

STABLE HYDROGEN AND OXYGEN ISOTOPE COMPOSITION  
 OF PRECIPITATION IN NORTHEASTERN COLORADO<sup>1</sup>

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**ABSTRACT:** Where data are available, hydrologic studies may use precipitation's stable oxygen and hydrogen isotope composition to investigate streamflow, ground water/surface water interaction, and ground water recharge. Paleoclimate studies utilize the  $\delta^{18}\text{O}_{\text{precipitation}} - T_{\text{air}}$  relationship, in conjunction with lake sediments, fossils, or old ground waters, for example, to estimate paleotemperatures. Ecological studies utilize precipitation and soil water isotope composition to track moisture uptake in plants, and to trace species migration patterns. Such studies require that the isotopic composition of precipitation be known. Oxygen-18 ( $\delta^{18}\text{O}$ ) and deuterium ( $\delta^2\text{H}$ ) data for precipitation are lacking in the semi-arid portion of the north-central U.S. Great Plains, and thus there is a need to establish additional 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. This study determined the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  composition of precipitation in the Pawnee Grasslands of northeastern Colorado from 1994 through 1998 using archived National Atmospheric Deposition Program samples. The resulting local water line follows the relationship  $\delta^2\text{H} = 7.86 \delta^{18}\text{O} - 7.66$ , and the data show a  $\delta^{18}\text{O}_{\text{weekly}} - T_{\text{weekly}}$  relationship of  $\delta^{18}\text{O} = 0.560 \cdot T (^{\circ}\text{C}) - 18.8$ .

(KEY TERMS: meteorology/climatology; precipitation; stable oxygen and hydrogen isotopes; northeastern Colorado.)

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INTRODUCTION

Stable oxygen ( $^{18}\text{O}$  and  $^{16}\text{O}$ ) and hydrogen ( $^1\text{H}$  and  $^2\text{H}$ ) isotopes are useful in hydrologic studies and can be used in surface water investigations to examine the dynamics of river mixing (Yang *et al.*, 1996), irrigation canal leakage (Harvey and Sibray, 2001), and

in hydrograph separation (Buttle, 1994). Oxygen and hydrogen isotopes can also be used to investigate ground water recharge (Mathieu and Bariac, 1996), determine the effects of evaporation on ground water systems (Hendry 1988), to trace ground water and surface water interaction (Krabbenhoft *et al.*, 1990), and to examine plant water use and uptake (Eggenmeyer *et al.*, 2004) and species migration patterns (Smith *et al.*, 2003). In addition to their use in hydrological and ecological studies, oxygen isotopes can be used to assess regional climate change by evaluating the relationship between the oxygen ratios of precipitation and air temperature often referred to as the  $\delta$ -T relationship. If this  $\delta$ -T relationship is known, it is possible to measure the oxygen-18 value of paleoclimate indicators such as fossil teeth or bone (Harvey *et al.*, 2003; Koch, 1998), or older ground water samples (Stotler *et al.*, 1999), for example, and to use the oxygen data to estimate paleotemperatures within a region.

Since 1953, isotope ratios in precipitation have been measured at numerous monitoring stations world-wide by the International Atomic Energy Agency (IAEA), but few IAEA stations in the U.S. 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, and the distribution of data sets across the continental U.S., and especially the Great Plains region, is sparse.

In the absence of long term monitoring stations, Harvey (2001) suggests that the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of precipitation can be determined using archive precipitation samples collected at monitoring stations managed by the National Atmospheric Deposition

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Program (NADP) as part of their weekly precipitation chemistry monitoring program. Harvey (2001) cautions, however, that before using NADP derived precipitation isotope data, two conditions must be met to ensure that the data are truly representative of the monthly and yearly meteoric input functions at the given location: (1) 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 largest and most frequent precipitation events; and (2) 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.

The objectives of this study were to measure the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of archived precipitation samples from the NADP monitoring station in the Pawnee Grasslands of northeastern Colorado, for years 1994 through 1998, to determine the local meteoric water-line and the local  $\delta$ -T relationship. The Pawnee Grasslands lies in the west-central portion of the Great Plains, and is representative of the semi-arid portion of this region.

## STUDY AREA

Stable isotope ratios were determined on NADP Precipitation samples collected at the Pawnee National Grassland station (Figure 1) outside the town of Dover, Colorado. The station (CO22) is located in Weld County in northeastern Colorado at latitude  $40^\circ 48' 23''$  N, longitude  $104^\circ 45' 17''$  W, and at an elevation of 1,641 meters (m) above sea level. The NADP site is operated by the Shortgrass Steppe Long Term Ecological Research (SGS-LTER) project, and the State Agricultural Experiment Station (SAES) at Colorado State University.

Additional climate data (temperature and some precipitation amounts) were compiled from a National Weather Service (NWS) station operated in Fort Collins, Colorado (latitude  $40^\circ 34' 05''$  N, longitude  $105^\circ 05' 05''$  W, and elevation 1,525 m) and were provided by the High Plains Regional Climate Center (HPRCC, 2005) of the University of Nebraska-Lincoln. 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 Fort Collins NWS station. Comparisons of the NADP precipitation data with the Fort Collins NWS station

precipitation values over the five-year monitoring period show good agreement between weekly recorded precipitation amounts, so this occasional substitution of the precipitation amounts is acceptable. Information regarding comparisons/calibrations with other stations is available from NADP.

## METHODOLOGY

### *Precipitation Collection*

Precipitation samples were collected weekly by the NADP network with the aid of site operators (Bigelow, 1991) from January 1, 1994, until December 31, 1998. Precipitation samples were collected using a modified Aerochem Metrics wet/dry precipitation collector (Bigelow, 1991). The precipitation falls into a collector that is covered by a mechanical lid assembly having a semi-gas tight 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 recorder gage.

Prior to January 11, 1994, weekly composite precipitation samples collected at the CO22 site were shipped to the Illinois State Water Survey (ISWS) in the sealed 13.25 liter (l) plastic bucket taken from the collector. If sufficient water was present in the collector, pH and conductivity were measured on each sample by the field technician at the collection site. At the ISWS laboratory, the sample was transferred from the collector to 1,000 ml plastic bottles for processing, and the amount of sample was recorded. After January 11, 1994, composite samples were transferred to the 1,000 ml bottle at the field collection station, and this bottle was sealed and mailed to ISWS. In the laboratory, 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  $4^\circ\text{C}$ .

### *Archive Sample QA/QC*

Several unpublished internal studies have been conducted by the NADP to determine if samples have evaporated during collection and/or storage (NADP, 2005). Collector efficiency studies compared precipitation amounts recorded by the Belfort collectors to

STABLE HYDROGEN AND OXYGEN ISOTOPE COMPOSITION OF PRECIPITATION IN NORTHEASTERN COLORADO

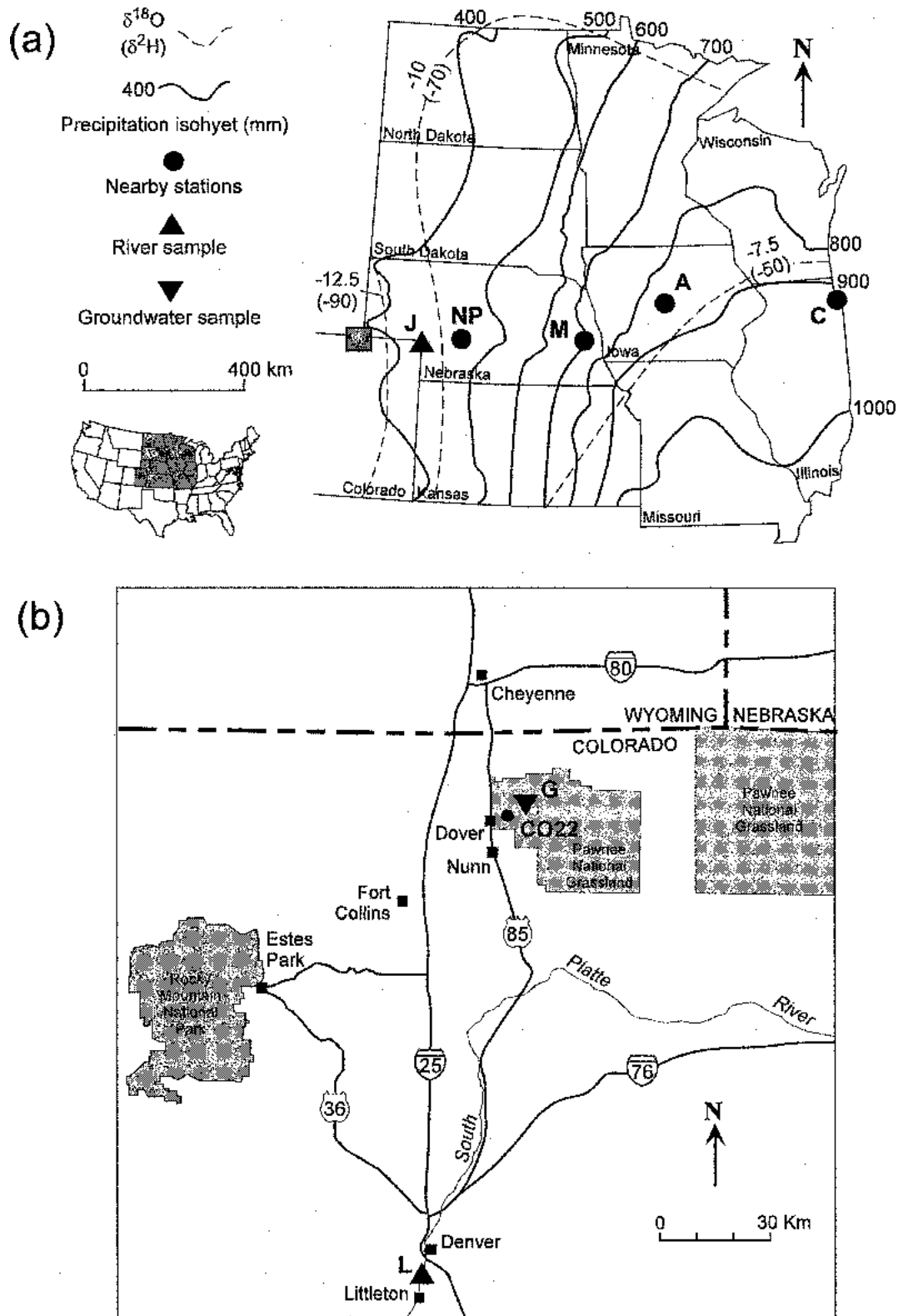


Figure 1. (a) Location of the IAEA Station at Chicago, Illinois (C); the Ames, Iowa (A), Station of Simpkins (1995); the Mead, Nebraska (M), Station of Harvey (2001); and the North Platte, Nebraska (NP), Station of Harvey and Welker (2000). Predicted oxygen and deuterium (in parentheses) contours were taken from Sheppard *et al.* (1969). Isohyets for precipitation were modified from Simpkins (1995). Also shown are the locations where the South Platte River samples (Kendall and Coplen, 2001) at Littleton (L) and Julesburg (J), and the ground water sample from the 18 m deep well of Dodd *et al.* (1998) at the CPER (G) were collected. (b) Expansion of the Shaded Area in (a) Showing the Location of the NADP Precipitation Station CO22 in the Pawnee Grasslands and the Fort Collins NWS Station.

HARVEY

TABLE 1. Stable Isotope Data for Precipitation in the Pawnee National Grasslands, Colorado, at the NADP CO22 Station (years 1994 through 1998).

Week Sampled	Average Weekly Temperature (°C)	Weekly Precipitation (mm)	$\delta^{18}\text{O}$ (per mil V-SMOW)	$\delta^2\text{H}$ (per mil V-SMOW)	$d$ (per mil V-SMOW)
<b>Year 1994</b>					
January 25 to February 01	-3.4	10	-15.9	-119	7.7
March 01 to March 08	6.7	2	-10.9	-87	0.2 <sup>†</sup>
April 05 to April 12	4.4	18	-23.0	-175	9.0
April 19 to April 26	14.9	11	-10.4	-78	5.1
April 26 to May 03	4.2	8	-19.7	-159	-1.5 <sup>†</sup>
May 03 to May 10	14.1	1	-11.0	-87	0.5 <sup>†</sup>
May 10 to May 17	16.0	14	-7.4	-51	9.0
May 31 to June 07	20.5	32	-5.6	-44	1.3 <sup>†</sup>
July 19 to July 26	21.7	12	-6.7	-48	5.6
July 26 to August 02	21.5	55	-6.7	-46	8.0
August 02 to August 09	21.8	6	-5.4	-31	12.3
August 09 to August 16	21.9	4	-6.9	-44	10.7
August 30 to September 06	18.4	3	-4.9	-39	0.5 <sup>†</sup>
September 13 to September 20	16.9	3	-22.0	-164	12.7
October 11 to October 18	10.3	24	-21.2	-154	15.4
November 08 to November 15	4.9	3	-13.9	-104	7.3
<b>Year 1995</b>					
April 11 to April 18	6.6	13	-17.4	-133	6.4
April 25 to May 02	6.4	15	-15.4	-113	9.6
May 02 to May 09	10.1	32	-14.2	-116	-2.0 <sup>†</sup>
May 09 to May 16	12.7	2*	-11.8	-89	5.6
May 16 to May 23	10.6	61	-12.9	-91	12.1
May 23 to May 30	8.8	43	-11.0	-82	6.5
May 30 to June 06	16.2	34	-8.9	-62	9.7
June 06 to June 13	14.8	29	-3.2	-10	15.7
June 13 to June 20	20.2	8	-8.9	-68	3.1
June 20 to June 27	18.5	30	-7.7	-65	-3.5 <sup>†</sup>
June 27 to July 04	16.5	12	-2.5	-20	-0.1 <sup>†</sup>
July 11 to July 18	22.3	19	-5.4	-56	-12.5 <sup>†</sup>
July 18 to July 25	20.1	12	0.2	-17	-18.5 <sup>†</sup>
August 08 to August 15	24.0	7	-6.6	-49	3.3
September 05 to September 12	17.7	8	-20.2	-149	11.9
September 19 to September 26	7.4	18	-11.0	-91	-3.8 <sup>†</sup>
September 26 to October 03	13.0	7	-16.6	-134	-1.2 <sup>†</sup>
October 03 to October 10	9.8	1	-17.3	-138	0.8 <sup>†</sup>
<b>Year 1996</b>					
January 30 to February 06	-12.5	5	-29.3	-225	9.5
March 12 to March 19	5.0	20	-18.2	-135	10.4
March 26 to April 02	5.6	2	-9.3	-66	8.2
April 02 to April 09	9.6	5	-17.3	-138	-0.3 <sup>†</sup>
April 09 to April 16	9.7	7	-15.5	-120	4.2
May 07 to May 14	13.8	6	-8.7	-68	1.4 <sup>†</sup>
May 14 to May 21	19.1	5	-6.2	-55	-0.3 <sup>†</sup>

## STABLE HYDROGEN AND OXYGEN ISOTOPE COMPOSITION OF PRECIPITATION IN NORTHEASTERN COLORADO

TABLE 1. Stable Isotope Data for Precipitation in the Pawnee National Grasslands, Colorado, at the NADP CO22 Station (years 1994 through 1998) (cont'd.).

Week Sampled	Average Weekly Temperature (°C)	Weekly Precipitation (mm)	$\delta^{18}\text{O}$ (per mil V-SMOW)	$\delta^2\text{H}$ (per mil V-SMOW)	$d$ (per mil V-SMOW)
<b>Year 1996 (cont'd.)</b>					
May 21 to May 28	12.1	60	-11.1	-78	11.2
May 28 to June 04	14.1	2	-8.0	-68	-4.5 <sup>†</sup>
June 04 to June 11	18.9	10	-4.3	-43	-8.7 <sup>†</sup>
June 11 to June 18	19.5	10	-4.0	-32	-0.1 <sup>†</sup>
June 18 to June 25	20.1	46	-3.0	-21	3.8
June 25 to July 02	21.2	4	-1.0	-7	1.6 <sup>†</sup>
July 02 to July 09	23.8	28	-5.5	-44	-0.7 <sup>†</sup>
July 09 to July 16	20.4	27	-10.3	-71	11.5
July 16 to July 23	23.3	13	-1.9	-20	-4.4 <sup>†</sup>
July 28 to July 30	20.6	15	-8.9	-62	8.8
July 30 to August 06	21.7	21	-5.9	-43	4.2
August 06 to August 13	21.1	4	-5.5	-61	-17.0 <sup>†</sup>
August 13 to August 20	21.0	17	-3.0	-26	-1.2 <sup>†</sup>
August 27 to September 03	18.8	2	-9.8	-69	10.1
September 03 to September 10	19.1	3	-3.1	-27	-2.6 <sup>†</sup>
September 10 to September 17	17.2	2	-7.2	-53	4.3
September 17 to September 24	13.1	14	-12.6	-96	4.9
September 24 to October 01	11.1	7*	-14.0	-107	4.4
October 15 to October 22	8.2	2	-13.5	-99	8.3
November 12 to November 19	-0.6	10	-18.7	-136	13.3
<b>Year 1997</b>					
February 11 to February 18	2.2	4	-17.0	-132	3.7
February 25 to March 04	-0.1	5	-20.0	-151	9.0
March 11 to March 18	3.8	7	-18.5	-134	13.8
April 01 to April 08	4.7	8	-12.7	-97	4.7
April 22 to April 29	8.3	13	-17.0	-129	6.5
May 20 to May 27	14.6	26	-10.7	-85	0.8 <sup>†</sup>
May 27 to June 03	16.7	49	-11.3	-85	4.9
June 03 to June 10	17.3	20	-9.8	-67	10.8
June 10 to June 17	17.0	17	-6.1	-47	2.0 <sup>†</sup>
June 17 to June 24	21.7	34	-7.6	-57	3.8
July 01 to July 08	19.2	3	-7.7	-71	-9.0 <sup>†</sup>
July 15 to July 22	23.0	11	-2.7	-12	9.4
July 22 to July 29	23.3	41	-5.3	-31	10.7
July 29 to August 05	21.9	88	-6.8	-41	13.5
August 05 to August 12	18.3	55	-6.5	-40	11.9
August 12 to August 19	19.2	23	-7.9	-54	9.6
August 26 to September 02	22.1	8	-3.5	-30	-2.3 <sup>†</sup>
September 02 to September 09	19.9	11	-2.2	-12	5.6
September 16 to September 23	14.3	31	-9.8	-63	14.7
October 07 to October 14	11.7	3	-10.2	-97	-15.5 <sup>†</sup>
October 21 to October 28	3.5	22	-15.0	-104	15.9

TABLE 1. Stable Isotope Data for Precipitation in the Pawnee National Grasslands, Colorado, at the NADP CO22 Station (years 1994 through 1998) (cont'd.).

Week Sampled	Average Weekly Temperature (°C)	Weekly Precipitation (mm)	$\delta^{18}\text{O}$ (per mil V-SMOW)	$\delta^2\text{H}$ (per mil V-SMOW)	$d$ (per mil V-SMOW)
<b>Year 1998</b>					
February 10 to February 17	1.8	8	-15.8	-120	6.2
March 03 to March 10	-2.0	9	-18.4	-134	13.8
March 17 to March 24	4.6	48*	-16.3	-114	16.2
March 24 to March 31	10.8	2	-16.2	-118	11.9
March 31 to April 07	6.7	24*	-9.5	-57	18.1
April 07 to April 14	9.0	12	-17.4	-123	16.5
April 14 to April 21	4.6	4	-16.0	-118	9.7
April 28 to May 05	12.7	6	-7.8	-63	0.0 <sup>†</sup>
May 05 to May 12	12.0	14	-10.9	-84	3.2
May 19 to May 26	16.3	23	-7.3	-53	5.4
June 02 to June 09	11.8	28	-11.6	-83	10.4
June 09 to June 16	15.8	5	-5.6	-58	-12.4 <sup>†</sup>
June 16 to June 23	17.5	4	-6.9	-62	-6.8 <sup>†</sup>
June 30 to July 07	22.5	1*	0.8	-15	-20.8 <sup>†</sup>
July 07 to July 14	22.7	9	-2.8	-33	-11.4 <sup>†</sup>
August 11 to August 18	21.7	18	-5.4	-47	-3.5 <sup>†</sup>
September 08 to September 15	21.2	2	-5.4	-48	-5.2 <sup>†</sup>
September 15 to September 23	16.9	31	-7.4	-42	17.1
September 29 to October 07	11.1	14	-12.8	-87	15.8
October 20 to October 27	9.5	3	-11.1	-84	5.3
October 27 to November 03	6.9	37*	-11.9	-84	12.0
November 03 to November 10	1.9	14	-19.1	-187	15.6

Note: Temperature data are taken from a National Weather Service station located at Fort Collins, Colorado. Precipitation data are taken from the National Atmospheric Deposition Program (NADP) station CO22 except where noted (\*). The deuterium excess ( $d$ ) is calculated as  $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$ . Analytical precision for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are 0.2 and 2.0 per mil (‰), respectively. <sup>†</sup>Samples may have been impacted by evaporation during collection since their  $d$ -excess values are less than 3 per mil.

amounts captured in the Aerochem Metrics collector, to evaluate the potential for evaporation during collection. NADP also periodically removes random archive samples from storage and performs a repeat chemical analysis to determine if ion concentrations match those of the initial analyses done on the original sample at the time of collection. These comparative tests indicate that the majority of precipitation samples collected have not undergone evaporation during collection and/or storage, and in the small number of cases where evaporation was detected, the total amount of evaporation did not exceed 1 percent of the total volume of sample collected (Van Bowersox, NADP, personal communication).

Another way to evaluate the integrity of the archive samples is to examine their  $d$ -excess values, defined by Dansgaard (1964) as  $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$ , as an indicator of potential sample evaporation. The

$d$ -excess in precipitation is determined 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 unchanged as air masses move across the continents and lose moisture by rainout. 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 (i.e., recycling of water) (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 either as it falls through the air (Gat, 1996), or as it sits in the rain collector. It can be shown using the moisture exchange model of Merlivat and Jouzel (1979) that for reasonable ranges

of temperature (20 to 30°C) and relative humidity (70 to 95 percent) over the ocean, the initial *d*-excess value of transported moisture should be between 3 and 15 per mil. Thus, NADP archive samples (or any samples) with *d*-excess values less than 3 per mil 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.

Examining this data set (Table 1) shows that 37 of the 104 samples were likely impacted by evaporation. These samples were typically collected during weeks when very small precipitation amounts were recorded (Table 1) in the collector. Several samples were collected in winter or early spring and may have fallen in the form of snow. Most, however, were collected in summer or early fall, and it may be that the warmer air temperatures, coupled with the low collector volumes resulted in partial evaporation of the sample while it was sitting in the collector. Evaporation observed in the summer *d*-excess values could also have occurred beneath the cloud base as the precipitation fell through the air column, and not on the ground in the collector. The hot, dry conditions present in the Pawnee Grasslands during the summer months could easily give rise to this effect.

The reader is cautioned that if it can be determined that the depleted *d*-excess samples have been evaporated while sitting in the collector, then those individual samples are not representative, and should not be included in the final data analysis. However, if it is determined that the samples have not been compromised, but rather that their low *d*-excess values record a natural meteorological occurrence, they should be included in the data analysis. Since it could not determine with certainty which of these two phenomena produced the evaporation that resulted in the low *d*-excess values observed in the data, the complete dataset will be reported in this paper in both tabular and graphical time-series form. However, the presented statistical and regression analyses will have been performed only on a selected subset of the data containing only those samples with *d*-excess values greater than 3 per mil.

#### Stable Isotopic Analysis

Archived precipitation samples from the Pawnee Grasslands NADP site for the years 1994 to 1998 were analyzed for <sup>18</sup>O and <sup>2</sup>H 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 (per mil or ‰) with respect to the international V-SMOW standard using the  $\delta$  notation, where

$$\delta_{\text{sample}} = [R_{\text{sample}} - R_{\text{standard}}] / (R_{\text{standard}}) \times 1000 \quad (1)$$

$R_{\text{sample}}$  is the ratio of <sup>18</sup>O/<sup>16</sup>O or <sup>2</sup>H/<sup>1</sup>H in the sample and  $R_{\text{standard}}$  is the ratio of the standard. The analytical precision for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  are 0.2 and 2.0 per mil (‰) (1 $\sigma$ ), respectively.

Yearly weighted mean values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were calculated by the equation

$$\delta_w = \{ \sum P_i \delta_i / \sum P_i \} \quad (2)$$

where  $\delta_i$  is the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (per mil) weekly composite sample;  $P_i$  is the recorded total weekly precipitation (mm) of the *i*th week; and *n* is the total number of weekly samples (67) over which the summation (*i* = 1 to *n*) is performed. Monthly weighted means were calculated in a similar fashion where  $\delta_i$  is the monthly average  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  (per mil) value over the five-year period (1994 to 1998),  $P_i$  is the average monthly precipitation (mm) of the *i*th month over the five-year period (1994 to 1998); and *n* is the number of months (12).

#### STABLE ISOTOPE COMPOSITION OF PRECIPITATION

Values for weekly precipitation and corresponding  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values and deuterium excess "*d*" for the entire data set are presented in Table 1 and plotted in Figure 2. Values of  $\delta^{18}\text{O}$  for the *d*-excess corrected data subset range from -2.2 to -29.3 per mil, with  $\delta^2\text{H}$  values ranging from -10 to -225 per mil. These ranges are typical of mid-continental stations globally (Gat and Gonfiantini, 1981), and they are similar to the range of limited precipitation values reported for sites in northeastern Colorado by Dodd *et al.* (1998), and north-central Colorado by Welker (2000). Arithmetic mean values for the Pawnee station were -12.2 per mil and -88 per mil, respectively (Table 2). Weighted yearly mean values over the five-year monitoring period were -10.6 per mil for  $\delta^{18}\text{O}$ , and -74 per mil for  $\delta^2\text{H}$  (Table 2). These values were isotopically similar to values interpolated for Nebraska (Figure 1) from a regional scale map of meteoric waters across the

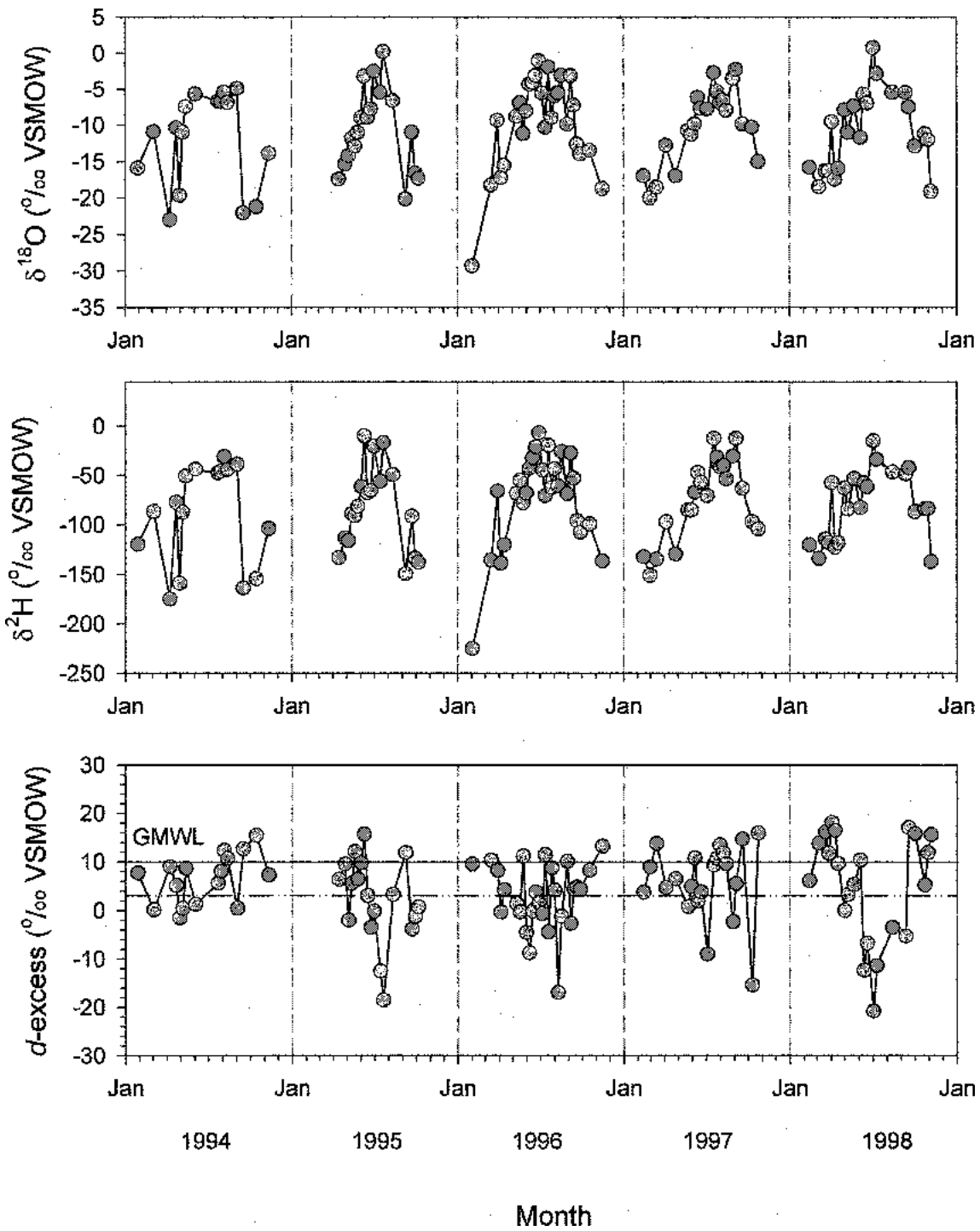


Figure 2. Time Series Plot of  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $d\text{-excess}$  for CO22 Site for the Entire Data Set. Global meteoric waterline (GMWL) from Craig (1961). Values of  $d\text{-excess}$  plotting below 3 per mil (the dashed-dot-dot-dashed line) may have experienced evaporation during collection (see text for explanation).

United States constructed by Sheppard *et al.* (1969), and compare well with predicted isotopic values for northeastern Colorado precipitation reported by Kendall and Copen (2001) based on isotopic values measured in streams and rivers in the region.

Arithmetic and weighted mean values for nearby stations are presented in Table 2. The annual means were more depleted than values reported for North Platte, Nebraska (Harvey and Welker, 2000), for Mead, Nebraska (Harvey, 2001), and for Ames, Iowa

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

Station	Slope (A)	Intercept (B)	Weighted Mean $\delta^{18}\text{O}$ (per mil)	Arithmetic Mean $\delta^{18}\text{O}$ (per mil)	Weighted Mean $\delta^2\text{H}$ (per mil)	Arithmetic Mean $\delta^2\text{H}$ (per mil)
Chicago, Illinois <sup>a</sup>	6.98	0.08	-6.0	-6.9	-43	-50
Ames, Iowa <sup>b</sup>	7.26	4.65	-8.0	-7.7	-54	-52
Mead, Nebraska <sup>c</sup>	7.40	7.32	-7.4	-8.1	-48	-53
North Platte, Nebraska <sup>d</sup>	7.66	4.96	-9.6	-9.8	-69	-71
Pawnee National Grasslands, Colorado <sup>e</sup>	7.86	7.66	-10.6	-12.2	-74	-88

Note: The water line equation is  $\delta^2\text{H} = A \cdot \delta^{18}\text{O} + B$ .

<sup>a</sup>IAEA, 1992.

<sup>b</sup>Simpkins, 1995.

<sup>c</sup>Harvey, 2001.

<sup>d</sup>Harvey and Welker, 2000.

<sup>e</sup>This study.

(Simpkins, 1995). They were even more depleted in comparison to the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  mean values from Chicago precipitation collected from 1962 to 1979 (IAEA, 1992). While comparison between the three stations documents the isotopic variations across the north-central Great Plains region, without more detailed event sampling to determine the source of moisture for a given precipitation event, it is not possible to determine the cause of the differences between the three stations. These differences may reflect one or more of the following: different meteorological regimes, varying distances from the source area (assumed to be the Gulf of Mexico), varying collection site elevation, or differences due to local processes that modify the isotopic composition of local precipitation. For example, the Chicago station is located near Lake Michigan, where precipitation may have been affected by evaporation of nearby lake water (Machavaram and Krishnamurthy, 1995).

The Pawnee Grasslands data can be compared to other precipitation data sets by constructing a linear plot of  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  values (Figure 3). The relationship between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in precipitation is controlled primarily by condensation processes related to Rayleigh distillation. Precipitation  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values globally generally plot along the global meteoric water line (GMWL), defined by Craig (1961) as

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \quad (3)$$

A local meteoric water line (PCMWL) for northeastern Colorado was constructed from the Pawnee precipitation data by using the linear least squares regression technique (Lapin, 1980). The equation of the line was

$$\delta^2\text{H} = 7.86 \delta^{18}\text{O} + 7.66 \quad \{r^2 = 0.991\} \quad (4)$$

The Pawnee meteoric water line plots close to the global water line but is slightly below it at heavier values. Such deviations result from differences in climatic factors such as air temperature, secondary evaporation, seasonality of precipitation and moisture source (Clark and Fritz, 1997), and occur in precipitation globally (Simpkins, 1995; Rozanski *et al.*, 1993; Fritz *et al.*, 1987).

Studies suggest that the isotopic composition of precipitation may be more related to air mass trajectories than to temperature relationships alone (Fritz *et al.*, 1987; Lawrence and White, 1991; Rozanski *et al.*, 1993). However, temperature (as related to altitude) appears to be the controlling factor in northwestern Colorado. A reasonably strong correlation can be seen between weekly  $\delta^{18}\text{O}$  values and weekly temperature; however there is scatter within the data (Figure 4). This scatter likely results from errors in assigning a weekly average temperature to the weekly precipitation samples, but might also be attributed to the effects of highly conductive summer storms, or any of the other factors mentioned previously. If the exact temperature at the time of the storm event could be determined, the  $\delta$ -T correlation might be stronger. However, the time and actual temperature of a specific storm event could not be determined with certainty because the precipitation sample represents a composite of all of the storm events in a given week. The regression equation relating the weekly Pawnee oxygen values to weekly temperature is

$$\delta^{18}\text{O} = 0.560 \cdot T \text{ (}^\circ\text{C)} - 18.8 \quad \{r^2 = 0.605\} \quad (5)$$

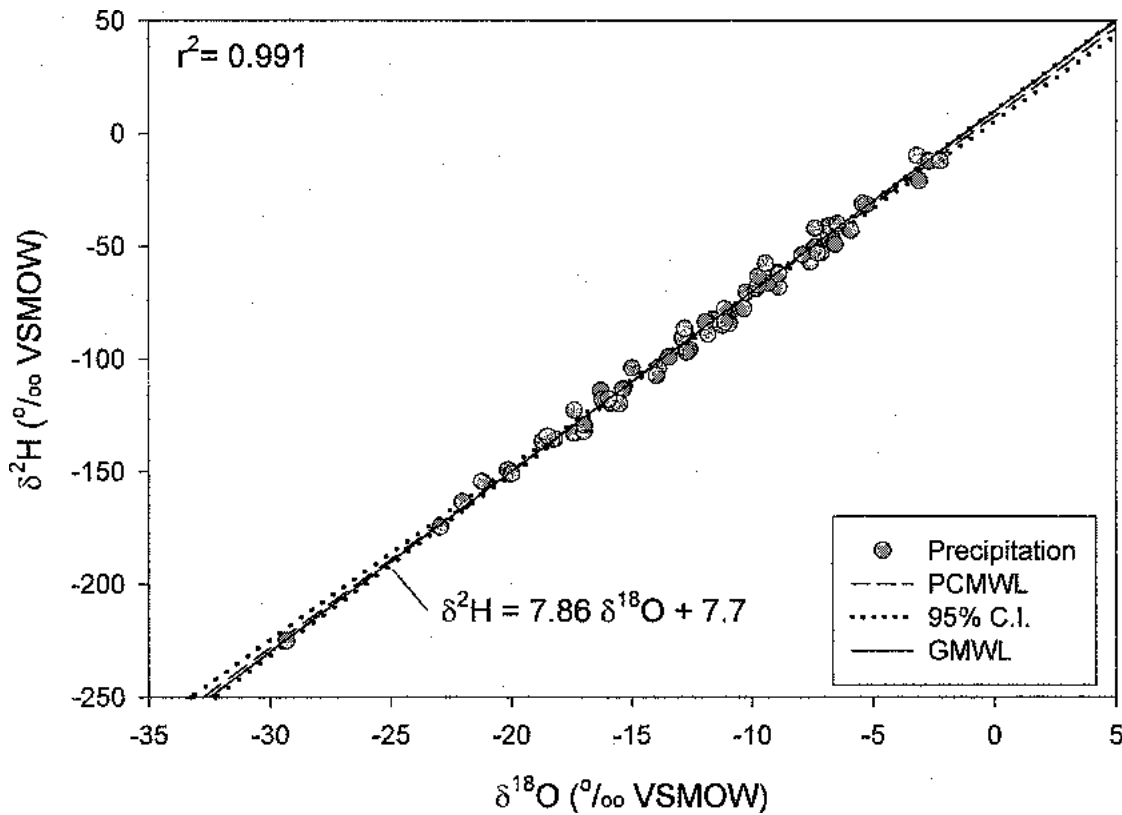


Figure 3.  $\delta^{18}\text{O}$  Versus  $\delta^2\text{H}$  Plot for Years 1994 to 1998 for CO22 Site (includes only those samples with  $d$ -excess values greater than 3 per mil).

A plot of weekly  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values (Figure 5) for 1994 to 1998 shows the seasonal effect on precipitation resulting from increasing precipitation events and amounts and higher temperatures over the summer months (April to September). Winter precipitation (October to March) has a more depleted signature while summer precipitation is enriched relative to the yearly arithmetic and weighted monthly  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  averages.

The deuterium excess values for the subset (those greater than 3 per mil) of the Pawnee station data ranged from a high of 18.1 per mil to a low of 3.1 per mil (Table 1) with an arithmetic mean of 9.2 per mil and a weighted mean of 10.0 per mil. These values were within the range of the  $d$ -excess values reported for other sites in North America (Harvey, 2001; Harvey and Welker, 2000; Welker, 2000; Simpkins, 1995; Rozanski *et al.*, 1993; Gat *et al.*, 1994), and elsewhere globally (IAEA, 1992; Dansgaard, 1964; Rozanski *et al.*, 1993). All  $d$ -excess values in this study were within the ranges reported at IAEA stations globally (IAEA/WMO, 2004; IAEA, 1992). The Pawnee  $d$ -excess subset values were very close to the global average of 10 per mil. The yearly means of the Pawnee  $d$ -excess subset are also very similar to the arithmetic and weighted means reported for the IAEA

station located at Waco, Texas (10.1 per mil and 9.9 per mil), which are taken to represent the composition of moisture derived from a Gulf of Mexico source (Harvey, 2001, Gat *et al.*, 1994). However, slight deviations from these means in many of the weekly samples also suggest that many precipitation events represent mixtures of Gulf moisture and moisture from other sources.

#### COMPARISON TO AREA GROUND WATER AND SURFACE WATER COMPOSITION

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 reported by Dodd *et al.* (1998) compare well with the yearly weighted precipitation average of -10.6 per mil. A ground water sample (G) collected from an 18 m deep well (Figure 1) at the Central Plains Experimental Range (CPER) in northeastern Colorado (40° 51' N, 104° 43' W, elevation 1,650 m) by Dodd *et al.* (1998) had  $\delta^{18}\text{O}$  values between -10.6 per mil and -11.5 per mil when sampled in 1995 and 1996.

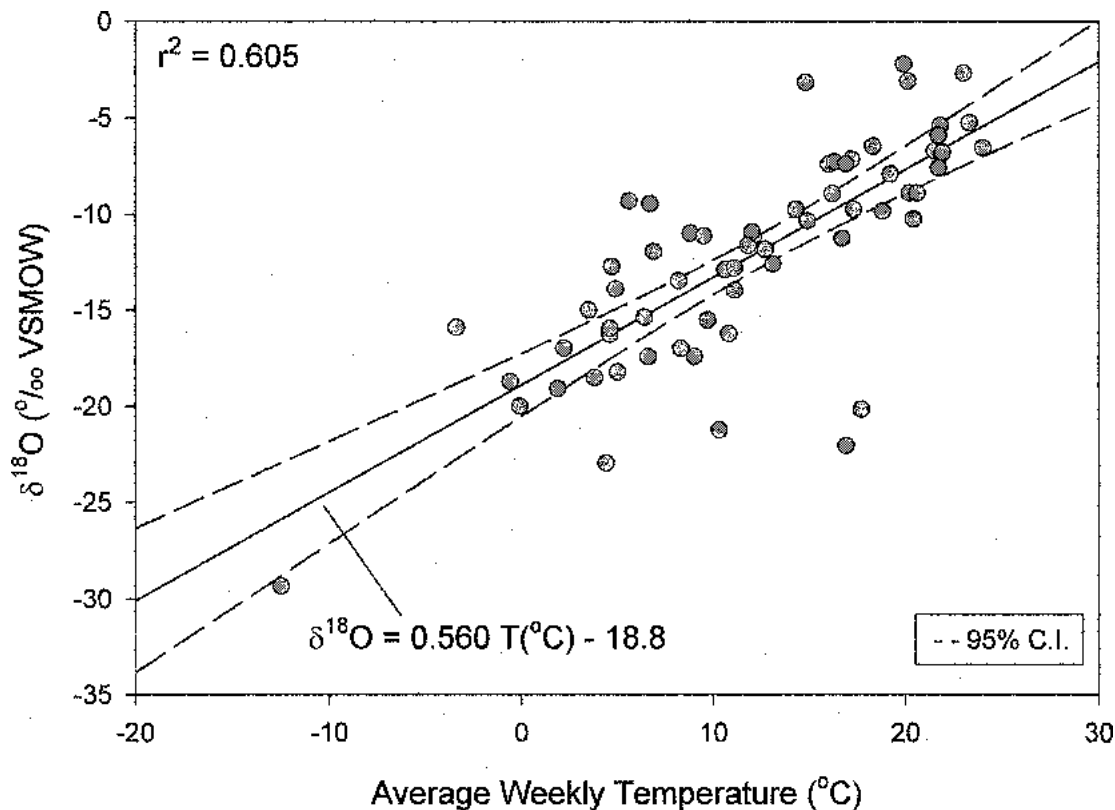


Figure 4. Temperature Effects on Weekly  $\delta^{18}\text{O}$  Values for Years 1994 to 1998 for CO22 Site (includes only those samples with  $d$ -excess values greater than 3 per mil).

Coplen and Kendall (2000) determined the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of river samples across the United States and found them to be good proxies for average precipitation values within a given region. One river monitored in their study was the South Platte River (Figure 1), which flows through northeastern Colorado adjacent to the Pawnee Grasslands. The average yearly  $\delta^{18}\text{O}$  composition of the South Platte River was reported to be about -13.3 per mil upstream of the Pawnee Grasslands site near Littleton (L) (latitude  $39^\circ 37' 08''$  N, longitude  $105^\circ 01' 07''$  W, elevation 1617 m), and -12.3 per mil farther downstream from the site near the city of Julesburg (J) (latitude  $40^\circ 58' 46''$  N, longitude  $102^\circ 15' 15''$  W, elevation 1,051 m). These yearly average river values, which represent a combination of both base flow and surface runoff, are similar to the arithmetic precipitation value (-12.2 per mil), and are only slightly more depleted than the weighted value (-10.6 per mil) perhaps due to the influence of winter snow melt runoff.

The strong agreement between the mean precipitation values and those of local ground water and surface water values lends support to the use of NADP archive samples to determine the meteoric input function. It should also be noted that this agreement further validates the decision to omit samples believed to

have been impacted by evaporation ( $d$ -excess less than 3 per mil) from the final analysis.

## SUMMARY AND APPLICATIONS

The isotopic attributes of precipitation collected at the Pawnee National Grasslands, Colorado, are similar to the findings from other mid-continental regions across the globe, including a strong isotopic enrichment between winter and summer precipitation and a strong  $\delta^{18}\text{O}$ -T correlation. The results differ however, in that the local meteoric water line is slightly below the global meteoric water line for heavier samples, and that yearly  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  means are more depleted than means from nearby stations in North Platte and Mead, Nebraska, Ames, Iowa, and Chicago, Illinois. The results are also consistent with groundwater and surface water isotope data from the region.

The data compiled by this research will be used in ongoing investigations related to regional ground water recharge, wetland hydrology, and ground water/surface water interaction, and the strong seasonal variation in the isotopic abundance of precipitation will allow us to ascertain whether grassland plants

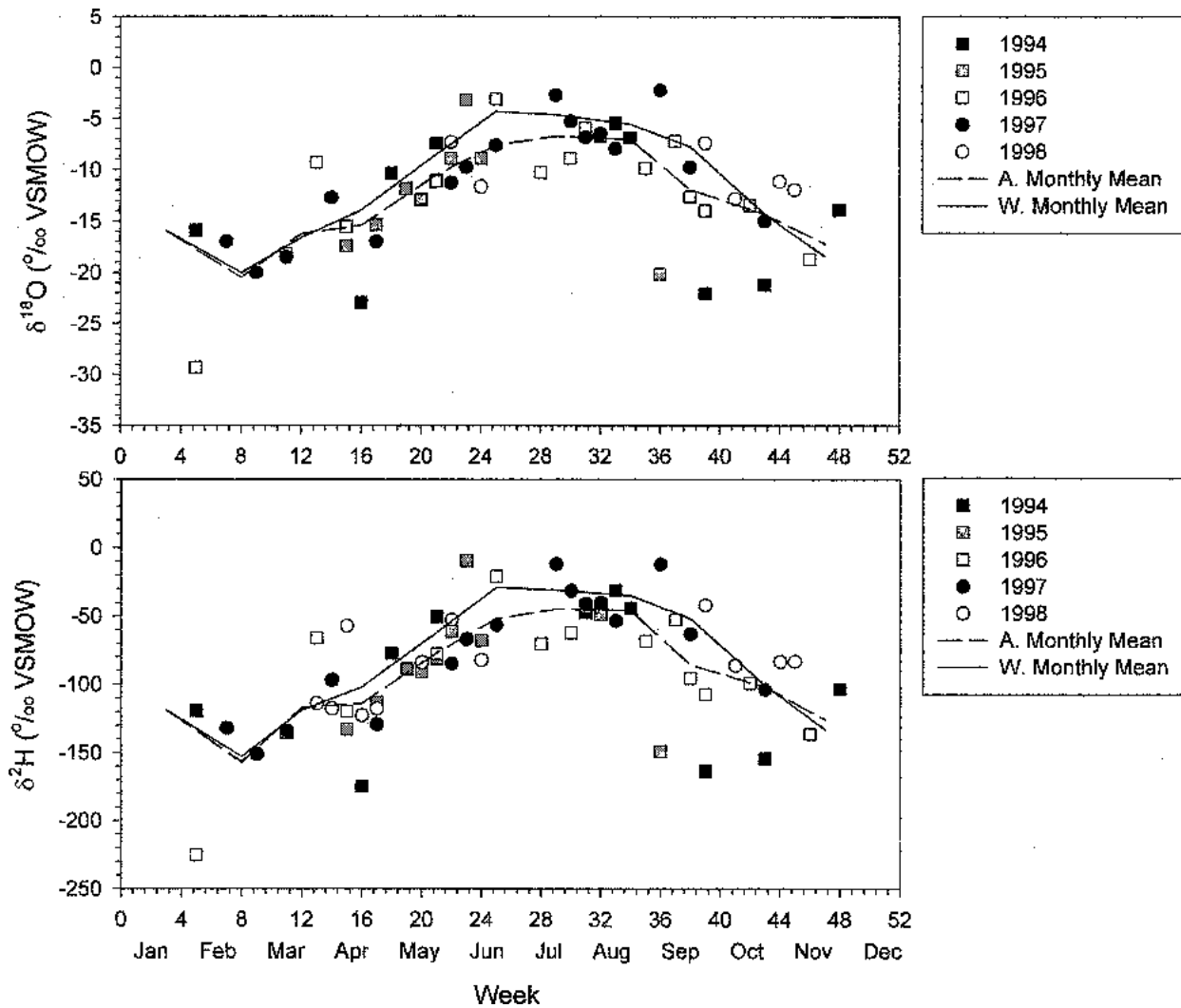


Figure 5. Weekly  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  Values for Years 1994 to 1998 for CO22 Site (includes only those samples with  $d$ -excess values greater than 3 per mil) Showing Seasonal Changes in Precipitation. Also plotted are the arithmetic and weighted monthly means for the site.

are using winter or summer precipitation during growth periods. In addition, the  $\delta$ -T correlation can be applied to the reconstruction of paleoclimate in the central Great Plains, a location of great interest to climatologists, as it is a region where different air masses converge.

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