

Use of NADP Archive Samples to Determine the Isotope Composition of Precipitation: Characterizing the Meteoric Input Function for Use in Ground Water Studies

by F. Edwin Harvey¹

Abstract

Stable oxygen and hydrogen isotopes have been used in ground water studies to investigate recharge, mixing, ground water/surface water interaction, advective-diffusive transport, paleohydrogeologic interactions and to estimate ground water ages. Such studies require that the isotopic composition of precipitation be known, as precipitation is a major input to ground water and surface water systems. As oxygen-18 and deuterium data for precipitation are lacking across much of the United States, there is need to establish additional local meteoric water lines as isotope input functions across the region, as well as to develop better understanding of the isotopic climate linkages that control oxygen and hydrogen isotope ratios in precipitation. In the absence of long-term monitoring stations, one possible solution to this problem is to determine the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation using archive samples collected at monitoring stations managed by the National Atmospheric Deposition Program (NADP). This study describes and interprets the seasonal $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of archived precipitation samples collected in eastern Nebraska near the town of Mead during the years 1992–1994. Values for $\delta^{18}\text{O}$ range from -23.6 to -0.7‰ . Values for $\delta^2\text{H}$ range from -172 to 0‰ . Yearly arithmetic mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the Mead station are -8.1‰ and -53‰ , respectively. Weighted yearly means for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were -7.4‰ and -48‰ , respectively. Mead values show a strong isotopic enrichment between winter and summer precipitation, and a strong $\delta^{18}\text{O}$ -T correlation ($r^2 = 0.91$) for mean monthly values of about 0.5‰ per degree Celsius. The local meteoric water line for the Mead site is $\delta^2\text{H} = 7.40 \delta^{18}\text{O} + 7.32$. Deuterium excess values suggest that most of the moisture across the region is derived primarily from a Gulf of Mexico source. The results of this study demonstrate that in the absence of long-term monitoring stations such as those operated globally by the International Atomic Energy Association, NADP archive samples can be used to determine the isotopic composition of precipitation, to characterize the local meteoric water line and establish the various climatic relationships, and define the meteoric input function for use in ground water studies.

Introduction

Purpose and Scope

The use of stable oxygen (^{18}O and ^{16}O) and hydrogen (^2H and ^1H) isotopes is well established in ground water studies (Clark and Fritz 1997; Mazor 1991; Fontes 1980). Oxygen and hydrogen isotopes have been used to investigate ground water recharge (Mathieu and Bariac 1996; Stimson et al. 1993); to determine the effects of evaporation on ground water systems (Hendry 1988; Clark 1987); to estimate advection/diffusion rates in fine grained terrestrial (Desaulniers and Cherry 1989) and lake sediments (Harvey 1996); to explore ground water and surface water interaction (Krabbenhoft et al. 1990), and as a relative age dating tool to identify ground waters that were recharged under colder climates dur-

ing the Pleistocene (Siegel and Mandle 1984; Matheney and Gerla 1996). Stable ^{18}O and ^2H isotopes have also been utilized in surface water studies to examine the dynamics of river mixing (Yang et al. 1996; Krouse and Mackay 1971); irrigation canal leakage (Sibray et al. 1997; Harvey and Sibray 2001); hydrograph separation (Buttle 1994); for investigating evapotranspiration (Gat et al. 1994; Ingraham and Craig 1993) and to examine the paleohydrology of lakes as it relates to climate change (Smith et al. 1997).

Such studies, however require that the oxygen and hydrogen isotope ratios of precipitation be known, as precipitation is a major input to ground water and surface water systems. Since 1953, isotope ratios in precipitation have been measured at numerous monitoring stations worldwide by the International Atomic Energy Agency (IAEA). However, few IAEA stations in the United States recorded $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data, and many IAEA stations that did are no longer in operation; thus, modern analyses are lacking.

Ground water and surface water studies in the northeastern Great Plains region, for example, must use data from the closest IAEA station in Chicago, Illinois (≈ 1275 km) or data from a study by Simpkins (1995) which collected and analyzed precipitation samples near Ames, in central Iowa (≈ 750 km), for 1992. While data

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have been successfully extrapolated to nearby locations with a similar climate and precipitation pattern (Harvey et al. 1997; Harvey 1996), the northeastern Great Plains region has climate and precipitation patterns which differ greatly from those present at Chicago, and although more similar, central Iowa as well. Recent studies have attempted to define a long-term isotopic trend for the central United States (Rozanski et al. 1993); however, the data sets are too widely spaced to be beneficial in the Great Plains, where the climate varies from subhumid in the eastern portion to semi-arid in the western portion. Thus, there is a need for more localized data that are representative of the various climatic zones.

In the absence of long-term monitoring stations, one possible solution to this problem is to determine the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation using archive samples collected at monitoring stations managed by the National Atmospheric Deposition Program (NADP) as part of their weekly precipitation chemistry monitoring program (NADP 1998; Bigelow 1991). The NADP is a nationwide network of precipitation monitoring sites maintained as a cooperative effort between many groups, including the State Agricultural Experiment Stations, USGS, the U.S. Department of Agriculture, and numerous other governmental and private entities. The NADP network is made up of more than 200 sites spanning the continental United States, Alaska, Puerto Rico, and the Virgin Islands. Site locations, information concerning acquisition of archive samples, and/or additional information about the program can be obtained on the NADP website (at <http://nadp.sws.uiuc.edu/>), or by contacting the Illinois State Water Survey.

Before using data derived from NADP precipitation samples for hydrological investigations, two conditions must be met in order to ensure that the data are truly representative of the monthly and yearly meteoric input functions at the given location. First, the samples analyzed must be representative of the yearly distribution of precipitation at the station, such that each of the four seasons are represented, and that a majority of the samples represent that portion of the year with the largest and most frequent precipitation events. Second, the precipitation samples must not have been impacted significantly by post-depositional modification effects (primarily evaporation), ensuring that the isotope values obtained are representative of meteoric water at the monitoring site at the time of collection. If these conditions are met, stable isotope values obtained from precipitation samples collected at NADP monitoring stations can be used to provide local meteoric water lines, and define the precipitation input function for a given location. Both of these criteria have been met by the data presented in this study.

This paper reports stable isotope data for precipitation in the eastern subhumid portion of the northeastern Great Plains determined using archived samples collected by the NADP. The study determined the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ concentrations of precipitation samples collected in Mead, Nebraska, from 1992 to 1994. The results of this study augment the more continental work of Coplen and Huang (2000) in the eastern United States, and Fritz et al. (1987) in Canada, and the more global work of Craig (1961), Gat (1980), and Gat and Gonfiantini (1981). However, they are unique in that they provide a much needed, local isotope database for use in ground water, surface water, and paleoclimate studies across the region. This study also demonstrates that in the absence of data collected at long-term monitoring stations, NADP archive samples can be used to establish local meteoric water lines, and to determine the meteoric input function.

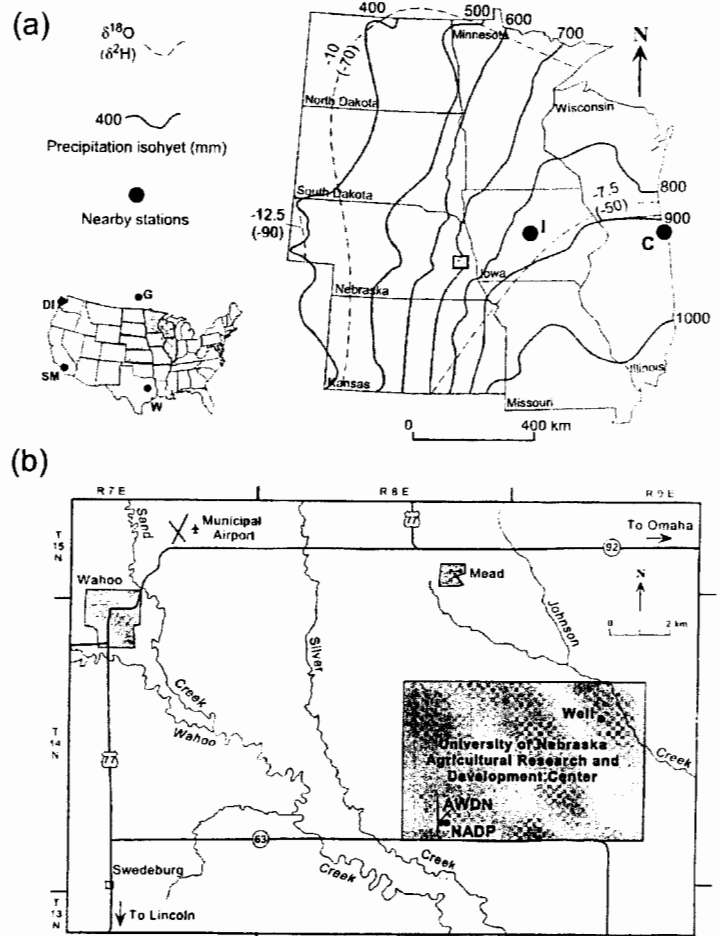


Figure 1. (a) Locations of the IAEA station at Chicago (C) and the Iowa (I) station of Simpkins (1995). Isohyets for precipitation were taken from Simpkins (1995). Predicted oxygen and deuterium (in parentheses) contours of Nebraska meteoric waters expressed as ‰ V-SMOW are from Sheppard et al. (1969). Also shown on the inset are the IAEA stations at Santa Maria, California (SM), Destruction Island, U.S.A. (DI), Gimli, Manitoba, Canada (G), and Waco, Texas (W). (b) Expansion of the shaded area in (a) showing the location of precipitation and meteorological monitoring stations in Mead, Nebraska.

Study Area

The data presented in this paper were collected from two meteorological stations at Mead, Nebraska, north of the capital city of Lincoln. Stable isotope ratios were determined on NADP Precipitation samples collected at the University of Nebraska Agricultural Research and Development Center (ARDC) in Mead, Nebraska (Figure 1). The station is located in eastern Nebraska, north of Lincoln and west of Omaha at latitude $41^{\circ} 09' 11''$, longitude $96^{\circ} 29' 34''$, and at an elevation of 352 m above sea level. The NADP site is operated by the University of Nebraska-Lincoln's School of Natural Resource Sciences.

Climate data were compiled from a station operated at the ARDC site by the University of Nebraska-Lincoln's High Plains Climate Center. The station is an Automated Weather Data Network (AWDN) station (Figure 1), located 15 m away from the NADP station.

Reported precipitation amounts (Table 1) were taken from the NADP station, except on several dates when an amount was not recorded due to instrument malfunction, or human error. For those dates the precipitation values reported were taken from the nearby AWDN station. Comparisons of the NADP data with the AWDN

Table 1
Stable Isotope Data for Precipitation in Mead, Nebraska
(Years 1992–1994)

Week Sampled	Cum. Week No.	Average Weekly Temp. (°C)	Weekly Precip. (mm)	¹⁸ O (‰ V-SMOW)	² H (‰ V-SMOW)	d (‰ V-SMOW)
Year 1992						
01-21 to 01-28	4	1.0	11	-17.4	-126	13.2
02-04 to 02-11	6	-0.6	2	-11.5	-86	6.5
02-11 to 02-18	7	1.0	20	-12.8	-80	22.9
03-03 to 03-10	10	10.0	43	-10.4	-73	10.4
03-17 to 03-24	12	4.1	8	-8.7	-59	10.6
03-24 to 03-31	13	5.2	15	-4.7	-28	9.7
03-31 to 04-07	14	9.7	12	-7.1	-47	10.2
04-14 to 04-22	16	8.8	20	-11.4	-77	14.5
04-22 to 04-28	17	7.7	8	-9.9	-67	12.0
05-12 to 05-19	20	16.9	17	-2.8	-12	10.7
05-19 to 05-26	21	17.2	31	-3.7	-5	14.8
05-26 to 06-02	22	12.8	14	-3.3	-13	13.6
06-02 to 06-09	23	18.5	9	-6.6	-55	-2.4†
06-09 to 06-16	24	20.5	4	-1.7	-8	5.9
06-16 to 06-23	25	21.1	15	-2.3	-11	7.2
06-23 to 06-30	26	21.0	3	-7.3	-66	-7.6†
06-30 to 07-07	27	22.0	48	-5.4	-34	9.7
07-07 to 07-14	28	23.6	94	-5.5	-30	13.5
07-21 to 07-28	30	20.0	20	-7.7	-53	9.1
07-28 to 08-04	31	20.6	24	-6.6	-37	15.8
08-04 to 08-11	32	22.7	14	-4.6	-30	6.7
08-11 to 08-18	33	18.3	6	-5.3	-36	6.3
08-18 to 08-25	34	22.1	13	-3.8	-13	17.0
08-25 to 09-01	35	16.8	6	-6.8	-40	14.3
09-01 to 09-08	36	20.5	24	-4.9	-27	12.3
09-08 to 09-15	37	17.9	18	-4.2	-16	18.0
09-15 to 09-22	38	19.2	6	-0.7	-3	3.0
09-22 to 09-29	39	14.2	8	-4.9	-19	19.9
10-06 to 10-13	41	9.9	50	-9.3	-50	24.7
10-27 to 11-03	44	6.3	26*	-16.6	-115	17.4
11-17 to 11-24	47	1.2	20	-15.1	-101	19.6
12-08 to 12-15	50	0.8	19*	-14.1	-91	21.4
Year 1993						
01-19 to 01-26	56	-6.0	9*	-17.2	-121	16.9
02-02 to 02-09	58	-1.5	3*	-15.9	-116	11.0
02-09 to 02-16	59	-4.5	5*	-15.5	-103	20.5
02-23 to 03-02	61	-9.3	10	-15.8	-110	16.9
03-02 to 03-09	62	1.3	4	-17.8	-126	16.5
03-30 to 04-06	66	2.8	18	-15.0	-104	15.8
04-06 to 04-13	67	8.4	19	-9.2	-58	15.0
04-13 to 04-20	68	7.2	31	-11.9	-81	14.3
04-27 to 05-04	70	12.2	10	-8.0	-61	3.4
05-04 to 05-11	71	16.4	36	-9.2	-64	9.5
05-11 to 05-18	72	16.5	5	-2.9	-26	-2.4†
05-18 to 05-25	73	14.0	41	-6.0	-32	15.9
05-25 to 06-01	74	18.4	4	-6.0	-39	8.8
06-01 to 06-08	75	16.0	36	-6.8	-38	16.7
06-08 to 06-15	76	20.8	45	-6.3	-37	13.4
06-15 to 06-22	77	22.8	32	-6.8	-42	12.5
06-22 to 06-29	78	22.4	90	-7.9	-54	9.0
06-29 to 07-06	79	24.8	18	-5.3	-35	7.2
07-06 to 07-13	80	22.8	47	-7.0	-39	16.5
07-13 to 07-20	81	24.0	62*	-7.7	-51	10.4
07-20 to 07-27	82	22.1	113*	-5.5	-36	8.6
07-27 to 08-03	83	24.3	4	-1.7	-12	2.0†
08-10 to 08-17	85	26.3	42	-4.0	-18	13.9
08-17 to 08-24	86	25.2	13	-3.9	-27	4.8
08-24 to 08-31	87	23.2	98	-4.9	-24	14.5
08-31 to 09-07	88	16.8	9	-9.8	-74	4.3

Table 1 (continued)

Week Sampled	Cum. Week No.	Average Weekly Temp. (°C)	Weekly Precip. (mm)	¹⁸ O (‰ V-SMOW)	² H (‰ V-SMOW)	d (‰ V-SMOW)
09-07 to 09-14	89	18.0	6	-5.6	-35	9.9
09-14 to 09-21	90	13.1	33	-7.0	-39	16.6
09-21 to 09-28	91	14.1	43	-5.8	-36	10.9
10-05 to 10-12	93	13.2	14	-8.7	-49	19.8
10-12 to 10-19	94	10.7	19	-11.9	-80	14.7
10-19 to 10-26	96	10.8	2	-13.8	-101	9.4
11-09 to 11-16	98	4.0	13	-11.5	-72	19.8
12-07 to 12-14	102	2.3	3	-19.0	-135	17.3
Year 1994						
04-05 to 04-12	119	5.3	15	-9.7	-62	15.0
04-26 to 05-03	122	5.2	17*	-12.5	-81	18.5
05-03 to 05-10	123	12.3	14	-8.3	-52	13.9
05-10 to 05-17	124	18.0	4	-4.4	-35	0.5†
05-17 to 05-24	125	22.1	13	-1.6	0	12.1
05-24 to 05-31	126	20.6	4	-5.8	-36	10.5
05-31 to 06-07	127	19.6	113	-5.7	-31	13.8
06-21 to 06-28	130	22.4	70	-4.4	-23	12.7
06-28 to 07-05	131	22.9	52	-5.6	-33	11.4
07-05 to 07-12	132	22.1	20	-0.7	-2	3.3
07-12 to 07-19	133	22.2	22	-7.2	-40	17.2
07-19 to 07-26	134	22.1	7	-5.9	-53	-5.6†
07-26 to 08-02	135	20.5	9	-5.1	-33	7.7
08-02 to 08-09	136	20.6	14	-4.9	-30	9.3
08-23 to 08-30	139	23.2	21	-2.9	-10	13.1
08-30 to 09-06	140	19.6	44	-5.4	-29	14.8
09-20 to 09-27	143	13.6	47	-13.2	-89	16.7
10-04 to 10-11	145	13.8	5	-4.6	-24	12.6
10-11 to 10-18	146	13.4	20	-9.4	-59	16.1
11-01 to 11-08	149	7.6	3	-10.1	-63	17.8
11-15 to 11-22	151	3.5	35	-17.2	-119	18.2
11-22 to 11-29	152	1.9	24	-8.8	-49	20.7
12-06 to 12-13	154	-7.8	18	-23.6	-172	17.3

Temperature data are taken from the AWDN station. Precipitation data are taken from the NADP station except where noted (*). The deuterium excess (d) is calculated as $d = \delta^2\text{H} - 8\delta^{18}\text{O}$. Analytical precision for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is 0.2 and 2.0‰, respectively. †Samples may have undergone evaporation in the collector owing to their d-excess values <3‰.

data, and additional data from other nearby weather stations reported here for all dates over the three-year period show excellent agreement between weekly recorded precipitation amounts, so this occasional substitution of the precipitation amounts is acceptable. Information regarding comparisons/calibrations with other stations are available from NADP.

Climate and Precipitation Sources

The isotopic composition of precipitation is determined by several factors including seasonal climate variations, geographic location and atmospheric moisture transport. Climate varies across the northern Great Plains ranging from dry, semi-arid climate in the west to moist subhumid climate in the east. Nebraska, located at the center of the region, also experiences this west to east variation. The state's continental position, and relatively clear skies throughout the year result in a wide range of annual temperatures (Lawson et al. 1977). Average yearly temperatures across the state range from 11.0°C in the southeast to 6.9°C in the northwestern portion of the panhandle (Owenby and Ezell 1992). In addition, Nebraska lies in a zone of the northern plains where precipitation diminishes rapidly

Methodology

Precipitation Collection

Weekly precipitation samples were collected every Tuesday morning at the Mead station by the NADP network with the aid of site operators (Bigelow 1991) from January 1992 through December 1994. Precipitation samples were collected using a modified Aerochem Metrics wet/dry precipitation collector (Bigelow 1991). The precipitation falls into a collector which is covered by a mechanical lid assembly having a semigasket seal on the bucket to prevent evaporation. During precipitation events, a 75 ohm sensor is activated and the lid opens. The lid closes after the precipitation event. Precipitation amounts are measured at the station using a Belfort Model 5-780 weighing bucket recording gauge.

Prior to January 11, 1994, the collected weekly composited precipitation sample was shipped to the Illinois State Water Survey (ISWS) in the sealed 13.25 L plastic bucket taken from the collector. If sufficient water was present in the collector, pH and conductivity were measured on the sample by the field technician at the collection site. At the ISWS lab, the sample was transferred from the collector to 1000 ml plastic bottles for processing, and the amount of sample was recorded. After January 11, 1994, the composited sample was transferred to the 1000 mL bottle at the field collection station, and this bottle was sealed and mailed to ISWS. In the lab, samples were filtered and split into two 60 mL subsamples. The subsamples were placed in plastic bottles. Cation and anion analyses were conducted on one subsample (Lynch et al. 1995) at the ISWS Central Analytical Laboratory. The second subsample was placed in storage (archived) on site, in a cold room at 4°C.

The NADP has conducted several internal studies to determine if samples undergo evaporation during collection and/or storage (see the NADP website for a complete list of the QA/QC reports). Comparisons are made between precipitation amounts collected in the Aerochem Metrics collector and amounts recorded by the Belfort gage, to evaluate the potential for evaporation during collection. Also, random archive samples are periodically removed from storage and reanalyzed for comparison of the chemical concentrations of the newly tested and original samples. These comparative tests indicate that the majority of precipitation samples collected have not undergone evaporation during collection and/or storage. In the small number of cases where evaporation was detected, the total amount of evaporation did not exceed 1% of the total volume of sample collected (Van Bowersox, NADP, personal communication, 1999).

The impact of evaporation on the NADP samples can also be evaluated by examining each sample's deuterium excess value (d-excess). The d-excess in precipitation is defined by the air-sea interaction processes over the ocean surface as described by Craig and Gordon (1965), Merlivat and Jouzel (1979), and Gat (1996). These processes fix the d-excess value, which remains invariant as air masses move across the continents and lose moisture by rain-out (as long as no direct formation of ice crystals is taking place). If however, the air masses are impacted by secondary processes which return moisture to the air such as evaporation from an open surface water body (Gat et al 1994; Machavaram and Krishnamurthy 1995), the inherited d-excess value can be altered as the air mass moves inland. The d-excess value may also be impacted by evaporation of the precipitation as it falls through the air beneath the cloud base (or possibly as it sits in the rain collector). Using the moisture exchange model of Merlivat and Jouzel (1979) it can be shown that

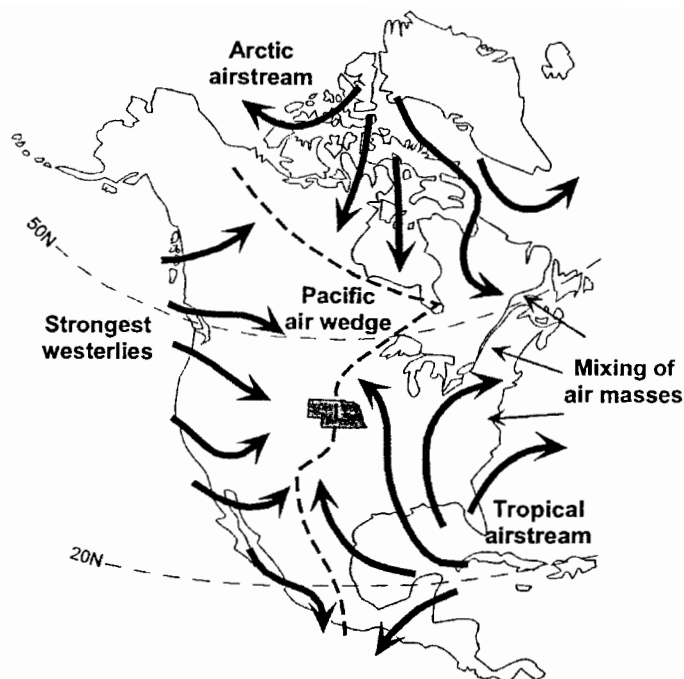


Figure 2. Map of North America showing location of competing airstreams and their relation to Nebraska's two major moisture sources (Pacific Ocean and Gulf of Mexico). Shaded area shows the location of Nebraska. (Modified from Bryson and Hare 1974).

from east to west. Values across the state range annually from 922 mm in the southeast corner, along the Missouri River, to 370 mm in the western panhandle near the Wyoming border (Lawson et al. 1977).

The climate of the northern Great Plains is largely influenced by four factors: distance from the equator, altitude, proximity to the Rocky Mountains, which block the eastward movement of Pacific Ocean moisture, and distance and direction from the Gulf of Mexico, the main moisture source for the region's precipitation (Colville and Myers 1965).

The climatology of the northern Great Plains, and Nebraska specifically, reflects the competing influences of the Arctic airstream, the Tropical airstream and the Pacific air wedge (Figure 2). Strong seasonal contrasts are produced by the alternation of cold, dry Arctic air, moist, warm air from the Gulf of Mexico and Pacific Ocean and mild, dry westerly winds (Court 1974; Bryson and Hare 1974; Lawson et al. 1977). In winter, Arctic air dominates the northern Great Plains weather, but with the lack of a land barrier to the south, unseasonably warm southern air frequently flows into the region. In summer, tropical air may be displaced by dry, cooler air from Canada. No other continental area experiences such severe contrasts in air mass conditions (Lawson et al. 1977).

These relationships are important because the various airstreams entrain moisture from different sources, which, in addition to temperature and altitude cause variations in the stable isotopic signature of precipitation. Nebraska's precipitation comes primarily from two moisture sources, the Pacific Ocean and the Gulf of Mexico or some mixture of both. Nearly 80% of the moisture precipitated in Nebraska comes from the Gulf (Allen Dutcher, Nebraska State Climatologist, High Plains Climate Center, personal communication 1999).

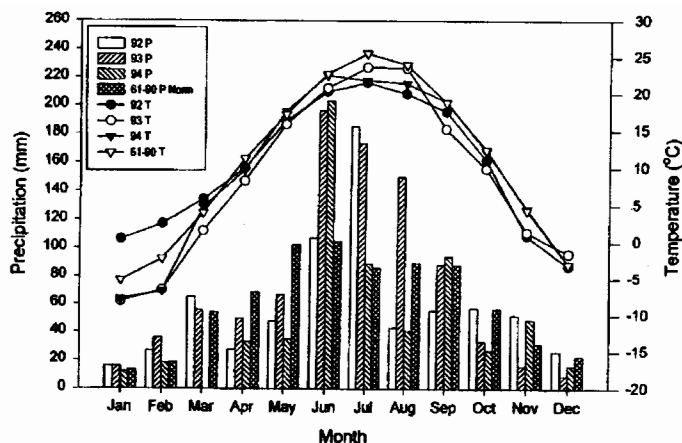


Figure 3. Precipitation (bars) and temperature (symbols) record for Mead, Nebraska (1992–1994). Also shown are the 1961–1990 (30-year) normal values taken from Owenby and Ezell (1992).

for reasonable temperature (20°–30°C) and relative humidity (70%–95%) conditions over the ocean, the initial d-excess value of transported moisture should be between 3–15 ‰. Thus, NADP archive samples with d-excess values less than 3 ‰ should be used with caution unless the source of their evaporative enrichment can be determined with certainty, as they may have been impacted by evaporation in the collector. Samples with values greater than 15 ‰ have likely been impacted by the addition of moisture from some secondary process during transport across the continent.

Evaluation of the data set used in this study using the previous criteria indicates that only six samples were impacted by evaporation (Table 1). All six samples were collected in summer months during weeks when small precipitation amounts were recorded (Table 1) in the collector. It may be that the warmer summer air temperatures, coupled with low collector volumes resulted in partial evaporation of the sample while it was sitting in the collector. If so, these samples are not representative of precipitation that fell during that collection week, and should be excluded from the final data evaluation. However, the observed evaporation could also have occurred beneath the cloud base as the precipitation fell through the air column, and not on the ground in the collector. This phenomena, which depends on a number of parameters such as raindrop radius, vertical temperature profile and/or relative humidity, for example, is often observed during light summer showers where the rain completely or partially evaporates before reaching the ground. In this case, the samples have not been compromised, but rather record a natural meteorological occurrence, and should therefore be included in the data analysis. Unfortunately, it could not be determined which of these two processes occurred for the low d-excess samples collected in this study. For this reason, and also because the impact of including the small number of samples in question relative to the total number of samples in the data set (Table 1) was minimal, all of the samples collected in this study were used in the final analyses.

Stable Isotopic Analysis

Archived precipitation samples from the Mead NADP site for the years 1992–1994 were analyzed for ¹⁸O and ²H abundance at the Environmental Isotope Laboratory (EIL) at the University of Waterloo in Waterloo, Ontario, Canada in August 1998. Oxygen determinations were made using a Micromass 903 triple collector SIRA mass spectrometer following the procedures of Epstein and Mayeda (1953). Deuterium determinations were made on a

Micromass 602C mass spectrometer following the zinc reduction preparation method of Coleman et al. (1982). Oxygen and hydrogen results are reported as parts per thousand (‰) with respect to V-SMOW using the (δ) notation where

$$\delta_{\text{sample}} = \frac{(R_{\text{sample}} - R_{\text{standard}})}{(R_{\text{standard}})} \times 1000$$

R_{sample} is the ratio of ¹⁸O/¹⁶O or ²H/¹H in the sample and R_{standard} is the ratio of the international standard. The analytical precision for δ¹⁸O and δ²H are 0.2 and 2.0 ‰ (1σ), respectively.

Yearly weighted mean values of δ¹⁸O and δ²H were calculated by the equation

$$\bar{\delta}_w = \left(\frac{\sum_{i=1}^n P_i \delta_i}{\sum_{i=1}^n P_i} \right)$$

where δ_i is the δ¹⁸O and δ²H (‰) of the weekly composite sample; P_i is the recorded total weekly precipitation of the *i*th week; and *n* is the number of weekly samples (89). Monthly weighted means were calculated in a similar fashion where δ_i is the monthly average δ¹⁸O and δ²H (‰) value over the three-year period (1992–1994); P_i is the average monthly precipitation of the *i*th month over the three-year period (1992–1994); and *n* is the number of months (12).

Meteorological Data

AWDN meteorological data for 1992–1994 were provided by the High Plains Climate Center. The AWDN station monitors hourly and daily temperature, precipitation, relative humidity, solar radiation, soil temperature, wind speed and wind direction. AWDN daily temperature is recorded using a Vaisalla HMP 45 temperature/relative humidity sensor. Daily precipitation is collected using a Sierra tipping bucket (1 mm/tip).

Results and Discussion

Meteorology of Mead, Nebraska

Monthly precipitation and temperature data for the Mead station are shown in Figure 3 for 1992–1994. Also shown are the 1961–1990, 30-year normal values for precipitation and temperature (Owenby and Ezell 1992). The normal yearly temperature is 10.8°C and normal precipitation is 736 mm.

Yearly average temperatures for 1992–1994 were slightly below normal, having values of 10.3°, 8.7°, and 9.7°C, respectively. Temperatures in 1992 were well above normal during January, February, and March, and dropped below normal during the summer months. In 1993 and 1994, temperatures in January and February were below normal, but rose in March to normal levels and remained near normal throughout the remainder of the year. With the exception of the January and February oscillations, monthly deviations from their respective norms are small.

Precipitation values show a great deal of variability during the monitoring period. The total yearly precipitation averages for 1992–1994 were 709, 890, and 617 mm, respectively. Year 1992 was slightly below normal while year 1993 was extremely wet, having more than 100 mm of additional precipitation. Year 1994 was a

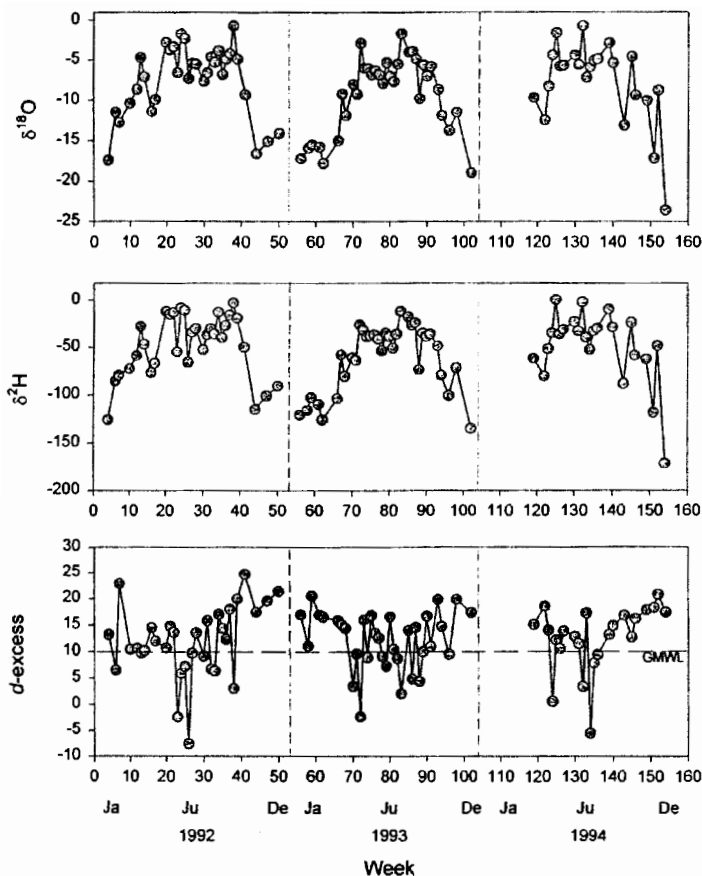


Figure 4. Three-year weekly time series plot of $\delta^{18}\text{O}$, $\delta^2\text{H}$, and deuterium (d) excess values for Mead.

drought year with rainfall falling more than 100 mm below normal. All three years had below normal precipitation values in the spring months (March–May), and above normal values in June and July.

Daily weather maps indicate that the warmer than normal temperatures in early 1992 resulted from the combination of mean zonal flow along the Canadian–United States border preventing cooler air from penetrating down into the Great Plains, and a series of low pressure zones present over the southern United States which forced warmer air into the plains from Mexico and the Pacific Ocean. January and February temperatures may also have been affected by the lack of precipitation and snow cover during the winter months (Allen Dutcher, State Climatologist, High Plains Climate Center, personal communication 1999).

In June 1991, and continuing into 1992, the Mount Pinatubo volcano erupted in the Philippines, blasting millions of tons of volcanic debris into the atmosphere and creating a massive sun-blocking aerosol cloud (Kerr 1993). This caused significant hemispheric cooling, resulting in temperatures that were lower than normal throughout 1992 (Figure 3), and with these cooler temperatures, increased precipitation. Residual effects of the eruption were also seen in the climate patterns of early 1993.

In 1993, the same climatic patterns which delivered unprecedented heavy rainfall to the upper Mississippi River Basin also caused above normal levels of summer rainfall in eastern Nebraska. During June and July 1993, the mean position of the polar jet stream extended from the northern Rocky Mountains to the upper Mississippi River Basin and a strong pressure height gradient occurred in the region (Kunkel et al. 1994). In June, below normal heights occurred over the Rockies and eastern Pacific, and off the Newfoundland coast, while

Table 2
Coefficients for Meteoric Water Lines and Arithmetic Mean Values from Stations in the Northern U.S. Great Plains Region

Station	Slope (A)	Intercept (B)	Weighted Mean $\delta^{18}\text{O}$ (‰)	Arithmetic Mean $\delta^{18}\text{O}$ (‰)	Weighted Mean $\delta^2\text{H}$ (‰)	Arithmetic Mean $\delta^2\text{H}$ (‰)
Chicago Illinois ^a	6.98	0.08	-6.0	-6.9	-43	-50
Ames, Iowa ^b	7.26	4.65	-8.0	-7.7	-54	-52
Mead, Nebraska ^c	7.40	7.32	-7.4	-8.1	-48	-53

The water line equation is $\delta^2\text{H} = A \cdot \delta^{18}\text{O} + B$.
^aIAEA 1992.
^bSimpkins 1995.
^cThis study.

above normal heights were present over the eastern United States. The July pattern was similar except that an additional area of above normal heights was seen over the eastern Pacific. This pattern was accompanied by a frontal boundary located over the basin on at least 40 days in June and July. This anomalous pattern again occurred briefly in August over the western United States and the eastern Pacific (Kunkel et al. 1994). Frequent low pressure waves developed in this region of horizontal surface temperature gradients and enhanced upper-air winds, bringing heavy rainfall to the area, including Mead which recorded nearly twice the average monthly precipitation during June, July, and August (Figure 3).

Statewide, 1994 was on average a normal year with respect to precipitation: However, several areas, including the area surrounding the Mead station, experienced drought-like conditions during several months resulting in below normal yearly precipitation values. This likely resulted from a weaker, nocturnal low level jet stream across the southern High Plains which produced fewer mesoscale convective complexes across eastern Nebraska, and thus less moisture. During 1994, a greater percentage of the rainfall activity across eastern Nebraska was from air mass thunderstorms. Under these conditions, it is not uncommon for some locations to receive above normal precipitation, while other areas as near as 30 km away experience drier than normal conditions.

Despite the abnormal variations in temperature and precipitation created by these weather patterns, averaging the isotopic content of precipitation over the three-year period should remove any anomalies and provide accurate values of the long-term stable isotope signature (i.e., the meteoric water line) of precipitation at Mead and across eastern Nebraska.

Stable Isotopic Composition of Precipitation

Values for weekly precipitation and corresponding $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and deuterium excess *d* (defined by Dansgaard [1964] as $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$) are presented in Table 1 and plotted in Figure 4. Values for $\delta^{18}\text{O}$ ranged from -23.6 to -0.7 ‰, and $\delta^2\text{H}$ values ranged from -172 to -0 ‰. These values are typical of a mid-continent station (Gat and Gonfiantini 1981). Arithmetic mean values for the Mead station were -8.1 ‰ and -53 ‰, respectively, with standard deviations of 4.7 and 35‰. Weighted mean values were -7.4 ‰ and -48 ‰. These values were consistent with those interpolated for Nebraska (Figure 1) from a regional scale map of meteoric waters across the United States constructed by Sheppard et al. (1969).

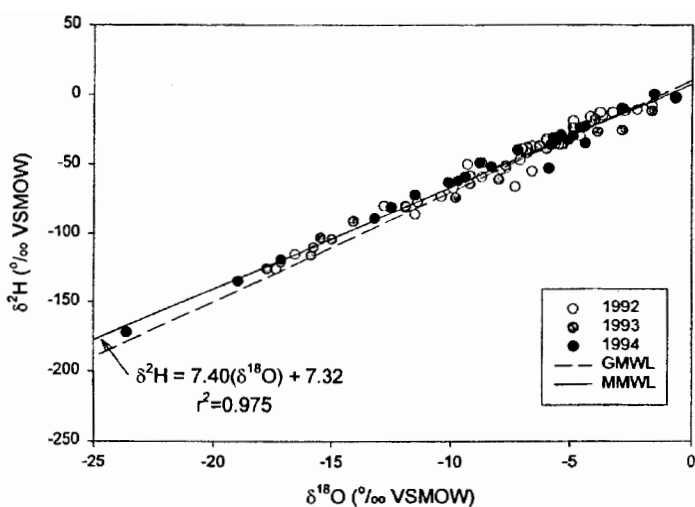


Figure 5. Oxygen-18 vs. deuterium plot showing Mead Meteoric Water Line (MMWL) for the 1992–1994 precipitation samples. The Global Meteoric Water Line (GMWL) of Craig (1961) is also plotted.

Arithmetic and weighted mean values for nearby stations are presented in Table 2. The annual means were more depleted than the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ mean values from Chicago precipitation collected from 1962 to 1979 (IAEA 1992), and just slightly more depleted than values reported for central Iowa collected in 1992 (Simpkins 1995). While comparison between the three stations documents the isotopic variations across the northeastern Great Plains region, without more detailed sampling to determine the source of moisture for a given precipitation event, it is not possible to determine whether the differences between the three stations reflects different meteorological regimes, or whether they are due to local processes which modify the isotopic composition of local precipitation (for example, the Chicago station lies adjacent to Lake Michigan, where precipitation may have been affected by evaporation of nearby lake water [Machavaram and Krishnamurthy 1995]).

A linear plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ values can be used to validate the Mead data (Figure 5). The relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation is controlled by condensation and evaporation processes related to Rayleigh distillation. Global precipitation values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ generally plot along the Global Meteoric Water Line (GMWL), defined by Craig (1961) as

$$\delta^2\text{H} = 8 \cdot \delta^{18}\text{O} + 10$$

A local Meteoric Water Line (MMWL) for eastern Nebraska was constructed from the Mead precipitation data by using the linear least-squares regression technique (Lapin 1980). The equation of the line was

$$\delta^2\text{H} = 7.40 \cdot \delta^{18}\text{O} + 7.32 \quad (r^2 = 0.975)$$

The Mead meteoric water line plots close to the global water line but does not parallel it, deviating slightly as oxygen values become more depleted. Such deviations occur in precipitation globally (Simpkins 1995; Rozanski et al. 1993; Fritz et al. 1987) and result from differences in climatic factors such as air temperature, seasonality of precipitation, secondary evaporation, and moisture source (Clark and Fritz 1997).

Recent studies by Fritz et al. (1987), Lawrence and White (1991), and Rozanski et al. (1993) have suggested that the isotopic composition of precipitation may be more related to air mass tra-

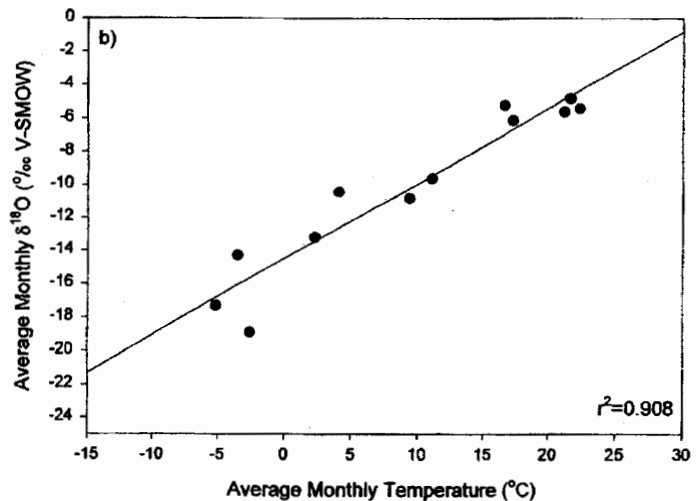
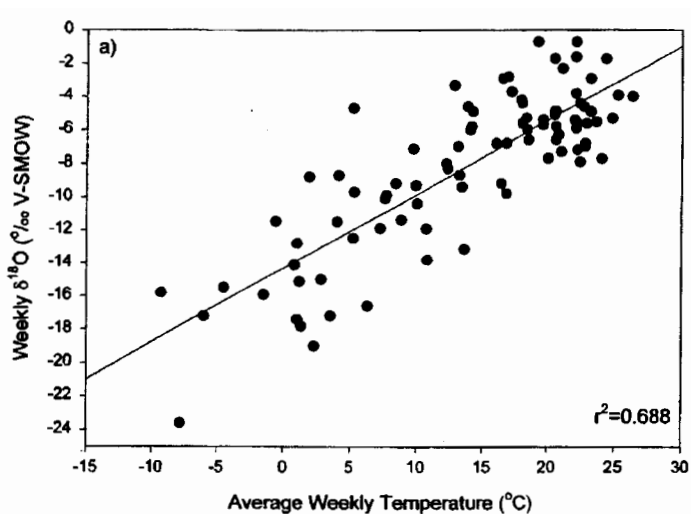


Figure 6. Temperature effects on (a) weekly $\delta^{18}\text{O}$ and (b) monthly $\delta^{18}\text{O}$ values for years 1992–1994. Monthly isotope and temperature values are plotted as arithmetic means.

jectories than to temperature relationships alone. However, temperature appears to be the controlling factor in eastern Nebraska. Weekly $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) values show a fairly strong correlation with weekly temperature; however, there is scatter within the data (Figure 6a). This scatter may be due in part to errors resulting from assigning a weekly average temperature to the weekly precipitation samples. Since the precipitation sample represents a composite of all the storm events in a given week, the time and actual temperature of a specific storm event could not be determined with certainty. If the exact temperature at the time of the storm event could be determined, the δ -T correlation might be stronger. The regression equations relating the weekly Mead oxygen and deuterium values to weekly temperature are

$$\delta^{18}\text{O} = 0.445 \cdot T (\text{°C}) - 14.3 \quad (r^2 = 0.688)$$

$$\delta^2\text{H} = 3.23 \cdot T (\text{°C}) - 98 \quad (r^2 = 0.646)$$

Monthly mean $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) values (during the three-year monitoring period) and monthly mean temperatures show a much stronger correlation than the weekly data (Figure 6b) as the effect of weekly anomalies in the isotope data are reduced. The regression equations for the Mead data are

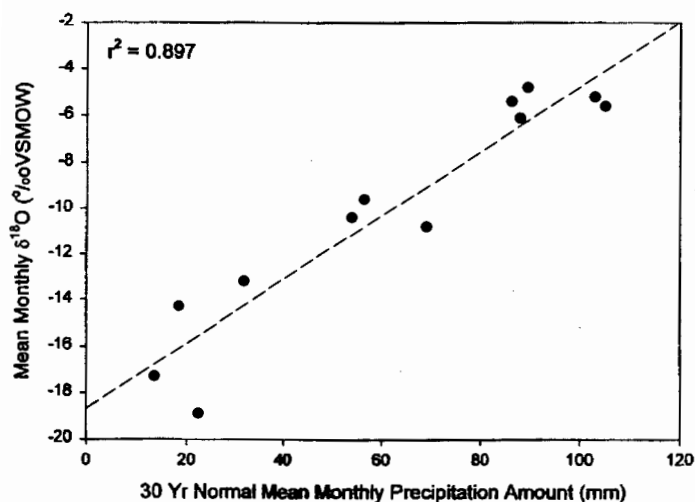


Figure 7. Amount effect on monthly $\delta^{18}\text{O}$. Isotope values are monthly averages for the three-year period (1992–1994). Precipitation amounts are the 30-year normal values for each month.

$$\delta^{18}\text{O}_{\text{monthly}} = 0.455 \cdot T (\text{°C}) - 14.5 \quad (r^2 = 0.908)$$

$$\delta^2\text{H}_{\text{monthly}} = 3.37 \cdot T (\text{°C}) - 100 \quad (r^2 = 0.905)$$

The amount effect, first observed by Dansgaard (1964), is a negative correlation between the amount of monthly precipitation and its isotopic composition. This effect is caused by the evaporation of rain as it falls and other in-cloud phenomena and mixing (Clark and Fritz 1997), and results in a depletion of the $\delta^{18}\text{O}$ content with increasing precipitation. Clark and Fritz (1997) point out that this effect is best observed in arid regions. Monthly mean $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) values at Mead show a strong positive correlation with monthly mean precipitation amounts (Figure 7); the reverse of the expected behavior. The regression equations relating the monthly Mead oxygen and deuterium values to monthly precipitation amounts are

$$\delta^{18}\text{O}_{\text{monthly}} = 0.14 \cdot P (\text{mm}) - 18.7 \quad (r^2 = 0.897)$$

$$\delta^2\text{H}_{\text{monthly}} = 1.02 \cdot P (\text{mm}) - 130 \quad (r^2 = 0.885)$$

This apparent reversal likely occurs because of the stronger influence of temperature on the isotope composition of local precipitation, as precipitation amounts are greater during the warmer, summer months (Figure 8). Thus, a true amount effect is not visible in the Mead data as it is mask by the temperature correlation, if present at all.

A plot of weekly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Figure 8) for 1992–1994 shows the seasonal effect on precipitation resulting from increasing precipitation amounts and higher temperatures over the summer months (April–September). Winter precipitation (October–March) has a more depleted signature while summer precipitation is enriched relative to the yearly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ averages (-8.1‰ and -53‰ , respectively).

Since the precipitation samples collected represent averages during a one-week monitoring period, it was not possible to evaluate the stable isotope values of individual storm events as the weekly sample may have contained precipitation from multiple events having different moisture sources. Therefore the isotopic signatures of the two primary precipitation sources (Gulf of Mexico and Pacific Ocean) could not be identified. Furthermore, it was not possible to evaluate if samples having deviations from the δ -T averages (Figure 6) resulted from anomalous temperature or δ values.

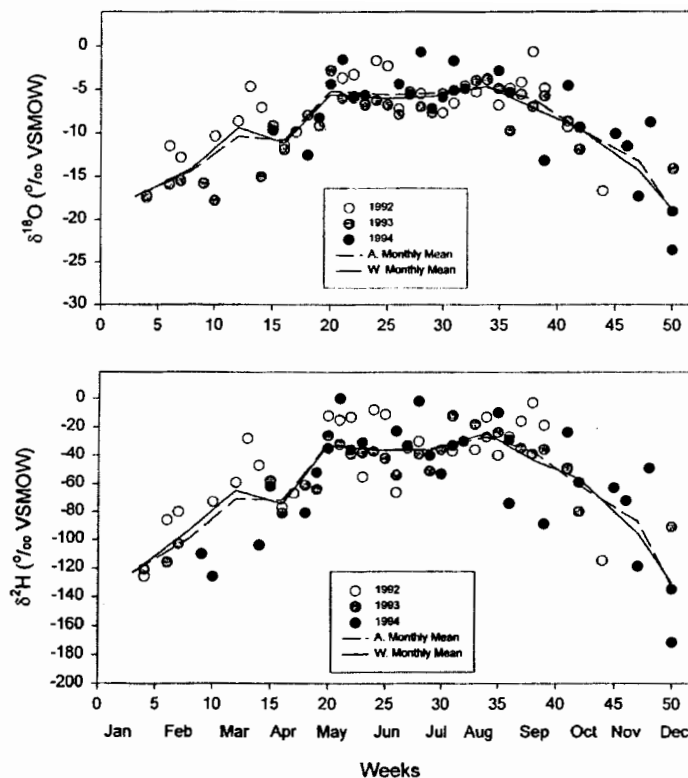


Figure 8. Weekly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for years 1992–1994 for Mead showing seasonal changes in precipitation. Also plotted are the monthly arithmetic and weighted means for each isotope.

Deuterium Excess

The deuterium excess values for the Mead station ranged from -7.6‰ to 24.7‰ , with a yearly mean value of 12.2‰ and a median value of 13.2‰ (Table 1 and Figure 4). These values are generally within the range of the d-excess values reported for other sites in North America (IAEA 1992; Rozanski et al. 1993; Gat et al. 1994); however, the yearly mean is slightly above the global average of 10‰ (Craig 1961). Weekly values were quite variable throughout the course of a given year (Figure 4) but show a repeating seasonal trend of lower values in summer than in winter.

There are two main sources for atmospheric moisture which mix in the east-central plains region: the Pacific Ocean and the Gulf of Mexico (the Gulf accounts for about 80% of the region's total moisture). Smaller amounts of moisture from the Arctic regions may also be added to the mix periodically during the winter months. Unfortunately, there are few isotopic data of precipitation available in the United States as only a few meteorological stations report the isotopic composition of precipitation to the IAEA-WMO network. Gat et al. (1994) suggest that precipitation data from Waco, Texas (Figure 1) can be used to represent air masses whose moisture originates in the Gulf of Mexico. Moisture which originates in the Pacific Ocean can be characterized by the precipitation sampled at Santa Maria, California, and Destruction Island (Figure 1). Precipitation data collected at the Gimli, Manitoba Station in central Canada (Figure 1) can be used to represent Arctic moisture.

Monthly average d-excess throughout the year for each of the four source stations are plotted in Figure 9. A seasonal trend is present in the monthly data at each of the four IAEA stations. Summer values (April to September) are more depleted than winter (October to March) values. This same trend is observed in Mead's monthly averages (Figure 9). Gat (1996) discusses several reasons for seasonal changes in the isotopic composition of rain, and suggests that

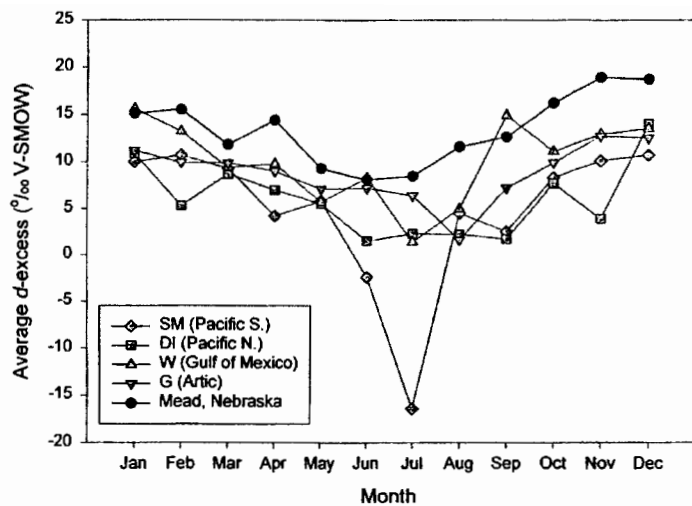


Figure 9. Monthly average d-excess values throughout the year reported by IAEA stations at Santa Maria, California (SM), Destruction Island, U.S.A. (DI), Waco, Texas (W), Gimli, Manitoba, Canada (G), and at Mead, Nebraska, for 1992–1994.

this summer dip (also observed in other continental stations at Ottawa, Vienna, and Ankara) results from a reduced degree of evaporation from falling rain droplets in winter when compared to summer conditions, and the effect of high d-values in snow (Jouzel and Merlivat 1984). Further, Gat (1996) suggests that these two processes apparently mask the effect of changes in temperature and humidity at the oceanic source area, which as Merlivat and Jouzel (1979) point out, would produce the opposite effect.

Comparison of the Mead precipitation's d-excess averages with those of the four moisture sources may also be used to identify the primary moisture source for the east-central plains region. However, Gat et al. (1994) caution that in order to avoid complications arising from the elevated winter d-excess values observed at times in snow and ice, as a result of kinetic effects (Jouzel and Merlivat 1984), comparisons should be made using d-excess data from summer and fall months.

To provide for both a yearly comparison, and a more rigorous summer-fall comparison as suggested by Gat et al. (1994), yearly and summer-fall (May to September) mean $\delta^{18}\text{O}$, $\delta^2\text{H}$, and d-excess values for Mead, Nebraska, and each of the four stations used to characterize the various moisture sources are given in Table 3. The yearly averages indicate that Pacific and Arctic air masses transport moisture which has a considerably lower yearly d-excess value than the global average of 10‰ (Craig 1961). Gulf moisture is roughly equal to the global value. Summer-fall averages show roughly the same trend, although the actual values differ slightly.

Comparison of the study results with the source averages in Table 3 indicate that precipitation across the east-central Great Plains has a d-excess value which is more characteristic of Gulf moisture, and thus originates from moisture transported from the Gulf of Mexico, as expected. In addition, this comparison also suggests that additional moisture is being returned to the air masses during transport inland from the various ocean sources. Yearly mean Mead precipitation d-excess values are 2.1‰ higher than Gulf source moisture, and 5.6 to 7.4‰ higher than Arctic and Pacific sources. Summer-fall Mead values are 3.1‰ higher than Gulf source moisture, and 4.3 to 11.4‰ higher than Arctic and Pacific sources. Weighted means behave similarly though the variation amounts may differ slightly. The source of this added moisture is uncertain; however, several possibilities exist in the regions between

the source areas and Mead including evaporation from surface waters such as lakes and reservoirs, and perhaps evaporation from center pivot and canal-furrow irrigated crop land. Without additional data, however, the relative contribution of each of these potential sources cannot be determined.

Relation to Ground Water Studies

The stable isotopic composition of ground waters is typically equal to the mean weighted annual composition of precipitation (Clark and Fritz 1997). This is true for this study as shallow ground water values compare well with yearly precipitation averages. A ground water sample collected from a shallow well approximately 5.8 km from the weather station (Figure 1) had $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of -8.4‰ and -58‰ , respectively. Shallow ground waters collected as part of several other ongoing studies in the surrounding area also have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values near -8‰ and -50‰ , respectively. This corroboration of the precipitation and local ground water values serves to further validate the use of NADP archive samples to determine the meteoric input function.

The meteoric input data compiled by this study will be used in several ongoing investigations (for which preliminary results have been presented at recent conferences). These studies are investigating regional ground water recharge to determine the rate and timing of recharge in the region (Harvey 1999; Gosselin et al. 1998), saline wetland hydrology, and the role of regional and local flow systems on wetland development, ground water-surface water interaction (Schellpeper and Harvey 1998), and regional paleohydrology (Stotler et al. 1999).

Conclusions

The isotopic attributes of precipitation collected at Mead, Nebraska, are similar to the findings from other midcontinental regions across the globe, including a strong isotopic enrichment between winter and summer precipitation and a strong $\delta^{18}\text{O}$ -T correlation ($r^2 = 0.91$) of about 0.5‰ per degree Celsius. The results differ, however, in that the local meteoric water line is slightly above the Global Meteoric Water Line. Also yearly $\delta^{18}\text{O}$ and $\delta^2\text{H}$ means differ significantly between Mead and the IAEA station in Chicago, Illinois. However, they do not differ significantly from the Ames, Iowa, station.

Deuterium excess values suggest that most of the moisture across the region is derived primarily from a Gulf of Mexico source. Deuterium excess values are slightly higher than the global average, and significantly higher than moisture in the source areas suggesting that additional moisture derived from secondary evaporation from open water or perhaps irrigation has been added to the air masses during travel to the region.

The three-year (1992–1994) precipitation isotope data set compiled by this study compares well with isotope data reported at long-term monitoring sites in North America (and elsewhere) by the International Atomic Energy Agency. The characteristics of the correlations with temperature, season, and the amount of precipitation are similar to what is seen with composited, event-based (nonweekly) samples. This indicates that National Atmospheric Deposition Program archive precipitation samples can be used successfully as proxies for establishing local meteoric water lines, and determining the meteoric input function for use in ground water studies.

The data compiled by this research will be used in ongoing investigations of regional ground water recharge, wetland hydrology,

Table 3
Yearly and Summer–Fall $\delta^{18}\text{O}$, $\delta^2\text{H}$, and d-Excess Means and Weighted Means (Expressed as ‰) for the Mead, Nebraska, Waco, Texas (W), Santa Maria, California (SM), Destruction Island, U.S.A. (DI) and Gimli, Manitoba, Canada (G) IAEA Stations

Station	Source	Yearly Means			Yearly W. Means			Summer–Fall Means			Summer–Fall W. Means		
		$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d	$\delta^{18}\text{O}$	$\delta^2\text{H}$	d
Mead	–	–8.1	–53	12.2	–7.4	–48	11.1	–5.4	–33	10.2	–5.5	–34	9.5
W	Gulf	–3.7	–20	10.1	–3.7	–20	9.9	–2.8	–16	7.1	–3.2	–18	7.7
SM	S. Pacific	–3.7	–24	4.8	–4.7	–28	9.2	–2.7	–23	–1.2	–4.8	–35	3.4
DI	N. Pacific	–7.0	–50	5.9	–7.6	–53	7.6	–5.5	–41	2.6	–5.4	–41	2.7
G	Arctic	–16.5	–123	8.7	–13.7	–102	7.4	–10.7	–79	5.9	–10.7	–79	5.9

Summer-fall averages are calculated for May through September. Data (except for Mead station) taken from IAEA/WMO (1998).

ground water/surface water interaction, and regional paleohydrology. The strong seasonal variation in the isotopic abundance of precipitation can be used by ecologists to ascertain whether plants are using winter or summer precipitation during growth periods. The δ -T correlation and d-excess relationships can be applied to paleohydrogeologic studies, and climate reconstruction and atmospheric moisture transport studies across the central Great Plains.

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