HYDROLOGICAL PROCESSES
Hydrol. Process. **15**, 1363–1393 (2001)
DOI: 10.1002/hyp.217

Distribution of oxygen-18 and deuterium in river waters across the United States

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Abstract:

Reconstruction of continental palaeoclimate and palaeohydrology is currently hampered by limited information about isotopic patterns in the modern hydrologic cycle. To remedy this situation and to provide baseline data for other isotope hydrology studies, more than 4800, depth- and width-integrated, stream samples from 391 selected sites within the USGS National Stream Quality Accounting Network (NASQAN) and Hydrologic Benchmark Network (HBN) were analysed for $\delta^{18}O$ and $\delta^{2}H$ (http://water.usgs.gov/pubs/ofr/ofr00-160/pdf/ofr00-160.pdf). Each site was sampled bimonthly or quarterly for 2·5 to 3 years between 1984 and 1987. The ability of this dataset to serve as a proxy for the isotopic composition of modern precipitation in the USA is supported by the excellent agreement between the river dataset and the isotopic compositions of adjacent precipitation monitoring sites, the strong spatial coherence of the distributions of $\delta^{18}O$ and $\delta^{2}H$, the good correlations of the isotopic compositions with climatic parameters, and the good agreement between the 'national' meteoric water line (MWL) generated from unweighted analyses of samples from the 48 contiguous states of $\delta^{2}H = 8{\cdot}11\delta^{18}O + 8{\cdot}99$ ($r^2 = 0{\cdot}98$) and the unweighted global MWL of sites from the Global Network for Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency and the World Meteorological Organization (WMO) of $\delta^{2}H = 8{\cdot}17\delta^{18}O + 10{\cdot}35$.

The national MWL is composed of water samples that arise in diverse local conditions where the local meteoric water lines (LMWLs) usually have much lower slopes. Adjacent sites often have similar LMWLs, allowing the datasets to be combined into regional MWLs. The slopes of regional MWLs probably reflect the humidity of the local air mass, which imparts a distinctive evaporative isotopic signature to rainfall and hence to stream samples. Deuterium excess values range from 6 to 15‰ in the eastern half of the USA, along the northwest coast and on the Colorado Plateau. In the rest of the USA, these values range from −2 to 6‰, with strong spatial correlations with regional aridity. The river samples have successfully integrated the spatial variability in the meteorological cycle and provide the best available dataset on the spatial distributions of $\delta^{18}O$ and $\delta^{2}H$ values of meteoric waters in the USA.

KEY WORDS rivers; USA; stable isotopes; oxygen-18; deuterium; deuterium excess

INTRODUCTION

Reconnaissance hydrogen isotope measurements of waters from across the United States demonstrated the profound effects of geography, especially the distance inland and elevation, on the isotopic compositions of precipitation and streamwater (Friedman *et al*., 1964). Similar studies on several continents have established that natural spatial distributions of the oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) isotopic compositions of precipitation over continental areas are primarily a function of the fraction of water remaining in the air mass as it moves inland over topographic features (Dansgaard, 1964; Gat, 1980). The $\delta^{18}O$ and $\delta^{2}H$ of precipitation are also influenced by temperature, altitude, distance inland along different stormtracks, environmental conditions at the source of the vapour, latitude, and humidity. In general, the δ values are higher (more positive) in the summer and lower (more negative) in the winter, and decrease with increasing altitude because of seasonal temperature differences.

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Received 18 September 2000
Accepted 30 September 2000

The only long-term regional network for collection and analysis of precipitation for δ^2H and $\delta^{18}O$ in the USA (and world) is the Global Network for Isotopes in Precipitation (GNIP) established by a collaboration between the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). GNIP maintained 12 stations in the continental USA in the 1960s and 1970s, where bulk rain samples were collected monthly for varying numbers of years, and average values were reported (IAEA, 1992). Other than this network, there is no long-term monitoring of the stable isotopic composition of rain, groundwater, or river water on a regional scale in the USA. The recent discovery that changes in the $\delta^{18}O$ of precipitation over mid and high latitude regions during the past three decades closely followed changes in surface air temperature (Rozanski *et al*., 1992) has increased the interest in revitalizing GNIP, sites where precipitation will be collected and analysed for isotopic composition.

Until now, perhaps the most detailed map of the hydrogen isotopic compositions of natural waters in North America was compiled by Sheppard *et al*. (1969). This map is based largely on stream samples collected during baseflow by Friedman *et al*. (1964), but also contains one-time 'grab' samples of rain and groundwater from various sites. Despite the limited data available for the map, it shows very prominent spatial distributions in δ^2H across the USA. Although many isotope hydrologists would agree that such maps should be constructed from long-term annual averages of precipitation compositions, there are some advantages of stream samples as indicators of precipitation compositions. First, stream samples are relatively easy to obtain by taking advantage of existing long-term river monitoring networks. Second, stream water is a better spatial and temporal integrator of the isotopic composition of precipitation intercepted by a large drainage basin than recent precipitation collected at a single location in the basin. Third, since groundwater is probably the dominant source of streamflow in most basins, the river provides information on the isotopic composition of waters that have infiltrated the soils to recharge the groundwater system. Finally, the remains of biota that lived in the soil, lakes, and streams that are used to reconstruct palaeohydrology and palaeoclimates record the integrated isotopic signal of recharge water, not the isotopic compositions of the precipitation.

Water in most rivers has two main components: (1) recent precipitation that has reached the river either by surface runoff, channel precipitation, or by rapid flow through the shallow subsurface flowpaths; and (2) groundwater. The relative contributions of these sources differ in each watershed or basin, and depend on the physical setting of the drainage basin (e.g. topography, soil type, depth to bedrock, vegetation, fractures, etc.), climatic parameters (e.g. precipitation amount, seasonal variations in precipitation, temperature, potential evapotranspiration, etc.), and human activities (e.g. dams, reservoirs, irrigation usages, clearing for agriculture, channel restructuring, etc.).

The $\delta^{18}O$ and δ^2H of rivers will reflect how the relative amounts of precipitation and groundwater vary with time, and how the isotopic compositions of the sources themselves change over time. Seasonal variations will be larger in streams where recent precipitation is the main source of flow, and smaller in streams where groundwater is the dominant source. As the basin size increases, the isotopic compositions of rivers are increasingly affected by subsequent alterations of the precipitation compositions by selective recharge and runoff, mixing with older groundwater and newer rain water, and by evaporation. (Gat and Tzur, 1967; Fritz, 1981; Gat, 1996). Local precipitation events are an important component of river water in the headwaters of large basins. For example, the average amount of new water in small forested watersheds during storms is about 40%, although during storms the percentage can be higher (Genereux and Hooper, 1998). In the lower reaches, local additions of precipitation can be of minor importance (Friedman *et al*., 1964; Salati *et al*., 1979), except during floods (Criss, 1999). For example, analysis of long-term tritium records for seven large (5000–75 000 km^2) drainage basins in the USA indicated that about $60 \pm 20\%$ of the river water was less than 1 year old (Michel, 1992). Frederickson and Criss (1999) showed that, for the 10 300 km^2 Meramac basin (MO), the recent rainwater contribution ranged from 50% during stream rises to 0% during baseflow.

The dual nature of river water (partly recent precipitation, partly groundwater) can be exploited for studying regional hydrology or climatology. Under favourable circumstances, knowledge of the isotopic compositions of the major water sources can be used to quantify the time-varying contributions of these sources to river water

(Sklash *et al*., 1976; Kendall and McDonnell, 1998). Alternatively, if the isotopic composition of baseflow is thought to be a good representation of mean annual precipitation (Fritz, 1981), then the $\delta^{18}O$ and $\delta^{2}H$ of rivers sampled during low flow can integrate the composition of rain over the drainage areas and be useful for assessing regional patterns in precipitation related to climate. A number of workers in North America have investigated meteorological processes largely on the basis of samples from small streams and shallow groundwater (e.g. Friedman *et al*., 1964; Brown *et al*., 1971; Hitchon and Krouse, 1972; Ingraham and Taylor, 1986, 1991; Yonge *et al*., 1989).

This paper contains $\delta^{18}O$ and $\delta^{2}H$ data on river samples collected at selected US Geological Survey (USGS) water-quality monitoring sites. The study utilizes river water to provide baseline data on the spatial distribution of $\delta^{18}O$ and $\delta^{2}H$ of meteoric waters for local hydrologic investigations and regional palaeoclimatic assessments, and it provides the foundation for future, more quantitative, evaluations of the relative contributions of recent precipitation and older groundwater in the rivers. The main objectives of the paper are to (1) describe the spatial and temporal variability in $\delta^{18}O$ and $\delta^{2}H$ of the rivers, (2) evaluate the correlations of the isotopic compositions with selected hydrologic, physiographic, and climatic parameters, (3) discuss the origin of the spatial distributions in $\delta^{18}O$ and $\delta^{2}H$, (4) compare the river isotopic data with available precipitation isotope data, and (5) discuss the validity of the spatial patterns of river samples as a proxy for precipitation and/or recharge compositions. Such fundamental information will be useful for many types of isotope hydrology study (Kendall and McDonnell, 1998; Coplen *et al*., 2000).

METHODS

Sampling network

More than 4800, depth- and width-integrated, stream-water samples from 391 selected sites (Figure 1a) in all 50 states and Puerto Rico were analysed for $\delta^{18}O$ and $\delta^{2}H$ (Coplen and Kendall, 2000). All the sites selected were part of the US Geological Survey's National Stream Quality Accounting Network (NASQAN) and Hydrologic Benchmark Network (HBN) water quality monitoring programs. These sites have been monitored for water quality for several decades to provide a representative picture of water quality conditions in the nation's rivers (Smith *et al*., 1987). Most of these NASQAN sites are no longer being monitored by the USGS; see Hooper *et al*. (2001) for a description of the current program. The Benchmark network is composed of 50–55, small, pristine watersheds that are expected to be little impacted by future human activities (Mast and Turk, 1999a, b; Clark *et al*., 2000; Mast and Clow, 2000); some of these are still being monitored for water chemistry. Basic hydrologic and climatic information of the NASQAN and HBN sites is available in Slack and Landwehr (1992) and Alexander *et al*. (1996). For the purposes of this paper, most of the discussion will focus on sites in the lower 48 states.

Stream-water samples from 339 selected NASQAN sites and all 52 of the then-extant Benchmark sites were collected bimonthly or quarterly (following the regular, fixed-time interval, sampling schedule for water-chemistry samples) for 2·5 to 3 years between 1984 and 1987. Samples were stored in 60 ml glass bottles with caps with conical plastic inserts and analysed for stable isotopic composition. The number of samples analysed from each station ranged from two to 35, with an average of 12 samples per site. Sample collection dates were distributed fairly evenly over the year, with 25% (±2%) of the samples collected each quarter of the year; hence, the potential for significant seasonal bias is probably small. NASQAN sites in small basins were preferentially selected; however, for completeness, some sites on major river systems were also included in the sampling program. Sizes of the drainage areas range from 6 km^2 to almost 3×10^6 km^2 (i.e. the Mississippi River at Arkansas City). The median drainage area is approximately 8000 km^2, which corresponds to a drainage basin of about 90 km on a side (about four times the size of the symbols in Figure 1a). About 93% of the sites have basin areas $<130\,000$ km^2.

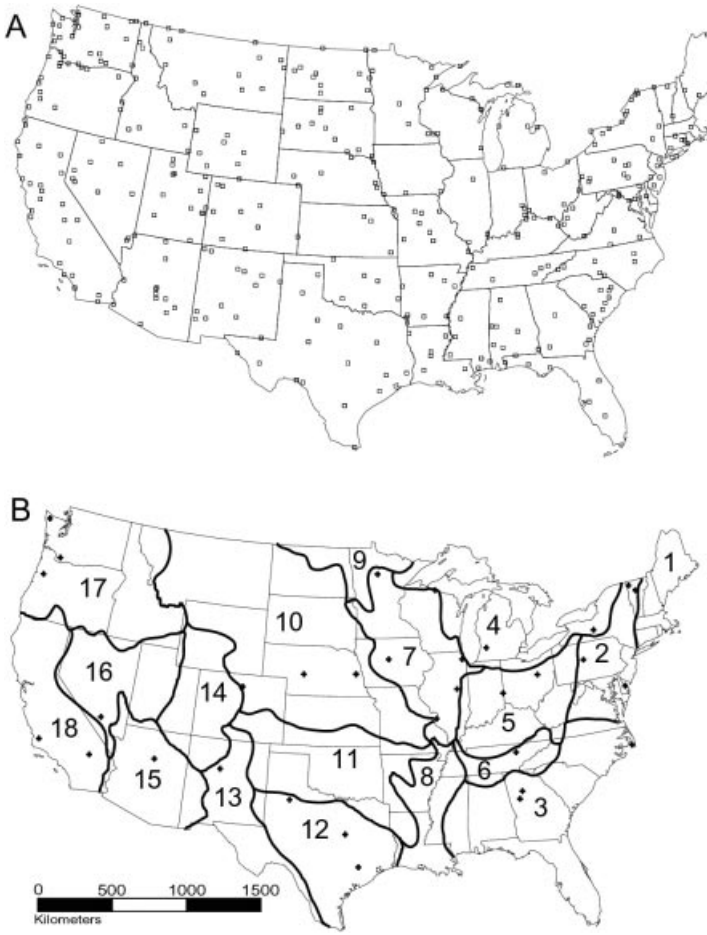

Figure 1. Index map showing (a) locations of the river sampling sites in the 48 contiguous states, and (b) locations of selected precipitation monitoring sites (isotope data from other studies). The locations of major drainage basins as defined by two-digit HUCs are indicated

Analytical methods

The $\delta^{18}O$ and $\delta^{2}H$ values are reported in per mil (‰) relative to VSMOW (Gonfiantini, 1978) on scales normalized to $\delta^{2}H$ and $\delta^{18}O$ values of SLAP reference water of -428‰ and $-55{\cdot}5$‰ respectively. All samples were analysed at least once for $\delta^{18}O$ using an automated version of the CO_2-H_2O equilibration technique of Epstein and Mayeda (1953), and two or more times for $\delta^{2}H$ by reduction of water with zinc (Kendall and Coplen, 1985). Analytical precisions (2σ) were better than $\pm 0{\cdot}2$‰ and $\pm 2{\cdot}0$‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively.

RESULTS

Averages and meteoric water lines

The $\delta^{18}O$ values of river waters ranged from $-25{\cdot}6$ to $+10{\cdot}4$‰. The $\delta^{2}H$ values ranged from $-198{\cdot}3$ to $+12{\cdot}4$‰. The entire dataset is given in Coplen and Kendall (2000). The dataset forms a flattened ellipse on a $\delta^{2}H-\delta^{18}O$ plot (Figure 2a). Note the asymmetry of the data points, with many points (mainly from Nevada and Montana) plotting below the ellipse. Most rivers with $\delta^{18}O$ values less than -20‰ are located in Alaska, Montana, and North Dakota, and most rivers with values greater than 0‰ are from Florida and Texas. Average

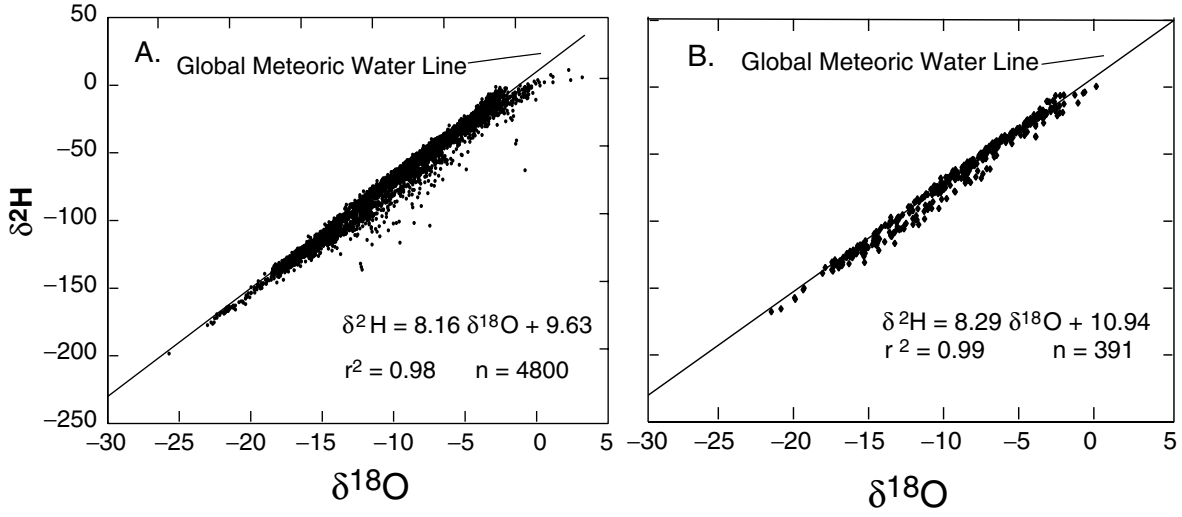

Figure 2. Relation between $\delta^{18}O$ and $\delta^{2}H$ values for (a) the entire dataset (4800 analyses) and (b) the arithmetic means for the 391 sites

$\delta^{18}O$ and $\delta^{2}H$ values for the sites in Hawaii are $-3{\cdot}2‰$ and $-10‰$ respectively; average values for Puerto Rico are $-3{\cdot}1‰$ and $-9‰$ respectively. The average values for each site produce a flatter ellipse (Figure 2b).

The 'national' meteoric water line (MWL) is the unweighted linear regression generated from these 4800 analyses: $\delta^{2}H = 8{\cdot}16\delta^{18}O + 9{\cdot}63$ ($r^2 = 0{\cdot}977$). The 'slope' of this local MWL (LMWL) equation is 8·16 and the 'intercept' or 'y-intercept' is 9·63. Perhaps this line should be called the 'river water line' or RWL, but we will retain the traditional usage because other kinds of non-precipitation samples (e.g. shallow groundwater and spring samples) are also used to define an LMWL. The MWL generated from the unweighted average values for the 391 sites is $\delta^{2}H = 8{\cdot}29\delta^{18}O + 10{\cdot}94$ ($r^2 = 0{\cdot}986$). The MWL for the unweighted analyses from the subset of 372 sites in the 48 contiguous states is $\delta^{2}H = 8{\cdot}11\delta^{18}O + 8{\cdot}99$ ($r^2 = 0{\cdot}975$). The slope of this equation is very similar to that of the 'unweighted' global MWL (GMWL) from GNIP sites of $\delta^{2}H = 8{\cdot}17\delta^{18}O + 10{\cdot}35$ (Rozanski *et al.*, 1993), and the intercept is 1·4‰ lower, less than the 2-σ analytical precision of $\delta^{2}H$ analysis.

The ellipse of data on Figure 2a is composed of many LMWLs for the individual stations. Equations of the LMWLs for the 391 sites are given in Coplen and Kendall (2000), along with $\delta^{2}H$–$\delta^{18}O$ plots of the individual datasets. The slopes of these LMWLs range from about -5 to $+13$, with an average of 6·1. Low slopes of LMWLs are commonly associated with low humidities and evaporation (Yurtsever and Gat, 1981). It might be expected that some of the anomalously low slopes were caused by making linear regressions of small datasets or ones where there was little seasonal variability. However, even when such sites (i.e. sites with less than six samples, less than 1‰ range in $\delta^{18}O$ values, and $r^2 < 0{\cdot}8$ for the LMWLs) were omitted from the calculation, the average slope of the remaining dataset is about 6. Hence, the low slopes are not artifacts of small datasets with limited variability, but are characteristics of the river datasets. Most of the sites where the $\delta^{2}H$–$\delta^{18}O$ slopes of the LMWLs are less than 5 are in the arid western states.

The *y*-intercepts of the LMWLs are, in general, substantially lower than $+10‰$, the value for the GMWL. The average intercept value of the LMWLs of the 391 sites is $-9{\cdot}3‰$. However, many sites show so little variability in $\delta^{18}O$ that fitting lines through the data may not provide useful information about the actual LMWLs of precipitation. For the 80% of the sites that had ranges of $\delta^{18}O > 1‰$ and slopes greater than 4, intercepts range from -55 to $+26‰$, with an average of $-7{\cdot}1‰$.

Many of the LMWLs of adjacent sites within some states or regions appeared to have similar slopes and intercepts, suggesting that the waters draining the basins have a similar origin. Although meteoric processes

are not affected by political boundaries, grouping the data by state provides a useful means for illustrating the observed similarities of LMWLs over regions roughly comparable in area to many western states. At a larger, multi-state level, the data can also be grouped by the regional (two-digit) USGS hydrologic unit code (HUC); the drainage basins defined by the HUCs are shown in Figure 1b. The slopes and intercepts for the LMWLs for states and HUCs are shown in Table I. For about 70% of the states and hydrologic units, the combined datasets define coherent regional MWLs with $r^2 > 0{\cdot}9$ (Table I). However, some states have sites with such heterogeneous $\delta^{18}O-\delta^2H$ relations (i.e. low r^2 values or low LMWL intercepts) that combining the data into a single equation is probably inappropriate (e.g. Nevada, Montana, and Wyoming). Because of the heterogeneous nature of these river data, the equations should not be viewed as representative of local precipitation without further evidence (e.g. groundwater or precipitation data).

Figure 3 shows the $\delta^{18}O$ and δ^2H values for selected states, chosen to reflect the range of compositions and LMWL slopes in the larger dataset. The figure includes the equations for the 'state' or 'regional' LMWLs derived from the samples collected from all sites within each state or region (e.g. data from western Oregon and Washington are combined, and data from North and South Dakota are combined). Note that the data from some regions (e.g. western Oregon and Washington, Alaska, North Carolina) show little scatter around the LMWL, whereas the data from other sites (e.g. Montana, Minnesota, North and South Dakota) show a wider range of values above and below the line.

The distribution of the state LMWLs around the GMWL can best be described as 'imbricate' (overlapping in sequence), and their lower slopes (below the GMWL) explain the asymmetry of the dataset observed in Figure 2a. The imbricate nature of the LMWLs for states is better shown in Figure 4a, where the data points are removed for clarity. The lengths of the LMWLs are fixed by the data used for the linear regressions.

Table I. Slopes and intercepts of the LMWLs for states and HUCs

State	LMWL		r^2	n	State	LMWL		r^2	n	HUC	LMWL		r^2	n
	slope	intercept				slope	intercept				slope	intercept		
AK	7·4	−5·6	0·93	95	NC	6·3	2·9	0·96	87	1	7·5	7·6	0·97	171
AL	5·3	−0·8	0·86	120	ND	6·8	−15·4	0·96	127	2	7·6	10·1	0·94	316
AR	6·3	1·1	0·93	104	NE	9·2	18·2	0·98	70	3	6·1	2·6	0·96	472
AZ	7·0	−5·1	0·87	146	NH	7·3	5·3	0·95	11	4	6·5	−3·9	0·94	328
CA	7·8	5·4	0·98	333	NJ	6·9	6·6	0·89	86	5	6·6	2·4	0·96	278
CO	6·3	−18·0	0·89	108	NM	6·7	−5·5	0·98	157	6	6·4	3·1	0·88	67
CT	6·5	0·7	0·94	48	NV	5·0	−37·7	0·70	126	7	7·6	5·1	0·95	133
FL	5·4	1·3	0·97	73	NY	6·5	−3·0	0·92	201	8	6·8	4·8	0·90	100
GA	5·5	0·5	0·89	83	OH	5·2	−8·2	0·73	82	9	6·8	−12·4	0·92	104
HI	7·3	13·2	0·77	107	OK	6·2	0·2	0·84	60	10	8·1	4·9	0·97	642
IA	9·3	18·8	0·98	52	OR	8·7	17·5	0·97	108	11	7·7	5·9	0·99	228
ID	7·9	6·6	0·90	106	PA	6·7	2·0	0·96	103	12	5·4	−2·5	0·82	115
IL	7·8	6·6	0·97	45	PR	6·0	8·2	0·76	20	13	7·3	−0·7	0·97	174
IN	5·9	−1·6	0·97	37	RI	5·5	−3·6	0·86	12	14	7·5	0·4	0·89	214
KS	8·4	10·9	0·95	30	SC	7·1	7·5	0·93	75	15	6·7	−7·7	0·81	194
KY	6·4	1·2	0·96	66	SD	7·1	−10·5	0·95	146	16	4·9	−42·2	0·78	207
LA	4·1	−3·6	0·82	24	TN	7·0	6·2	0·89	54	17	8·3	13·7	0·98	501
MA	5·5	−5·6	0·84	8	TX	7·5	2·3	0·91	215	18	7·8	5·5	0·97	334
MD	7·3	7·0	0·96	61	UT	6·7	−12·6	0·91	182	19	7·4	−5·6	0·93	95
ME	7·1	3·6	0·94	76	VA	6·7	4·3	0·97	53	20	7·3	13·2	0·77	107
MI	7·1	1·6	0·95	88	VT	6·5	−5·0	0·96	16	21	6·0	8·2	0·76	20
MN	5·7	−16·9	0·82	111	WA	8·5	15·5	0·99	240					
MO	8·8	14·0	0·98	116	WI	7·4	4·7	0·97	81					
MS	7·3	7·8	0·93	69	WV	6·4	−0·4	0·93	97					
MT	5·0	−46·5	0·82	164	WY	5·3	−39·2	0·95	121					

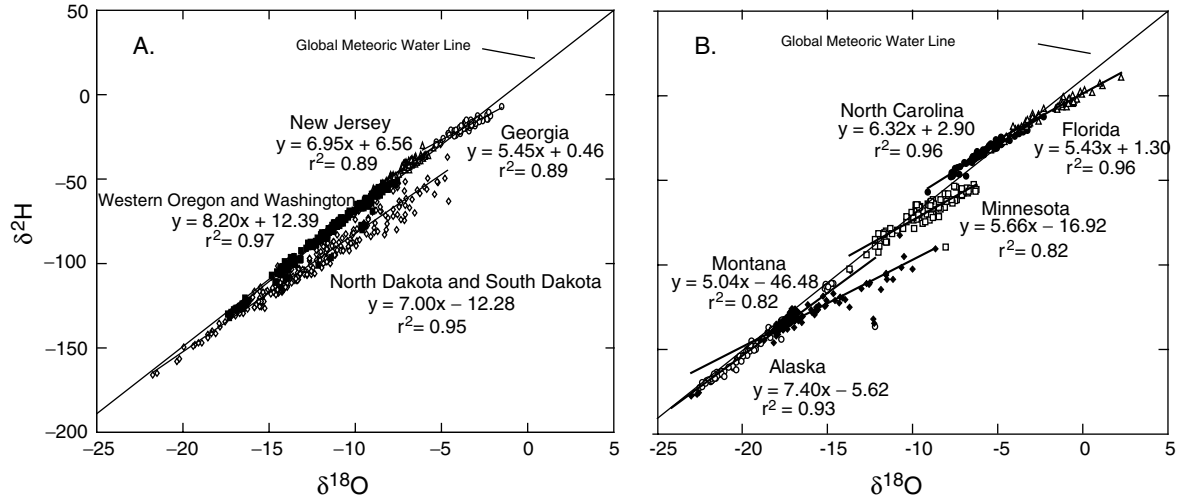

Figure 3. LMWLs for selected states or regions. (a) New Jersey, Georgia, western Oregon and Washington (combined), South Dakota and North Dakota (combined); (b) Florida, North Carolina, Minnesota, Montana, and Alaska

In general, the LMWLs for individual sites have ranges of slopes and intercepts that are similar to those of the state LMWLs. Hence, it is easy to see how the flattened ellipse of data (Figure 2a) reflects the imbricate nature of the LMWLs for individual sites.

Figure 4b gives two fairly typical examples of how similar the LMWLs and average δ values can be for adjacent sites in a state. This observation was the basis for combining the site data into state LMWLs, as a useful means for grouping the data to clarify spatial patterns. One of the sites in Nebraska (second from the right in Figure 4b) has so little range of values that a linear regression would be misleading; nevertheless, these data fall within the ranges of δ values for the other sites in the state. Data from one site in Missouri (the rightmost) appears to be affected by evaporation; nevertheless, most of the δ values are within the ranges of the adjacent sites.

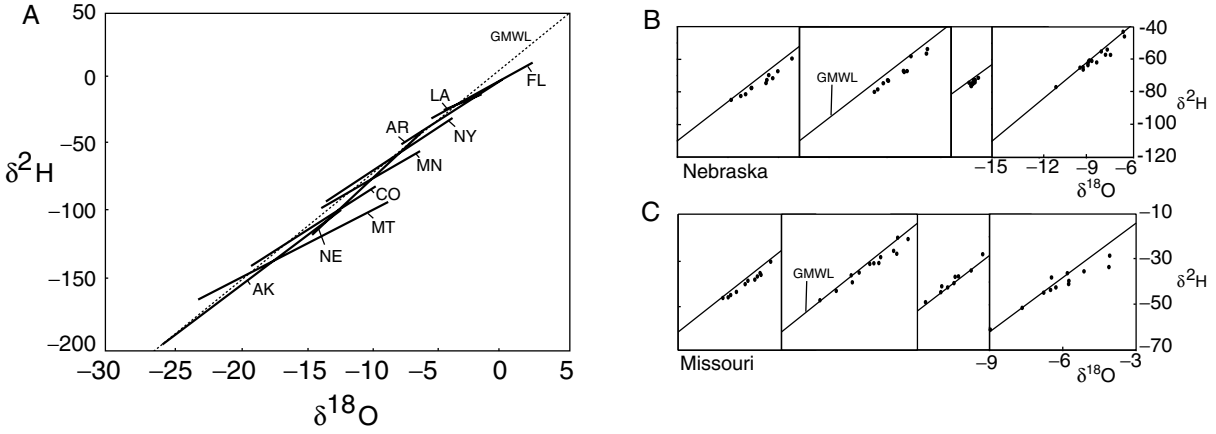

Figure 4. LMWLs for selected states. (a) The imbricate nature of the LMWLs relative to the GMWL is illustrated by omitting the data points and just leaving the lines; the lengths of the lines are fixed by the maximum and minimum values for each state. (b) Small plots of the $\delta^{18}O$ and $\delta^{2}H$ values for four sites from each of two states (Nebraska and Missouri) are overlapped to demonstrate how δ values from adjacent sites within a state appear to have similar LMWLs, making it reasonable to combine the site δ values into state LMWLs. The lines on the inset figures are the GMWLs. For more examples of the distribution of δ values for individual sites, see Coplen and Kendall (2000)

The 391 sites show very heterogeneous seasonal variations in $\delta^{18}O$ and $\delta^{2}H$. The maximum range of $\delta^{18}O$ values at any site is 15‰ (in North Dakota). About 17% of the sites had less than 1‰ range in $\delta^{18}O$ values; many of these sites were located below dams or lakes. Many sites, especially the smaller and less-managed HBN sites, show lower δ values in the late spring and higher values in the fall, similar to the seasonal changes in precipitation. However, more often the seasonal river patterns are difficult to decipher with the limited number of samples.

Site selection and other criteria for contour plots

Contouring the spatial distribution of average $\delta^{18}O$ and $\delta^{2}H$ values presents a number of challenges. First, and most important, is the question of how the data should be averaged—unweighted or weighted. Given the range in number of samples collected per site, and the small numbers of samples at most sites, it is unlikely that a simple arithmetic average of δ values correctly represents the theoretical volume-weighted average annual δ values of discharge from a basin. This problem is more serious for sites with large seasonal ranges in δ values. Only 15% of the sites show more than a 5‰ range in $\delta^{18}O$ values.

The δ values were weighted by their associated discharge values to remove the effect of the isotopic compositions of samples that are volumetrically unimportant, analogous to the volume-weighting of precipitation samples done by GNIP (IAEA, 1992). This computation was performed by multiplying the isotopic compositions of each individual sample by the discharge measured at the collection date, and dividing by the total discharge for the dates sampled. The discharge values are from Alexander *et al*. (1996); some values are mean daily discharges and some are instantaneous discharges. Unweighted average values were substituted for discharge-weighted values for the approximately 20 sites where more than 10% of the samples lacked discharge values.

A second complication arises from the fact that the values were contoured on the basis of the latitudes and longitudes of the gauge stations where the samples were collected. Although this is unimportant for small basins (e.g. for about half of the basins, where areas are less than 8000 km^2), for the drainage basins that are larger than most individual states (i.e. the Mississippi, Missouri, Ohio, Columbia, Rio Grande, and Colorado River basins) the samples probably integrate the isotopic compositions of waters derived much farther upstream (e.g. higher elevation or latitude) in the drainage areas than would be indicated by the position of the data point. Hence, the δ values for large basins are likely to produce artifacts in the contours.

All the contour plots presented herein were created using the programs Surfer[1] and MapViewer. The effects of different choices for several contouring parameters, including numbers of points, sizes of the grids, and type of gridding routine, were evaluated to ensure that the contouring algorithm used was not introducing bias in the plots. The positions of the contours were also frequently compared with the actual average δ values of the sites. The following contouring parameters were ultimately used for plots: a linear variogram weighting method, a quadrant search with three points per quadrant, a search radius of 2·5°, and a grid of 50 divisions E–W (60 °W to 130 °W) and 30 divisions N–S (20 °N to 55 °N). The effects of kriging (Figure 5a) were also compared with use of an inverse-distance gridding method (Figure 5c); the kriging produced contours that appeared more accurate.

In the early stages of this study, a number of plots were made of different subsets of the data, in an attempt to understand the potential effects of the heterogeneity of the dataset on contour plots. In particular, we evaluated the effects of excluding sites where the δ values were unlikely to resemble those of the original precipitation (e.g. sites with less than six samples, LMWL slopes less than 5, $r^2 < 0{\cdot}8$ for the LMWL, or where the range of $\delta^{18}O$ values was less than 1‰). We found that none of these exclusion criteria caused significant changes in the positions of contours on plots made with data from the remaining sites. However, the contours were sensitive to the inclusion of extremely large drainage basins (e.g. the Mississippi, Missouri, and Columbia River basins).

[1] Use of trade names in this report is for identification purposes only and does not constitute endorsement by the USGS.

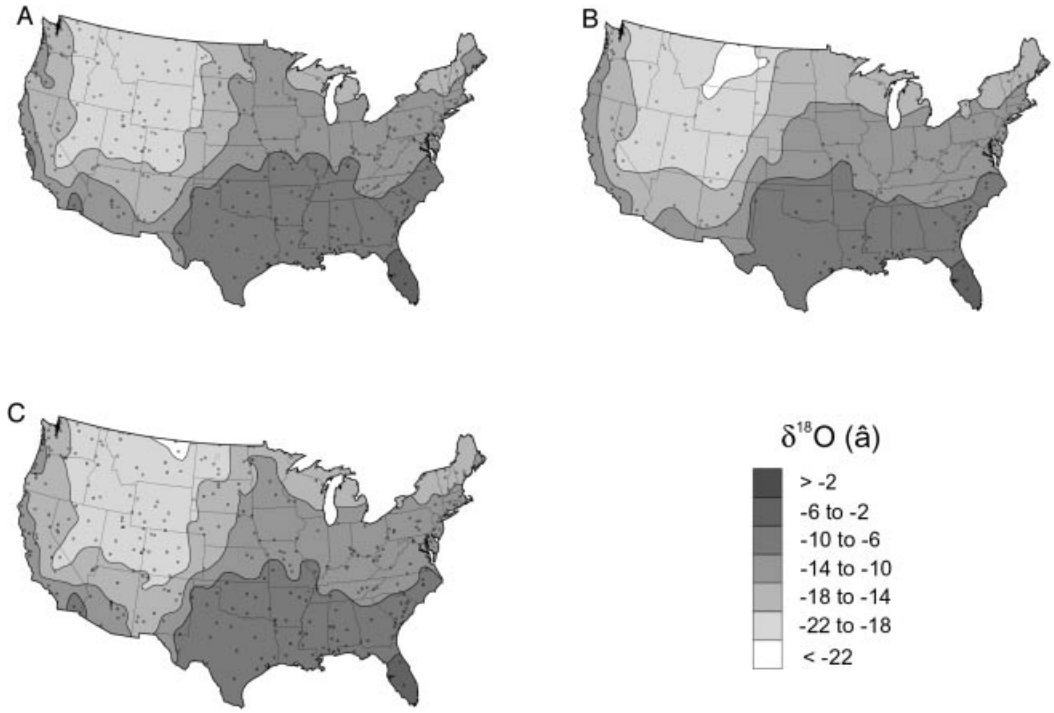

Figure 5. Effect of different choices of site and data-processing criteria on the spatial distributions of mean $\delta^{18}O$ values: (a) basins less than 130 000 km^2, unweighted data, gridded using kriging; (b) basins less than 8000 km^2, discharge-weighted data, gridded using kriging; (c) basins less than 130 000 km^2, discharge-weighted data, gridded using an inverse-distance method

We decided to use only the simplest and most defendable site selection criterion, drainage area, for the $\delta^{18}O$ and δ^2H plots because our investigation of various possible criteria showed that only exclusion of basins greater than 130 000 km^2 (27 sites) made any significant difference in the positions of the contour lines. For example, the unweighted $\delta^{18}O$ contour plot for all sites $<$130 000 km^2 (Figure 5a) is very similar to the contour plot for all sites of less than 8000 km^2 (Figure 5b). The locations of only the selected sites are denoted on each plot. Any differences are generally caused by the fact that the exclusion of sites may leave no data point for a large region of the country, causing other contours to shift substantially (e.g. note the change in the $-10‰$ contour southwest of the Great Lakes as large basins in northern Minnesota are removed in Figure 5c). Several conclusions can be drawn from the insensitivity of the contours to these various site selection criteria: (1) the kriging parameters were chosen appropriately to minimize artifacts caused by anomalous single-site compositions; (2) there are sufficient sampling points to make an adequate assessment of major spatial patterns; and (3) the spatial patterns are coherent and robust.

The site selection criteria for the contour plots for LMWL slope and d-excess (defined below) were more restrictive because we were concerned that performing regressions on a very heterogeneous dataset might introduce unexpected biases. Hence, LMWL slopes and d-excess values were not calculated for sites that fit the following criteria: number of samples less than six, and $\delta^{18}O$ range $<1‰$ and $r^2 < 0{\cdot}8$. These criteria were chosen empirically, on the basis of observations that small sets of data, with small ranges of δ values, did not provide sufficient constraint on the calculations. Basins greater than 130 000 km^2 were also omitted. This eliminated a total of 74 sites from these preliminary contour maps; hence, contour lines in some portions of the northwestern parts of the country are poorly constrained (note that only the locations of the selected sites are denoted on the plot). Despite these efforts to eliminate possible outliers, the dataset still was less spatially coherent than hoped. Therefore, contouring intervals were chosen to illustrate the major spatial patterns, some

poetic license was taken in hand-smoothing *d*-excess and slope contours in data-poor areas, and outliers defined by single points were sometimes ignored.

Spatial distribution of $\delta^{18}O$ and $\delta^{2}H$ values

The discharge-weighted average $\delta^{18}O$ and $\delta^{2}H$ for 345 selected sites (where basin areas are less than 130 000 km^2) in the contiguous 48 states were interpolated and contoured to produce Figure 6a and b. There is surprisingly little difference between the spatial distributions of unweighted (Figure 5a) and discharge-weighted $\delta^{18}O$ data (Figure 6a) for these sites. Given the variable seasonal distributions of δ values at different sites, and the small and variable number of samples collected to assess this variability, this close match is a testament to the success of this sampling effort at capturing the environmental signal.

The spatial distributions of $\delta^{18}O$ and $\delta^{2}H$ are very similar (Figure 6), as would be expected for the high correlation coefficient of the average δ values (Figure 2b). In the eastern side of the USA, δ values decrease northward, with contours that are roughly parallel to latitude. However, the contours curve downwards near the southern end of the Mississippi and downwards around the Great Lakes (see Figure 7a for the locations of these geographic features). The contours are slightly affected by the Appalachian Mountains, in that the contours move southward along the ridge and northward along the flanks. This pattern means that, along E–W transects across the Appalachians, δ values decrease with increasing elevation on both sides of the mountains. In the west, the isotope contours closely match topographic contours, with δ values decreasing eastward from the Pacific to the top of the Rocky Mountains, and then increasing eastward along the eastern flanks of the Rockies towards the Great Plains. The steepest increases in δ values are found at the southeastern edges of the Colorado Plateau, towards southern Texas. The uncoloured minor contour lines show that there are many small-scale variations, often defined by single sites, within the general pattern shown by the coloured intervals.

Seasonal patterns

Because of seasonal variations in the isotopic compositions of precipitation in many parts of the USA, contour plots of the minimum and maximum $\delta^{18}O$ values of river water sampled at each site were made (Figure 8). Only the $\delta^{18}O$ plots are shown, because the spatial patterns for $\delta^{2}H$ are almost identical. We had planned to contrast summer (June, July, and August) and winter (December, January, February) values, instead of maximum and minimum values. However, there was a poor correspondence of δ values with season for many sites. In snow-dominated areas, this shift in seasonal patterns relative to precipitation is probably caused by late releases of meltwater. Otherwise, the odd seasonal shifts probably reflect the high degree of river management at many sites (e.g. dams, irrigation return, diversions for agriculture or urban use), and contributions from groundwater. Therefore, detailed interpretation of seasonal patterns would require examining the sites on an individual basis. Nevertheless, the maximum values usually occur in the summer or fall, and the minimum values in the winter or spring.

These plots show more spatial heterogeneity than the plots of average $\delta^{18}O$ (Figure 6) because of the lack of averaging of the individual 'grab' samples. The general similarity of the spatial patterns of the minimum $\delta^{18}O$ values (Figure 8b) to those in Figure 6a probably is indicative of the large fraction of well-mixed groundwater, derived mostly from winter and spring precipitation, contributing to flow in many of these streams. As expected, contour lines move northward, away from the coast, and higher in elevation during the summer (i.e. when $\delta^{18}O$ values of rain are at their maximum), reflecting seasonal changes in temperature and precipitation amounts (Figure 7b and c). In general, sharp topographic features like the Appalachian and Rocky Mountains (Figure 7a) cause steeper isotopic gradients in the summer than the winter.

Spatial distribution of deuterium excess and LMWL slope values

The term 'deuterium excess' (often shortened to '*d*-excess' or '*d*') was defined by Dansgaard (1964) as $d = \delta^{2}H - 8\delta^{18}O$. This value is the $\delta^{2}H$ intercept value of a line of slope 8 fitted through a dataset, and typically

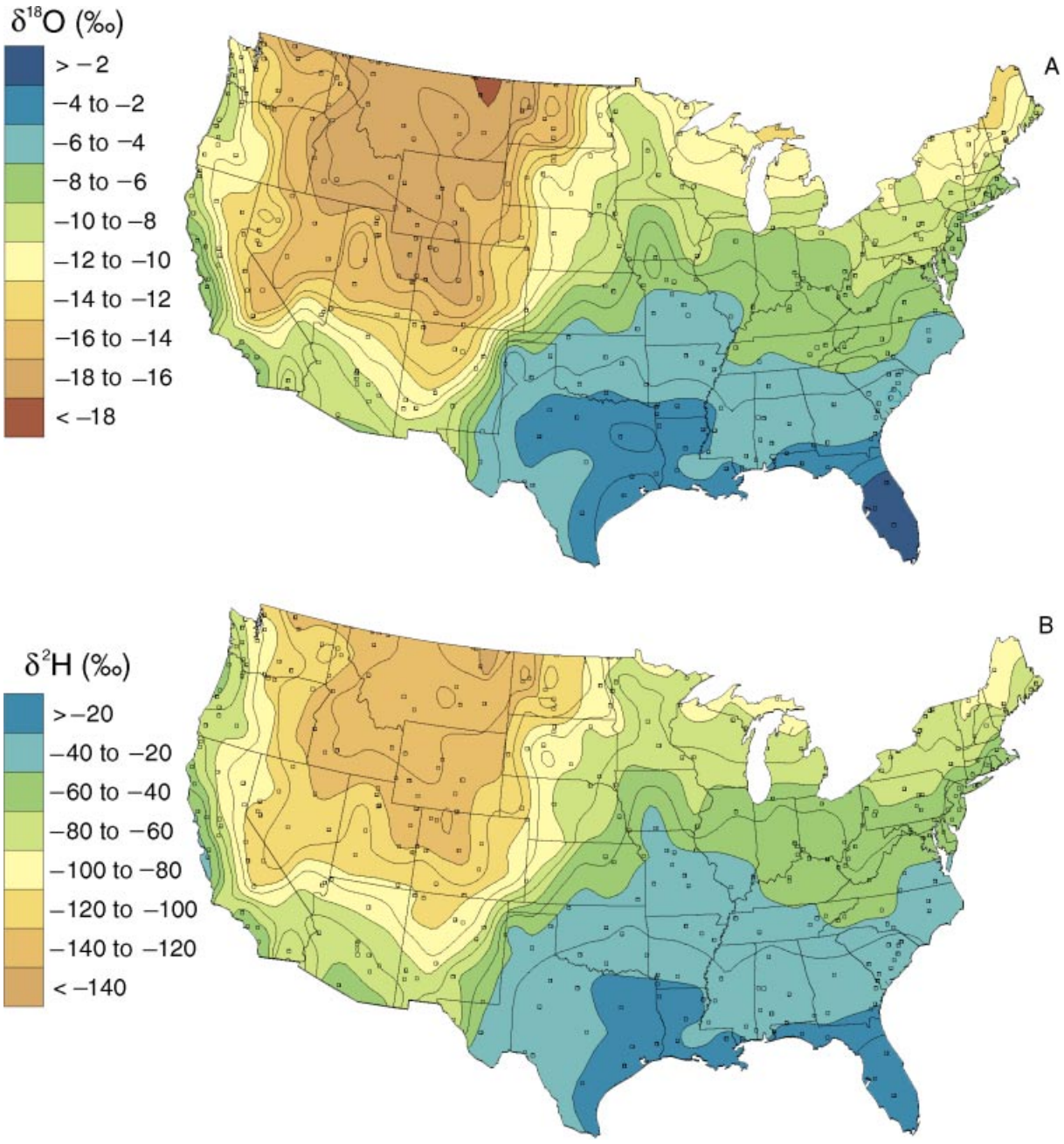

Figure 6. Spatial distribution of discharge-weighted mean (a) $\delta^{18}O$ values, and (b) $\delta^{2}H$ values

has values close to +10‰ for rain samples in temperate climates. Merlivat and Jouzel (1979) showed that the *d*-excess in air masses (and hence precipitation) depends on the relative humidity of the air masses at their oceanic origin, the ocean surface temperature, and kinetic isotope effects during evaporation. Because of the link to humidity, *d*-excess values are sensitive to evaporative processes, including whether summer or winter precipitation dominates recharge. During snow formation, *d*-excess increases as condensation temperatures

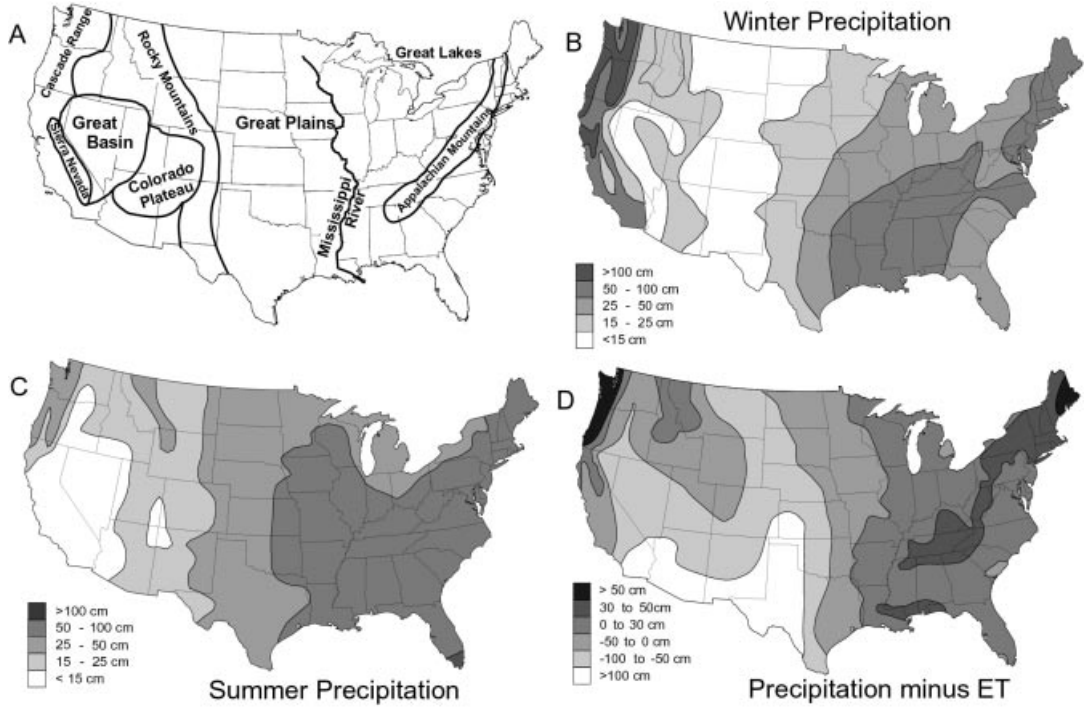

Figure 7. Spatial distribution of (a) physiographic provinces, (b) mean winter precipitation (cm), (c) mean summer precipitation (cm), and (d) mean precipitation minus open-air evaporation (cm). Precipitation data from the U.S. Department of Agriculture; (d) modified from Winter (1989)

Figure 8. Spatial distribution of (a) maximum $\delta^{18}O$, and (b) minimum $\delta^{18}O$. The legend is the same as for Figure 5

decrease from about -10 to $-20\,^{\circ}C$ (Jouzel and Merlivat, 1984). The *d*-excess parameter has been shown to be a diagnostic tool for measuring the contribution of evaporated moisture to the downwind atmosphere (Gat *et al*., 1994). High *d*-excess values generally indicate that more evaporated moisture has been added to the atmosphere (Gat and Matsui, 1991), and low values are associated with samples fractionated by evaporation.

The *d*-excess values for the 391 sites ranged from -8 to $+17‰$. About 8% of the 4800 river samples have *d*-excess values less than zero. The spatial distribution of average *d*-excess values for 317 selected sites within

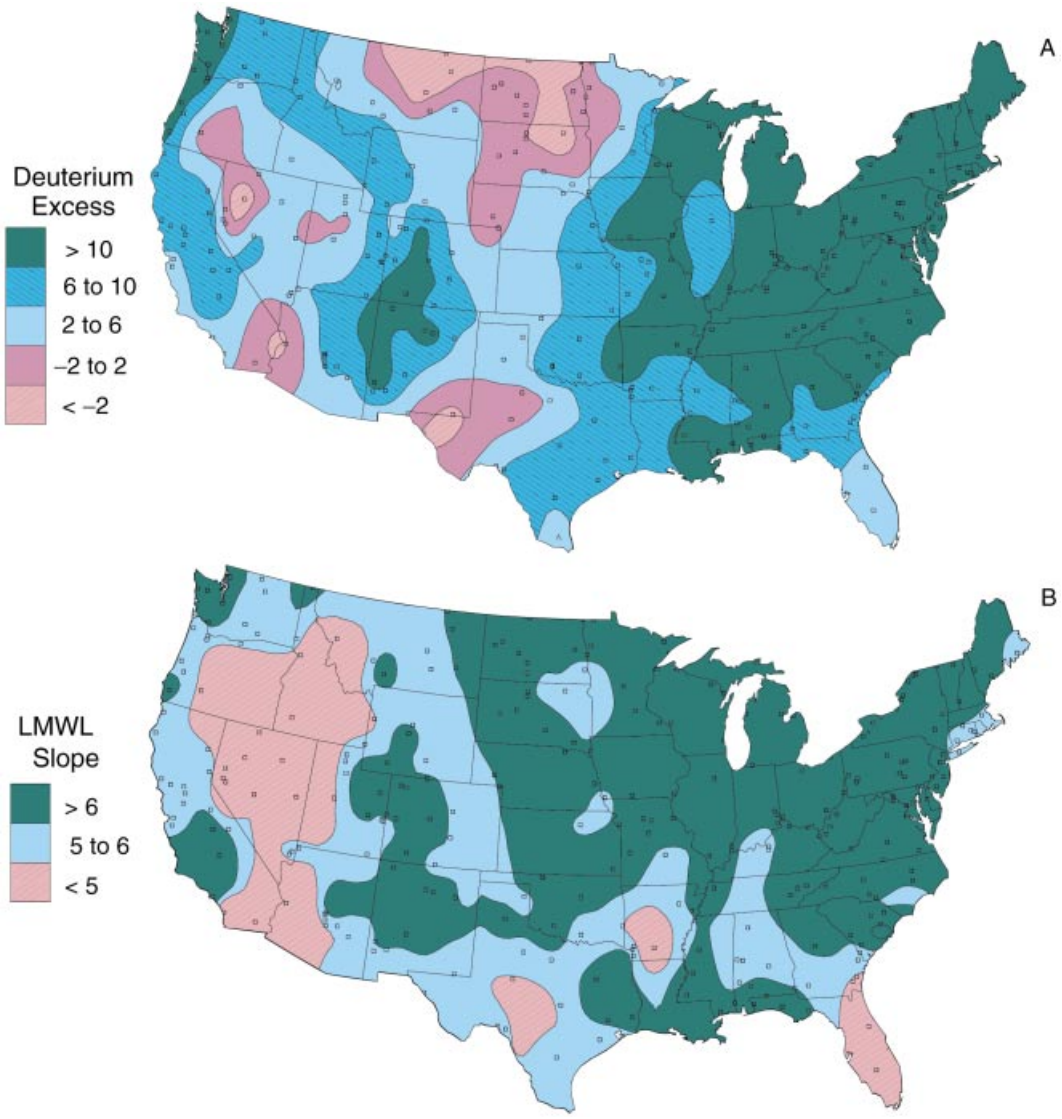

Figure 9. Spatial distribution of (a) deuterium excess values, and (b) slopes of LMWLs. Site selection criteria were chosen to enhance the major spatial patterns by reducing the number of outliers (see text)

the 48 contiguous states is shown in Figure 9a. Because of the conservative criteria used for site selection (discussed above), many areas, especially in the western states, do not have sufficient density of data points for accurate positioning of the contour lines (e.g. eastern Oregon, southern California and Nevada, western Kansas). Hence, the spatial patterns should be interpreted with caution.

The most striking feature of this plot is the sharp division of d-excess values between eastern and western sites. With the exception of a couple of sites in Florida, all sites east of a wavey line (Figure 9a) that cuts across Texas at about the 97th meridian and curves northeastward to about the 95th meridian at the Canadian border, have d-excess values greater than 6‰. Most sites in the eastern and east-central states have values in the range of 10 to 15‰. Most of the west shows d-excess values less than 6‰. There is a very steep decline in d-excess values starting just west of the $d = 10$‰ line; the gradient is steeper in the north than the south.

This gradient produces an N–S-trending 'saddle' of low *d*-excess values along the high-elevation parts of the southern Rockies.

The western sites show more spatial heterogeneity than the eastern sites. Although the average *d*-excess in the west is generally less than 6‰, there are several small locations (defined by few sites) where the *d*-excess values are less than −2‰, and there are two major zones with values greater than 6‰. The first of these includes the Cascades Range physiographic province along the west coast in Washington, Oregon, and northern California, plus a band of sites along the western slopes of the Sierra Nevada Mountains that extends into the Central Valley of California. The second zone of high *d*-excess values is centred around the Colorado Plateau physiographic province, is bordered on the east by the lower Rio Grande, and includes much of the south-central Rocky Mountains.

The spatial patterns of the slopes of LMWLs (Figure 9b) are less coherent than the 'robust' spatial patterns of average isotopic composition (Figure 6) and *d*-excess (Figure 9a). Hence, the slopes were divided into just three contouring intervals. The greater spatial heterogeneity of slopes than average $\delta^{18}O$ or $\delta^{2}H$ values or *d*-excess values suggests that slopes are more dependent on small-scale local processes or conditions. Nevertheless, large groups of adjacent sites, within regions that have sizes on the order of those of states or hydrologic units, have similar slopes (Table I), and outliers are relatively uncommon (e.g. areas with significantly different slopes, defined by only a few points). Although only 25% of sites have slopes in the range of 6 to 7, this range of values appears to be typical of more than 50% of the area in the lower 48 states. Most of the northeastern and north-central parts of the USA have LMWL slopes in the range of 6 to 8. Slopes greater than 8 are rare, and are generally found in isolated patches in the north-central part of the country. Values less than 6 are typical of most of the western, southwestern, and southeastern states.

The distribution of slopes exhibits some strong correlations with topography or physiographic region (Figure 7a), and also shows some strong correlations with the spatial distribution of *d*-excess values. In general, most of the sites with average *d*-excess values between 10 and 15‰ have slopes between 5 and 8. For example, the location of the NW–SE-trending line defining slope equal to 6 in the north-central part of the country is very similar to the eastern edge of the Rockies (Figure 7a) and trends in Figure 7d. The LMWLs for the Colorado Plateau have slopes less than 6; this region also has high *d*-excess values (Figure 9a). The Great Basin and other arid parts of the west (Figure 7c) have LMWL slopes less than 5; much of this region also has low *d*-excess values. And the parts of the west-coast that have high *d*-excess values also have slopes greater than 5. Although the spatial distributions of *d*-excess and slope have many similarities, there is no correlation between *d*-excess and slope for the dataset as a whole ($r^2 = 0{\cdot}04$).

Correlation of $\delta^{18}O$ and environmental parameters

As discussed earlier, the $\delta^{18}O$ of precipitation is affected by a number of interrelated climatic variables, such as temperature, precipitation amount, loss to evapotranspiration, and latitude. Figure 10 illustrates that the $\delta^{18}O$ values of river samples, like precipitation samples, show strong correlations with climatic parameters; the patterns of $\delta^{2}H$ are almost identical to those of $\delta^{18}O$. Average $\delta^{18}O$ values are compared with the mean annual values of the climatic parameters estimated for the locations of the gauge station. The precipitation and temperature data are from NOAA (1999). The potential evaporation data, which reflect the capacity of the atmosphere to hold water and are primarily a function of daylength and temperature, are from Farnsworth *et al*. (1982). For these plots, samples are divided into two groups based on their locations (longitudes east or west) relative to the 97th meridian (Figure 7a), which cuts across the USA from about the southern tip of Texas. This division represents the natural grouping of the data, noticed in previous plots (Figures 5 and 8a).

The $\delta^{18}O$–temperature gradient for the eastern sites is 0·51‰ °C (Figure 10a); this value compares well with values of 0·26 to 0·69‰ $^{\circ}C^{-1}$ reported for North America (Joussaume and Jouzel, 1993). The r^2 of 0·85 for this relation also compares well with what is typically observed for precipitation samples (Yurtsever and Gat, 1981; Rozanski *et al*., 1992) The western sites have a slightly higher $\delta^{18}O$–temperature gradient (0·58‰ $^{\circ}C^{-1}$) but, given the low r^2 (0·44), the difference in gradients is not meaningful. Removing the data

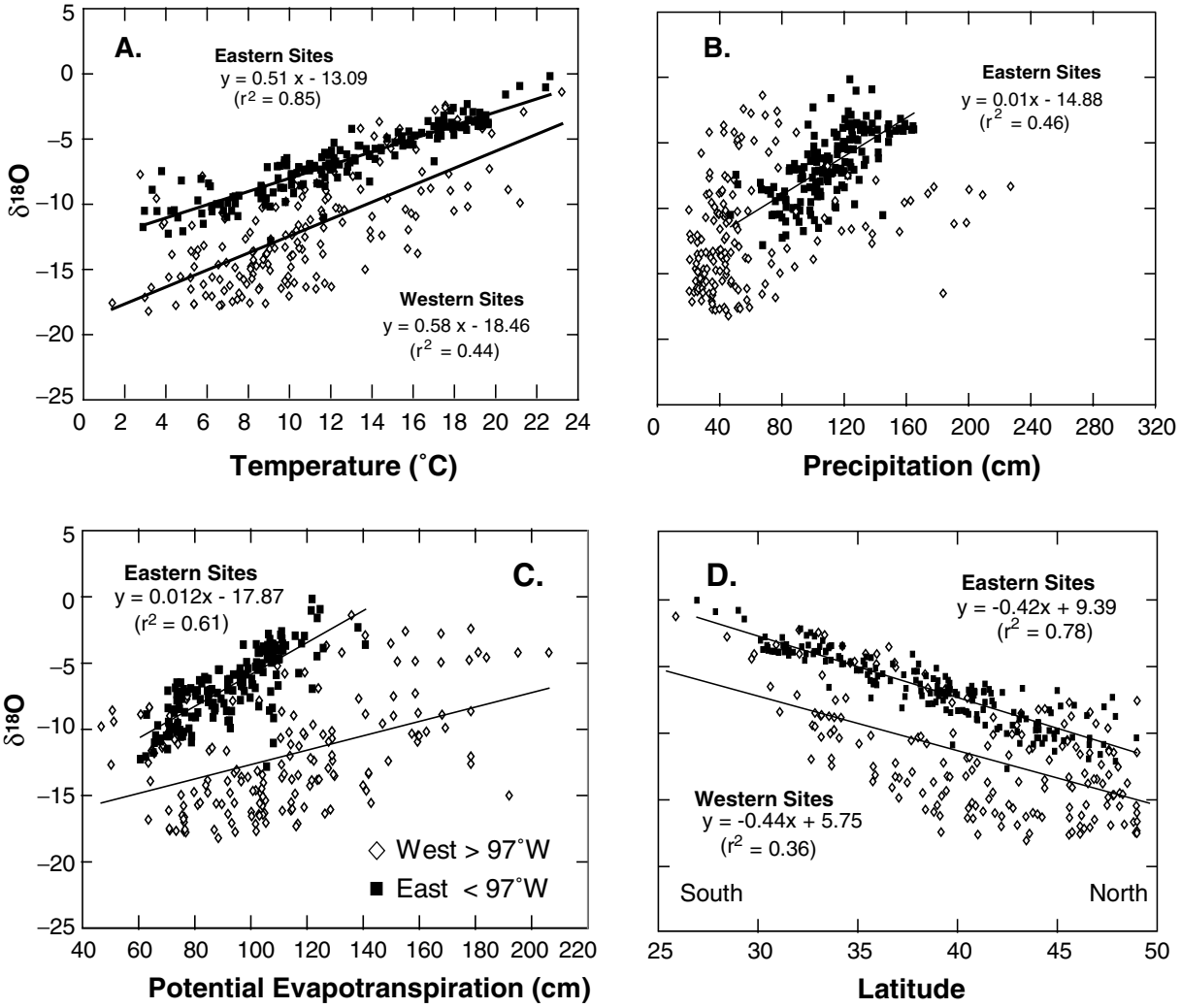

Figure 10. Relations between mean annual $\delta^{18}O$ and (a) temperature (°C), (b) precipitation (cm), (c) mean PET cm), and (d) latitude (°N). Temperature and precipitation data are means for 1961–90 (NOAA, 1999); PET data are from Farnsworth *et al.* (1982)

for large basins (>130 000 km^2) does not reduce the scatter in the western dataset. The greater scatter in the western samples is probably a function of the more irregular topography, and consequently larger seasonal ranges in temperature and $\delta^{18}O$ values, and the seasonal differences in sources of moisture in parts of the western states.

In the eastern sites, there is a weak positive correlation ($r^2 = 0{\cdot}46$) between $\delta^{18}O$ and mean annual precipitation (Figure 10b). Although western sites show two clusters of values (divided at about a precipitation of 100 cm) that 'envelope' the cluster of eastern values, neither cluster has a significant correlation with $\delta^{18}O$. About half of the high-precipitation sites are located along the rainy coastal areas of northern California, Oregon, and Washington (Figure 7b).

The $\delta^{18}O$ values of the eastern sites show a moderately strong positive correlation $r^2 = 0{\cdot}61$) with mean annual potential evapotranspiration (PET) loss (Figure 10c). Hence, it is not surprising that Figure 10a resembles Figure 10c. In the generally more arid western part of the USA, there is a very weak positive

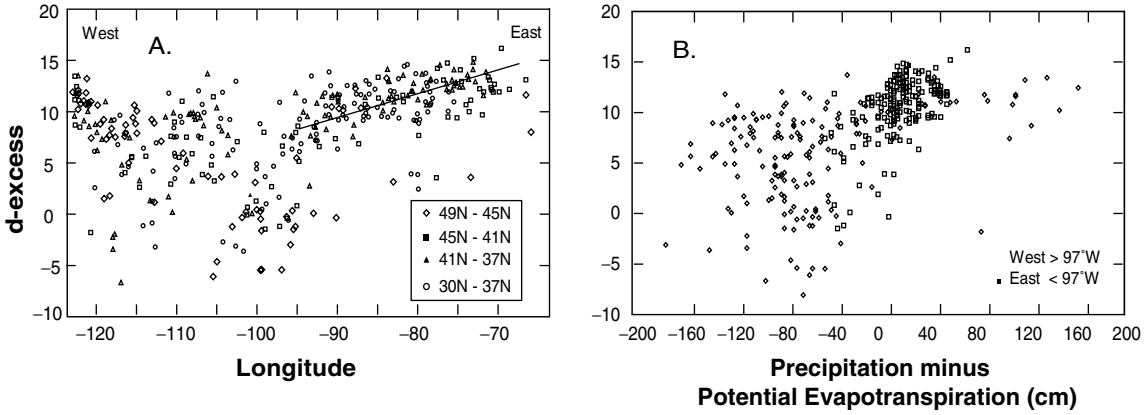

Figure 11. Relations between deuterium excess and (a) longitude (°W), and (b) mean annual precipitation minus PET (PMPE, in cm). Precipitation data from NOAA (1999) and PET data from Farnsworth *et al.* (1982)

correlation ($r^2 = 0{\cdot}18$) between δ^{18}O values and PET. The δ^{18}O–precipitation and δ^{18}O–evapotranspiration gradients for eastern sites are very similar. In contrast, only western sites with high precipitation amounts have similar δ^{18}O–precipitation and δ^{18}O–evapotranspiration gradients.

The δ^{18}O values of the eastern sites have a strong negative correlation ($r^2 = 0{\cdot}79$) with latitude (Figure 10d), reflecting the strong relation between mean annual temperature and latitude in this region ($r^2 = 0{\cdot}98$). The western sites, which have a weak relation between mean annual temperature and latitude ($r^2 = 0{\cdot}36$), show a weak negative correlation of δ^{18}O with latitude ($r^2 = 0{\cdot}35$). The weaker correlations in the west may also reflect greater seasonal variability in the amounts and sources of precipitation.

Correlation of d-excess and environmental parameters

The systematics of *d*-excess values in the east are different from those in the west (Figure 11a), somewhat similar to the east–west differences in systematics observed with δ^{18}O and δ^{2}H values. The *d*-excess values east of about the 97th meridian show a slight positive correlation ($r^2 = 0{\cdot}22$) with distance eastward from the 97th meridian, and are higher (on average) than those of western sites. The eastern sites also exhibit a much narrower range of values for any particular longitude (~7‰) than sites to the west (~20‰). The distributions of *d*-excess values in the west showed no correlation with latitude.

There is no correlation of *d*-excess and mean annual temperature ($r^2 < 0{\cdot}01$), and only very weak correlations ($r^2 < 0{\cdot}2$) with precipitation amount (positive) or PET (negative). Figure 11b is a plot of *d*-excess versus mean annual 'precipitation minus PET' (given the acronym PMPE); open-air (free-water surface) evaporation data are used as a substitute for PET (Farnsworth *et al.*, 1982). Values greater than zero reflect areas where annual precipitation exceeds PET, whereas values less than zero indicate that evapotranspiration exceeds precipitation (i.e. there is a water deficit). The spatial distribution of PMPE values is illustrated in Figure 7d (Winter, 1989). Most of the eastern sites have *d*-excess values in the range of 0–60 cm, whereas the western sites show a wide range of values that seem to cluster into two groups, one with a wide range of *d*-excess values and PMPE values less than zero and a high-precipitation group with a narrower range of *d*-excess values. This grouping is similar to the groupings seen in Figure 10b and c.

DISCUSSION

Slopes of the LMWLs

Although the slope of the national MWL for the entire set of 4800 samples is close to 8 (Figure 2), the data ellipse is composed of 391 very different LMWLs, each of which reflects local processes. These constituent

LMWLs have an average slope of 6·1. As shown in Figure 3a and b, these imbricate LMWLs (Figure 4a) commence at various positions along or above the GMWL and extend below and to the right of it. The generally lower slopes (below the GMWL) of most of the LMWLs explain the asymmetry of the dataset ellipse (Figure 2a). Although puzzling at first glance, the increase in slope (from 6 to 8) caused by averaging the data is just a natural by-product of averaging 'imbricate' data that are fairly evenly distributed along the GMWL (Figure 4a).

With the exception of some clearly evaporated samples, mostly from Nevada and Montana (Figure 3b), that have δ^2H values that plot up to 50‰ below the GMWL, the δ^2H range is generally less than 35‰ for any δ^{18}O value. The data ellipse for all 4800 samples (Figure 2a) is not much broader than some of the ellipses formed by plotting the δ^{18}O and δ^2H values of individual rain event samples (e.g. the datasets in Kendall (1993) and in Coplen and Huang (2000). However, since such datasets require expensive long-term precipitation monitoring to produce, are rarely published, and in most cases contain only monthly-composited samples (e.g. GNIP datasets), the short-term natural isotopic variability in rain-derived waters is not fully documented or appreciated.

The generally low slopes of the LMWLs might imply significant post-rain evaporation of the river samples prior to collection; if so, the data would not be representative of local rainfall. The pertinent questions are: (1) whether the low slopes of the LMWLs for many sites, in themselves, indicate extensive post-rainfall evaporation, and (2) if so, have post-rainfall processes (such as evaporation or mixing with groundwater) significantly affected the average isotopic compositions of the samples?

Many isotope hydrologists may have gained a biased perspective on what the slopes of LMWLs for precipitation 'should' be by exposure to the massive GNIP database, where all the large composites of data (e.g. IAEA, 1992; Rozanski *et al*., 1993) show MWL slopes of about 8 and $r^2 > 0{\cdot}9$ (similar to what we observe for our river dataset). A closer look at the GNIP data reveals that a number of sites also have LMWL slopes in the range of 6 to 7 (IAEA, 1992), despite the fact that most of the sites in that network are coastal, oceanic, and of low elevation. Humidities at these sites would be relatively high and evaporation minimal, conditions that should favour slopes near 8.

Long-term, multi-year investigations of the spatial and seasonal variability of rainfall in the arid southwestern part of the USA indicate that the slopes of LMWLs in these areas during the summer are often less than 8 (Friedman *et al*., 1992). The long-term average slope of the LMWL for summer rain in the southwest was 6·5, with slopes for individual years as low as 5 (Friedman *et al*., 1992). The low slopes during the summer are attributed to evaporation of falling raindrops in arid air masses (Stewart, 1975; Friedman *et al*., 1992), whereas the higher average slope for winter samples (9·2) was explained by the lack of isotopic fractionation during snow sublimation (Friedman *et al*., 1991). Based on the data in Friedman *et al*. (1992), LMWLs are likely to have slopes as low as 5 to 6 in arid regions where summer rain derived from the Gulf of Mexico is a major source of recharge and streamwater. Therefore, although many of the river samples, especially in arid zones, show LMWL slopes less than 6 that are indicative of evaporation, it is not clear whether the evaporation occurred during rainfall, within the soil zone, or in the stream.

Table II gives information about the isotopic compositions of precipitation at selected monitoring sites in the USA. The table includes the number of years that the data were averaged, and the number of collection sites at each monitoring site (e.g. data from 32 site in southern California were averaged). Most values represent multi-year averages. Complete sets of data were not available from some sites. About half the sites are from states east of the Mississippi. Except for one site (Hatteras, NC), all the eastern sites (where these data were available) were characterized by LMWL slopes between 7 and 8; all but three had intercepts in the range 5–12‰. Data from western sites generally had lower slopes and intercepts. About 70% of the LMWLs that were calculated for states or HUCs (Table I) are within the range of values for slopes and intercepts of precipitation sites (Table II). Hence, these regions show little direct evidence of post-rainfall isotopic fractionation.

The fact that the isotopic data from adjacent sites from the same state or region can be grouped together to produce 'regional' LMWLs for the state or region (Figure 3, Table I) implies that large geographic areas are responding similarly to some common process(es), perhaps evaporation. We speculate that the extent of

Table II. Comparison of the isotopic compositions of precipitation at selected monitoring sites with the isotopic compositions for these sites as interpolated from the river $\delta^{18}O$ and $\delta^{2}H$ maps (Figure 6). The estimated river data are in the two right-hand columns

Location	Data source[a]	HUC	Lat.	Long.	Years	Sites	LMWL		r^2	d-excess	Avg. $\delta^{2}H$	Avg. $\delta^{18}O$	River $\delta^{2}H$	River $\delta^{18}O$
							slope	intercept						
Flagstaff, AZ	6	15	35·13	−111·67	13	1	5·7	−18·5	0·88	3·5	−65·9	−8·1	−80·0	−11·0
Santa Maria, CA	6	15	34·90	−120·45	9	1	6·0	−0·8	0·84	9·4	−38·7	−6·0	−60·0	−8·0
So. California, CA	3	18	32·66	−114·61	2	32					−70·4	−8·6	−75·0	−10·0
Niwot Ridge, CO	13	10	40·06	−105·59	3	1						−14·6	−110·0	−15·0
Lewes, DE	1	2	38·77	−75·08	3	1	7·8	11·3	0·96	12·7	−35·7	−6·2	−45·0	−7·0
Georgia Station, GA	13	3	33·18	−84·41	3	1						−3·9	−30·0	−5·0
Panola, GA	8	3	33·63	−84·17	3	1	7·4	9·5	0·94		−29·5	−5·4	−30·0	−5·0
Ames, IA	12	7	42·00	−93·80	1	1	7·2	4·7	0·98		−53·6	−8·0	−50·0	−7·0
Bondville, IL	1	5	40·05	−88·37	3	1	7·7	9·8	0·97	12·3	−42·7	−7·0	−45·0	−7·0
Chicago, IL	6	7	41·78	−87·75	17	1	7·0	0·1	0·96	7·0	−43·0	−6·0	−55·0	−8·0
Williams Lake, MN	11	7	47·10	−94·62	2	2	7·8	6·4	0·97		−71·0	−10·0	−70·0	−9·5
St. Louis, MO	2	7	38·39	−90·15	4	2						−6·8	−40·0	−6·0
Hatteras, NC	6	3	35·27	−75·55	9	1	6·1	4·3	0·83	11·9	−22·5	−4·3	−35·0	−5·5
Mead, NE	4	10	41·15	−96·49	3	1	7·4	7·3	0·98	11·1	−48·0	−7·4	−55·0	−8·0
North Platte St., NE	5	10	41·06	−100·74	6	1	7·7	5·0	0·97	9·5	−69·0	−9·6	−80·0	−11·0
Albuquerque, NM	14	13	35·08	−106·67	2	1					−60·0		−95·0	−13·0
Las Vegas, NV	7	16	37·00	−116·25	6	14	6·9	−6·5	0·97			−11·9	−90·0	−13·0
Tompkins County, NY	1	2	42·40	−76·65	3	1	7·7	9·1	0·99	12·5	−65·9	−9·8	−65·0	−10·0
Coshocton, OH	6	5	40·37	−81·80	6	1	7·5	8·8	0·97	12·5	−47·3	−7·5	−55·0	−8·0
Oxford, OH	1	5	39·53	−84·73	3	1	7·8	11·2	0·97	13·0	−48·4	−7·8	−45·0	−7·5
Alsea, OR	13	17	44·39	−123·62	3	1						−7·4	−70·0	−10·0
Penn State, PA	1	2	40·78	−77·95	3	1	7·9	12·4	0·99	13·3	−65·2	−9·9	−60·0	−9·0
Walker Branch, TN	1	6	35·97	−84·28	3	1	7·9	12·1	0·97	12·8	−35·4	−6·2	−40·0	−6·5
Attwater Prairie, TX	13	12	29·66	−96·26	3	1						−2·9	−15·0	−3·0
Lubbock, TX	10	12	33·58	−101·33	1	5	6·9	1·5	0·94		−49·0	−7·4	−30·0	−4·0
Waco, TX	6	12	31·62	−97·22	9	1	6·5	5·6	0·91	9·4	−22·9	−4·0	−20·0	−3·0
Sleepers River, VT	15	2	44·5	−72·17	1	2						−11·1	−80·0	−11·5
Underhill, VT	1	2	44·53	−72·95	3	1	7·9	10·8	0·99	12·5	−72·9	−10·7	−80·0	−11·5
Destruction Is., WA	6	17	47·67	−124·48	5	1	6·9	−1·8	0·91	7·0	−52·9	−7·5	−65·0	−10·0
Trout Lake Station, WI	9	7	46·0	−89·6	1	1	8·0	9·3	0·99		−78·2	−10·9	−80·0	−11·5

[a] 1. Coplen and Huang (2000); 2. Criss (1999); 3. Friedman *et al.* (1992); 4. Harvey (2001); 5. Harvey and Welker (2000); 6. IAEA (1992); 7. Ingraham *et al.* (1991); 8. Kendall (1993); 9. Krabbenhoft *et al.* (1990); 10. Nativ and Riggio (1990); 11. Reddy, Michael M. (personal communication, 2000); 12. Simpkins (1995); 13. Welker (2000); 14. Yapp (1985); 15. Unpublished USGS data. All averages are volume-weighted except Welker (2000).

evaporative fractionation of rain in the region is controlled by the long-term average humidity and temperature of the region, which imparts a distinctive LMWL slope to rainfall within the area. Furthermore, post-rainfall evaporation is also affected by the same regional climatic conditions, producing a distinctive LMWL for river samples within the region. If the environmental conditions during rainfall and post-rainfall evaporation are similar then the river LMWL would be similar to the precipitation LMWL because continued evaporation of rain in the soil or stream would cause further increases in δ values but perhaps little change in the slope of the LMWL. An alternative explanation is that the similarity in slopes for adjacent sites reflects some regional characteristic of mixing of precipitation and groundwater.

At this point, we are unable to determine whether river or groundwater samples from a particular site have experienced sufficient post-rainfall evaporation to affect significantly the average δ values or LMWL slope, without closer investigation on a site-by-site basis. Although river LMWL slopes in the range of about 6 to 8·5 are within the normal range for precipitation and, hence, do not 'require' post-rainfall evaporation to explain the values, slopes in the range 6–7 may indeed reflect substantial amounts of post-rainfall evaporation. We clearly need more precipitation data, especially in arid regions, to interpret the meaning of slopes less than 6.

Spatial distributions of average $\delta^{18}O$, $\delta^{2}H$, and d-excess values

Surface waters are inherently subject to a greater variety of environmental conditions that may significantly affect the isotopic compositions than are rain samples. Hence, there is concern that the isotopic compositions of some river waters might be so altered that the dataset would be spatially biased by the occurrence of anomalous values at erratic locations. Instead, we find that contour plots for δ^{18}O and δ^{2}H (Figures 5 and 6) are similar in general patterns to the δ^{2}H contour map of Sheppard *et al.* (1969), but contain considerably more detail because of the much larger number of sampling sites. Having more sites increases the likelihood of 'capturing' more small-scale environmental detail, but it also increases the chance of perturbing general spatial trends with spurious values related to post-depositional processing of water in the drainage basin (e.g. dams, irrigation return flows, selective recharge, etc.). However, that does not seem to have happened; the contours have not been hand-smoothed, and it is clear that the patterns are spatially coherent.

In their pioneering investigation of the δ^{2}H of baseflow in small creeks in the eastern USA, Friedman *et al.* (1964) observed that the δ^{2}H contours were roughly parallel to latitude and closely matched the percentage of precipitation as snowfall; our larger dataset confirms this general pattern. The tight fit of the δ^{18}O–temperature relation for the eastern states (Figure 10a), and the less-good fit of the δ^{18}O–precipitation relation (Figure 10b), suggests that the regular decrease of temperature with elevation and latitude is primarily responsible for the trends, not the amount or type of precipitation; this has been observed in many precipitation datasets (e.g. Dansgaard, 1964; Yurtsever and Gat, 1981). The good correlations probably reflect the fact that most of the precipitation in the east is derived from storms from the nearby Atlantic and Gulf of Mexico (Bryson and Hare, 1974). By the time Pacific storms reach the Appalachians, the subsequent rain is likely to have spatially heterogeneous δ values. The regular decrease in δ values inland from the Atlantic and with increasing elevation in the Appalachians also implies an eastern moisture source.

The two major departures from the regular decrease in δ^{18}O with latitude for the eastern states are the southward-dipping contours around the Great Lakes and the southern end of the Mississippi River (Figure 6a). Higher *d*-excess in precipitation and river samples compared with that in the advecting air mass has previously been observed for the Great Lakes area (Gat *et al.*, 1994). This observation was interpreted as indicating that evaporated moisture from the lakes is mixed with atmospheric waters. Mass balance models indicate that 5–16% of the atmospheric vapour downwind from the Great Lakes is derived from lake evaporation in the summer (Gat *et al.*, 1994; Machavaram and Krishnamurthy, 1995).

In the lower Mississippi, several factors may be involved. Much of the water is derived from colder, northern areas and generally has δ^{2}H values in its lower reaches that are about 20‰ lower than the δ values of nearby small streams (Friedman *et al.*, 1964). Hence, one can speculate whether there might be sufficient evaporation from the lower Mississippi to local air masses, probably derived from the Gulf of Mexico, to

cause increases in the d-excess and decreases in δ values of local precipitation in this humid environment. The band of higher d-excess values and slopes of the LMWLs along the coastal and delta areas provide some support for this theory (Figure 9). An alternative explanation for the southward-dipping contours is that groundwater derived from the Mississippi River, with lower δ values typical of a source farther to the north, is a significant source of water to the nearby streams. More detailed examination of the characteristics of the individual sites would be needed to resolve this issue.

Topographical effects may also cause southwards-dipping $\delta^{18}O$ and $\delta^{2}H$ contours. The contours on Figure 6 wrap around the Rocky Mountains and the Appalachian Mountains, with decreasing δ values up the western sides and increasing δ values down the eastern sides. The lowest δ values in the contiguous 48 states are found in the northern Rockies and the foothill areas in Montana. The much steeper isotope gradients around the Rockies relative to the Appalachians reflect the differences in elevational and temperature gradients between the mountains.

Along the western and eastern sides of the Rockies, d-excess values decrease with decreasing $\delta^{18}O$. Sites dominated by oceanic moisture sources generally have decreasing d-excess with increasing $\delta^{18}O$ (Schotterer *et al*., 1993), whereas the d-excess decrease with decreasing $\delta^{18}O$ in Mongolia is attributed to precipitation derived from recycled continental vapour produced by evaporation of lakes and wetlands that appeared during summer in Siberia (Schotterer *et al*., 1993). Hence, the decreasing d-excess values at higher elevation sites in the Rockies probably reflects the aridity of much of the area. In contrast, there is a faint trend of increasing d-excess values with increasing elevation and decreasing δ values in the Appalachians (note the southward-dipping curve of the $d = 10‰$ and slope $= 6$ lines at the southern end of the Appalachians in Figure 9), as would be expected for precipitation largely derived from the Atlantic Ocean. On a regional scale, this minor trend is overwhelmed by the general increase in d-excess eastward from about the middle of the Great Plains, as shown on Figure 11a.

Although it might seem unjustified to take river data that have LMWL slopes less than 6 (or even lower) and fit the data to a slope of 8 to calculate d-excess, this calculation produces intriguing spatial patterns. The $d = 6‰$ line (Figure 9a) is slightly west of the line where open-air evaporation equals precipitation (Figure 7d). East of this line, precipitation exceeds evaporation, and west of this line, evaporation exceeds precipitation. The location of the curvy band of d-excess values ranging from 6 to 10‰ is approximately the same as the band of locations that receives 15–25 cm of winter precipitation (Figure 7b). Many of the areas with $d < 2‰$ correspond to arid zones where evaporation exceeds precipitation by 50 cm or more per year (Figure 7d).

Although there is no correlation of d-excess values and $\delta^{18}O$ for the entire dataset ($r^2 = 0{\cdot}08$), there is a general similarity between the spatial distributions of δ and d-excess values. Both show prominent N–S-trending contours in the north-central part of the USA. However, the steep gradient of δ values (Figure 6a) along the northeastern flanks of the Rockies is located west of the $d = 6‰$ line (Figure 9a). And where the steep δ gradient swings south around the southern edge of the Colorado Plateau (Figure 6a), it cuts across areas of low and high d-excess values as it bends around the plateau. Nevertheless, both datasets suggest that there are significant changes in climatic factors along the eastern foothills of the Rocky Mountains.

We speculate that the steep gradient in d-excess values coincident with the eastern edge of the foothills of the Rockies marks the boundary between the influence of wet, warm air from the Gulf and cold, dry air that has moved west from the Pacific. Westerlies originating in the Pacific, south-moving Arctic winds, and summer moisture from the Gulf of Mexico all converge in the Dakotas (Amundson *et al*., 1996), generating a steep gradient in δ values that extends into Canada. The increase in $\delta^{2}H$ and $\delta^{18}O$ eastward across the northern plains correlates with an increase in the summer/total precipitation ratios and decreasing mean annual temperatures (Amundson *et al*., 1996), related to the summer monsoon of the Great Plains (Tang and Reiter, 1984). Moisture from the Gulf of Mexico is expected to have higher $\delta^{2}H$ values because of less rainout and warmer temperature at the vapour source (Nativ and Riggio, 1990). Yonge *et al*. (1989) also note that large amounts of precipitation from storms tracking northwards up the Continental Divide from Montana into Canada can produce relatively high $\delta^{2}H$ values. Hence, the steep gradients in $\delta^{18}O$, $\delta^{2}H$, and d-excess probably reflect the seasonal interaction of, or changes in, air masses from different sources, and perhaps

subsequent evapotranspiration in this arid environment. The complex patterns in the western states suggest that it would useful to explore the effects of the varied topography, inland changes in precipitation amount, and recycled evapotranspiration on the estimated isotopic compositions of precipitation with simple models for Rayleigh condensation along several longitudinal transects. This will be left to a future paper.

The two zones with high *d*-excess values in the western states (Figure 9b) show no obvious correlation with $\delta^{18}O$ and $\delta^{2}H$ values. However, the zones correspond with known physiographic provinces (Figure 7a) and show striking similarities with seasonal precipitation patterns (Figure 7b and c) and the balance between precipitation and ET (Figure 7d). For example, the zones of high *d*-excess (6–10‰) values along the northwest coast and along the west side of the Sierra Nevada mountains in central California both correspond to areas of high winter precipitation (Figure 7b). The areas along the coast have dense forests. Hence, the higher *d*-excess values are likely to be related to the high humidity or high amount of transpiration in these areas. In a sense, these environments are more typical of 'eastern' environments than much of the arid west.

The high *d*-excess values along the Colorado Plateau and southwestward to the border with Mexico are a puzzle. This region has higher winter precipitation than most of the southern Rockies (Figure 7b), but is less rainy than other places where *d*-excess values are comparable. The area in question marks the southeastern extension of the zone of relatively high values of precipitation minus evaporation (Figure 7d) along the crest of the Rocky Mountains that extends to the Mexican border, and presumably continues along the crest of the Sierra Madre Mountains. The correspondence of the steep $\delta^{18}O$ gradients at the southern end of the Rockies (Figure 6a) suggests that the *d*-excess values may be caused by storms from the Gulf of Mexico and the Pacific that meet in this 'topographic saddle' between two mountain ranges as they move around the Rockies. Alternatively, it may reflect summer monsoonal moisture from the Gulf of California (Brenner, 1974).

Seasonal changes in moisture sources and precipitation

There are two major streams of atmospheric vapour onto North America: flow from the Pacific Ocean and from the Gulf of Mexico (Brubaker *et al*., 1994). Canadian air masses, either derived from the Pacific or the Arctic, and Atlantic air masses are minor sources in the northern USA, and rain from the Gulf of California is a minor source in the southwest (Brenner, 1974). The moisture flux from the Gulf of Mexico is strongest in the spring (March–May), and weakest in the fall (September–November), with higher fluxes at the western side of the Gulf than the eastern (Brubaker *et al*., 1994). The transport in the mid-latitudes is mainly westerly and relatively constant, with slightly higher fluxes in the fall and winter than in the spring and summer; the vapour contribution from the Gulf of Mexico seasonally either exceeds or is comparable to the supply from the Pacific Ocean (Brubaker *et al*., 1994). Most of the precipitation in the USA west of the Rockies falls during winter and spring (Figure 7b). In contrast, summer precipitation exceeds winter precipitation from the eastern flanks of the Rockies eastward to the Atlantic (Figure 7c).

Figure 8 shows that contour lines of $\delta^{18}O$ values move northward, away from the coast, and higher in elevation (Figure 7a) during the summer. In general, sharp topographic features like the Appalachian and Rocky Mountains have more effect (i.e. cause steeper isotope gradients) in summer months than winter ones. Many researchers have documented significant differences in the isotopic compositions of winter *versus* summer precipitation (e.g. Nativ and Riggio, 1990; Friedman *et al*., 1992), largely caused by seasonal differences in stormtracks. Air masses that derive their moisture from parts of the ocean with different surface temperatures, and which might encounter different elevational regimes and rainout histories in different seasons (e.g. Friedman *et al*., 1992), have different isotopic compositions. However, such changes can also be caused by seasonal changes in temperature at the precipitation site.

These possibilities for seasonal shifts in δ values can be evaluated by comparison of seasonal variations in $\delta^{18}O$ with the $\delta^{18}O$–climatic patterns shown in Figure 10. Note that the dividing line for eastern and western sites in Figure 10 roughly matches the division between the wetter east and drier western states in Figure 7. The general consistency of the $\delta^{18}O$–temperature relation for eastern sites (Figure 10a) implies that there was no significant seasonal difference in vapour sources or in the δ values of different sources. However,

the greater scatter of eastern $\delta^{18}O$ values for mean temperatures less than 7 °C (Figure 10a) and latitudes above 42°N (Figure 10d) could reflect differences in sources of moisture (e.g. from Arctic stormtracks or from additions of evaporated vapour from the Great Lakes). The $\delta^{18}O$–precipitation (Figure 10b) and $\delta^{18}O$-evaporation (Figure 10c) plots show considerably more scatter than the $\delta^{18}O$-temperature plot. This suggests that potential differences in precipitation amount and evaporation related to seasonal differences in stormtracks or sources are less important than static local conditions (primarily latitude, as shown in Figure 10d) on mean surface temperature.

In contrast to small seasonal changes in the eastern sites, the large amount of scatter in the $\delta^{18}O$ values of western sites in Figures 10 and 11 strongly suggests that more complex processes are affecting the values. The $\delta^{18}O$–temperature gradient for western sites is roughly the same as for the eastern sites (Figure 10a). However, the low correlation coefficient for the west ($r^2 = 0{\cdot}44$) suggests that other factors are involved. For example, the greater scatter of $\delta^{18}O$ values in the west is probably related to the larger ranges in amounts of precipitation (Figure 7b) and losses to evapotranspiration (Figures 10d and 11b) caused by the more complex topography in the west.

VALIDATION OF RIVER SAMPLES AS PROXIES FOR AVERAGE RAIN AND/OR RECHARGE COMPOSITIONS

At first glance, it may seem strange to consider the use of stream samples as indicators of rain or recharge isotopic compositions, since streamwater represents a time-varying mixture of groundwater with a spectrum of ages plus recent precipitation. However, there are several reasons for doing so. The main advantage of river samples relative to groundwater samples as proxies for precipitation is that they are readily available (i.e. no wells to drill). Also, many countries (like the USA) already have river monitoring networks in place, with large numbers of sites with long-term data to choose among. Also, because a sizable percentage of the river water is very recent rain (~40‰, on average; Genereux and Hooper, 1998), a smaller amount of the total water has been subject to local processes such as selective recharge and evaporation in the soil zone, which would tend to alter groundwater compositions from that of the original rain composition. For mid-channel, depth-integrated, volume-weighted river samples from small drainage basins—such as most of our sites—the effect of isotope fractionation due to surface evaporation is probably minimal (Fritz, 1981). Large rivers have a great advantage if one is interested in regional changes of the isotopes in precipitation because they integrate the isotopic signals of huge basins and, therefore, reduce the large spatial variability of isotopes in precipitation (Hoffman *et al*., 2000). A disadvantage of river 'grab' samples is that more samples are required to determine a reasonable regional average composition than with groundwater samples, because river samples have more seasonal and storm-related variations in isotopic compositions than local groundwater.

The isotopic compositions of shallow groundwater and small streams have been used by many researchers to define what are believed to be patterns in average precipitation (e.g. Friedman *et al*., 1964; Sheppard *et al*., 1969; Fritz *et al*., 1987; Ingraham and Taylor, 1986, 1991; Yonge *et al*., 1989). River samples are commonly used as substitutes for precipitation samples to determine LMWLs (e.g. Yonge *et al*., 1989), especially in environments where recent rainfall is believed to be a major component of streamflow. Additionally, the compositions during baseflow are commonly used to estimate the δ values of groundwater and annual mean precipitation (e.g. Friedman *et al*., 1964; Sklash *et al*., 1976) because the isotopic compositions of most groundwater systems are constant and thought to reflect closely the average annual isotopic composition of local precipitation (Yurtsever and Gat, 1981). These different usages reflect the dual (composite) nature of streamflow: recent precipitation and older groundwater (baseflow). However, the baseflow component should be viewed as reflecting a spectrum of ages of waters (Michel, 1992; Brown *et al*., 1999; McDonnell *et al*., 1999; Kirchner *et al*., 2000).

In many small drainage basins, the groundwater storage reservoir can be very limited and, therefore, discharge from the basin depends strongly on precipitation events. It might be expected that the magnitude

of the seasonal variations in the isotopic composition of the creeks would be inversely proportional to the size of the basin, i.e. the size of the sub-surface reservoir that can respond to precipitation events (Fritz, 1981). However, there is no correlation ($r^2 < 0{\cdot}004$) of the $\delta^{18}O$ range with basin size for the entire dataset. This result might be explained by the high degree of management of many of the rivers monitored by the NASQAN program (i.e. dams, irrigation return flow, etc.). Surprisingly, there is also no correlation for the smaller, more pristine, HBN sites (6–5200 km^2) either. This finding deserves further investigation.

Although the GNIP dataset is probably adequate in many locations for monitoring climatic change (e.g. Rozanski *et al*., 1992), it is not sufficiently detailed to determine the composition of precipitation for local recharge studies and other hydrologic investigations. Furthermore, despite a wealth of papers describing the climatic information available in the $\delta^{18}O$ and $\delta^{2}H$ of precipitation, this water probably does not have the same composition as the environmental water used by some plants and organisms. Hence, the $\delta^{18}O$ of river and groundwater samples might be, in this sense, more appropriate proxies for the water used by biota. And even if a much more detailed precipitation network existed (as is proposed by the Global Network of Isotopes in Precipitation, GNIP, program), it is unclear whether it would be satisfactory for determining the average isotopic composition of precipitation or recharge over areas of several to tens of square kilometres because of the problem of local topography affecting the composition of local rain.

Although most of the vertical and horizontal gradients in $\delta^{2}H$ of precipitation falling in various parts of the recharge areas may be characterized qualitatively, they cannot be characterized quantitatively (Friedman and Smith, 1970). There continues to be very little information about spatial differences in the δ values of precipitation on scales of tens of kilometres. The two precipitation monitoring sites in Georgia (Table II) are located at similar elevations, about 50 km apart; they have $\delta^{18}O$ values (each based on 3 years of data) that differ by 1·5‰. A few studies of convective storms have shown several per mil variation in $\delta^{18}O$ over areas of a few kilometres (Miyake *et al*., 1968; Kendall and McDonnell, 1993; Metcalf, 1995). Throughfall can be enriched in ^{18}O and ^{2}H by about 0·5‰ and 3‰ respectively, compared with rain collected in open sites within a few kilometres (Gat and Tzur, 1967; Saxena, 1986; Kendall, 1993; DeWalle and Swistock, 1994).

Because of the length of time required to obtain a reliable average δ value for precipitation (usually several years) and the problems of spatial variability of rain, shallow groundwater samples are often collected to determine the average precipitation composition. However, groundwater recharge is often a selective process, excluding rain that may runoff or fail to penetrate to the water table, and thus may be more reasonably considered to estimate the 'recharge' composition than the actual average rain composition. Since river samples contain a mixture of recent precipitation and older groundwater, estimation of average precipitation or groundwater compositions at each site requires fitting the data to a hydrologic model. These isotopic compositions can then be compared with available meteoric and ground-water data to improve the estimates of average rain and local recharge compositions.

Three approaches for demonstrating the validity of the river dataset as a proxy for the isotopic compositions of precipitation or recharge waters will be discussed below: (1) comparison of the average isotopic compositions of precipitation with the compositions of adjacent rivers sites; (2) demonstration that river samples show many of the same correlations with environmental parameters (e.g. temperature, precipitation amount, elevation) and spatial patterns as precipitation samples; and (3) evaluation of the spatial coherency or 'robustness' of the spatial distributions of the river isotopic compositions. A fourth approach is comparison with the isotopic compositions of groundwater samples from the equivalent drainage areas; such data are currently being assembled. During groundwater recharge, the original precipitation compositions are altered by much the same processes as affect river samples (i.e. sensitivity to short-term and/or local events and effects). However, groundwaters are better integrated than replicate grab samples of river water. In a sense, river samples are an intermediate between rain and groundwater samples in terms of sensitivity to short-term events.

Comparison with precipitation data

The most obvious approach for 'validating' the river dataset is to compare average δ values at selected sites with δ values determined for mean annual precipitation at nearby sites with long-term datasets. However,

there are problems with this approach. How does one demonstrate that the patterns seen in river samples reflect patterns that would have been observable in rain samples collected over equivalent drainage areas? Although groundwater, which is a major source of water to streams, is typically an integration of precipitation over a large area and usually over a long time period, precipitation occurs episodically, with each event often having different meteorological histories and many forms (e.g. rain, snow, hail, fog). Rain collectors have interception areas on the order of 100 cm^2, whereas the river sample sites integrate rain inputs over a median drainage area of 8000 km^2, with variable elevations. Given the differences in the interception areas of rain collectors versus the river basins, and the variability in the compositions of waters collected in rain collectors over short distances, validation of the river dataset with the compositions measured at the small number of sites where long-term averages of precipitation data are available is technically infeasible.

Nevertheless, comparison of the river and precipitation data is a useful exercise. Table II shows a comparison of $\delta^{18}O$ and $\delta^{2}H$ values for 30 sites (many of which represent averages of data from several nearby sites) that had at least one full year of precipitation data, with the estimated 'river' δ values at these sites interpolated from Figure 6. The list includes all the GNIP stations in the lower 48 states plus other readily available datasets; it is by no means a comprehensive list. Comparison of the precipitation data with interpolated river δ values, instead of to values at the closest river site, was considered preferable because this minimized the adverse effect of the heterogeneity of the river database.

There is excellent agreement between the river and precipitation data. In general, the $\delta^{18}O$ and $\delta^{2}H$ values interpolated from the river contour maps (Figure 6) are only slightly lower than those of precipitation. The average differences are $0{\cdot}5\pm1{\cdot}3‰$ ($n = 29$) for $\delta^{18}O$, and $5{\cdot}5\pm11‰$ ($n = 23$) for $\delta^{2}H$. The largest difference in $\delta^{18}O$ is for Lubbock (+3·4%); the higher $\delta^{18}O$ value for river samples probably reflects the aridity of the area. The largest difference in $\delta^{2}H$ is for Albuquerque (−35‰). Yapp (1985) noted that the Rio Grande in Albuquerque had a $\delta^{2}H$ about 30‰ lower than local precipitation, and that local groundwater had δ values that varied by about 30‰ over 20 km because of different recharge sources. The $\delta^{18}O$ values of Canadian groundwaters sampled by Fritz *et al*. (1987) were also within about 2–3‰ of the compositions of precipitation at nearby GNIP stations.

This dataset is too small to make sweeping statements about the comparability of precipitation and river δ values. Although it is unlikely that the close match is fortuitous, we still believe that this approach has logical flaws; the very different interception areas of rain collectors versus drainage basins is a serious problem. This is especially true in areas of sharp topographic relief (such as the Rocky Mountains just north of Albuquerque), where the isotopic compositions of local precipitation are overwhelmed by discharge from an adjacent area of higher precipitation. However, smaller differences (i.e. the 1·5‰ difference in $\delta^{18}O$ between two nearby precipitation sites in Georgia) are possible even in areas of gentle relief. Furthermore, the significantly higher $\delta^{18}O$ values of river samples near Lubbock than local rain highlights the complications caused by evaporation in arid regions for the interpretation of river δ values. Other factors that are likely to contribute to differences between precipitation and river datasets include insufficient sampling of the rivers to determine a reasonable average composition, selective recharge of certain types or seasons of storms (which biases recharge), and mixing of waters of different ages and sources. Nevertheless, the close agreement between the river and precipitation datasets (Table II) suggests that large-scale mean annual isotopic signatures of precipitation have been preserved in the river isotopic compositions. Small-scale variations in the δ values of precipitation and groundwater, such as the 30‰ range in $\delta^{2}H$ observed in southern California (Friedman *et al*., 1992; Smith *et al*., 1992), are not apparent in the more widely spaced river sample network (Figure 1a).

We can speculate why the datasets are in such close agreement. One obvious possibility is that most of the river water derives from precipitation falling on contributing areas located near the gauge. In this case, the slightly lower δ values of river samples than precipitation might reflect the fraction of precipitation derived from higher elevations than the gauge. This is supported by the higher δ values of river samples in mountainous areas (e.g. Table II: Albuquerque, Flagstaff, Walker Branch, Underhill) and in coastal areas (e.g. Table II: Santa Maria, Alsea, Lewes, Hatteras, Destruction Island) compared with rain δ values. In the case of the coastal samples, the lower river δ values might also reflect decreasing δ values inland caused by

rainout. Another factor to keep in mind is that the river δ values were contoured based on the location of the gauge station, which is downstream of the 'centre' of the contributing area; this fact alone can account for the slightly lower δ values of the river samples. More site-specific information would be required to resolve this question. However, the good agreement suggests strongly that the density of our sample network was generally satisfactory for averaging the natural variations in the precipitation for the average basin sizes and ranges of elevation of most of the country.

The slopes and intercepts for LMWLs for precipitation samples (Table II) can be compared with the values calculated for river samples within the same state and HUC (Table I). The differences in the slopes and intercepts for precipitation sites within the same state can be used for defining 'normal' variability in precipitation. For the four states (Illinois, Nebraska, Ohio, Texas) where two sets of values for the slopes and intercepts of the LMWLs of the precipitation data are available (Table II), the differences in slopes range from 0 to 0·7, and the differences in intercepts range from about 3 to 10‰. Based on these criteria, good agreements were found for the precipitation data with averages for both the state and corresponding HUC for Illinois, North Carolina, and Wisconsin. Good correlations were found for precipitation data with just HUC data for Iowa, Minnesota, Nebraska, New York, Pennsylvania, and Vermont.

The better correlations with river LMWL data averaged at the regional (HUC) basin size than for states probably reflects the larger size (and consequently larger number of data points) at the HUC scale. However, caution should be exercised when averaging river isotope data from different drainage systems, as suggested by the fact that several of the states where the HUC data matched better than the state data are divided into two HUCs (Figure 1b). With the exception of Nebraska, all the states where the precipitation data and river showed similar LMWLs are in the wet northeastern and northcentral parts of the USA. Hence, in these regions, the δ values of the river database are probably good proxies for the LMWLs of annual precipitation and recharge.

The general lack of agreement of river and rain LMWLs for the rest of the country is probably caused by: (1) the greater heterogeneity of precipitation δ values in the western states caused by heterogeneous topography, precipitation amounts, temperatures, and stormtracks; (2) the effect of evaporation on the δ values of river samples in some basins; and (3) mixing of the local precipitation with groundwater derived from higher elevations in mountainous areas (e.g. as is observed in Albuquerque; Yapp, 1985). Hence, the LMWL values calculated for western states and HUCs are only appropriate for estimations of large-scale climate patterns, not for determining the average recharge composition in small western drainage basins.

The differences between the δ values of precipitation and river samples provide some insight into whether the river data are providing information on the spatial distribution of the isotopic compositions of mean annual *precipitation* or mean annual *recharge*. On average, the dominant source of water to the rivers is groundwater; hence, most of the isotopic signal being transmitted by the rivers is that of recharge, not local precipitation. The close matches shown in Table II suggest that, within an error bar of about ±2‰ for $\delta^{18}O$ and ±10‰ for $\delta^{2}H$, mean annual recharge and mean annual precipitation have approximately the same isotopic compositions for much of the country. This is more likely to be the case in the northeastern and north-central states, where the topography is more subdued, rainfall is higher, and evaporation is less important, and is less likely to be true in the southwestern states, where the opposite conditions exist. The similarities in the slopes and intercepts of LMWLs for precipitation and rivers in many states and HUCs, mostly in the northeastern and north-central states, is further support of the general similarity of recharge and precipitation, in these areas. In these areas, the river data might often be a better indicator of recharge than precipitation, because much of the river water is actually groundwater. For example, local groundwater at the Trout Lake site ($\delta^{18}O = -11{\cdot}5$‰, $\delta^{2}H \approx -83$‰; Krabbenhoft *et al.*, 1990, 1994) is more similar to the interpolated δ values for river samples at this site than precipitation (Table II).

In the southwestern states, the low r^2 values for LMWLs for states and HUCs is indicative of the heterogeneous nature of recharge δ values in arid and mountainous regions. The general lack of similarity between the LMWLs of precipitation and those calculated for states and HUCs from river data provides ample evidence that the δ values of precipitation in this region are not representative of recharge compositions, except

perhaps on a very small scale where the effects of evaporation and selective recharge are minimized by local conditions. Whether the river samples are adequate for regional assessments of recharge compositions or LMWLs in western states will require a closer examination of both river and groundwater isotope data. The observation that the isotopic compositions of many adjacent river sites in the west can be combined to produce LMWLs at the state and HUC level with high r^2 values suggests strongly that these LMWLs reflect some 'characteristic' aspect of recharge compositions that is imprinted on the water at a regional scale. This unexpected coherence in the data from climatically heterogeneous environments deserves further investigation.

Correlation with environmental parameters

Another method for demonstrating the validity of river samples as proxies for precipitation is to examine the correlations of river δ values with environmental parameters that show good correlations with precipitation δ values. As discussed above, the correlations of $\delta^{18}O$ and $\delta^{2}H$ with climatic variables are quite good when one considers that the temperatures, precipitation amounts, and evaporation amounts were the average values for the gauge location, and may not adequately represent the actual 'mean' value for the basin as a whole. The higher degree of scatter in the various relations is a concern, but they may reflect the heterogeneity of this particular dataset rather than a fundamental problem of river data (i.e. if more samples had been collected at each site, would the improvement in average compositions result in less noise?).

Most of the noise is in the data for western sites that are subject to high amounts of evapotranspiration (Figure 7d). Continental recycling of precipitation (due to non-fractionating transpiration) can explain more than one-third of the variability in $\delta^{18}O$ that is not explained by temperature (Koster *et al.*, 1993). The low slopes of many of the LMWLs raises questions about the possibility that post-rainfall evaporation may have adversely affected the mean compositions. However, there is not enough information about the long- and short-term characteristics of precipitation in arid and semi-arid parts of the USA to resolve this question. For example, it is unclear what values of *d*-excess or slopes of LMWLs are actually diagnostic of evaporated samples. Welker (2000) concluded that the weekly precipitation samples he analysed had not suffered post-rainfall evaporation because few (5%) have *d*-excess values less than zero. Only 8% of the 4800 river samples had *d*-excess values less than zero (lowest: $-8‰$), which is not much higher than seen in Welker's data or that of GNIP sites in semi-arid areas (IAEA, 1992). Furthermore, Rozanski *et al.* (1982) observed that the average *d*-excess of summer precipitation at European sites was $-6{\cdot}3‰$. In summary, there is a lack of definitive evidence that the river samples are significantly isotopically fractionated and there are a variety of compelling lines of evidence that climatic signals have been retained in the river samples.

Robustness of patterns

If the contour plots of different subsets of the data produce similar spatial patterns, the patterns are 'robust' or spatially coherent. For example, about 35% of the total sites (those greater than 8000 km^2) were omitted to produce Figure 5b, yet the spatial distribution of $\delta^{18}O$ values is almost the same as Figure 5a and d, except for a few geographic regions where all the sites in a particular location were omitted and adjacent contours shifted to fill the gap in data (e.g. near the northwest edge of the Great Lakes). This means that removing the potentially least representative (i.e. large) sites has no major effect on the spatial patterns. The spatial distribution of minimum $\delta^{18}O$ values (Figure 8) is also similar to the distributions in Figures 5 and 6, suggesting that groundwater is the main source of water to most of the rivers. The similarity of patterns despite the different site or sample selection criteria indicates that these data are not very sensitive to the criteria tested. This test also demonstrates that the patterns are very robust (have strong spatial coherence). Although the robustness of the spatial patterns of river samples does not prove that the river samples are representative of precipitation, it is strong support that climatic signals that control the isotopic composition of precipitation samples have been preserved in the river samples. The spatial coherence suggests that the data reflect the spatial 'forcing' of some parameter, probably that of mean annual precipitation.

The robustness of the patterns suggests that the size of the database has successfully compensated for the inherent diversity of discrete river samples, at least for this scale of data analysis. In other words, although a multitude of complicating processes (e.g. storm events upstream, mixing with groundwater, and local evaporation) may act erratically on river samples to blur the original meteoric isotopic signal, and will act differently at different times and at different places, broad regional patterns are apparently preserved. Furthermore, it is likely that the river samples have done a better job of integrating the spatial variability in the meteorological cycle to produce spatially coherent $\delta^{18}O$ and $\delta^{2}H$ patterns across the USA than could have been determined with an equivalent number of precipitation samples. And finally, a network of river stations might be a superior means for establishing the isotopic compositions of recharge waters for calibrating potential palaeoclimatic and palaeohydrologic proxies than any comparable network of precipitation stations.

CONCLUSIONS

(1) A 'national' MWL based on unweighted analyses of river samples from the 48 contiguous states was calculated to be $\delta^{2}H = 8{\cdot}11\delta^{18}O + 8{\cdot}99$ ($r^{2} = 0{\cdot}98$). This relation is very similar to the unweighted GMWL of Rozanski *et al*. (1993) of $8{\cdot}17\delta^{18}O + 10{\cdot}35$, which was based on the GNIP precipitation network, and suggests the dominance of the isotopic signal of precipitation in this set of river samples.

(2) The 'national' meteoric water line is composed of water samples that arise in diverse local conditions where the LMWLs of river sites usually have much lower slopes. LMWLs from large sections of the western and southern parts of the USA have slopes less than 6, normally considered suggestive of evaporation. However, it is not known whether the changes in slopes took place during evaporation of rainfall, evaporation during recharge, or during some other recharge process.

(3) The broad regional patterns of LMWL slopes and the high r^{2} values for many LMWLs composed of sites from the same state or region imply that large geographic areas are being controlled by the humidity of the local air mass, which imparts a distinctive evaporative isotopic enrichment to rainfall and hence to stream samples within the area. Without additional information about isotopic compositions of local rain and groundwater, it is not possible to quantify the extent that LMWLs produced by evaporation of raindrops in an atmosphere of uniform humidity have been changed by later processes.

(4) Deuterium excess values range from 6 to 15‰ in the eastern half of the USA, along the northwest coast and on the Colorado Plateau; the rest of the USA shows values in the range of -2 to 6‰, with strong regional patterns. Although deuterium excess values are often interpreted as indicators of original air mass source, the superposition of evaporative isotopic effects in arid regions makes such interpretations problematic.

(5) Spatial distributions of $\delta^{18}O$ and $\delta^{2}H$ values are very similar to each other, closely match topographic contours, and show a high degree of spatial coherence. These contour plots represent the best available maps of the stable isotope ratios of hydrogen and oxygen of meteoric-derived waters in the USA.

(6) Although the robustness of the spatial patterns of river sample data does not prove that the river samples are representative of precipitation, it is strong support that climatic signals that control the isotopic composition of precipitation samples have been preserved in the river samples.

(7) There is excellent agreement of interpolated $\delta^{18}O$ and $\delta^{2}H$ values of river samples with the $\delta^{18}O$ and $\delta^{2}H$ values of precipitation measured at 30 sites, most of which have multi-year records and many of which reflect the compositions of one or more adjacent collection sites. Despite the fact that differences in the interception areas of precipitation collectors versus drainage basins makes such comparisons somewhat dubious, the agreement is nevertheless an encouraging indication that large-scale isotopic signatures of precipitation have been preserved in the river isotopic compositions.

(8) Until the average river isotopic compositions have been correlated with precipitation and groundwater data over the same area, care should be exercised when plots of average river composition are used to deduce average precipitation or recharge compositions, especially in the western states. However, regional patterns deduced from slopes of the LMWLs or from *d*-excess values probably reflect the patterns seen in precipitation.

(9) The good agreement of the correlations of mean $\delta^{18}O$ values of river samples to annual mean temperature, precipitation, and latitude, and their similarity to the correlations expected for precipitation samples, especially for the eastern sites, supports the usefulness of river isotope data for climatic reconstructions.

(10) Although it might be expected that the magnitude of the seasonal variations in the isotopic composition of the creeks is inversely proportional to the size of the basin, i.e. the size of the sub-surface reservoir that can respond to precipitation events (Fritz, 1981), there is no indication of this phenomenon in our dataset.

(11) Given the variable seasonal distributions of δ values at sites, and the small and variable number of samples collected to assess this variability, the minimal difference between the spatial distributions of average unweighted and discharge-weighted δ values is a testament to the success of this sampling effort at capturing the environmental signal.

(12) The main challenge in attempting to use stream samples to determine regional patterns of precipitation isotopic composition in the western states is the problem of evaporation. Because post-rainfall evaporation from the stream surface and in the soil zone in the same arid environment probably causes the isotopic compositions to plot along much the same evaporation line as for raindrops, determining whether samples from a particular site have experienced significant amounts of post-rainfall evaporation is extremely difficult. Surface-water evaporation effects have been minimized by collecting only depth-integrated samples.

(13) The robustness of the spatial isotopic patterns suggests that the size of the database has compensated successfully for the inherent diversity of grab-sampled river samples, and that the regional meteoric patterns (and perhaps many local patterns) have not been significantly overprinted by later post-rainfall effects such as evaporation, homogenization, and mixing with groundwater. In other words, the overprinting of local processes is insufficient to mask completely the regional isotopic patterns that reflect the origin of the vapour mass.

(14) The isotopic compositions of river samples produce spatially coherent $\delta^{18}O$ and $\delta^{2}H$ patterns across the USA. They appear to be primarily reflecting precipitation 'forcing', and so may do a better job of integrating the spatial variability in the meteorological cycle than could have been determined with an equivalent number of precipitation samples.

ACKNOWLEDGEMENTS

We would like to thank the many NASQAN program and other field technicians for their careful efforts collecting the samples. We would also like to thank Jessica Hopple, John Laughlin, and Stephanie Rieder for sample analyses, Steve Silva, Scott Wankel, Valerie Kelly, Eric Caldwell, and Dave Wolock for their help in preparing this report, and Bryan Bemis, Rick Hooper, Randy Hunt, Valerie Kelly, Jurate Landwehr, Bob Michel, Jim O'Neil, Adina Paytan, Steve Silva, Ike Winograd, and Tom Winter for their thoughtful reviews of versions of the paper.

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