cameron *et al*., 1995) and basins outside of Canada (Lee and Veizer, 2003). The Mackenzie River, draining an area of 1· 78ð10^{6} km^{2}, incorporates a diverse range of geographic source regions, including 8 of the 15 distinct ecoclimatic regions identified in Canada (Ecoregions Working Group, 1989). The basin is mountainous in the west and relatively flat-lying in the east, with strong north– south climatic gradients, and generally cold, dry climate conditions compared with other large river basins in the world. As a major contributor of freshwater discharge to the Arctic Ocean, the river is also distinct due to the occurrence of several large lakes (Lake Athabasca, Great Slave Lake, Great Bear Lake) that naturally act as flow, sedimentation, and biogeochemical

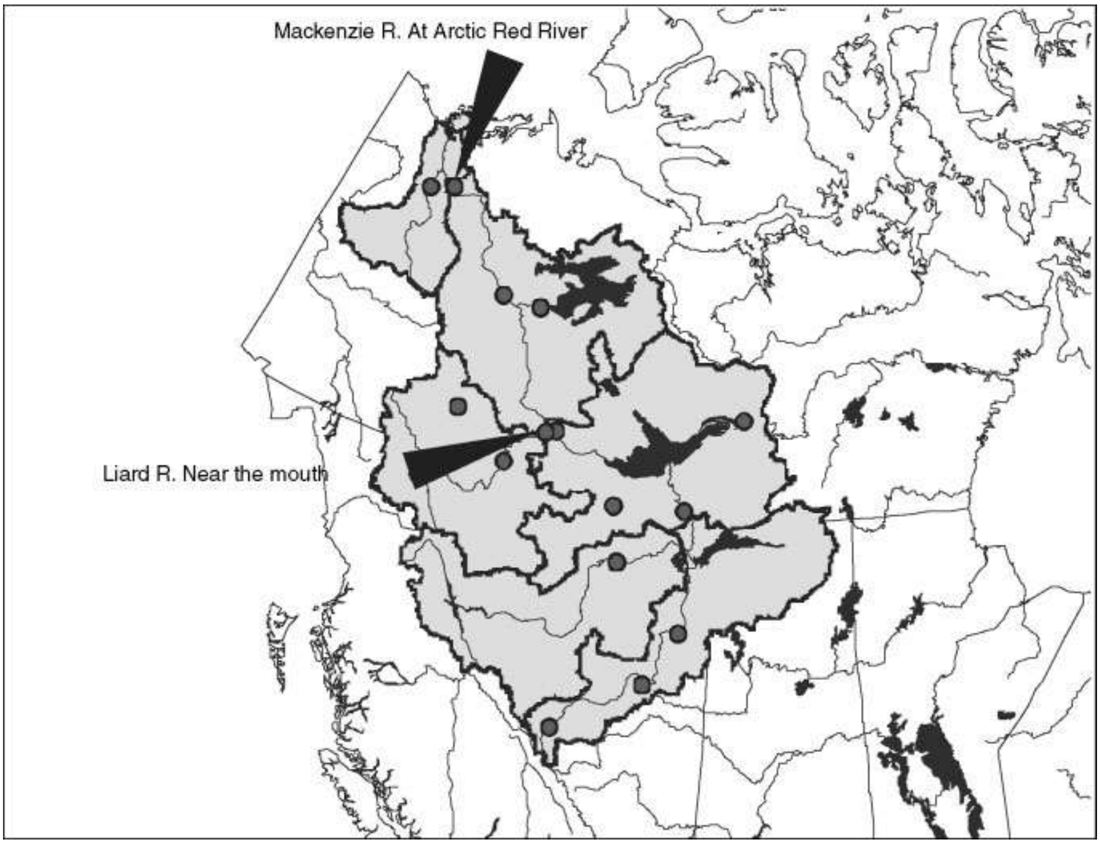


Figure 5. Map of northwestern Canada showing the water sampling network for isotopes initiated in 2002 within the Mackenzie basin (shaded). Labels indicate stations with longer time-series monitoring history. Note that the hydrometric station on the Mackenzie at Arctic Red River, which essentially incorporates the runoff of the whole basin, is situated slightly upstream of the mouth to avoid the complex Mackenzie delta region. Stations situated within Alberta are operated by Alberta Environment as part of the Long-term River Network. Stations situated in the Northwest Territories and Yukon are operated by the Water Survey of Canada. Water sampling for stable isotopes is coordinated by researchers at Environment Canada's National Water Research Institute. Seven additional water sampling stations in smaller tributaries are not shown

regulators along its main drainage network. Earliest work to define variations in υ^{18}O the Mackenzie Basin by Hitchon and Krouse (1972) showed systematic variations in discharge from tributaries and sub-basins. Notably, the most depleted isotope signatures (<Ð20‰ in υ^{18}O) were observed in tributaries of the Western Cordillera, especially the Mackenzie Mountains (minimum of —22ƭ9‰ in υ^{18}O), which are characterized by higher altitude precipitation, greater snowfall, and higher runoff/precipitation ratios than other parts of the basin. In shield-dominated areas to the east of Great Slave Lake and Lake Athabasca, and to a lesser extent in the central boreal– taiga plains, tributary runoff was found to be enriched in υ^{18}O, reflecting contributions from lake and wetland evaporation in low-relief areas where rivers traverse extensive string-of-lakes and bog– fen drainage networks. ^{18}O values in major tributaries typically ranged between– 16 andÐ14‰ in shield areas, with peak enrichment observed in wetland-dominated drainage of the south-central Boreal Plain (Wabasca River ¾Ð 9‰). A synoptic plot showing evolution of υ^{18}O along the Mackenzie– Athabasca River system (Figure 6) constructed from the data of Hitchon and Krouse (1972) reveals a pattern of regular fluctuations of ^{18}O from headwaters to mouth due to interaction of tributaries draining both western alpine regions (with depleted isotope signatures) and eastern lowlands (with enriched isotope signatures), overprinted by lake storage effects. In general, lakes serve a regulatory role in the runoff regime by reducing seasonality

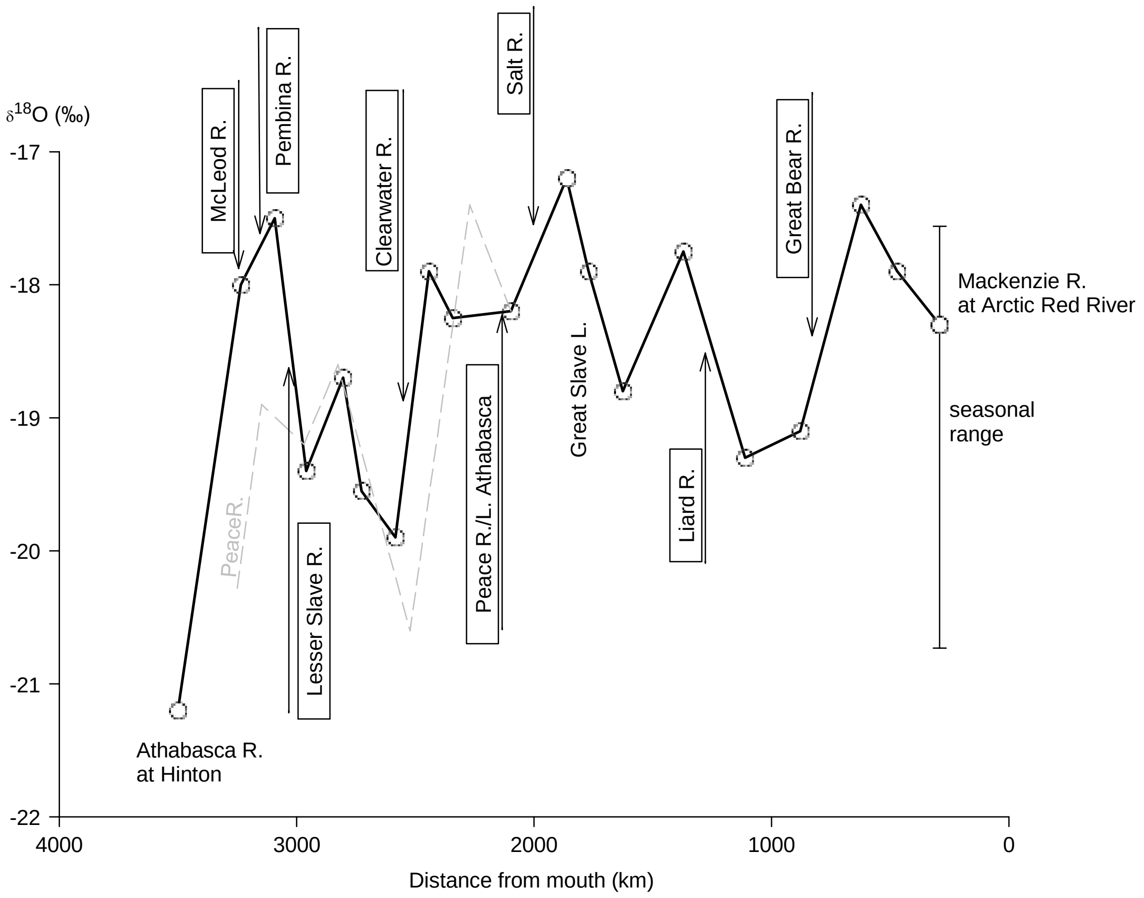


Figure 6. Synoptic survey of υ^{18}O along the Athabasca–Mackenzie River in summer 1969, based on data from Hitchon and Krouse (1972). Boxed text identifies the confluence of other major tributaries, with eastern tributaries shown above the curve and western tributaries shown below the curve. Dashed line denotes synoptic trends along the Peace River, a major tributary to the Mackenzie River

of discharge and amplitude of isotope variations. The 2– 3‰ overall enrichment of ^{18}O from headwaters to mouth, despite the north-flowing drainage network and northeastward decrease in ^{18}O in precipitation across the region (see Figure 4), emphasizes the cumulative importance of open-water evaporation losses in the basin water budget (¾0%).

Research within the Mackenzie GEWEX study has focused for the last 5 years on collection of isotopes in discharge and related hydrological components in the Liard Basin and five wetland-dominated tributary basins ranging from 200 to 2050 km^2 to assess the timing and relative contributions of snowmelt, groundwater and surface water sources to streamflow (Hayashi *et al.*, 2005; St Amour *et al.*, 2005). In addition to direct assessment of runoff generation mechanisms, the studies have endeavoured to develop isotope tracers as diagnostic variables for evaluating and tuning hydrological models (Stadnyk *et al.*, 2005). Seasonality in the isotope composition of discharge has been found to be pronounced, with systematic responses observed during the ice-on and ice-off periods due to changes in dominant source waters. A multiyear time series of υ^{18}O, as shown for the Liard River basin near the mouth (Figure 7a), reveals a strong decline in heavy isotope content during spring freshet due to enhanced snowmelt contributions and a steady increase in heavy isotope content during the ice-off period due to inputs of summer precipitation, groundwater and surface water. A substantial decline in heavy isotope content is also noted for the ice-on period, attributed to the increase in relative

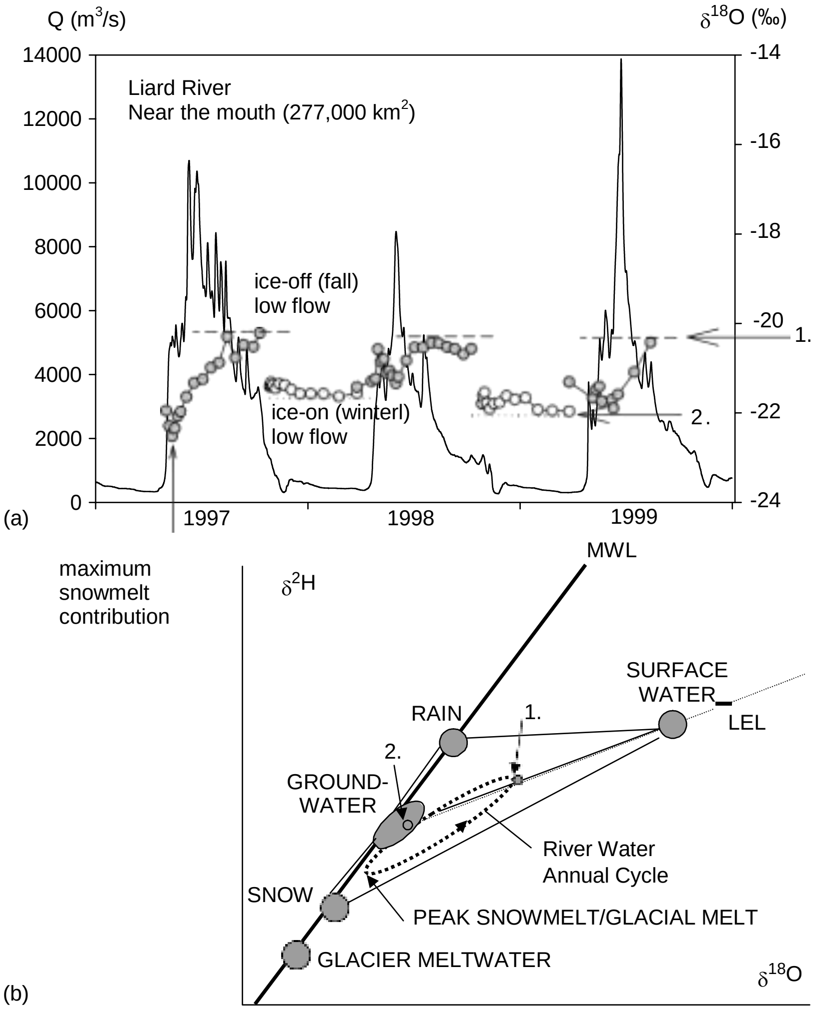


Figure 7. (a) Time series of discharge (solid line, m^3 s^{Ð1}) and $υ^{18}$O (circles) in the Liard River sampled near the mouth showing seasonal fluctuations. Grey circles denote isotope measurements during the ice-free period, whereas open circles depict ice-on conditions. (b). ^{18}O versus ^{2}H schematic showing major water sources (glacial meltwater, snow, groundwater, rain and surface water) that control the river water annual cycle. 1 and 2 denote the ice-off (fall) and ice-on (winter) low-flow set-points (see text for discussion)

contribution of deep groundwater versus precipitation and surface water sources under ice. Important set-points in the seasonal cycle include ice-off low-flow and ice-on low-flow conditions, which reflect the maximum surface water plus precipitation and the maximum deep groundwater contributions respectively (Figure 7b; see also Gibson and Prowse (2002)). Similar responses are observed at the basin outlet (Mackenzie River at Arctic Red River), where peak flow produced by snowmelt typically occurs in April (around day 150), and coincides with roughly a 2‰ depletion in $υ^{18}$O during typical years. Note that significantly higher depletions during freshet are often observed in smaller tributaries, where snowmelt tends to occur more uniformly over time. At the basin outlet, constant or subtle declines in $υ^{18}$O (to ¾Ð 19‰) may be observed during extended winter periods when groundwater becomes the dominant flow source, although increases in $υ^{18}$O to—17₤5‰

highlight periods when drainage of water from Great Slave Lake is the dominant flow source (Gibson *et al*., 2003).

Canadian research has also included analysis of winter streamflow and ice fractionation processes under river-ice cover (Gibson and Prowse, 1999, 2002). They described a multiyear isotope sampling survey conducted in the Liard– Mackenzie River basins, and show systematic isotopic patterns in vertical cores of congelation ice (black ice) obtained from rivers and from numerous tributaries. Gibson and Prowse (2002) attributed these patterns to primary streamflow signals, but with isotope offsets close to the equilibrium ice– water fractionation. The results, including comparisons with the isotopic composition of fall and spring streamflow measured directly in water samples, suggest that isotopic shifts during ice-on occur due to gradual changes in the fraction of flow derived from groundwater, surface water and precipitation sources, similar to the larger rivers (see Figure 7).

Longer term water sampling stations within the Mackenzie River basin were established in 2002 to capture both spatial and temporal variability in isotopic signatures better at gauged locations (Figure 5). These efforts are aimed towards partitioning of water from distinct geographical source regions previously identified by Hitchon and Krouse (1972), and to test and calibrate isotope-capable models (e.g. Stadnyk *et al.*, 2005). Importantly, these surveys will include both δ^{18}O and δ^{2}H to enable distinct labelling of cumulative evaporation losses. Ongoing studies, such as the NSF-funded Pan-Arctic Transport of Nutrients, Organic Matter, and Suspended Sediments PARTNERS, are also endeavouring to compare the isotope composition of discharge from the Mackenzie River with other major rivers of the northern circumpolar region, in part to understand and partition the freshwater sources and their interaction within the Arctic Ocean (B. Peterson, Marine Biology Lab, Woods Hole, personal communication). Synoptic surveys of isotope composition are also being conducted along the Mackenzie River during 2003 (T. Dick, University of Manitoba, personal communication).

One particularly exciting aspect of the river basin work is that monitoring of isotope signatures in discharge can be applied to characterize basin-integrated evaporation and transpiration as separate, coupled fluxes (e.g. Gibson *et al.*, 1993a; Gibson and Edwards, 2002). The ability to partition these vapour transfer mechanisms is based on the fact that evaporation causes predictable isotopic enrichment, whereas plant-mediated vapour exchange (transpiration) does not. The basic concept for partitioning is outlined below.

In conventionally gauged catchments, water budgets are normally calculated according to

$$P = \mathrm{ET} + Q \pm \Delta S \quad \text{(gauged, no isotope sampling)} \qquad (1)$$

where P is precipitation, ET is evapotranspiration, Q is discharge, and ΔS is change in storage (often assumed to be zero for long-term periods with stable climate).

Used independently, mean annual isotopic data from a river can be useful for partitioning the fraction of water loss by evaporation E from open waters and soils from the contributing catchment area and allows the following partitioning of the water balance:

$$P = E + (T + Q) \pm \Delta S \quad \text{(ungauged, isotope sampling)} \qquad (2)$$

This is particularly useful where evaporative enrichment is pronounced (i.e. open water or soil evaporation results in a substantial water loss as a percentage of total water losses).

In a situation where both physical and isotope information are used together, it may be possible to carry out a full partitioning of E and transpiration T to distinguish the following components:

$$P = E + T + Q \pm \Delta S \quad \text{(gauged, isotope sampling)} \qquad (3)$$

As CO_2 uptake during photosynthesis is coupled to the transpiration processes alone, this approach has allowed for better characterization of the net primary productivity, as demonstrated for the Ottawa and Mississippi river basins by Telmer and Veizer (2000) and Lee and Veizer (2003) respectively. Although further research is required to ground-truth evaporation and transpiration partitioning for individual terrain types, the distinct labelling of these fluxes has already been demonstrated from tower-based flux-gradient measurements (Brunel *et al*., 1992; Wang and Yakir, 1996).

LAKE AND CATCHMENT WATER BALANCE

The isotope mass balance approach for estimating water balance parameters has been demonstrated in previous studies of open water bodies (Dinçer, 1968; Gat, 1970, 1981; Zuber, 1983; Krabbenhoft *et al.*, 1990) and was reviewed in detail by Gat (1995). In general, an isotope mass balance calculation for a typical lake (Figure 8) requires measurement or estimation of the isotopic composition of all relevant water balance components. Liquid components, namely inflows, lake volume, and outflows, can often be directly sampled over time and appropriately weighted to provide mean estimates of their isotopic compositions. Owing to problems associated with direct sampling of evaporating moisture, the isotopic composition of evaporate is commonly derived indirectly using the linear resistance model of Craig and Gordon (1965), which requires estimates of temperature, relative humidity and the isotopic composition of ambient atmospheric moisture (υ_A). In a situation where all the isotope composition of all water balance components can be characterized, solution of the isotope mass balance allows for evaporation to be computed as a fraction of the total inflows (E/I).

A number of recent isotope-based studies have developed and refined approaches for application of isotope mass balance methods in seasonal climates of northern Canada. These studies include detailed comparisons of weekly to monthly evaporation in small, well-instrumented lakes using non-steady isotope balance methods (Gibson *et al.*, 1996a,b, 1998; Gibson, 2002a), regional comparisons of long-term water balance among lakes in boreal and Arctic areas (Gibson 2001, 2002a; Gibson *et al.*, 2002b; Gibson and Edwards, 2002), and application of evaporation pans and cryogenic vapour sampling to characterize isotopic composition of atmospheric moisture near the ground (Gibson *et al.*, 1999). Overall, these studies have shown that application of isotope mass balance using pan-derived atmospheric moisture and laboratory-determined values for kinetic fractionation parameters (see Gonfiantini (1986)) yields consistent results for short time periods when compared with a conventional water balance, where evaporation is determined using the Bowen ratio and aerodynamic profiling methods.

Various steady-state and non-steady-state formulations have been utilized, depending on the particular application (Gibson, 2002a,b). Owing to pronounced seasonal enrichment in lakes during the ice-free period in many parts of Canada, particularly the northern regions, it is often necessary to apply transient models for weekly or monthly studies (Gibson *et al.*, 1996a, 1998), although simplified steady-state models that account for seasonal fluctuations in the components have also been used for comparative analyses on longer time scales (Gibson *et al.*, 2002b). Evaporation calculations have commonly been performed independently for the isotopes of oxygen and hydrogen to provide a subsequent check on results. In general, it has been possible to simplify the number of required isotopic measurements through development of relationships between the

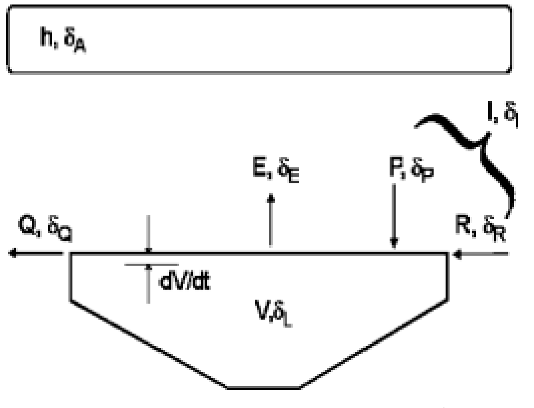


Figure 8. Schematic illustrating the major water and isotope mass balance components (fluxes and storages) for a well-mixed lake. Note that h is relative humidity of the atmosphere, Q is surface and subsurface outflow, V is lake volume, E is evaporation, I is combined

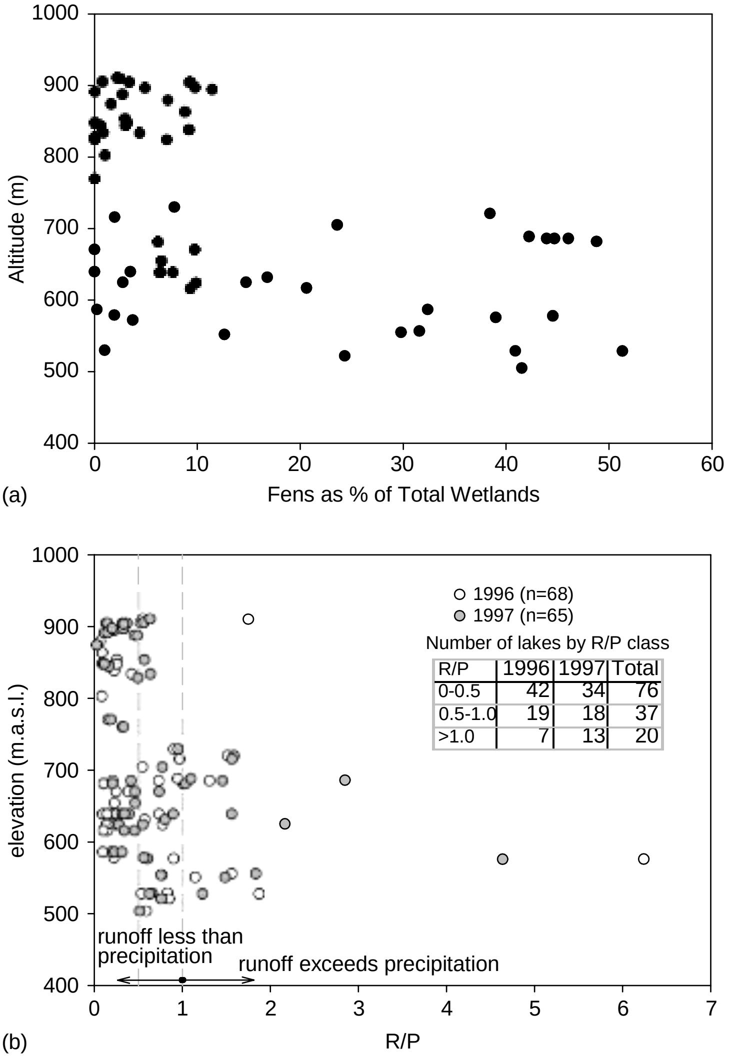
inputs, including precipitation on the lake surface P and surface and subsurface inflow R, and υ values refer to isotopic composition of the respective components various components. For example, shallow lakes are generally well mixed during the open water period, and outflows often acquire the isotopic signature of lake water, such that single water samples can be used to characterize υ_{L} and υ_{Q} for a given time. In addition, the isotopic composition of combined inflow sources is often close to that of mean annual precipitation, and atmospheric moisture is typically close to isotopic equilibrium with atmospheric moisture during the evaporation season, such that υ_{I} and υ_{A} can be evaluated from time-series records of υ_{P}. Although beyond the scope of this article, the validity of such assumptions have been discussed elsewhere (Gibson, 2001).

In stratified lakes, it is often necessary to account separately for epilimnion and hypolimnion volumes and exchanges, provided these have distinct isotopic compositions (Gat, 1995). Neglecting stratification can lead to overestimation of the importance of evaporation loss if sampling is conducted during dry, stratified periods, and underestimation of evaporation loss if sampling is conducted during wet, stratified periods (Gibson *et al.*, 2002b). Inflow bypass or short-circuiting of the system may also reduce the effective volume of the lake during wet periods or reduce the effective input in the opposite situation. Incomplete lateral mixing within the lake can also be a potential source of error when applying isotope mass balance to large lakes. In principle, incomplete mixing can be characterized by spatial and temporal sampling to constrain potential errors to any desired level of precision, although this is not always practical. A simple approximation for systems with similar epilimnion and hypolimnion compositions is to use an average value to represent the undifferentiated lake volume (Gibson *et al.*, 2002b).

Isotope mass balance methods have been applied in conjunction with regional sampling surveys to compare water balance parameters such as throughflow, water residence time and catchment runoff to lakes, thus providing a quantitative basis for examining natural landscape–lake connections and natural/anthropogenic impacts (e.g. forest fire or harvesting) on biogeochemistry of watershed systems (e.g. Gibson *et al.*, 2002b). In combination with physically based estimates of evaporation and precipitation, the method has also been applied to calculate catchment water yield parameters such as runoff/precipitation ratios (R/P). One significant ambiguity noted in a recent Boreal Shield study by Gibson *et al.* (2002b) was that derived water yields exceeded the available precipitation input in 15% of the headwater lake systems. Although uncertainty in the isotope mass balance approach and difficulty in defining catchment boundaries in low-relief terrain were clearly noted as contributing sources of error, the systematic influence of regional groundwater inflow was not considered. Closer examination of these results (Figure 9) suggests a frequent pattern of water yield excess ($R/P > 1$) in lower elevation catchments that were also typically dominated by fens, compared with higher elevation catchments that were typically dominated by bogs and tended to have modest water yields ($R/P < 1$). From this perspective, the results may imply that regional groundwater flow derived from outside the topographic catchment area is significant in many of the fen-dominated, lower elevation basins. This explanation is consistent with basic understanding of the origin and water cycle of fens in the region (Halsey and Devito, 2005).

As noted previously, local and regional sampling surveys in northern Canada have revealed a pronounced latitudinal steepening of the slope of local evaporation lines from about 5 to 7 in $\upsilon^{2}\mathrm{H}$– $\upsilon^{18}\mathrm{O}$ space over the latitude range of 50 to 71 °N (Figure 3). The slope of LELs reported from studies at lower latitudes typically range from about 4 to 5[5 (Dinçer, 1968; Gat, 1995). As explained by Gibson (2002b), the elevated slopes observed at high latitudes likely reflect a progressive decoupling of the hydrologic and atmospheric isotope signals with enhanced seasonality. Although the isotopic composition of input to the system varies closely with the mean annual υ_{P} in all systems, the isotopic composition of atmospheric moisture υ_{A} is strongly biased toward conditions during the evaporation season, which would tend to produce higher LEL slopes (see Gat (1996)). A revised conceptual model of isotopic enrichment in seasonal climates (Figure 10) illustrates that the use of evaporation-flux-weighted parameters significantly improves the reproducibility of the LEL slopes and improves the consistency of the water balance estimates predicted by each tracer, while maintaining the experimental values for the kinetic fractionations for both oxygen and hydrogen (see Vogt (1976) and

Gonfiantini (1986)). An interesting point that is particularly relevant to palaeoclimate studies is that temporal changes in seasonality may have altered the slope of the local evaporation in the past. Application of dual



Number of lakes by R/P class

R/P	1996	1997	Total
0-0.5	42	34	76
0.5-1.0	19	18	37
>1.0	7	13	20

Figure 9. (a) Systematic wetland distribution in headwater lake catchments, Boreal Plains region, northern Alberta, showing increase in percentage of fen cover with decreasing elevation. (b) Variations in isotope-based (υ^{18}O) estimates of runoff ratios (*R*/*P*) in the same network of lakes based on data from Gibson *et al*. (2002a,b). Plot and inset table show that the majority of lakes have $R/P < 1$, as expected for catchments with no external groundwater sources. Conditions where $R/P > 1$, observed primarily at lower elevations, and higher percentage of fen cover in these areas suggest contributions of groundwater flow to these systems from outside the catchment area

^{18}O and ^{2}H tracers to lake sediment archives may, therefore, be able to trace changes in palaeoslope of the evaporation line to provide a basis for examining past seasonality signals. For modern water balance applications, the use of non-weighted atmospheric moisture values and standard exchange parameters can result in substantial errors in computed long-term values for evaporation to inflow ratios, particularly for strongly seasonal climates, where errors may be as high as 50% for low throughflow, high-evaporation lakes (Gibson, 2002b).

One promising aspect of the isotope balance approach is that it is field based and can be readily incorporated in water quality surveys in remote or ungauged basins to provide hydrological control for evaluating the water quantity–quality relationships. Recent studies (McEachern *et al*., 2000; Prepas *et al*., 2001) have applied

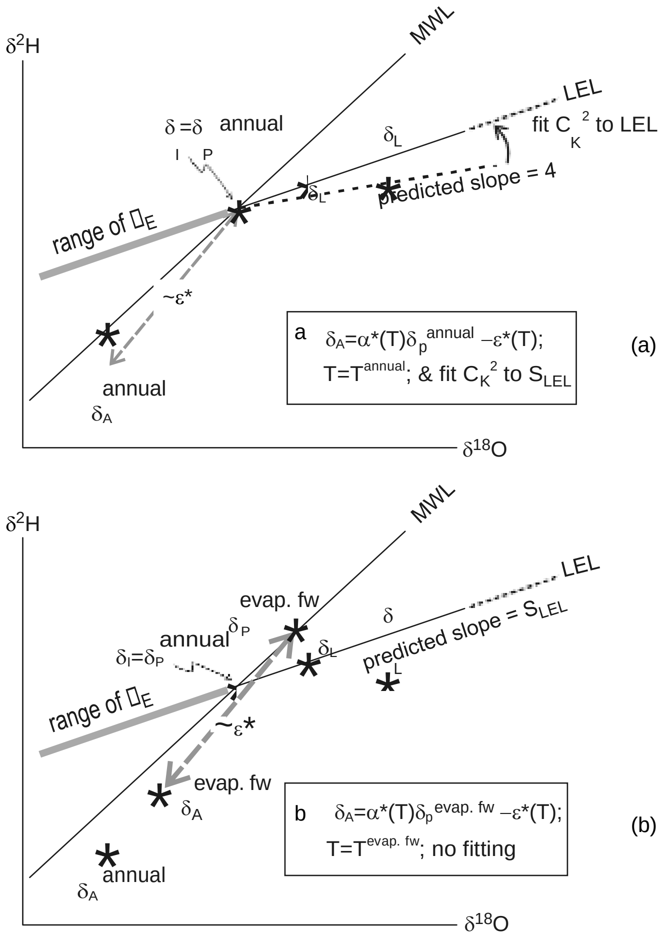


Figure 10. Conceptual models showing isotope composition of major water balance components relative to the MWL and LEL in υ^2H–υ^{18}O space: (a) original model assuming isotopic equilibrium between atmospheric moisture and precipitation (e.g. Gibson *et al*., 1993b). Predicted slopes fall close to 4 and require fitting of the isotope exchange parameters to obtain good agreement between tracers; (b) refined model assuming equilibrium between flux-weighted precipitation and atmospheric moisture. Predicted slopes are close to the observed LEL and do not require fitting of exchange parameters. υ values denote isotope compositions where υ_P is precipitation, υ_A is atmospheric moisture, υ_E is evaporating moisture, and υ_L are various lakewaters. C_K^2 is the kinetic fractionation constant for deuterium, ¸^{ł}*(T)* and $\varepsilon^{ł}$*(T)* are the equilibrium fractionation and separation factors respectively for each isotope species, and *T* is ambient temperature. Superscript ‘annual’ and ‘evap. fw’ denote mean annual and evaporation flux-weighted values (modified from Gibson (2002b))

the technique to study phosphorus loadings due to forest fire and landscape variables influencing nutrients and phytoplankton communities in Boreal Subarctic and Boreal Plains regions of northern Alberta. Notably, isotope-based methods enabled the latter study to ascertain that mean water residence time *t* was more than 20-fold longer for upland-dominated lakes than for wetland-dominated ones (11 years and 0ɫ5 years respectively), attributable to the deeper lake basins and smaller water yields within the upland-dominated systems. Positive associations (*r* D 0ɫ65) were also noted between lakewater residence time and alkalinity, conductivity, $HCO_3^{Đ}$, Mg^{2C}, and K^{C}, suggesting the influence of hydrological setting, specifically lake flushing rates for some but not all dominant ions. The isotope-based estimates of effective drainage basin area eDBA D *(R/P* ð DBA*)*, where DBA is the topographically defined basin area, were also positively related to colour and percentage bog cover (r^2 D 0Ð40 and 0Ð37 respectively, P < 0Ð001) and negatively related to drainage basin slope and percentage upland cover (r^2 D 0Ð30 and 0Ð47 respectively, P < 0Ð001). In wetland-dominated lakes, eDBA was found to be a stronger correlate with dissolved organic carbon and total nitrogen than DBA. Within the whole dataset, eDBA was more strongly associated with lakewater colour than DBA, suggesting a connection with colour-producing wetlands. Colour concentration, being highest in wetland lakes, was correlated with the ratio of isotopically defined effective drainage basin area to lake volume (eDBA/LV, r^2 D 0£63). Overall, the isotope-based indices allowed for better understanding of the relative differences between water balance among the lakes than the physical watershed characteristics alone, which illustrates the added value of incorporating isotopes in such water quality surveys. Several current studies are also incorporating isotope mass balance to the study of lake systems in the Peace–Athabasca delta region by Wolfe and others and the Oil Sands Regional Aquatic Monitoring Program (RAMP), both regional surveys being situated in northern Alberta.

ISOTOPE PALAEOHYDROLOGY FROM LAKE SEDIMENT RECORDS

Physically based understanding of stable isotope behaviour in modern lake systems, and the occurrence of robust archives of lake water υ^{18}O contained in inorganic and organic fractions of lake sediments, have also stimulated a wide range of palaeolimnological studies. These have generally focused on reconstructing past hydrology and hydroclimatology, inferred from isotopic records in bulk carbonate and molluscs, ostracodes, aquatic cellulose, and biogenic silica as reviewed elsewhere (Talbot, 1990; Talbot and Kelts, 1990; Edwards, 1993; Li and Ku, 1997; Holmes, 1996; Ito, 2001; Wolfe *et al*., 2001a,b; Schwalb, 2003). Interpretation of lake sediment-derived υ^{18}O stratigraphic profiles generally involves separating primary isotopic effects caused by shifts in the oxygen isotope composition of source water (i.e. precipitation and inflow) from those associated with secondary hydrological processes, such as evaporative ^{18}O-enrichment. Hydroclimatic factors controlling these isotopic effects have been discussed in detail above.

Over the past 30 years, lake sediment isotope palaeohydrological research in Canada has largely been concentrated along its southern border in the Laurentian Great Lakes and adjacent region, utilizing both carbonate and organic fractions. The Great Lakes have been at the forefront of this research, with multiple isotopic records recovered from Lake Huron (e.g. Lewis *et al*., 1994; Rea *et al*., 1994b; Dettman *et al*., 1995), Lake Michigan (e.g. Colman *et al*., 1994a,b; Forester *et al*., 1994), Lake Erie (e.g. Fritz *et al*., 1975; Lewis and Anderson, 1992; Tevesz *et al*., 1997), and Lake Ontario (e.g. Duthie *et al*., 1996; Wolfe *et al*., 2000), which have played a key role in reconstructing the hydrological evolution of these systems and climatic conditions since deglaciation. For example, some of these records have contributed to the debate over the cause and impact of the Younger Dryas in the Great Lakes region (Lewis and Anderson, 1992; Rea *et al*., 1994b; also see Yu and Eicher (1998) and Yu (2000)), a 1000 year long period of marked cooling that interrupted the deglacial transition into the Holocene. A major related focus has been to elucidate the history of meltwater drainage from Glacial Lake Agassiz upstream and the Laurentide Ice Sheet through the Great Lake basins (e.g. Colman *et al*., 1994a,b; Forester *et al*., 1994; Rea *et al*., 1994a; Dettman *et al*., 1995). A strongly ^{18}O-depleted signature has typically been used to trace the influx of Lake Agassiz waters, although this has been questioned by recent isotope studies of ostracodes, sediment cellulose and porewater from sediment cores retrieved from the Lake Agassiz basin (Last *et al*., 1994; Buhay and Betcher, 1998; Birks *et al*., 2005). These data suggest a more ^{18}O-enriched composition for Lake Agassiz, which has significant implications for late glacial– early Holocene drainage history through eastern North America, as well as the subsequent impact on North Atlantic oceanic circulation and climate (Broecker *et al*., 1989).

While many of the above-mentioned studies have strongly or exclusively relied on the oxygen isotope record from archives in lake sediments, stable carbon isotope records have also been used to assess past natural and human-induced hydrological variability in the Great Lakes. For example, a record of shifting interaction between Hamilton Harbour and the larger Lake Ontario was facilitated by comparison of harbour and offshore cellulose carbon isotope records, interpreted largely to reflect site-specific lake water dissolved inorganic carbon isotope composition (Wolfe *et al*., 2000). Results indicated that artificial excavation of a ship canal through the Burlington Bar in 1823, which had provided a natural impediment to exchange between

Hamilton Harbour and Lake Ontario, led to a 30– 100% increase in mixing between the two water bodies and attenuation of anthropogenic-driven eutrophication in the harbour. More conventional uses of carbon (and nitrogen) isotopes in lake sediment cores have been used to document nutrient loading history in Lake Ontario (e.g. Schelske and Hodell, 1991; Hodell and Schelske, 1998) and Lake Erie (e.g. Schelske and Hodell, 1995; Ostrom *et al*., 1998).

Lake sediment oxygen isotope records from several small lakes in the Great Lakes region of southern Ontario have also been used to reconstruct late-glacial and Holocene hydroclimatology (Edwards and Fritz, 1988; Edwards and McAndrews, 1989; Edwards *et al*., 1996; Yu *et al*., 1997; Yu and Eicher, 1998; Yu, 2000). For example, abrupt late-glacial– early Holocene υ^{18}O excursions to lower values at Twiss Marl Pond and Crawford Lake correspond to the timing of the Younger Dryas, as well as the Preboreal Oscillation, and provide evidence for atmospheric propagation of these climatic events into central North America (Yu and Eicher, 1998; Yu, 2000). Lake sediment isotope records from Little Lake, Inglesby Lake, Weslemkoon Lake, and Hamilton Harbour, in combination with an independent record of precipitation υ^{18}O from wood cellulose obtained from a site near Brampton (Edwards and Fritz, 1986), are consistent with progressive warming and moistening from the post-glacial to the mid-Holocene as the influence of Arctic air diminished and warm, moist ^{18}O-enriched air masses from the Gulf of Mexico became increasingly prevalent (Edwards and Fritz, 1988; Edwards and McAndrews, 1989; Duthie *et al*., 1996; Edwards *et al*., 1996). A strongly contrasting isotope-climate history marked by mid-Holocene aridity has been proposed by Yu *et al*. (1997), based mainly on interpretation of a marl υ^{18}O record from Crawford Lake, and thus apparent subregional inconsistencies remain to be resolved. Notably, a composite Holocene precipitation υ^{18}O record for southern Ontario presented by Edwards *et al*. (1996) compares well with a kerogen-inferred lake water υ^{2}H record from Austin Lake, Michigan (Krishnamurthy *et al*., 1995; Wolfe *et al*., 2001), and points to the intriguing potential of coupling oxygen and hydrogen isotope tracers in multiple archives from the same lake sediment record to deconvolute hydroclimatic controls on lake water isotope composition history unambiguously.

In north-central Canada, recent lake sediment isotope studies have extensively relied on aquatic cellulose to provide new quantitative insight into isotope-climate history associated with the expansion of forest– tundra vegetation during the mid-Holocene (MacDonald *et al*., 1993; Wolfe *et al*., 1996; Edwards *et al*., 1996). Cellulose-inferred lake water υ^{18}O records from three lakes in strongly varying hydrological settings along the northern boreal treeline were used to distinguish the effects of evaporative ^{18}O-enrichment from shifting precipitation υ^{18}O (Edwards *et al*., 1996).

Results from isotope mass balance modelling indicated that forest– tundra expansion between 5000 and 3000 ^{14}C years BP was associated with a 10– 15% increase in summer relative humidity compared with the present. Following 5000 ^{14}C years BP, estimated precipitation υ^{18}O is consistent with modern isotope-temperature relations, with higher values than present corresponding to a mean annual temperature increase of about 3 °C during forest– tundra expansion. In the early Holocene, however, precipitation υ^{18}O values of about 4‰ higher than present (when temperatures were at least as cold as present) are not in harmony with the isotope– temperature relation that was established after 5000 ^{14}C years BP. Edwards *et al*. (1996) suggested that these high values may, in part, reflect an increase in the efficiency of long-distance moisture transport (leading to a decrease in rain-out isotopic effects), consistent with a dominantly zonal air mass circulation and higher cloud base over the Western Cordillera (Bryson and Wendland, 1967; Dean *et al*., 1996).

New multidisciplinary studies of present and past hydro-ecology are currently being conducted in the Mackenzie basin deltas (MBDs) of northwestern Canada. These are being spearheaded by the use of isotope tracers to assess water balance in selected lakes and to detect events such as high-water flooding from distributary channels, which are difficult to monitor directly because of the remote setting and extremely subdued topography of the MBDs. Information about the present hydrological variability of lakes is crucial to the interpretation of a suite of palaeolimnological indicators that are being used in company with cellulose oxygen isotope data to reconstruct the hydro-ecological history of MBD lakes. Complementary isotope time-series are also being developed from tree-ring sequences in the MBDs to reconstruct past climate and flood frequency, the latter modelled after similar efforts in the Red River basin of southern Manitoba (Buhay *et al.*, 2002). Results will be used to address pressing concerns related to the potential environmental impact of river regulation, resource development and climate variability on the MBDs (see Wolfe *et al*. (2002) and Edwards *et al*. (2004)).

FUTURE DIRECTIONS

It can be argued that Canadian researchers have played an important role in the development and refinement of isotope hydrology techniques and in support of cooperative global monitoring. Improvement of Canadian infrastructure for isotope-based research, particularly in the last decade, and a growing awareness of the potential value of incorporating isotope tracers as a component of broadly based hydrological research programmes, has undoubtedly provided fertile ground for significant advances to be made in the future. It is important to note that Canadian progress in isotope hydrology will continue to rely extensively on international collaboration, expertise, and scientific exchange.

One emerging avenue of international research is the integration of stable isotopes of water into ocean, atmosphere, and land-surface hydrological models. These models provide capability for tracking the isotopic composition of reservoirs and fluxes, and simulating the isotopic fractionation processes. As such, they offer a potentially powerful tool for model evaluation and for examining the underlying causes of water-cycle variability. To date, isotopes are operationally implemented in several global climate models (e.g. ECHAM-4, GISS, FORSGC AGCM), and new regional climate models with isotope capability are also under development (e.g. REMO). A version of the Swedish HBV hydrological model incorporating stable isotopes has also been tested at the small catchment scale to simulate isographs (isotope hydrographs), and has been used to develop more realistic hydrological parameterization schemes based on a ‘soft data’ optimization procedure (J.J. McDonnell, Oregon State University, personal communication). A US DOE-supported water-cycle pilot study involving incorporation of isotopes into a mesoscale atmospheric model (MM5) and several land-surface models (NCAR-LSM, TOPMODEL, TOPLATS) is also planned over the next 10 years. Great potential also exists for application of isotopes in hydrological models at the continental scale (e.g. Stadnyk *et al*., 2005). In future, the coupling of continental-scale hydrological models with general circulation models (GCMs), including incorporation of evapotranspiration feedbacks to the atmosphere, could potentially improve the realism of the GCMs’ water and tracer fluxes. Likewise, such a coupled approach could benefit the study of hydrological processes and isotope distribution at the continental scale, and could serve as a model diagnostic used in a similar way to the HBV model run at the small scale. In order to benefit from advancements in new isotope diagnostic models, a commitment must be made to maintain and preferably expand the current scope of water sampling within hydrometric networks in Canada and globally.

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