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Application of isotope tracers in continental scale hydrological modeling

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Summary Isotope tracers are widely used to study hydrological processes in small catchments, but their use in continental-scale hydrological modeling has been limited. This paper describes the development of an isotope-enabled global water balance and transport model (iWBM/WTM) capable of simulating key hydrological processes and associated isotopic responses at the large scale. Simulations and comparisons of isotopic signals in precipitation and river discharge from available datasets, particularly the IAEA GNIP global precipitation climatology and the USGS river isotope dataset spanning the contiguous United States, as well as selected predictions of isotopic response in yet unmonitored areas illustrate the potential for isotopes to be applied as a diagnostic tool in water cycle model development. Various realistic and synthetic forcings of the global hydrologic and isotopic signals are discussed. The test runs demonstrate that the primary control on isotope composition of river discharge is the isotope composition of precipitation, with land surface characteristics and precipitation-amount having less impact. Despite limited availability of river isotope data at present, the application of realistic climatic and isotopic inputs in the model also provides a better understanding of the global distribution of isotopic variations in evapotranspiration and runoff, and reveals a plausible approach for constraining the partitioning of surface and subsurface runoff and the size and variability of the effective groundwater pool at the macro-scale.

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Introduction

Fractionation of the stable isotopes of water (^{18}O , ^2H) during phase changes and water cycle mixing produces a natural labelling effect that has been widely applied to local and regional-scale hydrological studies. In contrast to the case for small watershed studies, interpretation of isotopic signals arising from a complex overlay of hydrological processes at the large scale requires new model platforms for simulating isotopic fractionation, transport, and the mixing process. Water isotopes have previously been incorporated into global or regional climate models for simulating broad-scale features of isotope climatology, mainly for analysis of air mass/precipitation origin and paleoclimate archives of precipitation (Hoffman et al., 1998; Joussaume et al., 1984; Jouzel et al., 1987, 2000). Quantitative application of these heavy-isotope tracers and transferability of the approach is strengthened by the fact that the water isotopes are mass-conservative, incorporated within the water molecule ($\text{H}_2\ ^{18}\text{O}$, $^1\text{H}^2\text{H}^{16}\text{O}$), and are transported predictably but slightly differently than common water ($^1\text{H}_2\ ^{16}\text{O}$) among water phases, a property which can provide additional information on magnitude and the importance of water fluxes and pathways (Gibson et al., 2005).

Application of stable isotopes in large- (continental-) scale hydrological studies has lagged behind the small scale applications primarily due to the lack of a systematic collection of global-scale data. Long-standing efforts of the International Atomic Energy Agency (IAEA) – to coordinate a global monitoring network for deuterium (^2H) and oxygen-18 (^{18}O) in precipitation and more recently in large river discharge – will continue to provide new opportunities to utilize isotope information at the continental scale. To date, IAEA collects monthly precipitation data at over 550 stations worldwide, beginning as early as the 1960s as part of IAEA/WMOs Global Network for Isotopes in Precipitation (GNIP). This has permitted compilation of a global monthly climatology of ^2H and ^{18}O in precipitation (Birks et al., 2002). A similar effort to coordinate collection and analysis of monthly river discharge samples from large river basins is likewise under development (Gibson et al., 2002). Recent studies have also demonstrated integration of stable water isotopes into meso-scale hydrological models for specific basins or regions (Stadnyk et al., 2005; Henderson-Sellers et al., 2005).

The present paper demonstrates a global-scale application of an isotope-enabled hydrological model. We describe an approach used to modify a well-tested water balance model developed by researchers at the University of New Hampshire (Vörösmarty et al., 1998, 1996) to include a basic representation of isotope fractionation in evapotranspiration processes and isotopic mixing through all components of the terrestrial hydrological cycle. Primary forcing of the model is accomplished with the global monthly precipitation climatology for ^2H and ^{18}O developed from the IAEA precipitation observations (Birks et al., 2002), and validated for the contiguous United States using river data compiled by the US Geological Survey (Kendall and Coplen, 2001). Long-term average monthly climate data are also used to estimate interception/evaporation and transpiration, soil moisture change and runoff and to predict the isotopic com-

position of these elements of the hydrological cycle. The aim is to map and interpret some of the major spatial patterns associated with isotope fractionation during evaporation and runoff generation. The model is also tested with synthetic forcings, which help to better understand the sensitivity of the model to the parameterization of fractionation and mixing processes. Overall, through these baseline comparisons, we establish the potential value of an isotope-enabled global hydrology model as a tool for improving understanding of the relative significance of hydrological processes and to create a more realistic representation of these processes in the model.

Methods

We focus here on stable isotopes of hydrogen (^2H) and oxygen (^{18}O) that are naturally present in water molecules. Stable isotope compositions are expressed conventionally as delta values (δ), representing deviation in per mille (‰) from the isotopic composition of a specified standard (R_{ref}), such that

$$\delta = \frac{R}{R_{\text{ref}}} - 1 \quad (1)$$

where R values refer to $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ in sample and standard, respectively. The universal standard in water cycle applications is Vienna Standard Mean Ocean Water (V-SMOW) distributed by IAEA, which is the approximate isotopic composition of the present-day oceans, and has $\delta\ ^2\text{H}$ and $\delta\ ^{18}\text{O}$ values of 0 ‰ (Craig, 1961; Edwards et al., 2004). We treat the deviation (δ) values like conservative constituent concentrations.

The isotopic composition in precipitation shows clear seasonal cycles and spatial variations (Birks et al., 2002). This spatially and temporally varying signal of isotopic composition is altered through hydrological cycle via enrichment or depletion during water phase changes and mixing in various storage pools in vertical and horizontal water transport processes. A description of how each of these component processes is represented in the model and how the isotope response is simulated is described below. For a more general discussion of stable isotopes in the hydrological cycle the reader is referred to Gat (1996).

Isotopic transformations in hydrological processes

The water balance/transport model (WBM/WTM) (Vörösmarty et al., 1998, 1996, 1991) is designed to simulate the key hydrological processes at large scales operating at a monthly time step. The water balance model quantifies the vertical exchange of water between the soil/vegetation and the atmosphere. Water in excess of evaporations while passing through various storage pools follows two runoff pathways. Surface runoff immediately enters the river network, while recharge passes through the groundwater pool, which controls the subsurface flow to the organized river channels. The water transport model simulates the horizontal transport via a predefined channel network and a corresponding riverbed geometry that determines the residency time. Changes of the isotopic characteristics through the hydrological processes are the

result of isotope enrichment/depletion during phase changes (primarily evaporation) and mixing in the various storage pools (e.g. snow pack, soil moisture, ground water, river channel). These are detailed below.

Snow pack

The forms of precipitation as snow and rain are distinguished by considering mean monthly temperature. Precipitation falling in months when the mean temperature was below a threshold of -1°C is assumed to be snow, otherwise it is deemed to be rain. The snow accumulates during each month when the mean monthly air temperature is below this threshold. The entire accumulated snowpack then melts when the mean monthly temperature is above the 1°C threshold and the local elevation is <500 m above sea level. In mountainous regions (elevation >500 m) half of the snow pack melts in the first non-freezing month and the rest is released in the following month. The snowmelt is treated as water surplus from evapotranspirations discussed in the following section that either contributes to surface flow or recharges the groundwater.

Since this treatment of the snow accumulation and melting processes is rather simplistic, and the time steps are coarse, the simulation of the processes affecting the isotopic characteristics are limited to simple mixing without any fractionation/selection of the heavy isotopes as observed by Taylor et al. (2002) and others. In any case, these effects are expected to be short-lived and largely indiscernible at monthly time-steps. The simulations treat the snow pack (S_{sp}) as a mixing pool that collects snow precipitation (P_{sn}) during the freezing season. The isotopic composition change of the snow pack ($d\delta_{sp}/dt$) is defined as:

$$\frac{d\delta_{sp}}{dt} = \frac{P_{sn}(\delta_{pc} - \delta_{sp})}{P_{sn} + S_{sp}} \quad (2)$$

where δ_{pc} and δ_{sp} are the isotopic compositions of the precipitation and the snow pack, respectively. The accumulated snow pack (S_{sp}) with its isotopic composition (δ_{sp}) is then released during snowmelt as snow recharge ($S_{sr} = -dS_{sp}/dt$) and then runs off or enters the soil and groundwater pool.

Recent revisions of the WBM (Rawlins et al., 2003) added refined snow accumulation/snow melt and freeze/thaw dynamics and daily time steps. In the future, this permafrost version (P-WBM) of the water balance model will be used to implement more realistic simulations of the changes in the isotopic composition during freeze/thaw and snow accumulation processes. This version of the model will also be used to investigate the importance of snow fractionation on the global scale.

Soil moisture

From an isotopic perspective, soil moisture serves as another storage pool that mixes water over time. We assume that all the incoming water (precipitation and snow melt) mixes with the soil moisture before forming either direct surface runoff or groundwater recharge. The total amount of water mixed (W_{tl}) over in time ($t, t + dt$) is the sum of the precipitation as rain ($P_{rn}dt$), the snow melt and snow recharge ($S_{sr}dt$) and the soil moisture (S_{sm}):

$$W_{tl} = P_{rn}dt + S_{sr}dt + S_{sm} \quad (3)$$

The isotopic composition of this mixture (δ_{mx}) can be expressed as:

$$\delta_{mx} = \frac{\delta_{pc}P_{rn}dt + \delta_{sn}S_{sr}dt + \delta_{sm}S_{sm}}{W_{tl}} \quad (4)$$

where δ_{sm} is the isotopic ratio of the soil moisture. The total mixed water (W_{tl}) is available for evapotranspiration (E_{tot}), the sum ($r = r_d + r_g$) of direct surface runoff (r_d) and groundwater recharge (r_g), and soil moisture change (dS_{sm}/dt) that can be expressed as the classical (Thorntwaite, 1948) water balance equation:

$$P + S_{sr} = E_{tot} + r + \frac{dS_{sm}}{dt} \quad (5)$$

During evaporation, the heavier isotope molecules tend to stay in liquid phase, resulting in isotope depletion of the evaporated vapor, and isotope enrichment of the soil moisture and the excess water that forms direct runoff and groundwater recharge. This fractionation process affects only evaporation (i.e. evaporation from open water, soil or interception) and does not affect transpiration (biotically mediated vapour loss) as explained by Gat (1996). The water balance model can be configured with a variety of PET functions ranging from simple temperature based to complex cover dependent ones such as the Shuttleworth and Wallace (1985) also discussed by Federer et al. (1996) method that was used for this study. The Shuttleworth–Wallace method estimates the evaporation from soil and leaves (interception) and transpiration through plants separately. The potential evaporation (as the sum of evaporation and transpiration) was scaled down to total evapotranspiration by keeping the ratio of evaporation and transpiration constant. Evaporation from soil and leaves (E) was treated as isotopically fractionating and transpiration (E_T) as non-fractionating. The total evapotranspiration ($E_{tot} = E + E_T$) is the sum of the fractionating evaporation and the non-fractionating transpiration. The fractionating evaporation goes through a Rayleigh process:

$$\delta = (1 + \delta_0)f^\epsilon - 1 \quad (6)$$

where δ_0 is the initial isotopic composition of the evaporating water mixture (δ_{mx}), f is the ratio of the evaporating water volume and the total fractionating water mix ($f = E/W_{tl}$), ϵ is the isotope fractionation and δ is the isotopic composition of the remaining water ($W_{tl} - E$).

The isotope fractionation ($\epsilon = \epsilon_{V/L} + \epsilon_{diff}$) is a sum of the equilibrium fractionation ($\epsilon_{V/L}$) and the kinetic (diffusive transport) fractionation (ϵ_{diff}). The equilibrium fractionation is given by Majoube (1971) as:

$$\epsilon_{vl} = e^{c_0 + \frac{c_1}{T} + \frac{c_2}{T^2}} - 1 \quad (7)$$

where c_0 , c_1 , c_2 are coefficients and T is the air temperature (in K). The kinetic fractionation is (Gat, 1996):

$$\epsilon_{diff} = (1 - h_N) \left(1 - \frac{\rho_i}{\rho} \right) \quad (8)$$

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

Groundwater

The WBM maintains a simple runoff detention pool (δ_{gw}) to represent the runoff delay due to groundwater storage. The detention pool dynamics are expressed by the following differential equation:

$$\frac{dS_{\text{gw}}}{dt} = (1 - \gamma)r - \beta S_{\text{gw}} \quad (9)$$

where r is the groundwater recharge from Eq. (5), γ and β are empirical constants. The river runoff (r_r) then becomes:

$$r_r = \gamma r + \beta S_{\text{gw}} \quad (10)$$

The isotope composition of the groundwater (δ_{gw}) undergoes mixing similar to the snow pack and the soil moisture pools (Eqs. (2) and (4)) and takes the following form:

$$\frac{d\delta_{\text{gw}}}{dt} = \frac{(1 - \gamma)r(\delta_{\text{ro}} - \delta_{\text{gw}})}{(1 - \gamma)r + S_{\text{gw}}} \quad (11)$$

Water transport

The runoff released from the groundwater pool is propagated along a predefined 30' (longitude \times latitude) simulated network (Vörösmarty et al., 2000a,b) using a simple routing scheme. The routing model considers temporally uniform but spatially varying flow velocity to calculate residence time in each grid cell. The velocity field is computed using empirical relationships relating mean annual discharge to riverbed and flow characteristics (Bjerklie et al., 2003; Osterkamp et al., 1982), where the mean annual discharge is estimated for each grid cell by summing up the mean annual runoff upstream for each cell. The residence time calculated from the flow velocity is used to delay the transport of the runoff generated in individual grid cells along the predefined gridded network. The spatially varying but temporally uniform velocity (that ranged between 0.1 m/s and 5 m/s and averaged 0.7 m/s globally) was assigned to each STN30 gridcell based on mean annual discharge and local slope derived from GTOPO30 digital elevation (Gesch et al., 1999) applying hydraulic considerations (Bjerklie et al., 2003). The simple routing scheme has been demonstrated to be sufficient for monthly flow simulation (Vörösmarty et al., 1996, 1991) and can be applied easily to constituent transport as well (Green et al., 2004). Routing of water is considered to be a non-fractionating process, involving only quantitative mixing of heavy isotope content in admixed water.

Input data

The water balance simulations require forcing by climatic data (such as air temperature, precipitation, vapor pressure and wind speed) and land surface characterization (land-use, soil properties, elevation). Besides the water balance model inputs, the modeling of the isotopes requires a description of the spatial and temporal distribution of isotopes in the precipitation. All the simulations in the present study were performed at monthly time steps, using climatological (long term mean) input forcings (Fekete et al., 2002, 2004).

Climate forcings

The gridded mean monthly climate forcings (for air temperature, precipitation, vapor pressure, wind speed, solar radi-

ation) derived from meteorological station records at 30' (longitude \times latitude) resolution were available for the 1901–2000 period (New et al., 2000, 1999). In the present study, we used the climatologically averaged monthly means for the 1960–2000 period that corresponded the isotope records in IAEA's Global Network of Isotopes in Precipitation (GNIP) database.

Land-surface characterization

Land cover classification from Melillo et al. (Melillo et al., 1993) was converted to eight broad cover classes (conifer forest, broadleaf forest, grassland, savannah, cultivation, tundra, desert and open water) that were found to have characteristically different properties in evapotranspiration processes (Federer et al., 2003, 1996). Soil textures (differentiating seven classes: lithosol, coarse, medium, fine, coarse + medium, coarse + Fine, medium + fine, coarse + medium + fine) were from FAO/UNESCO (1986). The water balance model assigns uniform soil properties such as porosity, wilting point, field capacity from a lookup table to the individual soil texture. The rooting depth is assigned through a similar lookup table that combines the eight land-use categories with the seven soil texture types (Vörösmarty et al., 1998). Gridded elevation at 30' resolution was derived from GTOPO30 global 30" (30" \sim 1 km) resolution digital elevation model (Gesch et al., 1999).

Isotopes in precipitation

Gridded monthly climatology of the isotopic composition of precipitation at 2.5° (longitude \times latitude) resolution was obtained from Birks et al. (2002). This data set was developed from the Global Network of Isotopes in Precipitation (GNIP) database assembled by the International Atomic Energy Agency (IAEA) and contains over 100,000 measurements collected at 550 stations worldwide. These measurements do not necessarily represent complete time series records with regular observations, but an "ad hoc" sample of the isotopic composition of the precipitation in space and time. Fig. 1 shows the minimum and maximum monthly values from GNIP. The isotopic composition has clear spatial and temporal patterns. The precipitation is highly depleted isotopically at the high latitudes (exceeding -300% deuterium and -40% oxygen-18 depletion), while it remains more similar to the reference ocean water (Vienna Standard Mean Ocean Water, VSMOW) in the tropics. The ranges of the isotopic composition also show higher seasonal variation at the high latitudes than the low latitudes.

Validation data

As the IAEA global river program is in its early stages, widespread isotope data for world rivers is not yet publicly available. Therefore, we set out to validate the isotope-enabled water balance/transport model (iWBM/WTM) against isotope data from a fairly extensive national survey conducted during the 1980s across the contiguous United States (Kendall and Coplen, 2001). This data set is the most complete compilation of deuterium and oxygen-18 composition of river water currently available. Similar to the precipitation data used to produce the gridded isotopic composition fields of precipitation, the river isotope records can be described as being derived from "ad hoc" sampling rather than regular

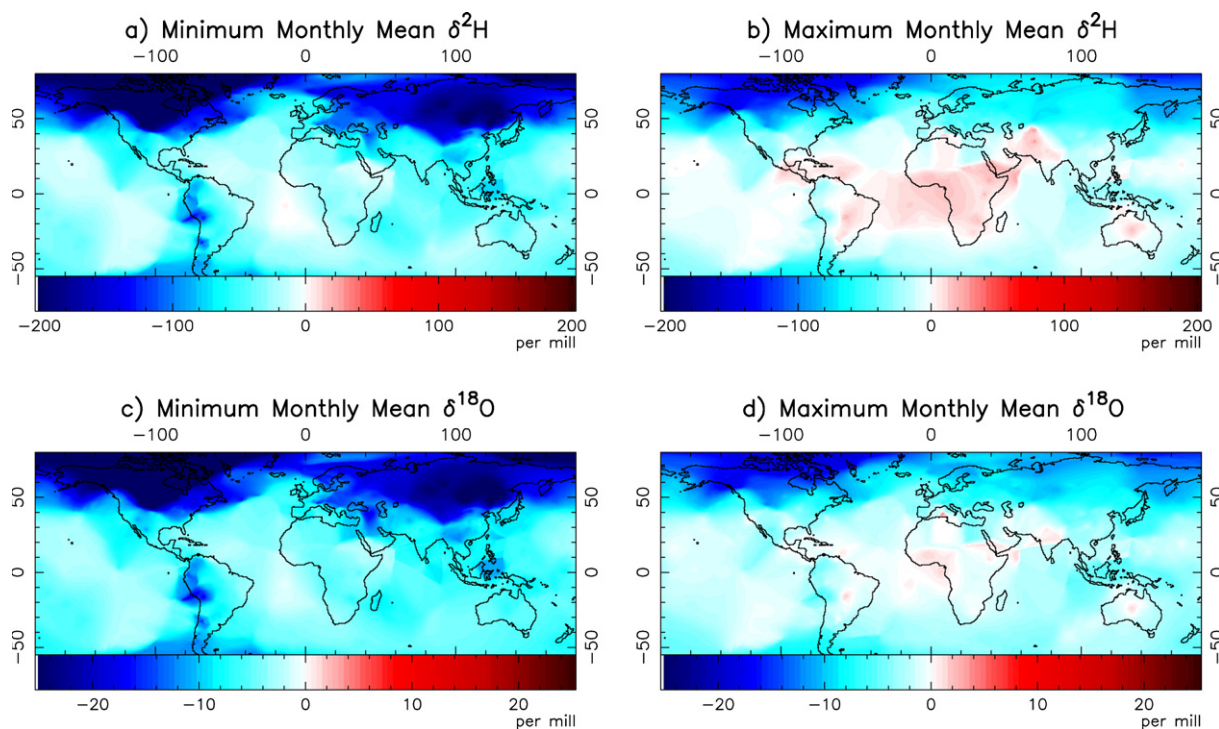


Figure 1 Minimum and maximum values of monthly oxygen-18 and deuterium composition of the precipitation from GNIP.

observation series for most sites. The rationale for this sampling strategy is described in Hooper et al. (2001).

Results

The iWBM was initially run at selected test locations to gain an appreciation for the fractionation and mixing processes at the point scale and to test if the model represents those processes realistically. The point scale testing was followed by application of the iWBM/WTM globally in the context of a 30' resolution simulated river network, which was validated against observed isotope compositions of river water with the United States from USGS stations.

Point scale testing

Point scale tests were performed at five selected locations (San Juan, *Puerto Rico*; Lake Charles, *Louisiana*; Madison, *Wisconsin*; Seattle-Tacoma, *Washington*; Fairbanks, *Alaska*) that were used in previous studies for evaluating different water balance model implementations with varying complexity (Federer et al., 2003, 1996). The five test sites represent characteristically different climate regimes. iWBM was first tested with isotopically uniform (VSMOW, $\delta^2\text{H} = 0.0\text{‰}$) deuterium composition in precipitation (Fig. 2). The model is generally consistent in simulating a significant heavy-isotope enrichment in groundwater recharge and a less significant, though present, heavy-isotope depletion in evapotranspiration on an annual basis. The peak summer evapotranspiration–precipitation and groundwater-precipitation separations are greater for Fairbanks (high-latitude site) than for the other low-latitude sites. Although the magnitude of the predicted monthly ground-

water-precipitation separations is high, the volume of water contributed to groundwater recharge is negligible for Fairbanks, and small or negligible for substantial periods during the summer in most locations except San Juan. Generally, in mid-summer, the monthly evapotranspiration is predicted to be enriched relative to the precipitation inputs, especially when monthly evapotranspiration is greater than precipitation, which may suggest contributions to evapotranspiration from isotopically enriched soil moisture. When the model is run with isotopically varying precipitation (sampled from the gridded GNIP at the test locations, third column in Fig. 2) it shows similar patterns (enriched groundwater recharge and depleted evapotranspiration). The "enriched" evapotranspiration appears to be an indicator of precipitation deficit (when the evapotranspiration is partly occurring from previously enriched soil moisture). Otherwise, the isotopic composition regime of the evapotranspiration and groundwater recharge follows the isotopic variation of the precipitation. The isotopic enrichment of groundwater recharge (which is the surplus from the surface water balance calculation) in mid-summer at Seattle-Tacoma and Fairbanks may seem to be too high and it is probably due to the lack of interaction between the groundwater and the vadose zone. In other words, when the excess water as a residual from evapotranspiration is small, the apparent enrichment will be high that is normally homogenized rapidly with in situ water storage.

Groundwater storage results in dampening of the isotopic variation of the groundwater recharge (the surplus water from the water balance calculation). Fig. 3 shows the monthly dynamics of the groundwater recharge, the storage, and the runoff leaving the groundwater pool and the simulated deuterium compositions. The groundwater storage size has a greater effect on the isotopic composition

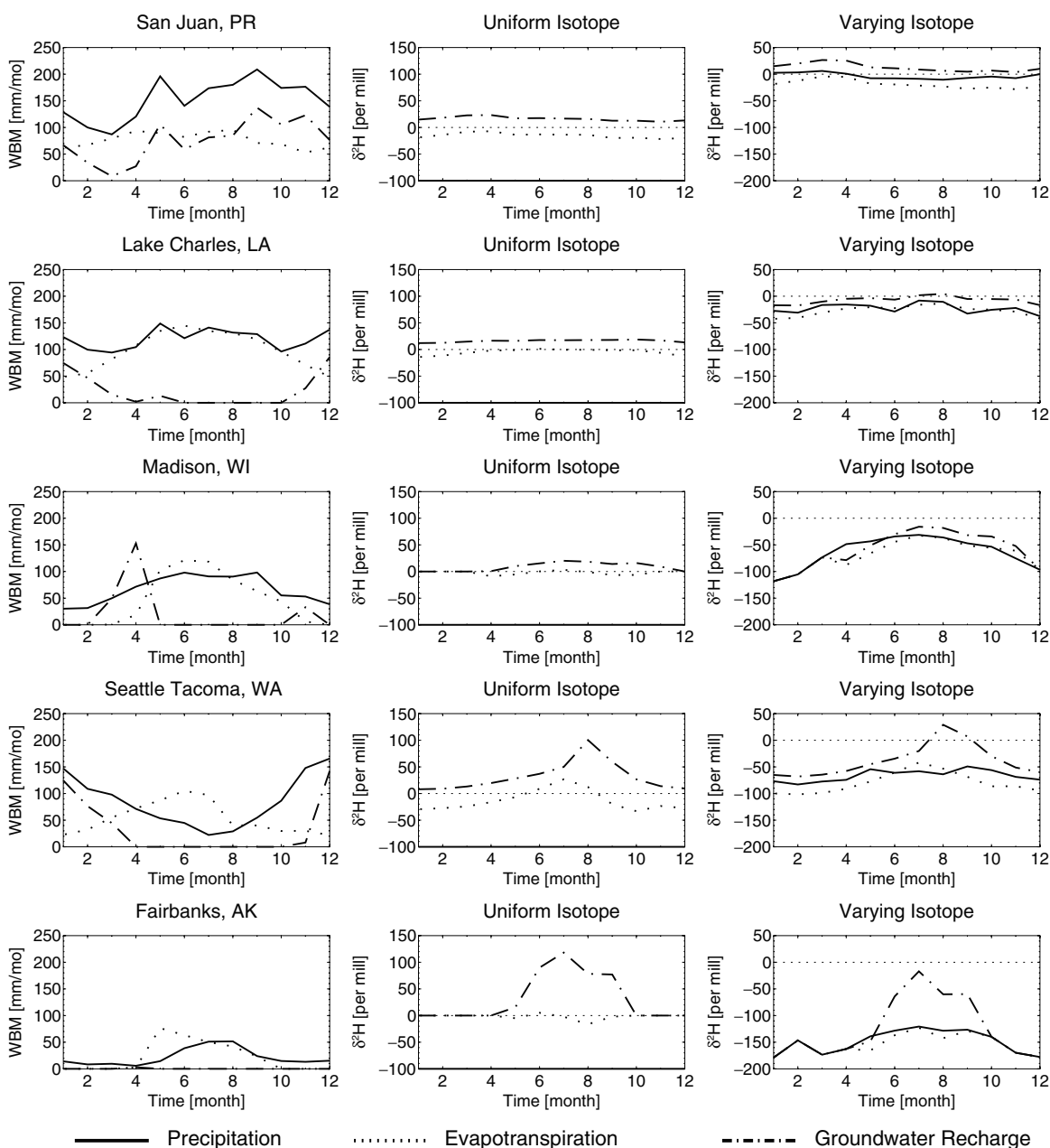


Figure 2 Isotope-enabled water balance results at selected test sites. The first column shows the monthly regimes of input precipitation, estimated evapotranspiration and groundwater recharge. The second column summarizes the isotopic composition of the same three water balance components using isotopically uniform (VSMOW) precipitation. The third column shows the simulated isotopic composition under isotopically varying precipitation input (from GNIP).

of the runoff than the runoff regime itself. An order of magnitude change in the groundwater release coefficient (β) from Eqs. (10) and (11) has little impact on the runoff signal (i.e. the runoff regime largely follows the groundwater recharge), but increases significantly the groundwater storage. The increased groundwater storage has a major impact on the isotopic composition of the runoff. Although further point-scale testing of the model is required to assess the validity and realism of the model under a wider range of conditions, the isotope composition of runoff therefore appears to be a sensitive indicator of the effective groundwater storage size. This is an important, yet poorly constrained

parameter influencing many water resources issues such as water quality and sustainability of groundwater development on a continental scale, and therefore should be an important target of future modeling efforts.

Global application

Following testing of the iWBM at the point scale we applied it globally in the context of the global 30' gridded river network (Vörösmarty et al., 2000a,b). The model was run with spatially and temporally uniform deuterium composition (VSMOW, $\delta = 0.0\text{‰}$) and uniform land characteristics to

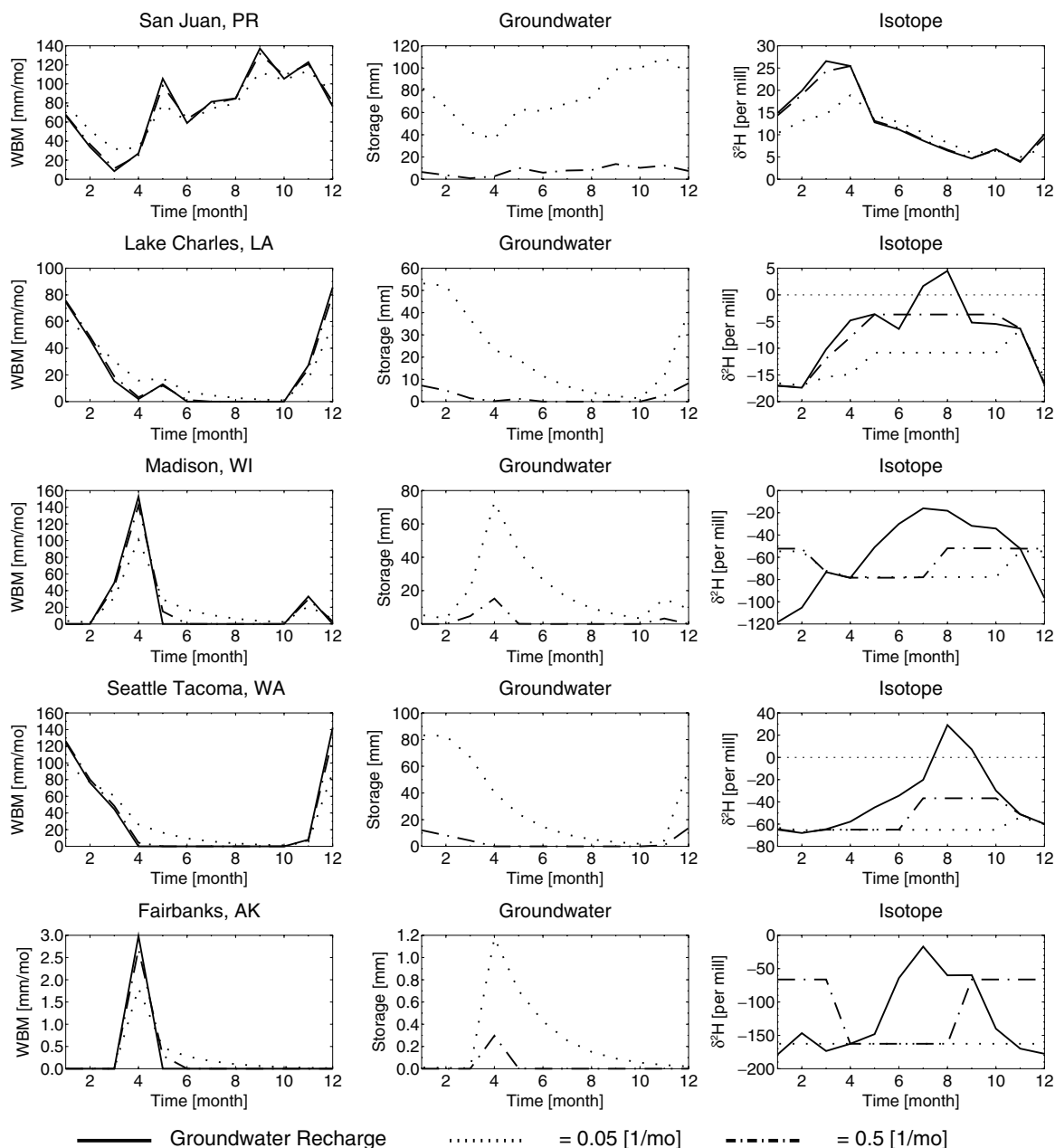


Figure 3 Impact of groundwater parameterization on the isotopic composition of the runoff. The figure shows the monthly dynamics of the runoff leaving the groundwater pool, the groundwater storage and isotopic composition of the runoff using different values of β (0.5 mo^{-1} and 0.05 mo^{-1}) in Eqs. (10) and (11). The change in the β coefficient appears to have little impact on the runoff regime leaving the groundwater pool but has dramatic impact on the groundwater pool size and as a consequence on the isotopic composition of the runoff.

assess the impact of the latter on the isotopic compositions of evapotranspiration and runoff. Finally, iWBM/WTM was applied with spatially and temporally varying precipitation input and spatially varying land cover properties to simulate a more realistic global pattern of atmosphere forcing and land surface characteristics. These tests are described below.

Impact of land cover characteristics

The model sensitivity to land cover properties was tested by simulating spatially and temporally varying climate inputs

with constant isotope concentrations in precipitation while carrying out five model runs with uniform land cover characteristics, i.e. broadleaf forest, conifer forest, grassland, tundra and desert as if the whole world had a single cover type that received precipitation with uniform VSMOW (i.e. $\delta = 0.0\text{‰}$) isotopic composition. Tall canopies such as conifer and broadleaf forests showed higher fractionation. The average deuterium compositions for these covers globally were found to be -6.2‰ for evapotranspiration (suggesting significant effect of evaporation during interception) and 21.3‰ in runoff. Because isotopes in precipitation are held

constant in these runs, such values closely reflect the mean isotopic separation of each component from monthly precipitation. Short canopies such as grassland and tundra appear to result in less fractionation, i.e. $\delta^2\text{H} = -3.6\text{‰}$, respectively, for evapotranspiration 11.1‰, respectively, for runoff. The magnitude of these values is substantially linked to the current formulation of the fractionation due to evaporation, particularly the interception loss and canopy storage.

Globally, systematic patterns are found in the range in mean annual deuterium composition of the evapotranspiration and runoff using the different uniform coverages (Fig. 4). These maps, which provide insight into the sensitivity of the vapour fractionation and runoff processes to the land surface scheme, show that some areas are likely to be more sensitive than others, and thus show a higher range in ^2H (Fig. 4). Land cover appears to be a weak factor in controlling fractionation potential by evapotranspiration across much of the southern continents (apart from moderate impact in the Amazon) and is a strong factor in far northern areas of Siberia, Tibet, the Canadian Arctic and Alaska. Regions, where the runoff ratio is high (i.e. where a significant portion of the precipitation forms runoff due to either high precipitation like in the tropics or low evapotranspiration in the Arctic) appear to be most sensitive in terms of fractionation potential during runoff.

Applying isotopically varying precipitation

The iWBM was then tested with natural, varying vegetation cover initially using the spatially and temporally uniform precipitation (VSMOW, $\delta = 0.0\text{‰}$) and against the use of GNIP isotope precipitation climatology. This test permitted evaluation of the contrast between changes in isotopic composition due to fractionation in the hydrological cycle and spatial variations in the isotopic composition of precipitation itself (Fig. 5). The left panels in Fig. 5 illustrate the uniform simulations, and essentially convey the isotopic separation between evapotranspiration and precipitation (Fig. 5a) and runoff and precipitation (Fig. 5c), respectively. The isotopic fractionation appears to be a weak signal compared to the spatial variation of the isotopic composition of the input precipitation. Therefore, the isotopic signal of both evapotranspiration and runoff remains largely determined by the local precipitation that is altered by depletion

in evapotranspiration and enriched in runoff. Besides fractionation, selective utilization of water during the growing season for evapotranspiration as discussed by Gat (2000) appears to be just as important process. Runoff not only appears to be enriched in the heavy isotopes compared to precipitation, particularly in regions with subdued seasonality, which is attributed mainly to the residual water effect, i.e. enrichment of runoff as a consequence of evaporation losses, but also to a lesser extent by seasonal selection in some regions (e.g. when annual runoff is mostly generated from depleted winter precipitation).

The dominant features of the isotopic variability predicted globally in evaporation and runoff (right panels, Fig. 5) appear to closely resemble precipitation input along with the imprint of some of the stronger regional signals of isotopic fractionation during evaporation. The left panels in Fig. 5a, c showing the isotopic compositions of evapotranspiration and runoff with varying land cover conditions assuming uniform (VSMOW) input seem to bear a relatively weak signal compared to the natural simulation when both land cover and isotopic composition varies.

Fig. 6, which compares the volume weighted mean annual isotopic composition of precipitation with evapotranspiration and runoff, is included to illustrate the impact of seasonal selections in the runoff generation processes. In most regions, both the evapotranspiration and runoff shows expected behavior in terms of isotopic depletion in evapotranspiration (blue shades) and enrichment in runoff (red shades). However, there is an apparent inconsistency (virtual "enrichment" in evapotranspiration and "depletion" in runoff) in some regions. This is due to the differences in the timing of the isotopic variations in the precipitation and the runoff regime. In temperate regions, the majority of runoff is generated during the winter season. In other words, the runoff generation efficiency (the fraction of the precipitation that forms runoff) is higher during the cold seasons. On the other hand, the isotopic composition of the precipitation tends to be depleted during the cold seasons compared to the annual average, while the summer precipitation that mostly evaporates is typically heavier than the annual average. Since, the annual runoff is selectively generated from the lighter winter precipitation the mean annual composition of the runoff appears to be lighter than the annual precipitation. The evapotranspirations (that

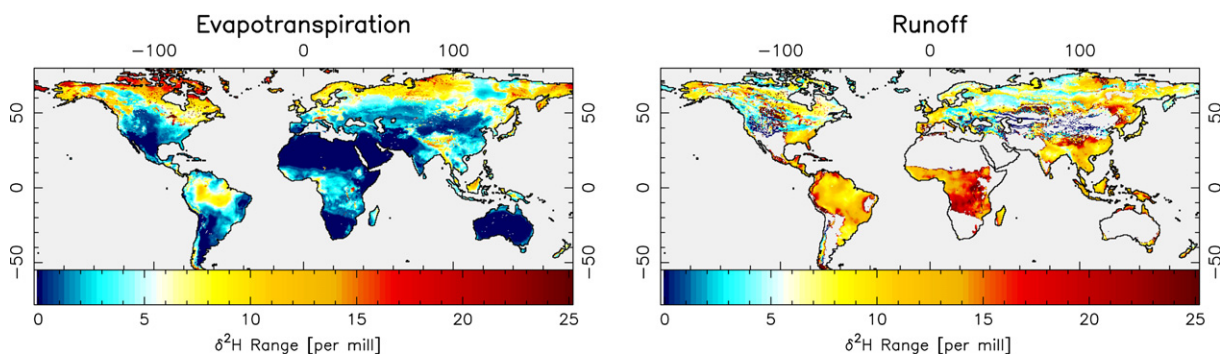


Figure 4 Impact of land characterization on the fractionation potential. This model run applied climate inputs from CRU with isotopically uniform (VSMOW) precipitation over uniform land cover (conifer, broadleaf, grassland, tundra and desert). The figure shows the range (the difference between the maximum and minimum deuterium composition) from the different simulations. The fractionation potential is higher in the wet regions, where substantial portion of the precipitation forms runoff.

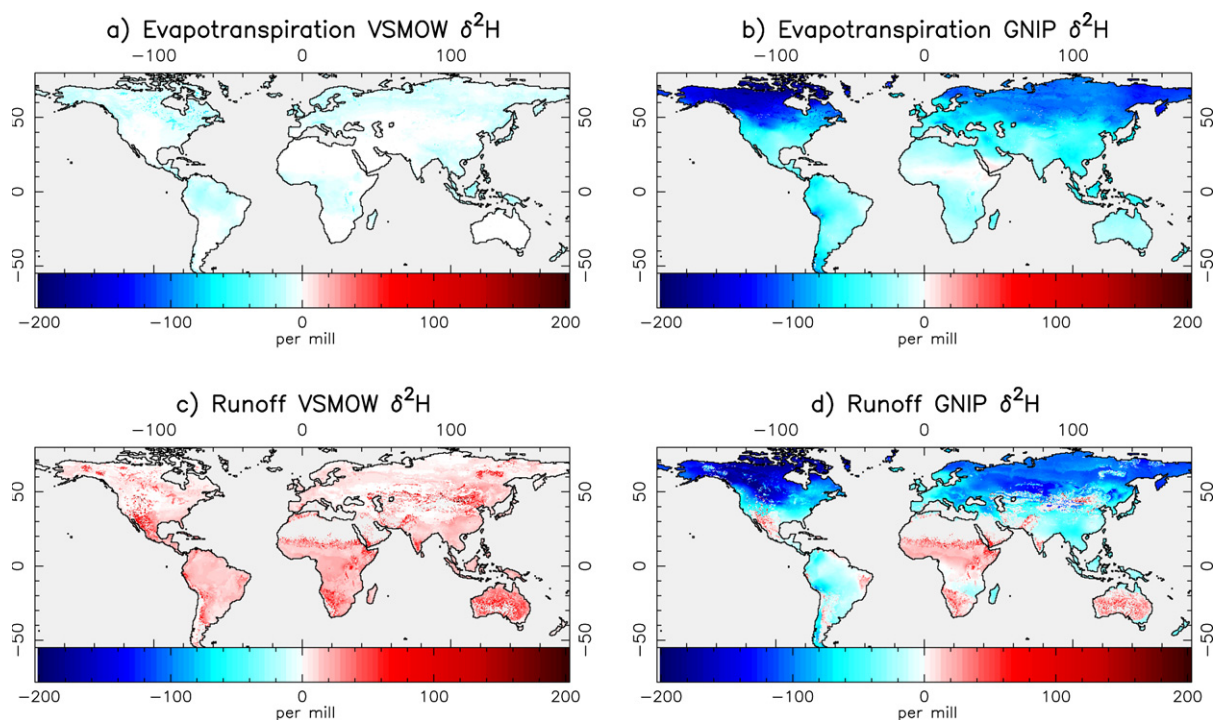


Figure 5 Global simulations of iWBM. Shown are the isotopic composition of evapotranspiration using: (a) constant V-SMOW precipitation (b) GNIP precipitation climatology, and runoff (c) constant V-SMOW precipitation and (d) GNIP precipitation climatology. The left panels illustrate synthetically modeled 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.

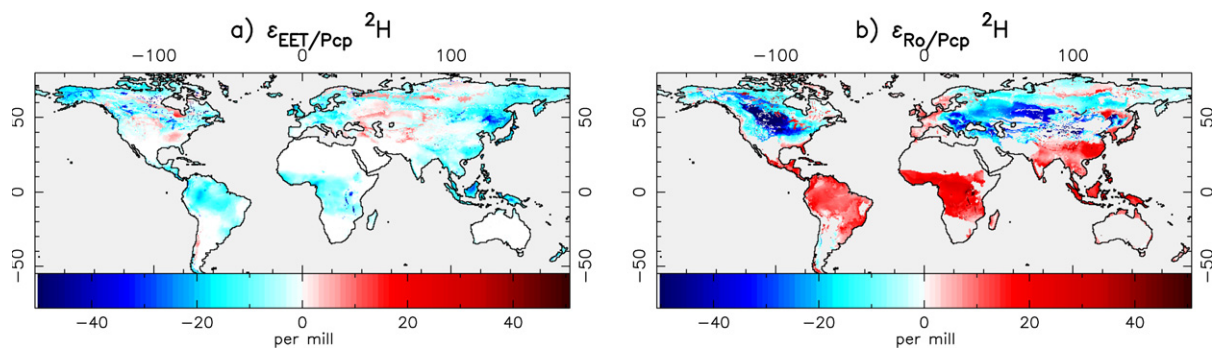


Figure 6 Estimated mean annual ratios: (a) $\epsilon_{EET/Pcp}^{2H}$ and (b) $\epsilon_{Ro/Pcp}^{2H}$ the isotopic composition of the precipitation.

occurred mostly during the warm seasons from enriched precipitation) is heavier than the annual precipitation average.

Model validation

The iWBM/WTM outputs were compared to river isotopic composition data for the United States (Kendall and Coplen, 2001). It is important to acknowledge when comparing this dataset with the GNIP precipitation climatology that measurements were not made over equivalent periods, although a general sense of systematic similarities and differences in isotopic composition of precipitation and runoff can still be identified. For these simulations, runoff calculated from the

vertical water balance is routed through a 30' gridded network using spatially varying but temporally-constant monthly flow velocity (described in the water transport section). The isotopic composition of runoff was treated like a conservative constituent and routed along with the runoff to estimate the isotopic composition of river discharge. Before comparing the model results to observed isotopic compositions we performed a series of simple back of the envelope calculations to better understand the consistency between GNIP precipitation and USGS runoff.

The impact of isotopic variations in precipitation over the catchment of the monitoring sites are demonstrated in Fig. 7a. The local (at gridcell values, where the USGS monitoring sites are located) isotopic composition of the

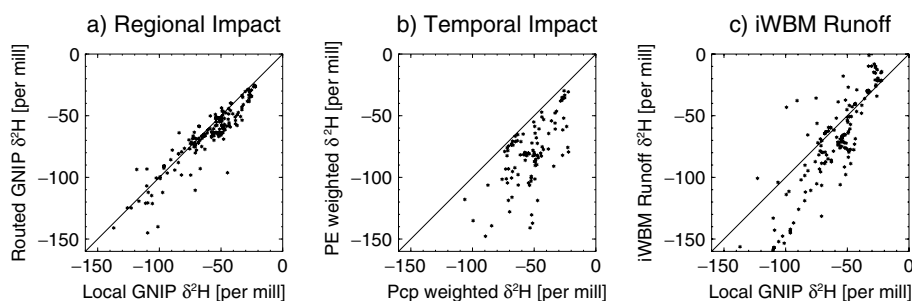


Figure 7 Preliminary analysis of isotopic inputs. Panel (a) demonstrates the difference between local precipitation and runoff weighted average upstream within the catchment of the monitoring site. Panel (b) shows the comparison of precipitation and precipitation minus evapotranspiration ($P-E$) weighted annual average of the monthly GNIP values at the USGS isotope monitoring sites. Panel (c) compares the local precipitation weighed annual average GNIP to runoff weighted average isotopic composition of the simulated local runoff.

precipitation is compared to runoff weighted average over the catchment upstream (defined by the 30' gridded network). Traditional application of stable isotopes (in small river basins) tend to neglect the isotopic variation of the precipitation within the river catchments. However, most of the USGS runoff samples are also from smaller basins (hence the good correspondence between local and spatially integrated isotopic compositions) but the few outliers representing larger basins clearly shows that the impact of spatial differences in the input precipitation can be significant at larger scales.

We compared mean annual isotopic composition at the USGS sites weighting with precipitation and with the residual of the precipitation after evaporation ($P-E$). Fig. 7b shows the (grid cell value) comparison of precipitation and $P-E$ weighted averages at the USGS monitoring sites. The $P-E$ weighted average is always more depleted than the precipitation weighted average. The $P-E$ weighted average can be viewed as the potential isotopic composition of the runoff without evaporational enrichment. The $P-E$ weighted isotopic composition is always lower than the precipitation weighted because the isotopically depleted precipitation corresponds to lower temperature when evapotranspiration is more limited, leaving larger portion of the precipitation to recharge storage pools (snow pack, soil and groundwater) and/or form runoff. This finding is consistent with the widely recognized notion that base flow (which isotopically tends to represent the long term average of the recharging runoff) is always more depleted than the local precipitation.

Fig. 7c shows the combined effect of isotopic fractionation and selective runoff generation on the local water balance by contrasting the isotopic composition of the local precipitation against the isotopic composition of the mean annual runoff simulated by iWBM in the local grid cell. While the isotopic fractionation always causes enrichments in runoff, the selective runoff generation acts in the other direction causing apparent isotopic depletion. The fractionating enrichment is stronger in the less depleted (warmer) regions, therefore the upward shift is more pronounced when the precipitation input is more enriched. In those regions, the fractionating enrichment can overcompensate the virtual depletion due to selective runoff generation, so the isotopic composition of the runoff becomes more enriched than the precipitation (points over the one-to-one line on Fig. 7c).

After the preliminary analysis, we compared δ -values of both the local and catchment integrated average precipitation and the iWBM/WTM simulated runoff to the USGS runoff (Fig. 8). Fig. 8a compares the isotopic composition of the runoff at the USGS sites to the local isotopic composition of the precipitation. Apparently, the runoff in the warmer regions with less depleted ($0-50\text{‰}$) δ -value follows more closely the isotopic composition of the local precipitation than in colder, therefore more depleted, regions. When the isotopic composition of the USGS runoff is below the -50‰ δ -values, the precipitation is often more enriched than the runoff. Besides the possibilities of data inconsistencies between GNIP and USGS data, the most likely explanation is the effect of selective runoff generation discussed

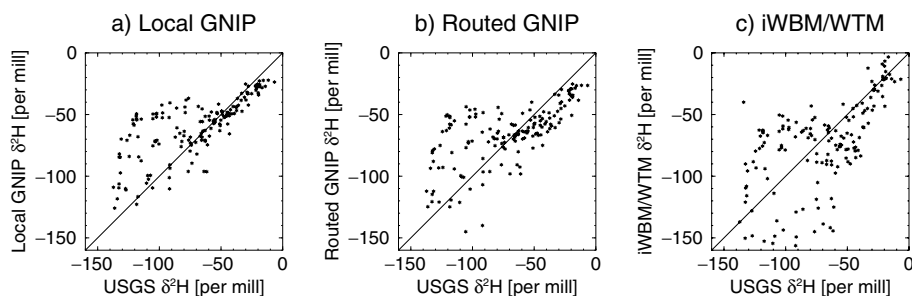


Figure 8 Comparing USGS runoff isotope data: (a) local GNIP precipitation, (b) runoff weighted average over the tributary of the monitoring sites and (c) iWBM/WTM simulated isotopic composition of the river discharge.

earlier. Interestingly, the correspondence between isotopic composition of the runoff and the precipitation is weaker when the USGS runoff is compared to runoff weighted average of the precipitation within the contributing area of the monitor sites (Fig. 8b). One possible explanation is that the USGS data tends to represent the local runoff more than the entire catchment upstream. Further explanation might be that the tighter fit in Fig. 8a is actually the result of counteracting impacts of fractionation (enriching the runoff) and selective runoff generation (from more depleted precipitation).

Model predictions of the isotope composition of annual river discharge across the contiguous United States are compared with observations in Fig. 8c. This figure broadly supports the previous assertion that the isotopic composition of the discharge is largely dominated by the precipitation input. In general, the model predictions are found to be fairly consistent with the observed values for regions with $\delta^2\text{H}$ values in the range of -50 to 0‰ . The bulbous deviation from the 1:1 line below -50‰ appears to be a deficiency of the current iWBM/WTM configuration in colder regions. Fig. 9 reveals a spatial pattern suggesting an explanation. iWBM/WTM simulated isotopic composition is more depleted than the observed values in the upper Mississippi regions while more enriched at higher elevations in Western regions. A possible explanation to this spatially consistent deviation is the partitioning of the snowmelt into surface and subsurface flow. In the upper Mississippi region, iWBM/WTM forms too much surface runoff from snow melt instead of recharging the groundwater pool and allowing the vegetation to draw from the groundwater to transpire larger portions of the depleted winter precipitation. The opposite effect occurs in the Western regions, where too little portions of the snow melt is released as surface runoff, which makes the depleted winter precipitation available for evaporation. In other words, the selective runoff generation in the current configuration of iWBM/WTM is too selective in the upper Mississippi region and not selective enough in the Rocky Mountains.

Overall, the results indicate that the vertical water budget solution estimated using the iWBM/WTM is fairly effective at predicting runoff amounts on monthly or annual time-steps. However, as it is currently configured, the mod-

el storages and fluxes are not effectively capturing and reproducing the isotopic response of the system, at least not in seasonal climates, where isotope differentiation among water cycle components is most pronounced, and, where isotope composition of discharge is more depleted than about -50‰ in ^2H .

Concluding remarks

This paper provides a description of the basic approach required to incorporate isotopes into a well-known continental-scale water cycle model, the University of New Hampshire's WBM/WTM. The paper has illustrated some of the basic strengths and shortcomings of this and similar models. In general, the model is extremely effective at reproducing global-scale variations in runoff amounts (Vörösmarty et al., 1998; Fekete et al., 2004, 2002). The model performs better when the precipitation is moderately (0 – 50‰) depleted. The poorer isotopic reproducibility of more depleted settings is probably partly due to data inconsistencies (GNIP precipitation and USGS runoff). The model obtains the correct mean annual isotopic compositions without capturing the structure of internal storages (the subsurface pools in particular). Groundwater storage and fluxes are often and rightfully neglected in large-scale hydrological modeling simulating runoff since they have little impact on the large scale water fluxes and cannot be validated by considering observed discharge only. Stable isotopes have the potential to provide much needed validation data necessary to make improvements in the representation of these subsurface storages and their runoff generating mechanisms.

While it is clear that the model is potentially valuable for global-scale hydrologic applications, it certainly needs further refinement and validation. Both the partitioning mechanism for representing fractionating and non-fractionating vapour loss and calculation of the fractionation effect itself needs improvement. Beyond partitioning evaporation and transpiration, these enhancements should include separate representations of soil evaporation and canopy interception, the latter coupled to a partial re-evaporation and throughfall mechanism. Fractionation during snowmelt, which would delay the release of heavy isotopes from the

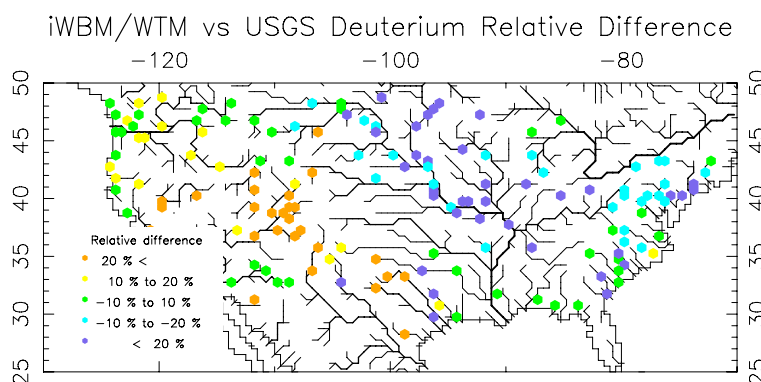


Figure 9 USGS runoff isotope monitoring stations. The stations are colored by the relative difference between iWBM/WTM simulated isotopic composition in river discharge vs. USGS monitored record. Blue and cyan colored stations represent underestimation of the isotopic composition (points under the one-to-one line of Fig. 8c) while yellow and brown point represent over estimates (points over the one-to-one line of Fig. 8c).

snowpack, could also be important at shorter time steps. Both the groundwater component and the horizontal water transport requires improved calibration and the incorporation of lakes and reservoirs (Dynesius and Nilsson, 1994; Vörösmarty et al., 1997) should be considered as additional storage pools that could buffer seasonal isotopic variations and lead to an overall enrichment of heavy isotopes in discharge. The implementation of the listed processes will increase the model complexity that is often difficult to validate. Stable isotopes represent an additional constrain that have different sensitivity to hydrological processes than runoff, therefore they can provide valuable validation data for more complex models.

The overall realism of the global isotope simulations is expected to improve if more detailed models with more realistic internal architecture are used to resolve the vertical water budget (Henderson-Sellers et al., 2005; Braud et al., 2005). An array of such models is currently being tested as part of iPILPS (Isotopes in Project for Intercomparison of Land-surface Parameterization), a contribution to GLASS (Global Land Atmosphere System Study) coordinated by the World Climate Research Program under the auspices of the Global Energy and Water Cycle Experiment (GEWEX). Coupled with global runoff routing schemes, such models could improve the ability to simulate global isotopic responses. Despite the apparent limitations of the model at present, this study will serve as a baseline comparison for future model development efforts. Importantly, this work has also identified an important target for future modeling efforts, the global characterization of groundwater pool sizes and recharge/discharge dynamics, which is a quantity that has been difficult to estimate using non-isotopic techniques.

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