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	Abstract	<p>Measurement and modeling of the stable isotope signature of water in continental runoff provides unique information for large scale hydrological process studies and global water budget assessment. This chapter presents theory and case studies that illustrate isotopic signals relevant to understanding large scale hydrological processes. We provide examples illustrating isotopic labeling arising from isotopically varying runoff sources, open-water evaporation from lakes and wetlands, and river channel evaporation. Incorporation of isotopes in global and regional distributed runoff models may support the formal implementation of water isotopes as tools for monitoring large scale changes in continental water budgets and for model validation, but this work will require more comprehensive monitoring efforts for both surface water and meteoric precipitation isotopic composition.</p>

Chapter 18

Stable Isotopes in Large Scale Hydrological Applications

John J. Gibson, Balázs M. Fekete, and Gabriel J. Bowen

18.1 Introduction

The seminal water budget studies of L'vovich et al. (1990), Baumgartner and Reichel (1975), and Korzoun et al. (1978) provided the first practical synthesis of global-scale variations in climatology of major water budget components. Although based on limited data, these studies presented fairly consistent first-approximations of the long-term continental water fluxes; estimates that are still being refined today, both spatially and temporally, using a variety of observational and modeling techniques (Browning and Gurney 1999; Oki et al. 1999; Vörösmarty et al. 1998; Fekete et al. 2002; Raschke et al. 2001). Early on, the establishment of global patterns and recognition of continental, regional (and local) variability in water budgets provided a unifying framework and context for widespread analysis of water cycling processes.

While it can be argued that a similar conceptual framework has been established for global isotope balance processes, the practical (quantitative) closure of the modern-day isotope mass balance for the continents has not yet been achieved, due mainly to a lack of long-term systematic measurements for the riverine fluxes to the oceans. As a result, a perspective of isotope variations in hydrological systems has emerged

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from piecemeal studies, predominantly via small-scale and short-term measurement programs, from analysis of local variations of paleoclimate archives recording deep time variations of the Earth's water cycle, and from analysis of modern-day global-scale precipitation patterns. This perspective, until recently, has not included a sophisticated understanding of climatological-scale runoff patterns, despite the added value that closure of the isotope mass balance provides as an integrated, cumulative indicator of water cycling and related processes.

Hydrological studies primarily rely on the stable isotopes of oxygen and hydrogen (^{18}O , ^2H), which are incorporated within the water molecule (H_2^{18}O , $^1\text{H}^2\text{H}^{16}\text{O}$), and exhibit systematic variations as a result of isotope fractionations that accompany water-cycle phase changes and diffusion. The broad features of global isotope variations were reported shortly after the discovery of the heavy isotope water molecules in the 1930s, followed by more systematic descriptions of the global isotope climatology in the 1950s and 1960s (Craig 1961; Dansgaard 1964; Friedman et al. 1964; Craig and Gordon 1965; Gat and Gonfiantini 1981). Isotope fractionation produces a natural labeling effect within the global water cycle, which has been applied to study a wide range of hydrological and climatic processes at the local, regional, and global scales.

A relatively sophisticated understanding of global isotope variations in precipitation processes and related modeling capabilities has emerged in recent years (Jouzel and Merlivat 1984; Hoffmann et al. 1998, 2000; Ciais and Jouzel 1994; Rozanski et al. 1993; Cole et al. 1993, 1999), primarily as an outgrowth of concerted efforts at the national and international level to systematically monitor the isotope composition of precipitation (IAEA/WMO Global Network for Isotopes in Precipitation (Birks et al. 2002; Aggarwal et al. this volume). Considerable advances have also been made to apply precipitation isotope data to the study of regional atmospheric water balance (Gat 1980, 1996; Gat and Gonfiantini 1981; Gat et al. 1994; Merlivat and Jouzel 1979), and the use of more localized (point) datasets for the study of paleoclimatic trends (Jouzel et al 2000; von Grafenstein et al. 1999) and water budget and runoff studies at the micro- to meso-scale (Kendall and McDonnell 1998). This dataset has provided the basis for a growing body of work focused on interpolation, prediction, and analysis of the spatial distribution of precipitation isotopic composition at national to global scales (Birks et al. 2002; Bowen and Revenaugh 2003; Lykoudis and Argiriou 2007; Bowen this volume). The large-scale patterns in the precipitation isotopic distribution reflect the transport of vapor from the tropics to higher latitudes, while going through repeated cycles of precipitating and evaporating resulting in increasing depletion of the heavier isotope species. The precipitation is depleted in the heavy isotopes of H and O at high latitudes (exceeding -300‰ and -40‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively), and resembles more closely the reference ocean water (Vienna Standard Mean Ocean Water, VSMOW) near the Equator. The difference between minimum and maximum monthly values indicates strong seasonal variations in isotopic composition, such that winter precipitation tends to be more depleted than summer precipitation, which is also more pronounced at high latitudes (Fig. 18.1; Bowen 2008).

[AU1]

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The principal uncertainty in closure of the isotope mass balance for the continents, however, remains a lack of systematic measurements of some of the important budget components, such as the isotope composition of river discharge and atmospheric moisture (Gat 2000). Notwithstanding notable contributions from individual scientists and research groups, systematic sampling within efforts by national programs, such as the U.S. Geological Survey's National Stream Quality Accounting Network (Kendall and Coplen 2001), and more recent international initiatives, such as the International Atomic Energy Agency's coordinated research project on large river basins (Gibson et al. 2002), have sought to build capacity for a network for monitoring the isotope composition of river discharge. Isotopes of water (^{18}O and ^2H) have also been part of a suite of tracers measured in the six major rivers flowing to the Arctic Ocean within a U.S. National Science Foundation sponsored program called PARTNERS (Pan-Arctic River Transport of Nutrients, Organic Matter and Suspended Sediments) to constrain the riverine input amounts used to assess the freshwater balance of the Arctic Ocean (McClelland et al. 2008). Among the important contributions of such programs is their ability to build consensus on sampling and data analysis techniques for improving the closure of the isotope balance for large river basins.

This chapter describes the rationale and potential benefits of incorporating isotope tracer measurements in existing hydrological monitoring networks as a complimentary tool for understanding some of the underlying causes of hydrological and biogeochemical variability, and for tracking future impacts due to land use changes, deforestation, and climate change. Notably, closure of the isotope balance for stable isotopes of water permits a sharper focus on variations in contributions and interaction between various water sources such as: surface water and groundwater, their contributions to flow in major rivers, the role of these interactions as biogeochemical regulation mechanisms, and partitioning of vapor losses by evaporation and transpiration, the latter being the quintessential link between the water and carbon cycles via photosynthesis. These are among the key mechanisms not routinely described from field-based data collected within current observational networks, nor are they readily discernible from today's remote sensing satellite observations. As with the water budget studies, fundamental characterization of integrated isotope signals at the continental scale may be of paramount importance to understanding the global climate system.

18.2 Theoretical Background

The use of stable oxygen and hydrogen isotopes as tracers in hydrologic studies has expanded over the past half-century following initial characterization of variations in world precipitation (Craig 1961; Dansgaard 1964), development of theory describing isotopic fractionation during evaporation (Craig and Gordon 1965; Gibson et al. 2008b) and testing and validation of process studies under a range of

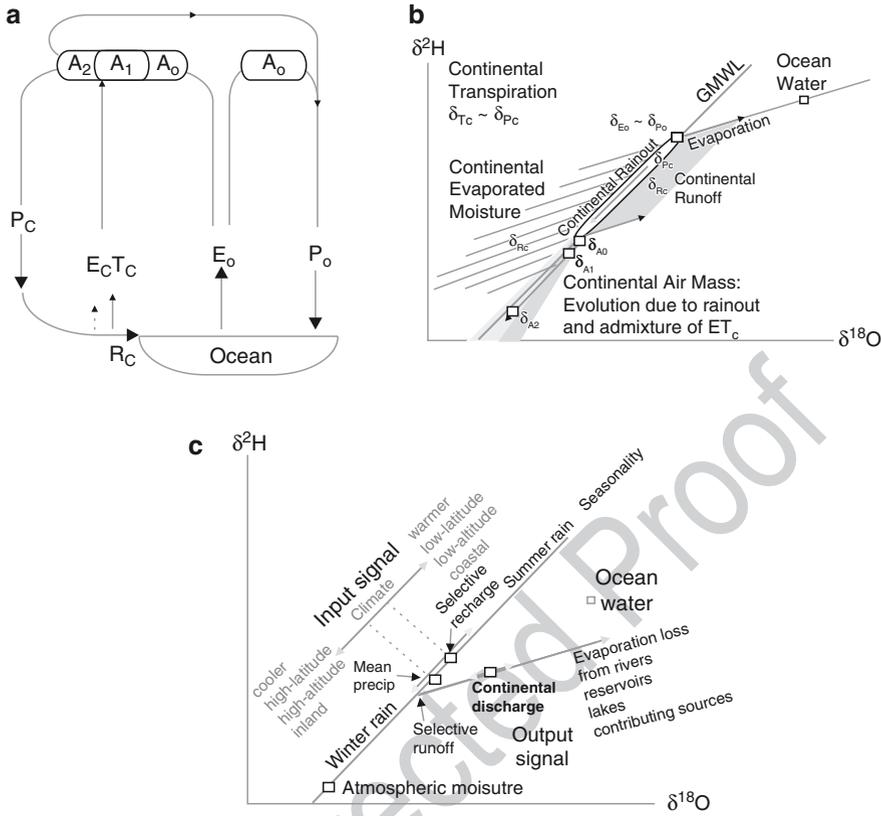


Fig. 18.1 Conceptual model of the ocean-continent water cycle. (a) Schematic of the global water cycle fluxes. (E_o and P_o are the oceanic evaporation and precipitation, E_c , T_c , R_c and P_c are the continental evaporation, transpiration, runoff and precipitation, A_o , is water vapour transport over the oceans, and A_1 to A_2 denotes water vapour composition over continental areas as modified by evaporation and transpiration feedback and moisture recycling. (b) Isotope signatures (δ values) for the ocean-continent system, where subscripts denote signature of components shown in (a). GMWL = global meteoric water line, ET = evapotranspiration. (c) Primary forcings on isotope composition of hydrological inputs and outputs from large river basins

field conditions (Gat and Gonfiantini 1981; Gat 1996; Clark and Fritz 1997; Kendall and McDonnell 1998; Gibson and Prowse 2000).

International programs, such as the recently completed IAEA coordinated research project on “Isotope tracing of hydrological processes in large river basins,” have increased scientific awareness of the potential value of incorporating isotope tracers in large-scale water cycling studies to trace water origin and residence times, snowmelt processes, surface-groundwater exchange, evaporation–transpiration partitioning, precipitation variability, and climate/land use changes (Gibson et al.

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2002; Vitvar et al. 2007). Although isotope techniques have been widely tested and are operationally applied at the small catchment-scale, theoretical development and testing of isotope-mass balance approaches at the continental scale are still in progress.

We begin by presenting a quantitative framework within which isotopic variation can be related to large scale land-surface hydrological processes (Fekete et al. 2006). Tracing stable isotopes in the hydrological cycle is analogous to the tracing of conservative constituents, except that fractionation mechanisms during phase changes must also be computed and tracked. While the mathematically correct computation of isotopic composition mixing using absolute concentrations is desirable for its accuracy, particularly over large ranges of isotopic composition, we adopt the common approximation of isotopic composition as δ values for notational simplicity. Herein we use $\delta = \frac{R}{R_{ref}} - 1$, where R, R_{ref} values refer to $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ in sample and V-SMOW standard, respectively).

For long time periods, the mass and isotope balances for the oceans and continents, respectively, are given by

$$P_o = E_o - P_c \quad (18.1)$$

$$\delta_{P_o} P_o = \delta_{E_o} E_o - \delta_{P_c} P_c \quad (18.2)$$

and

$$P_c = R_c + E_c + T_c \quad (18.3)$$

$$\delta_{P_c} P_c = \delta_{R_c} R_c + \delta_{E_c} E_c + \delta_{T_c} T_c \quad (18.4)$$

where P_o and E_o is oceanic precipitation and evaporation, and P_c, R_c, E_c and T_c are continental precipitation, runoff, evaporation, and transpiration (Fig. 18.1a). Changes in atmospheric moisture are expected due to admixture of evaporated and transpired moisture to air masses over the continents. Oceanic moisture in coastal areas is shown as A_o which becomes subsequently modified as it moves across the continent to inland areas (shown here as ranging from A_1 to A_2).

The approximate isotope compositions (δ) of components are shown in Fig. 18.1b. Long-term differences in precipitation arise from Rayleigh-type fractionation of atmospheric moisture and precipitation during rainout over the continents. Transpired moisture is expected to be isotopically similar to precipitation or groundwater recharge for a given location, whereas evaporated moisture will be heavy-isotope depleted (plotting on or above the MWL) and river discharge will tend to be heavy-isotope enriched (plotting on or below the MWL). Figure 18.1c shows specific hydro-climate forcings on ^2H and ^{18}O isotopic compositions, including those related to long-term precipitation input signals (temperature, latitude, altitude, distance from ocean source), seasonal signals (temperature, monsoon

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cycles, moisture sources, glacial melt), bias in recharge due to selection of high-precipitation or thaw-season events, and seasonal oscillations in evaporative enrichment from the river or contributing sources (soil water, lakes, reservoirs, wetlands, etc.). In addition to the monitoring of volumetric fluxes, the characterization of long-term and seasonal isotope signals is expected to provide additional insight into hydro-climatic changes in each hydrologic regime. In some cases, such as rainfall-runoff climates, primary precipitation signals may be preserved in river discharge. In others, such as arid or seasonally arid climates, the selection processes and evaporative enrichment effects often result in more pronounced differences between river discharge and precipitation. A more quantitative description of this difference is presented below.

While systematic surveys of flux-weighted isotope signatures of discharge are not very common, the anticipated long-term separation can be postulated based on the isotope and mass balance shown in Fig. 18.1b and depicted in Eqs. 18.3 and 18.4. The isotope separation between flux-weighted continental runoff and continental precipitation ($\delta_{R_c} - \delta_{P_c}$) is expected to depend on

$$\delta_{R_c} - \delta_{P_c} = \frac{E_c (\delta_{R_c} - \delta_{E_c}) + T_c (\delta_{R_c} - \delta_{T_c})}{P_c} \quad (18.5)$$

which is obtained by rearranging Eq. 18.4 with substitution of $R_c = P_c - E_c - T_c$ from Eq. 18.3. If it is also assumed that continental transpiration is similar to continental precipitation, i.e. $\delta_{T_c} \approx \delta_{P_c}$ then this further simplifies to

$$\delta_{R_c} - \delta_{P_c} = \frac{E_c (\delta_{R_c} - \delta_{E_c})}{P_c - T_c} \quad (18.6)$$

Equation 18.6 demonstrates that the long-term isotope separation between runoff and precipitation will approach zero only as $E_c \rightarrow 0$ or as $\delta_{R_c} \rightarrow \delta_{E_c}$. While very low (free-surface) evaporation may be characteristic of some humid areas dominated by vegetation, the latter condition where

$$\delta_{R_c} \approx \delta_{E_c} \quad (18.7)$$

is not expected to occur due to isotope effects associated with evaporation. This can be shown by substitution of the Craig and Gordon model (Craig and Gordon, 1965):

$$\delta_{E_c} \approx \frac{\alpha^* \delta_{R_c} - h \delta_{A_c} - \epsilon}{1 - h + 10^{-3} \epsilon_K} \quad (18.8)$$

into Eq. 18.7 assuming $\delta^* \approx 1$, which shows that $\delta_{R_c} \rightarrow \delta_{E_c}$ only as:

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$$\delta_{R_c} \rightarrow \frac{h\delta_{A_c} + \varepsilon}{h - 10^{-3}\varepsilon_K} \quad (18.9)$$

which is the limiting isotope enrichment under prevailing atmospheric conditions. Note that in this case δ_{A_c} is the average isotope composition of continental atmospheric moisture over the continent as comprised of a mixture of δ_{A_0} , δ_{A_1} and δ_{A_2} (δ_{A_0} being oceanic moisture, and δ_{A_1} and δ_{A_2} representing oceanic moisture altered by progressive rainout and potential feedback of re-evaporated continental moisture). Limiting enrichment is only expected to occur under conditions where waters evaporate to dryness and is therefore unlikely for the case of sustained discharge. Variation in evaporative enrichment of heavy isotopes in continental discharge is therefore expected to depend mainly on the fraction of water loss by (free-surface) evaporation in the river basin, as well as on the atmospheric humidity, its isotope composition and the ambient temperature.

The isotope fractionation $\varepsilon = \varepsilon_{V/L} + \varepsilon_K$ is the sum of the equilibrium fractionation ($\varepsilon_{V/L}$) and the kinetic (diffusive transport) fractionation (ε_K). The equilibrium fractionation is given by Majoube (1971) as:

$$\varepsilon_{V/L} = e^{c_0 + \frac{c_1}{T} + \frac{c_2}{T^2}} - 1 \quad (18.10)$$

where c_0 , c_1 , c_2 are coefficients and T is the air temperature (in kelvin). The kinetic fractionation is:

$$\varepsilon_K = (1 - h_N) \left(1 - \frac{\rho_r}{\rho}\right) \quad (18.11)$$

where controlling factors include relative humidity (h_N), the atmospheric resistances to diffusion of water molecules containing the rare, heavy (ρ_r) and common, light (ρ) water molecules, where ρ_r / ρ is close to 1.0125 for deuterium and 1.0142 for oxygen (Gat 1996).

This conceptual model provides an example at the global scale for development of quantitative approaches to examining river discharge signals. Specifically, it provides an initial basis for understanding and quantifying the hydrological significance of the long-term precipitation-runoff isotope separation, which is expected to vary with the ratio of $E_c / E_c T_c$. Such information is not available via conventional hydrometric monitoring. One key assumption of this derivation is that the isotopic composition of continental groundwater is similar to that of precipitation, although due to selective recharge and storage effects this may not be an appropriate representation for some large river basins. Other long-term storages such as glaciers need to be explicitly included in some areas. This, and similar models, need to be developed and tested to account for seasonal variations in the hydrological processes and specific influences of long-term storage reservoirs such as groundwater and glacier melt. A recent review by Gat and Airey (2006) provides additional discussion on scaling issues related to working with stable isotopes at the continental scale.

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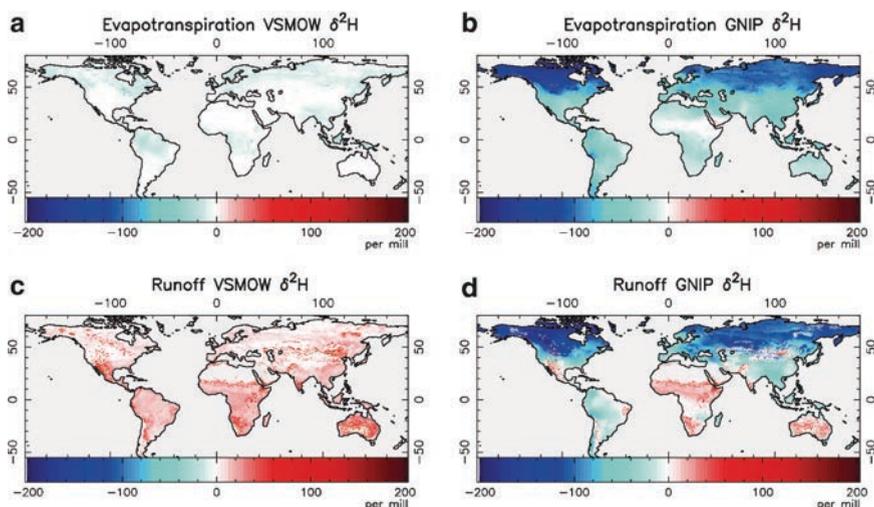


Fig. 18.2 Global isotope simulations using the iWBM distributed hydrology model. Shown are the isotopic composition of evapotranspiration using (a) constant V-SMOW precipitation, (b) GNIP precipitation climatology, runoff (c) constant V-SMOW precipitation and (d) GNIP precipitation climatology. The *left panels* illustrate modeled isotopic separation from precipitation, whereas the *right panels* show predicted isotopic compositions that might be measured in nature. These effectively constitute a spatial hypothesis awaiting verification when global observations become available (Reprinted from Fekete et al. 2006, Application of isotope tracers in continental scale hydrological modeling, Journal of Hydrology, vol. 330, p. 452, Copyright 2006, with permission from Elsevier)

These isotopic processes were implemented in the continental scale hydrological model iWBM by Fekete et al. (2006). Figure 18.2 shows the simulated mean annual deuterium composition of the evapotranspiration and runoff under isotopically uniform (V-SMOW) and spatially and temporally varying precipitation forcings (Birks et al. 2002). The salient features of these simulation results include: (1) the dominant control of spatial variation in precipitation isotopic composition on that of the evapotranspiration and runoff, particularly at high latitudes, and (2) pronounced heavy isotope enrichment in runoff, which is a function of fractionation during evaporation and the runoff ratio (the ratio of runoff to precipitation).

18.3 Large Scale Isotopic Patterns

18.3.1 Sources and Generation of Runoff

A limited number of traditional, basin-scale isotope hydrology studies have explicitly considered the spatial variation in precipitation isotope ratios (e.g., McGuire et al. 2005). At these scales, the primary spatial signal of interest is variation in precipitation

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isotopic composition with elevation, which must be considered in hydrograph separation studies that attempt to quantify the contribution of storm event water to runoff, in that the isotopic composition of storm water may vary significantly throughout high-relief catchments. At the scale of major catchments to continents, these spatial patterns are often significant and are useful means to identify water source areas. Figure 18.3 illustrates a hypothetical example: the runoff weighted mean annual isotopic composition is shown for a 30' gridded stream network (Vörösmarty et al. 2000) in the Yenisei basin, Mongolia and Siberia. Isotopically heavier runoff originating from the mid-latitude headwaters is transported downriver through the main channel, and maintains a characteristically different isotopic composition from the surrounding lower-order streams that more closely reflect the isotopic composition of local precipitation.

River water and tap water datasets from the contiguous U.S.A. illustrate the potential for water isotopes to be used as an indicator of runoff sources (Dutton et al. 2005; Bowen et al. 2007b). Both studies show that meteoric waters across large, high-relief areas of the western U.S.A. tend to be ^2H - and ^{18}O -depleted relative to local precipitation due to the altitude effect on the isotopic composition of high-elevation precipitation contributing to runoff. Unambiguous identification and

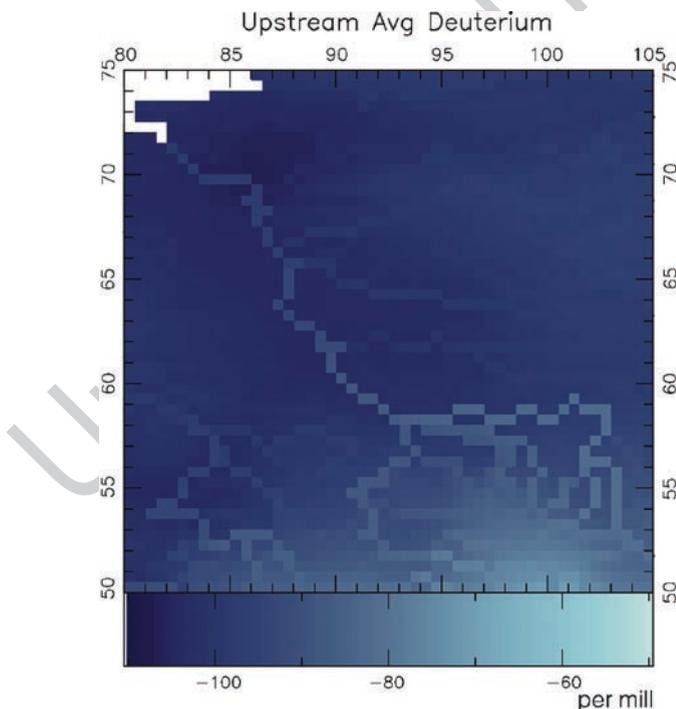


Fig. 18.3 Average, runoff weighted hydrogen isotopic composition of the precipitation in the Yenisei basin in Mongolia and Siberia, propagated down a river network derived from a 30' digital elevation model

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quantification of these effects is only possible for watersheds and continental areas when both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are applied together to identify isotope effects of evaporation.

An additional factor that may contribute to the observed pattern is the selective (e.g., seasonally-biased) generation of runoff. The influence of this effect on large-scale isotopic patterns can be observed in the Fekete et al. (2006) simulations, where contrary to the theory presented above the isotopic composition of evapotranspired water in some snow-dominated regions is predicted to be isotopically heavier than annual average precipitation whereas the excess water (that forms surface runoff and groundwater recharge) is lighter (Fig. 18.2). Winter precipitation is more depleted than summer precipitation due to the greater degree of rainout between relatively warm ocean vapor source regions and cool wintertime continents, supplemented by enhanced equilibrium fractionation at lower temperature (Eq. 18.10). This heavy-isotope depleted precipitation is more prone to form excess water, due to the lower evaporation rates in winter time, therefore the excess water weighted mean annual isotopic composition of the surface runoff and groundwater recharge forming water surplus carries more of the winter precipitation signal than the summer precipitation that tends to evaporate more. In addition to its significance for understanding seasonal water balance, this process of selective excess water generation also has implications for hydrograph separation in that the isotopic composition of groundwater will gravitate towards the mean precipitation value weighted by the temporally varying runoff ratio.

18.3.2 *Evaporative Processes*

Isotope ratios measured in surface waters have provided important information on evaporative processes and their impact on hydrological mass balance across a wide range of spatial scales. Among the unique and important potential contributions of isotopic data is their ability to partition evaporation (fractionating) and transpiration (non-fractionating) fluxes and their capacity to quantify evaporative loss in ungauged areas.

Gibson and Edwards (2002) applied spatially distributed sampling of lake water isotope ratios to quantify land surface evaporation across a large region (275,000 km²) of northern Canada, illustrating systematic, spatial patterns in the ratios of evaporation to transpiration and evaporation to inflow. Within some parts of the study domain, as much as 60% of catchment-integrated precipitation was lost as evaporation, leading to substantial heavy-isotope enrichment in runoff. The larger-scale manifestation of this pattern is apparent in early data from the PARTNERs program, which show that river discharge in Arctic rivers deviates strongly from the Global Meteoric Water Line of Craig (1961), particularly for the North American rivers (Mackenzie and Yukon R.) draining catchments containing extensive lakes and wetlands. The comparative proximity to the GMWL of the four Eurasian rivers sampled (Ob', Yenisey, Lena and Kolyma, see Fig. 18.4) suggests more

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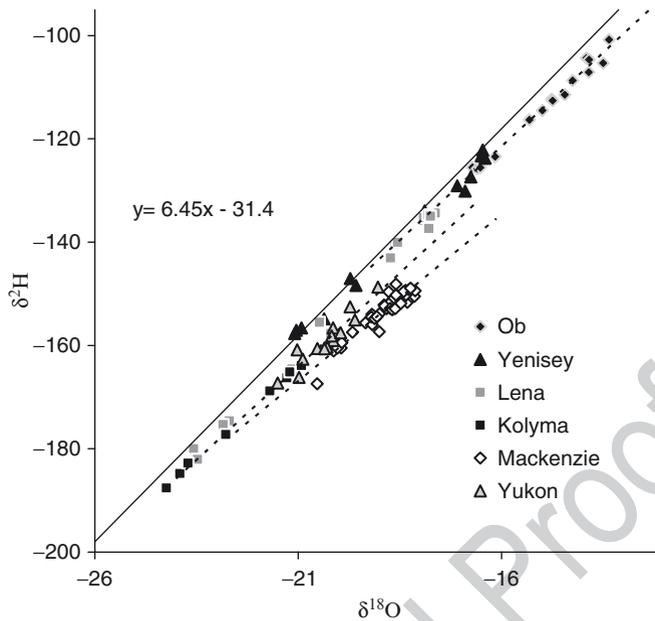


Fig. 18.4 $\delta^2\text{H}$ - $\delta^{18}\text{O}$ plot showing isotopic data for major Arctic flowing rivers collected during the PARTNERS study. *Solid line* is the Global Meteoric Water Line. *Dashed lines* represent best fit lines through individual river datasets. Slopes range from 6.5 to 8 reflecting mixing between evaporated and non-evaporated sources (Based on unpublished provisional data, <http://ecosystems.mbl.edu/partners/>)

limited wetland/lake sources, and potentially more atmospheric recycling of evapotranspired water crossing the Asian landmass relative to the North American rivers (Yukon and Mackenzie) where the distance to humid, saturated air masses at sea level is shorter. Drainage to the Arctic Ocean represents 10% of global runoff and therefore is a critical component of the global water budget, which may be better understood through continued isotopic monitoring (McClelland et al. 2008; Cooper et al. 2008).

In contrast to the Arctic flowing rivers, for which evaporative isotopic signals are strongly linked to wetland sources distributed widely across the watershed, some dryland rivers such as the Barwon-Darling River, Southeastern Australia display isotopic signals which are more consistent with evaporative enrichment of water from the river channel and floodplain itself (Fig. 18.5). Gibson et al. (2008a) described a technique for evaluating reach water balance using isotopic enrichment signals and applied it to the Barwon-Darling River dataset. Among the most interesting outcomes of this study is the development of a potential tool for characterizing the monthly dynamics of ungauged water losses and gains for individual river reaches based on a combination of physical and isotopic monitoring. Notably, ungauged inflows to upper, middle and lower reaches of the river, expressed as

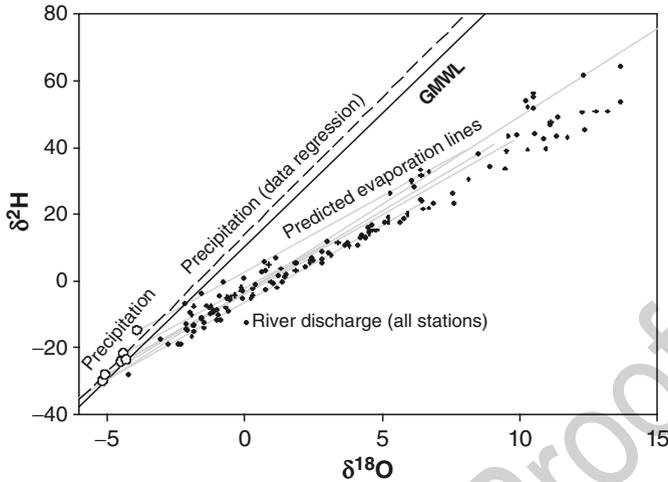


Fig. 18.5 $\delta^2\text{H}$ - $\delta^{18}\text{O}$ plots showing Barwon-Darling River discharge data at nine stations. Global Network for Isotopes in Precipitation (GNIP) annual data for Australian stations and a linear regression are shown in comparison to the Global Meteoric Water Line (GMWL). Predicted evaporation lines for GNIP input are simulated using an evaporation flux-weighting technique assuming an ideal precipitation-fed open-water reservoir as discussed in Gibson et al. (2008b). Agreement between data and modeled slopes close to 4 suggests dominance of evaporation by open-water rather than soil evaporation processes, the latter characterized by lower evaporation slopes

runoff ratios (Fig. 18.6), were found to be consistent and vary systematically in time within the expected range of between 0% and 10% of incident precipitation. Although requiring additional real-time isotopic data for operational use, the method demonstrated potential as a complimentary tool for detecting and quantifying water contributions and diversions, one that can be easily incorporated within existing water quality monitoring networks.

Strong deviations from the GMWL also characterize some surface and tap water samples from the U.S.A., although these effects are highly regionalized. The survey of Kendall and Coplen (2001) demonstrated both low deuterium excess values and temporal isotopic variation along evaporation lines for many rivers within the Rocky Mountain and western Great Plains regions. Given the diverse collection of rivers represented in the dataset, it is not clear the extent to which in-stream evaporation versus evaporation from natural lakes and reservoirs contributes to the observed patterns. Isotopic values of tap waters samples from the contiguous U.S.A., many of which were derived from surface water sources, reflect a similar pattern of variation in deuterium excess (Bowen et al. 2007b). Comparison of isotopic values (hydrogen and oxygen) and deuterium excess values with those of local precipitation suggest that some of the spatial structure in deuterium excess

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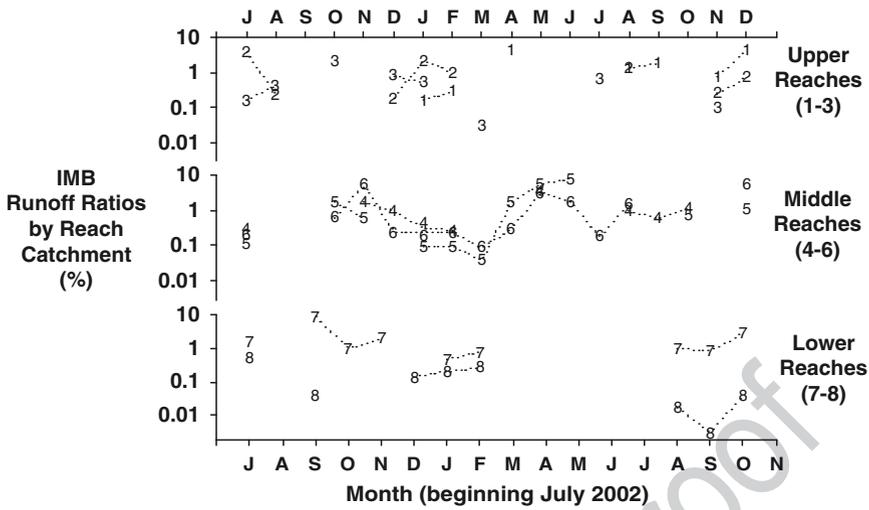


Fig. 18.6 Derived runoff ratios by month based on isotopic estimates of ungauged inflow over reach catchments along upper, middle and lower reaches of the Barwon-Darling River (Modified from Gibson et al. 2008b).

observed in U.S.A. tap and river waters is inherited directly from precipitation, but that particularly strong evaporative effects can be observed in the western Great Plains. The semiarid climate and relatively low relief of this region may contribute to relatively intense evaporation from surface water systems, reflected as strong evaporative enrichment of the heavy isotopes and deviation from the GMWL. Estimates of the fraction of catchment water lost as evaporation based on tap water data from reservoir-fed sites in central Texas and Oklahoma are as high as 45% (Bowen et al. 2007a). In addition to improved understanding of natural systems, quantification of the evaporative water flux in these human-managed systems provides information in support of planning and management decisions.

18.4 Concluding Remarks

As scientists contemplate the future of hydrology and potential for monitoring large river discharge from space (Alsdorf et al. 2003), there is still considerable insight to be gained in the present and future by improving ground-based observational networks to target many of the poorly understood interactions between the hydro-spheric, atmospheric, and biospheric cycles. Isotopic and geochemical measurement programs, such as the U.S. Geological Survey's National Stream Quality Accounting Network (Hirsch 2001), and IAEAs coordinated rivers project (Gibson et al. 2002; Vitvar et al. 2007), serve as more than an exercise in validation for

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land-atmosphere-ocean modeling, but rather as a resource of new information to understand the factors that contribute to water and biogeochemical variability. Some of the key processes controlling water, carbon, and nutrient cycling remain to be adequately understood for homogeneous landscapes, let alone for the complex melange of terrain types that typify regional and continental scales. Variations in contributions and interaction between various water sources such as surface water and groundwater, their contributions to flow in major rivers, the role of these interactions as biogeochemical regulation mechanisms, and partitioning of vapor losses by evaporation and transpiration, the latter being the quintessential link between the water and carbon cycles via photosynthesis, are examples of key mechanisms that are not routinely described from field-based data collected within current observational networks, nor are they readily discernible from today's remote sensing satellite observations. Fundamental characterization of integrated signal is nevertheless of paramount importance to understanding the global climate system.

Only 60% of runoff (Fekete et al. 2002; Bjerklie et al. 2003) from the continents is currently monitored, and some important regions such as the Pan-Arctic drainages have experienced widespread declines in hydrological monitoring, which have seriously limited the potential for study of global change impacts (Shiklomanov et al. 2002; Vörösmarty et al. 2002). The importance of modeling and prediction in ungauged basins is an obvious target for future analysis. But optimizing the array of parameters measured in field-based surveys is as important now as ever to develop an understanding of the response of the key hydrological processes to climate changes at the continental scale. The IAEA proto-network of large rivers will monitor drainage from approximately 23% of the land surface. Improved coverage through widespread integration of water quality and water quantity networks will be required to close the stable isotope balance of the continents with accuracy similar to the early climatological water balance studies of the early 1970s.

The success of large scale applications of stable isotopes in surface hydrology also hinges on adequate monitoring of the isotopic composition of precipitation. Whereas surface and subsurface waters act as integrator in hydrological processes, and are therefore ideal targets for point measurement (since the measurement is less sensitive to the density and the exact location of the sampling locations), monitoring of the isotopic composition of precipitation with "in-situ" observations is more challenging. In order for isotope hydrology to fulfill its promise in large scale applications, continued improvement in techniques for measuring precipitation isotopic composition and generating time-explicit precipitation isoscapes are needed. Recent advancements such as the use of the Tropospheric Emission Sensor (TES) on NASA's Aura satellite to estimate the deuterium contents of the atmospheric vapor (Worden et al. 2007; Helliker and Noone this volume), and improvements in isotope-enabled GCM simulations, including nudged simulations that replicate time-explicit isotope climate, (Noone and Sturm this volume) may in combination with surface-based monitoring networks (Aggarwal et al. this volume) and statistical data assimilation tools (Bowen this volume) fill critical data gaps and advance large scale isotope hydrology from an experimental research topic to an operational tool in monitoring the water cycle.

[AU2] **References**

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Author Queries

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Queries	Details Required	Author's Response
AU1	The citation 'Rozanski 1993' (original) has been changed to 'Rozanski et al., 1993'. Please check if appropriate.	
AU2	<p>Following references are not cited in text:</p> <p>Bennett KE, Gibson JJ, McEachern P. Water yield estimates for critical loadings assessment: comparisons of gauging methods vs. an isotopic approach. <i>Can J Fish Aquat Sci.</i> 2008;65:83-99.</p> <p>Coplen TB, Kendall C (2000) Stable hydrogen and oxygen isotope ratios for selected sites of the U.S. geological survey's NASQAN and benchmark surface-water networks.</p> <p>Henderson-Sellers A, McGuffie K, Noone D, Irannejad P. Using stable water isotopes to evaluate Basin-Scale Simulations of Surface Water Budgets. <i>J Hydrometeorol.</i> 2005;5: 805-22.</p> <p>Koster RD, de Valpine DP, Jouzel J. Continental water recycling and H218O concentrations. <i>Geophys Res Lett.</i> 1993;20(20):2215-8.</p>	
AU3	Please confirm the details inserted in Gat JR (1980), Gibson JJ, Edwards TWD (2002)	

Uncorrected Proof