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Abstract: This article provides an overview of recent progress in isotope tracer hydrology in Canada during 2003-2008, identifying over 85 published scientific articles. The cornerstone of Canada's contribution to isotope hydrology has been and continues to be via contributions from independent university-based researchers and students to the peer reviewed literature. Long-standing networks, such as the Canadian Network for Isotopes in Precipitation, and scientific steering groups, such as the Canadian Geophysical Union Committee on Isotopic Tracers, have also been important coordinating bodies for data collection, analysis and dissemination, and have sought to improve awareness of current interests, as well as to promote meetings and community activities. Research linkages to international programs such as the International Atomic Energy Agency (IAEA)/World Meteorological Organization's Global Network for Isotopes in Precipitation, IAEA Coordinated Research Programs such as Large River Basins and Geostatistical Spatial Analysis, and recent involvement with the International Association of Hydrological Sciences International Commission on Tracers have been some of the more visible contributions to Canada's international efforts.

Résumé : Dans le présent article, nous proposons une revue des progrès récents dans le domaine des traceurs isotopiques en hydrologie au Canada de 2003 à 2008, en identifiant plus de 85 publications scientifiques de chercheurs universitaires et gouvernementaux. La pierre angulaire de la contribution canadienne à l'hydrologie isotopique s'est faite et continue de se faire à travers la contribution indépendante de chercheurs et étudiants universitaires aux publications avec comités de lecture. Les réseaux à long terme tels le Réseau Canadien pour les Isotopes dans les Précipitations et les regroupements scientifiques comme le Comité des Traceurs Isotopiques de l'Union Géophysique Canadienne ont aussi contribués, en tant qu'organisme de coordination, de façon importante à la collection de données, l'analyse et la diffusion, et ont aspiré à améliorer la prise de conscience ainsi que la promotion de congrès et autres activités de la communauté. Les liens de recherche aux programmes internationaux tels le Réseau Global pour les Isotopes dans les Précipitations de l'Agence Internationale de l'Energie Atomique (AIEA)/Organisation Météorologique Mondiale, les Programmes de Recherche Concertés de l'AIEA comme ceux des Bassins des Grandes Rivières et de l'Analyse Spatiale Géostatistique, et les implications récentes

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Introduction

The utility of isotope techniques in hydrological investigations stems from their ability to label water sources and cycling processes including surface/groundwater interaction, water residence times, flow pathways, evaporation fluxes, and solute processes, to name a few. The stable isotopes of water ($^{18}$O, $^2$H) are most commonly employed as tracers as they are incorporated within the water molecule (H$_2$O, $^1$H$^2$H$^{16}$O) and because they undergo measureable and systematic fractionations as they move between phases in the water cycle. The study of hydrological processes that control water quality has also been an important avenue of investigation. Water-related biogeochemical studies have also tended to rely extensively on solute isotopes, namely carbon, nitrogen, strontium, sulphur, and chloride.

This article follows a recent review of Canadian progress in isotope hydrology that included a more complete historical description of contributions including precipitation networks, hydrograph separation and groundwater studies, river basin hydrology, lake and catchment hydrology, and paleohydrology (Gibson et al., 2005). From this and other international review articles (Darling et al., 2005) it can be argued that Canadian researchers have played a significant role in the development and refinement of isotope hydrology techniques and in support of cooperative global monitoring. It is important to note that Canadian progress in isotope hydrology has continued to rely extensively on international collaboration, expertise, and scientific exchange.

Coordinated Research Programs (2003-2008)

One current trend in Canadian isotope tracer research has been towards sustained long-term monitoring of precipitation and river discharge to enable better characterization of spatial and temporal variability in isotope signatures and their underlying causes. Finding methods to obtain hydrological information from remote, under-monitored or ungauged basins remains a significant challenge for Canadian hydrologists, one that is a priority of the Canadian component of the Prediction in Ungauged Basins (PUB) initiative of the International Association of Hydrological Sciences (IAHS). Isotope tracer techniques are particularly well suited for research in ungauged basins as they integrate hydrological and climatological information over time and space and therefore provide a first-approximation of long-term conditions. Driven by this need Canadian researchers continue to lead the development and application of isotope tracer techniques in remote areas and have collectively supported a long-standing precipitation isotope network.

A number of large-scale research programs using water isotope tracers are currently under way in Canada including: (i) the Mackenzie River basin program as a contribution to the Global Energy Water Cycle Experiment (GEWEX) and IAEAs Coordinated Research Project (CRP) on Large River Basins (see Gibson et al., 2002a; 2005); (ii) water and carbon studies in the St. Lawrence River basin (Hélie and Hillaire-Marcel, 2006); (iii) low-flow water sources in the Grand River basin, (Environment Canada/University of Western Ontario/University of Victoria; see also Stadnyk-Falcone (2008)); (iv) regional water balance in the Fort McMurray region, where isotope tracers are being used to evaluate lake sensitivity to atmospheric deposition as part of the Cumulative Environmental Management Association Acid Sensitive Lakes Program, and for evaluating potential regional water resources impacts related to surface mining and in-situ oil extraction (Alberta Research Council/University of Alberta, e.g., Bennett et al. (2008)); (v) the North and South Saskatchewan River basin where isotope tracers have been used to delineate water-carbon cycle linkages (Ferguson et al., 2007a); and (vi) the Peace-Athabasca Delta where the hydrology and paleohydrology of delta lakes are being assessed using isotope tracers (Brock et al., 2007; Yi et al., 2008).

Hydrograph Separation and Groundwater Studies

The stable isotope labeling of different water sources continues to be a major application of isotope
techniques in runoff generation and hydrogeological studies. Emili and Price (2006) showed the application of isotopes for partitioning surface/groundwater flow in steep forested slopes of north coastal BC and discuss topography as a major control on groundwater residence time on hypermaritime forested-peatland hillslopes. Water isotope tracers were used to explore the topographic control on streamflow sources and groundwater residence times during snowmelt in a paired-basin study by Monteith et al. (2006). Murray and Buttle (2005) also report on a study utilizing isotope tracers to investigate snowmelt infiltration and soil water mixing in forested and harvested hillslopes in the Turkey Lakes watershed. St. Amour et al. (2005) and Hayashi et al. (2004) both applied isotope techniques, the latter also applying selected major ions to partitioning streamflow components in wetland dominated forest catchments near Ft. Simpson, Northwest Territories. Carey and Quinton (2004; 2005) use tracers as part of an ensemble of approaches to understand runoff generation during snowmelt in an alpine discontinuous permafrost catchment.

Smerdon et al. (2005) used isotope techniques in their investigation of groundwater interaction with shallow lakes on outwash sediments in the sub-humid boreal plains of Canada. Work has also continued on understanding of groundwater in crystalline bedrock, including the Lac du Bonnet batholith (Gascoyne, 2004), and deep crustal fluids, including Canadian Shield brines (Bottomley et al., 2005). Isotope techniques have also recently been used in the field of permafrost hydrogeology to better understand the development of permafrost (Lacelle et al., 2007; 2008). Stable isotopes have been used in combination with other major and minor ions used to understand geochemical processes and flow systems within low permeability aquifers (Hendry et al., 2004a; b; Hendry and Wassenaar, 2005) and regional aquifers (Aravena et al., 2004; Wassenaar et al., 2006). Isotopic labeling of gases has been used to partition gas fluxes from soils and waste-rock piles (Hendry et al., 2002; Birkham et al., 2003; 2007; Lee et al., 2003). The distribution of δ18O and δD has been used to better understand the origin and flow of groundwater across large sedimentary aquifers such as the Williston Basin (Rostron and Holmden, 2003) and the Winnipeg aquifer (Ferguson et al., 2007b).

Lake and Catchment Water Balance

Recent progress in the application of stable isotope techniques to lake and catchment water balance studies includes the development of an isotope mass balance method for determining water yield estimates, which can be incorporated into critical load models (Bennett et al., 2008). This approach builds on techniques developed in previous isotope mass balance studies of lakes in Alberta (Gibson et al., 2002b). This method is currently being applied to other lake monitoring networks within Environment Canada’s acid rain program and various provincial government supported surveys. Isotope mass balance approaches have also shown great potential for partitioning of evaporation and transpiration (Gibson and Edwards, 2002), overwinter flow sources (Gibson and Prowse, 2002), and short-term evaporation losses from lakes in Arctic regions (Gibson, 2002).

River Basin Hydrology

On the basin-scale, isotope techniques continue to provide insight into sources of water, watershed evaporation, information on the sources of solutes as well as the potential for linking the carbon and hydrological cycles.

Researchers at the University of Calgary have focused on characterizing water sources in the headwater tributaries (Rock and Mayer, 2007). Combinations of hydrometric, chemical and isotope approaches have also been used to identify sources of sulfate and nitrate in the hydrosphere and to study their transformation processes in watersheds (Mayer, 2005; Rock and Mayer 2004; 2006a; b; Mayer et al., 2007; Prietzel et al., 2004). These techniques were successfully used to study the sources of riverine nitrate and sulfate in headwater streams in the northeastern United States (Campbell et al., 2006; Mitchell et al., 2006; Shanley et al., 2005), in the Seine River of France (Sebilo et al., 2006), in the Jordan River in Israel (Farber et al., 2005; Segal-Rozenhaimer et al., 2004), and in karst groundwater in southern Germany (Einsiedl and Mayer, 2005; 2006).

Research at GEOTOP-UQAM-McGill has focused on using isotope tracers in the St. Lawrence River to couple the carbon and hydrological cycles as well as improve the understanding of nutrient cycling in the watershed. Bi-weekly sampling of the St. Lawrence
River's inflow and outflow as well as the outflow of the Ottawa River began in 1997 and is ongoing. Analyses include dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC) as well as the isotopic composition of water ($\delta^2$H and $\delta^{18}$O). This research has shown that the carbon isotope composition of the St. Lawrence tracks seasonal changes in the sources of discharge and carbon sources, with the Great Lakes being the dominant source of summer discharge and carbon to the St. Lawrence, compared to smaller tributaries which dominate during the rest of the year (Hélie et al., 2002). Carbon isotopes also shed light on the sources of POC in the St. Lawrence discharge with the depleted $^{13}$C showing the dominance of aquatically derived POC over terrestrial sources (Hélie and Hillaire-Marcel, 2006). Studies are also under way in the St. Lawrence estuary hypoxic layer project using $\delta^{15}$N and $\delta^{18}$O of nitrates to constrain the source of nitrates. This approach of identifying carbon sources based on their isotopic signatures is also being applied to hydroelectric reservoirs where stable carbon isotopes can be used to constrain sources and fluxes of greenhouse gas emissions from flooded boreal hydroelectric reservoirs (Hélie and Hillaire-Marcel, 2005a; b).

Researchers at the University of Ottawa continue to make advances in the coupling of the carbon and water cycles (Telmer and Veizer, 2000; Lee and Veizer, 2003; Karim et al., 2008). Recent research based on the Saskatchewan River basin used the water isotope mass balance approach to partition evaporation and transpiration water vapor fluxes in the northern Great Plains region of western Canada (Ferguson et al., 2007a). This research has highlighted the need for longer-term data on the isotopic composition of river water, precipitation, and atmospheric moisture.

In addition to these university-based research programs, Canada has been a participant in the IAEA CRP on Large River Basins that includes 17 research groups worldwide who are actively collecting and analyzing water samples for stable isotopes of water. While official Canadian participation was via the National Water Research Institute's Mackenzie River Basin project, there were several other groups who were also active in large river basins including the St. Lawrence River basin (GEOTOP-UQAM-McGill, Montreal) and Saskatchewan River (Ferguson et al., 2007a). Several related studies have also been undertaken in the basin that support the IAEA program, including a synoptic survey of river water and tributaries that was conducted along the Mackenzie River from Great Slave Lake to the mouth during summer 2002, during a Department of Fisheries and Oceans cruise. Water samples from an isotopic survey of 140 locations in the Mackenzie Basin drainage network were also obtained from a 1996–1999 survey of Mackenzie Basin waters (Millot et al., 2003), and these samples have been analysed for $^2$H and $^{18}$O. This will be a valuable resource for comparison with the original isotopic surveys of the Mackenzie Basin by Hitchon and Krouse (1972). The National Science Foundation funded Pan-Arctic River Transport of Nutrient, Organic Matter, and Suspended Sediments (PARTNERS) project has also included measurement of stable water isotopes in Mackenzie River discharge as part of a study of six large Arctic rivers (Cooper et al., 2008). The isotopic and hydrologic datasets assembled as part of the Mackenzie Basin project are now a valuable resource for testing the capability of hydrological models to correctly partition different sources of runoff.

**Paleohydrology**

Over the past five years, research at Wilfrid Laurier University and the University of Waterloo has focused on hydrology, climate, and paleohydrology studies using various archives including lake sediment and tree ring chronologies (Brock et al., 2007; Birks et al., 2007; Edwards et al., 2008; Wolfe et al., 2005; 2007a). A review of progress in isotope paleohydrology using lake sediment cellulose was also prepared and is presented elsewhere (Wolfe et al., 2007b). Efforts are currently focussed on the Peace-Athabasca and Slave Deltas in the Mackenzie Basin where isotopic archives of climate and hydrology are providing the context for evaluating modern hydrology. Isotopic water balance techniques have proven to be particularly well suited for evaluating hydrolimnological conditions and hydroecological evolution of lakes in the delta landscapes (Brock et al., 2007; Wolfe et al., 2007a; Yi et al., 2008). Edwards et al. (2004) reviewed the use of water isotope tracers in high-latitude hydrology and paleohydrology.

Tree-ring $\delta^{13}$C chronologies from 1901–2001 were used to infer changes in hydrology on the Slave River Delta (Buhay et al., 2008).
Biosphere-Atmosphere Interactions

Advances in the use of isotope tracers to examine atmosphere-biosphere interactions have benefited from the involvement of atmospheric scientists from the Air Quality Research Branch at Environment Canada. Understanding biogeochemical cycles is fundamentally linked to our understanding of the water cycle and the distinctive isotopic labeling of oxygen in atmospheric and soil moisture can be used to understand and quantify the different sources of CO$_2$. Researchers at the Stable Isotope Laboratory and the Carbon Cycle Modelling Group have been collaborating with national and international colleagues in the measurement and interpretation of stable isotopes $\delta^{13}$C and $\delta^{18}$O of atmospheric CO$_2$. The Carbon Cycle Modelling Group has a number of isotope measurement campaigns and initiatives under way, including: measurement of the $\delta^{13}$C and $\delta^{18}$O of CO$_2$ from weekly air samples collected at a series of Canadian baseline stations (Alert, Estevan Point, Sable Island, Fraserdale, East Trout Lake/Prince Albert and Egbert; Huang and Worthy (2005)); a series of intensive summer aircraft measurement campaigns over the Fraserdale and Boreal Ecosystem Research and Monitoring Sites (BERMS) providing vertical profiles of $\delta^{13}$C and $\delta^{18}$O of CO$_2$; and measurements of $^{17}$O in atmospheric water vapour at Alert (Lin, 2006). These detailed field campaigns are now beginning to provide sufficient isotopic datasets of $\delta^{13}$C and $\delta^{18}$O of atmospheric CO$_2$ and soil water to develop our understanding of the isotopic labeling of different carbon pools as well as to test our understanding of the relative contributions of photosynthesis and respiration to atmospheric CO$_2$ (Chen et al., 2006; Higuchi et al., 2003; Shashkov et al., 2007).

Through collaborations with university-based scientists, researchers at Environment Canada are using isotope tracers to evaluate Canadian guidelines for dissolved oxygen in river systems as well as developing stable isotope techniques that can be used to assess ecosystem metabolism. Isotopic labeling of gases is being used to better understand the fundamental dynamics of gaseous and dissolved gases (Venkiteswaran et al., 2007; 2008; Wassenaar and Hendry, 2007).

Isotopic Labeling of Precipitation

Added insight into isotope labeling of precipitation has been gained from the recent results of research from the University of Calgary. The ten-year record of weekly precipitation isotope compositions measured at Calgary has provided a local meteoric water line for the region as well as a better understanding of local isotope-climate relations (Peng et al., 2004; 2005; 2007). Progress was also made towards understanding the influence of altitudinal gradients (Moran et al., 2007) as well as the potential for post-depositional modifications (Sinclair and Marshall, 2008) on the isotopic labeling of the snowpack in the Rocky Mountains.

Collection and analysis of precipitation isotope data in Canada from local studies, such as those described above, as well as more regional sampling has shown that the distribution of amount-weighted isotope fields across Canada reflects differences in the dominant meteorological regimes (Pacific, Arctic and/or Gulf Stream) associated with each region. While these efforts were fundamental in providing local hydrological input functions and calibration for paleoclimate archives, there was growing awareness of the significant value of longer-term networks to monitor ongoing and dynamic evolution of the global water cycle. Essentially, these snapshots of the isotope climatology of Canada were limited by the spatial and temporal patchiness of the existing Canadian data.

Efforts were made in 1997 to improve this situation with the establishment of the Canadian Network for Isotopes in Precipitation (CNIP) as a joint venture between university and government researchers, and supervised by a scientific sub-committee of the Canadian Geophysical Union. One of the objectives of this network is to provide the spatial and temporal data necessary to examine the sensitivity of isotope fields to changes in circulation patterns, particularly in northern areas where the signal to noise ratio is much lower. The network consists of 19 stations (for locations see Figure 1 in Gibson et al. (2005)) distributed across Canada (spanning almost 40° of latitude and 70° of longitude) collecting weighted monthly precipitation samples for $\delta^{18}$O and $\delta^{2H}$ analyses. This marks the first time that both the southern and northern regions of the country have been simultaneously sampled capturing a large range in latitude and continentality (Figure 1). With ten years of data the CNIP dataset is now at
the stage where regional interannual variations can be examined (Birks et al., 2004; 2005). In addition, CNIP also includes three stations where daily precipitation samples are collected for $\delta^{18}$O and $\delta^2$H analyses. This partnering between CNIP and Canadian Air and Precipitation Monitoring Network (CAPMON) has benefited both parties by creating a comprehensive dataset that includes full geochemical characterization of precipitation, providing both isotopic and major ion tracers to constrain source areas and transport history.

In addition to maps and animations of the distribution of climatological averages of isotopes in

Figure 1. Time-series of monthly $\delta^{18}$O of precipitation from the 19 stations operating between 1997-present (first five years shown) with some of the air-mass indices influencing Canadian climate. There are currently ten years of data from stations spanning the entire country allowing for assessment of the role of circulation patterns such as the El Niño Southern Oscillation (ENSO), the Pacific North American pattern (PNA) and Arctic Oscillation (AO) on the isotopic labeling of precipitation.
precipitation (Birks et al., 2002), the CNIP and Global Network for Isotopes in Precipitation (GNIP) datasets are also being used to develop more specialized products (e.g., growing season precipitation isotope composition) to facilitate the use of isotope tracers in ecology (Bowen et al., 2005) where the spatial distribution of isotopes in precipitation can be used to quantify large scale movement of migratory organisms. The CNIP and GNIP datasets have also been used with gridded climate datasets to use isotope mass balance models to investigate differences in slopes of local evaporation lines (Gibson et al., 2008).

**Isotope Equipped Models**

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 model evaluation, and for examining the underlying causes of water-cycle variability.

Incorporating the isotopes of water in climatological and hydrological models provides a critical test of the model's capabilities to consistently partition and conserve both mass and isotopes in the water cycle. Reproducing the distribution of $\delta^{18}O$, $\delta^2H$ and $d$-excess in precipitation by an atmospheric General Circulation Model (GCM) tests the model's representation of the entire hydrological cycle, including the source area of precipitation, transport pathways, air-mass mixing, recycling of moisture and conditions during condensation. The growing capability of isotopic GCMs has been a major factor in the emerging science of isotope climatology, since the distribution of isotopes in precipitation provides fundamental information about the partitioning of the global atmospheric water budget that is not directly accessible using other means (Edwards and Birks, 2001).

To date, isotopes are operationally implemented in several GCMs (e.g., ECHAM-4, GISS, FORSGC AGCM), and new regional climate models with isotope capability are under development (e.g., REMOiso). As the spatial and temporal resolution of isotopic AGCMs improves, and with the development of isotopic regional climate models (RCMs), datasets such as GNIP as well as national networks such as CNIP have become increasingly important. The CNIP dataset is the most comprehensive high-latitude precipitation dataset available and continues to be a key validation tool for isotope equipped GCMs and RCMs (Birks et al., 2005). Progress on incorporation of isotopes in hydrological models includes WATFLOOD (Stadnyk et al., 2005) and University of New Hampshire Water Balance Model (Fekete et al., 2006).

Likewise, simulating the $\delta^{18}O$ of CO$_2$ provides a rigorous test of the model's representation of the carbon cycle, requiring correct representation of $\delta^{18}O$ fractionation processes in both the atmospheric and the ecosystem models. A new Canadian initiative through a Canadian Foundation for Climate and Atmospheric Sciences (CFCAS) collaborative project with the University of Toronto and the Carbon Cycle Modelling Group at Environment Canada will incorporate isotope tracers in a three-dimensional coupled atmosphere-biosphere model. Fractionation processes for $\delta^{18}O$ will soon be incorporated into a global ecosystem model of the carbon cycle coupled with the hydrological processes of the Canadian weather forecast model Global Environmental Multiscale (GEM). Isotopic data from CNIP and GNIP will be used for validation and verification of the coupled model in a coupled atmosphere-biosphere three-dimensional model.

Although GCMs equipped with water isotope tracers have provided important information about the global water cycle, their representation of the hydrological cycle is limited by their relatively coarse spatial resolution. RCMs have the potential to improve spatial details of simulated climates, particularly in regions of complex topography. The water-isotope tracer routine from ECHAM4 has recently been implemented into the regional circulation model REMO 5.0 (Sturm et al., 2005). Preliminary results from REMOiso for modern isotope fields over Europe have demonstrated superior representation of precipitation isotope fields as compared with AGCM-derived output (Sturm et al., 2005), particularly in areas with steep topography. In collaboration with Kristof Sturm (University of Stockholm), REMOiso has been run using a domain that includes Canada. Preliminary results show the improved resolution of the expected altitude effects over the Rockies as well as a fairly good representation of climate and isotope time-series for CNIP stations (Figure 2).
Conclusions

Development and refinement of isotopic measurement capabilities, techniques, and infrastructure over the past four decades has greatly extended Canadian scientific capacity in isotope hydrology and related sciences. As such, the effectiveness of future research is likely to be limited only by the degree of cooperation within the Canadian and international scientific community, by strategic integration within baseline monitoring programs, and by educational resources. One of the goals of the Canadian Geophysical Union – Hydrology Section Committee on Isotopic Tracers is to support and facilitate this cooperation by encouraging information exchange between isotope specialists and hydrologists both within Canada and internationally, and to address issues of importance to isotopic investigations including integration within broadly-based hydroscience research programs.

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References


