Variations in the stable isotope compositions of water vapor and precipitation in New Mexico: links to synoptic-scale weather

Mel Strong

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VARIATIONS IN THE STABLE ISOTOPE COMPOSITIONS
OF WATER VAPOR AND PRECIPITATION IN
NEW MEXICO: LINKS TO SYNOPTIC-SCALE
WEATHER

by

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DISSERTATION

Submitted in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY IN
EARTH AND PLANETARY SCIENCES

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This dissertation investigates the stable isotope composition ($\delta D$ and/or $\delta ^{18}O$) of water vapor and precipitation in New Mexico. Water vapor and precipitation samples were collected and analyzed for stable isotope compositions over a 30 month period between 2005 and 2007. The outcomes of this project are as follows:

A. *The development of two independent methods of measuring the isotopic composition of water vapor.* One system is designed to capture a small volume of air (~650 mL) in an evacuated glass flask. This system is extremely portable (easily transported by automobiles and airplanes) and very quick to implement in the field (samples are taken in ~1 second). The second system is a cryogenic trap capable of gathering at least 1 mL of liquid water condensate. This second system is also portable (though not as portable as the flask system) and has the advantage of being able to measure both oxygen and hydrogen isotopes. Both of these systems required several steps including the inception and building of the capture devices, development of the field protocol, and refinement of the lab technique.

B. *The creation of a long (30-month) high temporal resolution (2-3 samples per day) record of the $\delta D$ of water vapor over Albuquerque.* Prior to this project, published records of water vapor had temporal resolutions of one day or less, and studies typically only lasted a few weeks. The most thorough study to date was completed in Germany, a climatic setting very different from that of the American Southwest. One product of this dissertation is a nearly-continuous 30-month record of
atmospheric water vapor (δD) that illustrates temporal and isotopic variations not yet reported in the literature. Such a record is necessary to realize the full range of variability of δD at different times scales (hourly to seasonally).

C. The description of 23 profiles of δD of water vapor up to 3.5 km AGL in the atmosphere. Prior to this study, atmospheric profiles of the D-content of water vapor were restricted to two studies done in the 1960s. In those studies, the efforts were focused on high altitude sampling with vapor samples taken every ~1km or so in altitude up to the tropopause. Variations in the δD of water vapor in and directly above the boundary layer are important to determine mixing and transport processes occurring near the surface. For this reason, 23 profiles of atmospheric water vapor were collected in increments of ~300 meters of altitude in an effort to detail the isotopic structure in the lower atmosphere. Variations in δD with height are investigated and found to correlate to wind direction.

D. The correlation of synoptic-scale weather events to variations in water vapor isotope chemistry. The majority of the work in this dissertation is devoted to determining atmospheric processes responsible for the variability in δD we observe in atmospheric water vapor near the surface at Albuquerque. While many factors can ultimately control the δD values of water vapor, a thorough investigation into the meteorologic processes at work reveals that synoptic-scale weather fluctuations have a first-order affect on the isotopic composition of water vapor in Albuquerque. I have diagnosed δD variations in terms of weather variability as shown on standard
weather maps, providing the most comprehensive analysis presented to date describing the relationship between meteorology and isotope geochemistry.

E. Investigation into the relationship between precipitation and vapor. Daily collection of water vapor and precipitation (when available) allows for the investigation of any relationships between the isotopic values of these two measurements. Despite the abundance of precipitation studies, there has been very little investigation into the relationship between water vapor and concurrent precipitation. In this study, pairs of precipitation and water vapor samples are examined. While in some instances they are reasonably close to being in equilibrium, in other cases they are clearly different.

F. The creation of the atmospheric water vapor line. The meteoric water line (constructed from both δD and δ¹⁸O of precipitation values) has been used for decades to map out the isotopic composition of precipitation from around the world. However, until now there has not been an attempt to collect and analyze a significant number of vapor samples sufficient to construct a plot of δD and δ¹⁸O similar to that of the meteoric water line. Such a plot has been constructed in this project, showing that vapor lies slightly above the meteoric water line. Water vapor samples collected from Albuquerque, Arizona, and Texas show that the deuterium excess is relatively constant. The position of the water vapor samples on a graph of δD vs δ¹⁸O is consistent with known fractionation processes between vapor and precipitation.
G. *The use of stable isotopes to find moisture sources.* One practical application of stable isotopes in the water cycle is in the determination of moisture sources. This project assesses the utility of δD as a tracer in determining the source for New Mexico's atmospheric moisture during the summer monsoon. In short, it appears that there is no unique isotopic signature of either the Gulf of CA or the Gulf of MX. Instead, any isotopic composition of water vapor that may be inherit to either gulf is secondary to variations produced by meteorological processes. Most notably, variability in convective activity can lead to considerably isotopic variability.

This dissertation is organized into the following chapters: Chapter 1 is a manuscript originally published by the Geophysical Research Letters in 2007 under the authorship of Strong, Sharp, and Gutzler. As first author, I contributed more than 50% of the work. Chapter 1 serves as an introduction to the technique and focuses on variations of δD values of water vapor observed in the spring of 2005. Chapter 2 summarizes the entire 30-month dataset, and investigates the meteorological and climatological processes responsible for the observed δD variations. Chapter 3 examines the relationship between water vapor and precipitation through the δD and δ^{18}O compositions of each.
Variations in the stable isotope compositions of water vapor and precipitation in New Mexic: links to synoptic-scale weather

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ABSTRACT

The D content of atmospheric water vapor over Albuquerque, New Mexico was measured for 30 months with air samples captured one to three times daily on the roof of a three story building. In addition, the D and O isotopes for 106 samples of surface water vapor and 40 samples of precipitation from the southwestern US were also measured. The relationship between the isotopic ratios of water vapor (δD_v) and humidity, in the form of vertically integrated precipitable water (PW), is explored. Midlatitude waves are responsible for a great deal of δD_v variation throughout the fall, winter, and spring. As the wave passes over NM, advection shifts to a westerly to northwesterly flow with subsidence aloft, which decreases δD_v and PW. Variations in
δDν throughout the summer monsoon season are due to a combination of factors but are primarily the result of circulation around a dominant high pressure system over North America. Periods of anticorrelated δDν - PW in the summer occur when Albuquerque is downwind of vigorous convective activity. The deuterium excess (d) of Albuquerque's vapor samples are remarkably consistent, especially when compared to reported values of d from other studies of water vapor. Our water vapor samples plot parallel to the Global Meteoric Water Line with an average d of 13.5‰, while higher values of d (up to 24‰) are observed in water vapor from AZ and eastern NM. Highly variable d is observed in precipitation samples; this variability is due to evaporation during precipitation events and is not related to variations of the d of the source vapor. Vertical profiles of δDwv in the lower troposphere exhibited considerable structure that cannot be ascertained from standard meteorological measurements. Trajectory analyses provide consistent evidence that the large temporal variations of surface δDwv and vertical variations of δDwv are primarily due to advection of water from different source regions.
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Chapter 1: Diagnosing moisture transport using D/H ratios of water vapor

Mel Strong, Zachary D. Sharp, David S. Gutzler

ABSTRACT

Water vapor transport paths into the American Southwest were deduced from a high temporal resolution record of hydrogen isotope compositions of atmospheric water vapor ($\delta D_{\text{wv}}$) collected over a six-week period in late spring, 2005, at Albuquerque, New Mexico. Daily fluctuations of $\delta D_{\text{wv}}$ routinely exceeded 20‰ in magnitude, while $\delta D_{\text{wv}}$ variations up to 80‰ occurred on the time scale of weather (a few hours to ~ a week). Vertical profiles of $\delta D_{\text{wv}}$ in the lower troposphere exhibited considerable structure that cannot be ascertained from standard meteorological measurements. Trajectory analyses provide consistent evidence that the large temporal variations of surface $\delta D_{\text{wv}}$ and vertical variations of $\delta D_{\text{wv}}$ are primarily due to advection of water from different source regions. The lack of mixing inferred from our analyses indicates that $\delta D_{\text{wv}}$ can be used as a sensitive tracer of the moisture transport history of air parcels.
1.1 Introduction

Stable isotope compositions of precipitation have been used for decades as a diagnostic tool for understanding the worldwide hydrologic cycle, including climatological moisture transport and recycling (Rozanski et al., 1993; Welker, 2000) and would seem to be an appropriate tool for deducing moisture transport paths in the American Southwest (Wright et al., 2001). Precipitation-based studies, however, are difficult in semi-arid regions where dry periods lasting from weeks to months are common. Most precipitation that reaches the surface is isotopically heavier than the initial cloud water due to evaporation below cloud base (Friedman et al., 1964). Thus, attempts to resolve moisture transport issues by isotopic studies of precipitation in this region are hampered by low temporal resolution and local fractionation processes.

In order to directly study the isotopic composition of moisture within an air mass, we developed a technique to collect air samples nearly instantaneously for deuterium analysis of water vapor. Such studies are rare and tend to focus on local recycling, surface exchange, and mixture of water vapor (Lai et al., 2006) rather than on large-scale transport. Previous studies of isotopic variations of atmospheric water vapor with a focus on meteorological processes (Jacob and Sonntag, 1991; White and Gedzelman, 1984) were conducted in relatively humid and well-vegetated areas and concluded that local evapotranspiration (ET) was a major contributor to the stable isotopic composition of water vapor. However, no corresponding study has yet been
conducted in an arid or semi-arid environment where transpiration fluxes are relatively low.

We present here an isotopic study of water vapor at a site in the American Southwest, where the relative importance of different water vapor transport paths into the Southwest has been much-debated over the past several decades (Adams and Comrie, 1997). At different times of year this region potentially receives moisture from three different oceanic sources: the Pacific Ocean, the Gulf of Mexico, and the Gulf of California (Adams and Comrie, 1997; Schmitz and Mullen, 1996). Temperature, humidity, and evaporation rates over the possible oceanic source regions are typically quite different, as are the pathways from source to inland regions. These factors should lead to detectable differences in the isotopic composition of atmospheric water reaching the Southwest.

In this study we present analyses of water vapor in air collected 1-3 times a day on the roof of a three-story building at the University of New Mexico (UNM) in central Albuquerque (the terminus of trajectories in Figs. 1 and 2). In addition, air samples at and above the surface were periodically collected in early morning over desert scrubland 40 km west of Albuquerque. Vertical profiles were collected in approximately 300 m intervals using a light aircraft with a ceiling of 2-3 km above ground level (AGL).

1.2 Data Collection and Analysis Technique

We have developed a system by which relatively small volumes of air can be captured quickly for subsequent deuterium analysis in the laboratory. Prior to sample
collection, 650 mL glass flasks were evacuated in the laboratory and sealed with a valve. These flasks were filled in the field with air samples by simply opening and closing the valve, a process that takes ~ 1 second. In the laboratory, water was isolated by bleeding the sample \( P_{\text{max}} = 15 \text{ mbar} \) through a liquid nitrogen (LN\(_2\)) filled trap. The glass flask was heated with a torch to approximately 400ºC to remove absorbed water from the interior flask walls. \( \text{CO}_2 \) was removed from the sample by replacing the LN\(_2\) with a mixture of ethanol and dry ice. The remaining water was then transferred to a glass tube containing zinc, where it was then reduced to hydrogen (Friedman, 1953). The hydrogen gas was then analyzed on a Finnigan Delta XL mass spectrometer. Data are reported relative to SMOW, defined such that IAEA water standards VSMOW and SLAP have \( \delta^D \) values of 0.0 and -428‰, respectively (Coplen, 1988). Replicate analyses of air samples collected simultaneously have a precision of +/- 1‰. The accuracy of our system was tested by placing ~2 ml of waters of known composition into dry flasks. Our reproducibility of known water standards is +/- 2‰.

Surface samples were taken on the upwind side of the roof of the three-story Earth and Planetary Sciences building at UNM. A Davis Weather Monitor II at the same location records meteorological conditions every 15 minutes. Sampling began in April 2005 and is ongoing.

Vertical sampling was accomplished by transporting a set of evacuated glass flasks (described above) onto a light experimental aircraft. Our goal was to obtain samples as quickly as possible to resolve the structure of \( \delta^D \) variability at scales
comparable to synoptic wind and humidity fluctuations. Prior isotopic studies of atmospheric water vapor required long integrated sampling times, requiring hours of flight time to obtain a single profile (Ehhalt, 1974; He and Smith, 1999; Taylor, 1972). Flights were conducted early in the morning as soon as enough daylight permitted launch and conducted on days that had weak or no surface-level winds, no precipitation, and few clouds (normal conditions for this area). After the maximum altitude was reached, which depended on conditions, the aircraft’s engine was shut off, and samples were collected during descent. Samples were usually taken every ~300 meters. The total time taken for descent was 15 - 25 minutes. This method captures isotopic profiles of vapor in the lower atmosphere at much greater temporal and spatial resolution than has been achieved in earlier studies (Taylor, 1972; Ehhalt, 1974; He and Smith, 1999), with the result that vertical structures not previously observed are documented.

1.3 Atmospheric δD Variations and Airmass Trajectories

The time series of near-surface δD_{wv} and collocated dewpoint (T_d) values, for the period May 25-July 5, 2005, are shown in Fig. 1a. δD_{wv} values range from -200‰ to -50‰. Variations as large as 80‰ can occur in less than a day. The correlation between δD_{wv} and T_d is high on daily/weekly time scales but seasonal scale trends are different. Thus r^2(δD_{wv}, T_d) = 0.65 if the dataset is first split in half, with correlations calculated separately for periods
before and after June 15. However the mean $\delta_{D_{wv}}$ value is significantly higher in the second half of the dataset.

Four representative vertical profiles of $\delta_{D_{wv}}$, temperature ($T$), and $T_d$ are shown in Fig. 2. In general, major vertical variations in $\delta_{D_{wv}}$ do not correspond to vertical variations in $T$ or $T_d$. While water vapor typically becomes lighter with altitude, exceptions to this can be observed (e.g., Profiles 1 and 4). To help interpret $\delta_{D_{wv}}$ variability in the time series of Fig. 1a, 48-hr reverse-calculated trajectories for air parcels at select times were performed using the NOAA HYSPLIT model (Draxler and Rolph, 2003), using the EDAS 40 km analysis. Vertical motion was modeled using the vertical velocity option.

The HYSPLIT model is designed for regional scale trajectory analysis. It has been used extensively for studies of regional transport of aerosols (e.g., Lee et al., 2004). Pollutant transport in the absence of active atmospheric chemistry is similar to isotopic transport, to the extent that the $\delta_{D_{wv}}$ value of air is preserved (i.e. no fractionation or mixing of parcels with different isotopic signatures). The version of HYSPLIT used for this study advects air parcels through the resolved 40-km grid. The trajectories are subject to errors associated with the EDAS analysis and computational inaccuracies in the model formulation. Furthermore, HYSPLIT does not simulate any isotopic fractionation or include a convective mixing parameterization, such as would be needed to explicitly simulate the isotopic changes associated with condensation and evaporation associated with moist convection.
During periods of high $\delta D_{wv}$ (e.g. times A, C, E), trajectories show low-level advection from the southeast or east (Fig. 1b), suggesting the Gulf of Mexico as the primary source of water vapor. Periods of low $\delta D_{wv}$ (e.g. times B, D, F) correspond to advection from the southwest, suggesting origin over the Pacific Ocean. Additionally, the HYSPLIT model simulates a sheared flow at time E, in which air below 1500m AGL is being advected from the southeast while air above 1500m AGL is being advected from the southwest. Similar inspection of trajectories at other times confirms that the large $\delta D_{wv}$ variations observed in Fig. 1a can generally be attributed to changes in low-level atmospheric circulation.

Trajectory calculations are also useful in the interpretation of vertical variations of $\delta D_{wv}$ (Fig. 2). Profile 2 represents the simplest of the four vertical trajectory histories. Although air at all three altitudes follows nearly the same path in map view, HYSPLIT's simulation of vertical motion suggests that air below 1100m AGL has been in close proximity to the ground 24-36 hr prior to sampling. Air above 1100m AGL has been transported directly from the Pacific Ocean without much mixing with ground-level air, resulting in extremely low $\delta D_{wv}$ values near -280‰.

The trajectories associated with Profiles 1 and 3 imply more complicated transport paths. In both cases, differential advection over Albuquerque correlates with observed vertical variations of $\delta D_{wv}$. For Profile 1, HYSPLIT shows that near-surface air (up to 1000m AGL) is being advected from the southeast, mid-level air (~1000 - 1500m AGL) from the south, and air above 2000m AGL from the west. Corresponding
variations in the $\delta D_{wv}$ values of Profile 1 include a pronounced increase in $\delta D_{wv}$ values above 700m at the base of a layer in which air is advected from the south.

Similarly, for Profile 3, HYSPLIT predicts that sub-1200m air has either been advected from the southeast or did not move significantly in the previous 24 hours, while air above 1200m was advected from the southwest. In the $\delta D_{wv}$ values from profile 3, we see a corresponding decrease in the $\delta D_{wv}$ values above 1200m. Profile 4 was sampled late in the study period, when the large-scale circulation was shifting from springtime conditions, with dry westerly winds aloft, to a more summerlike monsoonal circulation. The southwesterly winds in the uppermost trajectory are associated with a very unusual increase in $\delta D_{wv}$ with altitude.

1.4 Interpretation and Discussion

Previous research on isotopic fractionation between water phases provides a general guide to expectations in isotopic variability in meteorological systems. Water vapor evaporated from a warmer body of water (e.g., Gulf of Mexico) should have higher $\delta D_{wv}$ values than vapor from cold bodies of water (e.g., North Pacific). When an airmass experiences rainout as it moves inland, the remaining water vapor will become lighter (Dansgaard, 1964). Above the surface, $\delta D_{wv}$ values should decrease with height approximately following a Rayleigh fractionation pattern (Taylor, 1972). Transpiration should increase $\delta D_{wv}$ values, while evaporation of soil water could lower or raise $\delta D_{wv}$, depending on the proportion of water remaining in the soil (Sharp, 2006).
The trajectories associated with Profile 2 suggest that air below 1100m was in close contact with the ground during the 36 hr prior to collection, so that near-surface air accumulated isotopically heavy water from ET. Above 1100m the vapor is light, indicating transport from the Pacific Ocean without much continental contribution from evapotranspired water.

From the above discussion, we conclude that advection is the primary cause of $\delta D_{wv}$ variability. Although local ET certainly contributes to the observed variations in $\delta D_{wv}$, multiple lines of evidence point toward a secondary role for ET. First, we compared $\delta D_{wv}$ values from surface air sampled ~40 km west of Albuquerque, over sparsely vegetated scrubland, with nearly simultaneous samples collected at UNM amidst relatively abundant, well-watered urban vegetation. The $\delta D_{wv}$ values for each of these pairs of samples are nearly identical (Fig. 1a), implying that ET fluxes from these two disparate environments have not affected $\delta D_{wv}$ values of the surrounding vapor, or else affected them in exactly the same amount.

Second, water vapor collected from the transpiration of native vegetation shows little $\delta D$ variation over several months of sampling (Fig. 3), unlike the atmospheric samples. We sampled vapor from selected sagebrush (Artemisia filifolia) and Juniper (Juniperus communis) trees in an area 20 to 40 km west of Albuquerque. Plastic bags were placed over a portion of the plant and left for 24 hr. Water vapor was collected in the bags and analyzed for deuterium content. Five sampling periods were conducted between early July and mid October. For each sampling period, an effort was made to
collect from the same plant. If that plant was not available, another plant of similar size
was selected in the same area, within a few meters of the original. As illustrated in Fig.
3, the total temporal variation observed in sagebrush vapor is ~ 30‰, while junipers
show ~ 40‰ variation, much smaller than atmospheric $\delta D_{wv}$ variations (Fig. 1a).

Third, water vapor was collected periodically over bare soil in the vicinity of the
sampled plants. This was accomplished by placing a plastic box over an area of
unvegetated bare soil. After 24 hr the water vapor inside the box was collected. The $\delta D$
values of evaporated water from one representative location are shown in Fig. 3.
Similar to transpired water, the evaporated water from soil at each of the sampling sites
shows much smaller fluctuations in $\delta D$ values than atmospheric $\delta D_{wv}$. This suggests that
the rapid and large variations in $\delta D_{wv}$ (Fig. 1a) are not caused by variations in the $\delta D$ of
evaporated soil water.

Finally, our collection of water vapor from plants and soil indicates that ET
contributes water vapor that is heavier than that normally present in the atmosphere.
Thus if atmospheric conditions were such that convection was stifled and ET
contributions accumulated within the boundary layer, one would expect elevated $T_d$ and
higher $\delta D_{wv}$ values as suggested by White and Gedzelman (1984). However, in the time
series present, we find no such correlations between meteorological conditions, $T_d$, and
$\delta D_{wv}$.

Recycled precipitation can also provide a major contribution to D-enriched water
evapor in the lower troposphere. During condensation processes in clouds, heavy
isotopes preferentially enter the liquid phase. If raindrops partially evaporate during descent, the air column below cloudbase will become enriched with isotopically light water vapor. However, if 100% evaporation occurs, as is common in the Southwest, then water vapor of isotopic composition equivalent to that of the bulk precipitation is added to the air column, typically increasing $\delta D_{wv}$ values.

Over the time period of our dataset, hot and dry conditions necessary for the complete evaporation of raindrops were often met. Spring 2005 was warm and dry in NM, as expected climatologically. The monthly average daytime high temperatures recorded at the Albuquerque airport in May and June 2005 were 26°C and 32°C respectively, with an average relative humidity of 39% and 29%. May had a total of 10 mm of rain, most of which fell on May 4th (7 mm), while June's total rainfall was only 2 mm.

We propose that Profiles 1 and 3 include layers of air containing water vapor originating from recycled precipitation. The outstanding example of this is Profile 3, where the sub-1200m air had $\delta D_{wv}$ values that are among the highest recorded in 2005. The trajectory analysis of profile 3 (Fig. 2) indicates that low-level air over Albuquerque was transported westward from an area that experienced widespread thunderstorms the previous afternoon.

Similarly, weather conditions leading up to the collection of Profile 1 were also conducive to precipitation recycling. For more than three weeks prior to 5/27/05, south-central NM was mostly free of precipitation, with daily relative humidity near
20%. In the two days leading up to the collection of Profile 1, thunderstorm cells occurred ~100km south of Albuquerque. At the time of Profile 1, mid-level advection (~1000 - 1500m AGL) was from the south, passing through the convectively active area. Evaporation of raindrops from the previous afternoon's thunderstorms followed by northward advection could explain the isotopically heavy mid-level layer.

The trajectory ending at 2000m AGL above Albuquerque traces back to a location near the Gulf of California. The northern Gulf is much warmer than the Pacific Ocean so moisture from this source would be expected to be isotopically heavy, consistent with the increasing $\delta$Dwv values at the top of Profile 4. Thus the range of isotopic variability in the data seems to be sufficient to distinguish the principal sources of moisture for the American Southwest.

Our study indicates that the primary control on $\delta$Dwv variability is atmospheric circulation in this semi-arid area, with local ET playing a secondary role. The magnitude of $\delta$Dwv variability over time and altitude, the correlation between multi-day $T_d$ and $\delta$Dwv fluctuations, and the trajectory analyses are all consistent with atmospheric circulation being the primary control on $\delta$Dwv variability.

The $\delta$Dwv data are characterized by rapid, pronounced temporal and vertical isotopic shifts that can be related to large-scale airmass trajectories. The $\delta$Dwv value at a given altitude captures the history of the air, suggesting that the isotopic values of the water vapor may be 'set' and retained for hundreds of kilometers without much fractionation or mixing. Air parcels retain their isotopic identity within narrow vertical
bands that are consistent with low-level wind shear but not apparent in temperature or dewpoint data.

We propose that geographically widespread sampling of $\delta D_{wv}$ could provide a powerful new diagnostic tool for monitoring air parcel trajectories and validating atmospheric models. The geochemical fingerprints of different moisture source regions and transport paths now promise to yield a new observational database that complement existing dynamical tracers. This study was conducted during the dry spring season, when there was minimal chance for recycled precipitation to contribute to our measurements. We are continuing this study into the rainy monsoon season and hypothesize that the temporal and vertical variability of $\delta D_{wv}$ may be different, potentially yielding insights into moisture recycling processes.

**Acknowledgements.** The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.html) used in this publication. Funding for this project was provided by the Kelly-Silver Foundation through UNM. We thank Joe Galewsky, Jim O'Neil, Roland Draxler and manuscript reviewers for helpful comments.
1.6 Figures

Figure 1 - Caption next page
Figure 1 - Caption

(a) Time series of $\delta D_{wv}$ (red) and dew point $T_d$ (blue) for samples collected at UNM. Stars indicate ground-level measurements taken with each vertical profile at the flight site 40 km west of UNM. Numbers 1-4 denote vertical profiles shown in Figure 2. Letters A-F refer to times of trajectories shown in (b). (b) HYSPLIT reverse-calculated 48-hour trajectories ending at Albuquerque for times A-F from (a). For each trajectory model, the green, blue, and red lines in map view represent the path of air parcels terminating at 3000, 1500, and 500 meters AGL over Albuquerque for the 48-hr period prior to the specified date. Tick marks indicate 12-hr increments. Vertical motion for each air parcel as calculated by HYSPLIT is shown below each map. In general, high (low) values of $\delta D_{wv}$ correspond to advection of air from the southeast (southwest).
Figure 2 - caption next page
Figure 2 - Caption

Four vertical profiles (times 1-4 from Figure 1a) of δD$_{wv}$, T, and T$_d$ (colored black, red, and blue, respectively) shown next to their associated HYSPLIT reverse trajectory models. The green, blue, and red lines in map view represent paths of air parcels of differing elevations terminating at different elevations over Albuquerque; the modeled vertical motions are shown beneath each map.
Figure 3.

δD values of transpired water from four Sage plants (short dash) and two Juniper trees (solid) compared to δD values of evaporated water from bare soil (long dash); all sampled 20 to 40 km west of Albuquerque.
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Chapter 2: The meteorological and climatological mechanisms behind observed variations in the isotopic composition of atmospheric water vapor over New Mexico

Abstract

The D content of atmospheric water vapor over Albuquerque, New Mexico was measured for 30 months with air samples captured one to three times daily on the roof of a three story building. The relationship between the isotopic ratios of water vapor (δDᵥ) and humidity, in the form of vertically integrated precipitable water (PW), is explored. For most of the year δDᵥ and PW correlate, but significant exceptions to this relationship exist, particularly in the summer. The causal relationship between synoptic-scale atmospheric conditions and resulting variations in δDᵥ is investigated. Midlatitude waves are responsible for a great deal of δDᵥ variation throughout the fall, winter, and spring. When New Mexico is downwind of the trough axis of an approaching wave in westerly flow, advection is initially from the southeast to southwest, typically causing an increase in δDᵥ and PW. As the wave passes over NM, advection shifts to a westerly to northwesterly flow with subsidence aloft, which decreases δDᵥ and PW. Variations in δDᵥ throughout the summer monsoon season are due to a combination of factors but are primarily the result of circulation around a dominant high pressure system over North America. The exact position of this high pressure is critical to the behavior of δDᵥ over Albuquerque. Variations in δDᵥ during the monsoon season are also due to easterly wave activity, gulf surges, and the occasional Pacific hurricane remnant.
Periods of anticorrelated $\delta D_v - \text{PW}$ in the summer occur when Albuquerque is downwind of vigorous convective activity.

2.1 Introduction

The mass of an individual water molecule depends on the combination of different possible isotopes of H and O. Isotopically "heavy" water molecules, relatively rare in the hydrosphere, include isotopologues HD$^{16}$O and H$_2^{18}$O, whereas the overwhelming majority of water molecules are the "light" isotopologue H$_2^{16}$O. Stable isotope ratios (R) of HD$^{16}$O:H$_2^{16}$O or H$_2^{18}$O:H$_2$O measure the relative abundance of heavy isotopes within a body of water. Isotopic ratios are expressed as a departure from standard mean ocean water ($R_{SMOW}$) and are written in delta notation ($\delta$) as:

$$\delta = \left[ \frac{R - R_{SMOW}}{R_{SMOW}} \right] \times 1000 \tag{2.1}$$

The isotopic composition of precipitation depends on several known factors, the most important of which are the degree of rainout, the temperature of condensation, and the temperature of the source body of water (Dansgaard, 1964). In the past few decades, the isotopic compositions ($\delta D$ or $\delta^{18}O$) of precipitation have been used to study a variety of processes in the water cycle. The most common application in such studies surrounds the known correlation of stable isotopic composition with temperature, making isotopic analysis particularly useful for paleoclimate reconstructions from ice cores (e.g., Jouzel et al., 1982; Petit et al., 1991; Barlow et al.,
1993; Delmotte et al., 2000; Stenni et al., 2001; Hoffman et al., 2001; Vimeux et al.,
2002; Werner and Heinmann, 2002), groundwater (e.g., Edmunds and Wright, 1979; Gat
and Dansgaard, 1972; Rozanski, 1985) and tree rings (e.g., McCarroll and Loader, 2004).
However, the use of deuterium and $^{18}$O as tracers has also helped to decipher several
atmospheric processes that have otherwise been difficult to observe or quantify. For
example, widespread precipitation collection and analysis over many decades has
enabled investigation into meteorological problems such as identifying large-scale
circulation patterns responsible for isotopic variability on large spatial scales
(Dansgaard, 1964; Salati et al., 1979; Rozanski et al., 1993; Celle-Jeanton et al., 2001;
Friedman et al., 2002; Longinelli and Selmo, 2003; Argiriou and Lykoudis, 2006; Lykoudis
and Argiriou, 2007), and identifying moisture sources for a particular area (Lawrence et
al., 1982; Gedzelman and Lawrence, 1982; Rindsberger et al., 1982; Friedman et al.,
2002; Burnett et al., 2004; Peng et al., 2004; Barras and Simmonds, 2008; Pfahl and
Wernli, 2008).

Although isotopic studies of precipitation have yielded insights into atmospheric
processes, precipitation studies have an inherit limitation in that the isotopic
composition of precipitation collected at the surface is not necessarily representative of
the composition of the moisture that left the cloud. Falling drops are subject to
evaporation and exchange with the moisture in the air column - processes that are
dependent on the temperature, humidity, and isotopic composition of the vapor in the
air column (Stewart, 1975). These attributes of an air column can vary widely with
altitude, allowing for a complex series of processes (mostly evaporation and exchange
reactions) to occur on raindrops during their descent. In addition, precipitation studies are difficult in dry locations such as Southwestern North America, where entire months may be void of any measurable precipitation. A direct study of the isotopic composition of water vapor would sidestep these problems, providing an alternative method for studying atmospheric moisture and thereby complementing the existing literature based on precipitation. Variations in the $\delta D$ and/or $\delta^{18}O$ values of atmospheric moisture may be helpful in identifying a number of water vapor transport processes, including moisture source and history, moisture recycling, and boundary layer dynamics. The temporal resolution of such a study would only be limited by the resources involved in sampling and analysis, not by the occurrence of random precipitation events.

The transport and fractionation of stable isotopes in water vapor have been simulated in models with a wide range in complexity. Isotope models fall into two categories. The first type are dynamically simple models that deal with isolated air masses and the isotopic fractionation processes that are occurring within that airmass. Generally, this type of model uses some form of Rayleigh distillation, such as that used by Dansgaard (1964) and then later refined in Friedman et al. (1964), Taylor (1972), Siegenthaler and Matter (1983), and Jouzel and Merlivat (1984). These models can explain many of the observations of stable isotopes in precipitation, but do not simulate all of the complex processes involved in the formation of precipitation, especially over a broad spatial domain (Ciais and Jouzel, 1994).
This inherent deficiency in isolated air mass models eventually led to the incorporation of isotope physics into global circulation models (GCMs), the second major category of models attempting to simulate isotopes in the water cycle. The first successful isotope-enabled GCM is credited to Joussaume et al. (1984) and Jouzel et al., (1987), who incorporated isotope physics into the Goddard Institute for Space Studies General Circulation Model (GISS), a three-dimensional GCM first described by Hansen et al. (1983). Isotope physics were then embedded into the European Centre Hamburg Model (ECHAM) (Hoffman et al., 1998). Both the isotope-enabled GISS and ECHAM models were considered successful in generating the main features observed in global precipitation patterns. Mathieu et al. (2002) incorporated isotope tracers into the Global Environmental and Ecological Simulation of Interactive Systems (GENESIS 2.0 GCM as first described by Pollard and Thompson, 1994); the GENESIS model claimed to have a more sophisticated parameterization of interactions between precipitation and atmospheric water vapor than previous GCMs. Additional work with GCMs was completed by Noone and Simmonds (2002) who added isotope parameterizations to the Melbourne University GCM (MUGCM), a spectral primitive equation model based on Bourke et al. (1977) and McAvaney et al. (1978).

In the past ~10 years, isotope-enabled models have become more realistic with the incorporation of forcing/nudging techniques from observed data or reanalysis products. For example, Vuille et al. (2003) added sea surface temperature (SST) forcing with observed data to both the GISS and ECHAM GCM models. Yoshimura et al. (2003) used gridded reanalysis data sets (NCAR and ECMWF) with Rayleigh equations to create a
model considered to be intermediate between the Rayleigh-type and isotope-enabled GCMs. This model was then expanded by Yoshimura et al., (2004) to enable longer timeframes and subsequently by Yoshimura et al. (2008) to include spectral nudging. Similarly, Risi et al. (2010) used a nudging technique with reanalysis data and the LMDZ4 GCM. Improved representation of physical processes in models through better parameterization in isotope-enabled GCMs is ongoing (e.g., Lee and Fung, 2008; Bony and Emanuel, 2001; Smith et al., 2006; Lee et al., 2009; Wright et al., 2009).

While GCMs have been a useful tool to help interpret global patterns in stable isotopic ratios of precipitation and vapor, isotope-enabled GCMs have been used to diagnose more specific scientific problems in atmospheric dynamics. For example, Schmidt et al. (2005) used a version of the GISS model to study the exchange of water vapor between the stratosphere and troposphere. Lee et al. (2009) used the isotope-enabled NCAR-CAM2 GCM to investigate deuterium excess during the last glacial maximum. In other instances scaled-down, simplified, or customized process models other than full GCMs have been run to address specific problems. Ciais and Jouzel (1994) created a one-dimensional model to simulate the physics of mixed clouds (ice and liquid) and the resulting isotopic fractionation. Dessler and Sherwood (2003) studied HDO in the tropical tropopause layer by combining Rayleigh distillation with a convective model utilizing Emanuel parameterization. Likewise, Bony et al. (2008) developed a one-dimensional model utilizing Emanuel parameterization to investigate the role of tropical convection in the transport of water to the upper troposphere and lower stratosphere. Blossey et al. (2010) developed cloud-resolving simulations of an
idealized equatorial Walker circulation to investigate the tropical tropopause layer. Galewsky and Hurley (2010) created an advection-condensation model to diagnose the maintenance of subtropical water vapor. These models each provide a different quantitative framework to address the isotopic ratios of water vapor in various locations in the atmosphere.

In addition to Eulerian GCMs and one-dimensional models, Lagrangian trajectory models have been used to explain isotopic variations in the hydrosphere. Some of the earliest use of trajectory analysis was for determining moisture source for precipitation in the eastern US (Lawrence et al., 1982), the Mediterranean Sea area (Rindsberger et al., 1983), and the Great Basin (Friedman et al., 2002). Trajectory analysis has been extended to help explain isotopic compositions of water vapor by inferring the source of the water vapor in question (Lawrence et al., 2004; Strong et al., 2007; Pfahl and Wernli, 2008; Noone et al., 2011).

To date there are hundreds of thousands of published analyses of stable isotopic compositions of precipitation. By comparison, there have been very few published datasets for water vapor. Thus while there has been considerable work to build up the quantitative and theoretical framework for understanding stable isotopes in the atmosphere (as previously described), very little observational data exists. After the pioneering work of Dansgaard (1953, 1954) and Craig and Gordon (1965), one finds virtually no published studies on water vapor until the works of White and Gedzelman (1984) and Schoch-Fischer (1984). Both of these latter studies attempted to link
meteorological conditions to the isotopic variations in the surface-level moisture.

Another hiatus appears in the literature until a flurry of more recent work, with analyses of vapor above the ocean (Uemura et al., 2008), in the tropics (Lawrence et al., 2004); in or near hurricanes (Gedzelman et al., 2003), above the Mediterranean Sea (Gat 2003), on the Tibetan plateau (Kurita and Yamada, 2007), above marshland in northeastern US (He et al., 2001), inland Europe (Dirican et al., 2005; Carreira et al., 2005) and at various altitudes around Hawaii (Galewsky et al., 2007).

The vapor studies listed above have used the rather laborious method of capturing water vapor through a cryogenic trap, which limits the number of analyses that can be reasonably made. With the advent of tunable laser diode (TLD) wavelength-scanned cavity ringdown spectroscopy (Lee et al., 2005; Crosson, 2008; Brand et al., 2009; Gupta et al., 2009) isotopic analysis of water vapor have become more prolific, and now include datasets from a one-year study from northeastern US (Lee et al., 2005), a one-year period from Beijing, China (Wen et al., 2010), a four-week period from the Mauna Loa Observatory in Hawaii (Noone et al., 2011), and a ~3-week period from the Chajnantor Plateau in Chile (Galewsky et al., 2011).

In addition to recent datasets from TLD instruments, isotopic studies of water vapor on a regional scale have been gathered from a variety of airborne platforms such as the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment aboard the Space Shuttle (Moyer et al., 1996; Kuang et al., 2003; Ridal, 2002), from stratospheric balloons (Johnson et al., 2001; Stowasser et al., 1999), and from aircraft (Webster and
Heymsfield, 2003; Hanisco et al., 2007). These studies almost exclusively focused on the isotopic composition of water vapor in the stratosphere or tropopause region. Satellite platforms such as the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument on ENVISAT (Steinwagner et al., 2007; Payne et al., 2007) and the Tropospheric Emission Spectrometer (TES) instrument on the Aura satellite (Worden et al., 2007; Brown et al., 2008) are now returning global coverage of isotopic compositions of tropospheric water vapor.

Broadly speaking, the majority of the theoretical and observational work in atmospheric stable isotopes described above has been concerned with either interpreting the isotopic composition of precipitation collected at the surface or using stable isotopes as a diagnostic tool for determining stratospheric or upper tropospheric moisture sources. The resolution of the GCMs, while adequate for tackling global-scale circulation problems, is far too coarse for resolving small-scale meteorological processes occurring close to the surface. Most of the observing platforms (TDLs aside) integrate over a thick vertical layer of the atmosphere or are designed for middle-atmosphere and higher altitudes.

Until now, there have been few studies that report time series of surface-level isotopic variations of water vapor with daily resolution with timescales greater than a few weeks (Lee et al., 2005). Additionally, there have not been attempts to link observed isotopic variations to synoptic-scale atmospheric conditions on the (daily) timescale of weather. Although scientific awareness of water vapor isotopic ratios and
their potential for diagnosing hydrometeorological processes is increasing with the advance of new instrumentation, very little is still known about the role that daily weather has on stable isotope ratios of water vapor. In this paper we present a 30-month long study of the isotopic composition of water vapor and precipitation in an arid/semi-arid region in the southwestern US. We describe the variability of δD of water vapor (δDv) at both seasonal and daily time scales, investigate the meteorological and climatological processes that are responsible for the observed variability, and explore relationships that exist between the δD ratios of precipitation and water vapor. Our underlying goal is to understand the interplay between meteorological events and the resulting variations in δDv. Our dataset include air samples collected regionally from neighboring states as well as a number collected above the surface from aircraft flights, though the main thrust of our efforts is to understand the variability of δDv observed in surface-level air samples at Albuquerque.

2.1.1 Setting

Water vapor and precipitation samples were collected primarily in Albuquerque, NM, with some vapor samples collected periodically in Arizona (AZ), Eastern NM, and Texas (TX) (Figure 1). Albuquerque, with an altitude of 1620 m, is considered arid/semi-arid desert with 215 mm of average annual rainfall. Approximately half of the yearly precipitation falls in July-August-September with the arrival of monsoonal moisture from the south. NM lies in the northern portion of the North American Monsoon System (NAMS), a convective circulation system that is centered in northwest Mexico.
(MX) but greatly affects the US states of AZ and NM (Douglas et al., 1993; Adams and Comrie, 1997). NM occasionally receives precipitation from the remnants of Pacific cyclones in late summer (Etheredge et al., 2004; Ritchie et al., 2011) while midlatitude storms originating over the Pacific Ocean provide precipitation for the remainder of the year (Tuan et al., 1973).

2.2 Methods

Atmospheric vapor was collected and analyzed for δD by two independent methods. Primarily, evacuated 650 mL glass flasks were evacuated and then used to capture air samples. The moisture from the flasks was isolated and then reduced with zinc to produce hydrogen gas as described in Strong et al. (2007). In 2007, we introduced a cryogenic method of capturing water vapor, which was used in conjunction with the glass flasks to give larger volumes of water for oxygen isotope analysis. The hydrogen isotope data from samples collected via the cryogenic procedure is included with hydrogen data collected with the flask method in this paper. The oxygen isotope data and the procedure for the cryogenic sampling are described in Chapter 3.

The majority of the air samples were taken from the roof of a three-story building at the University of New Mexico in Albuquerque. Samples were always taken upwind from any steam or exhaust vents to prevent possible contamination. The sampling regiment was variable, but in general 1 to 3 vapor samples were taken every 24-hour period. Typically one sample was taken in the morning, one in the late afternoon, and one close to midnight local time. Meteorological conditions on the roof were recorded
every 15 minutes by a Davis Weather Station. During the spring and summer months of 2007, we initiated a sampling campaign outside of Albuquerque in an effort to compare the isotopic compositions of water vapor on a regional scale. We conducted nine sampling trips to Arizona and six to eastern NM/west TX (Figure 1).

Glass flasks were also taken aloft in an airplane ~25 km west of Albuquerque to capture water vapor at different altitudes. 23 flights were conducted over 2005 and 2006 throughout spring, summer, and fall. We collected 6 to 10 samples on each flight, sampling at every 300-500 vertical meters with final altitudes reaching between 1.5 and 5.5 km above the surface. Flights were only conducted in early mornings on days with little or no surface wind.

2.3 Data

The entire 30-month time series of $\delta D_v$ and precipitable water (PW) is shown in Figure 2 to highlight the seasonal cycles, while Figure 3 shows the same data expanded into greater detail. In general, isotopically lighter water vapor (i.e., relatively depleted in deuterium) occurs in the winter while isotopically heavier vapor (i.e., relatively enriched in deuterium) occurs in the summer, with heaviest samples collected in June just prior to monsoon onset. PW reaches a relatively sharp maximum in early August, but minimizes over several months throughout the winter and early spring. Although $\delta D_v$ correlates temporally with PW to a first order, there are periods of time when $\delta D_v$ and PW are decorrelated. Most notably, $\delta D_v$ does not peak in early August with PW, but in fact decreases somewhat at the PW maximum (most noticeable in 2006). In addition
to the general seasonal cycle of higher δDᵥ values during the summer and lower δDᵥ values during the winter, variations in δDᵥ tend to be greatest in the winter and spring, where δDᵥ can change by ~100‰ in 24 hours. The onset of the summer monsoonal moisture, marked by elevated PW in July, is coincident with more subdued variations in δDᵥ. The observed δDᵥ values reached a minimum of -283‰ (1/21/07), and a maximum of -52‰ (6/25/05).

We present a climatological summary of the δDᵥ and precipitation (δDₚ) at Albuquerque in Figure 4. Each gray box represents the summation of all surface-level (rooftop) vapor samples for that month over 2005-2007. Because of the scarcity of precipitation samples (especially in the winter months), we have included precipitation collected in the three years preceding our vapor study. In general, the values of δDₚ within a given month are higher than δDᵥ values, though some overlap occurs on the monthly timescales (though δDᵥ is never higher than δDₚ on individual days).

2.4 Comparison with meteorologic variables

The positive correlation between the isotopic enrichment of precipitation and temperature (T) has been known since Dansgaard’s initial work (1964) and has been refined throughout the years (e.g., Rozanski et al., 1993). To assess whether any such δDᵥ - T relationship exists within our vapor data, we have split the data into four seasonal groups based on regional climatology. These groups include ‘spring’ (April-May-June), ‘monsoon’ (July-August), ‘post-monsoon’ (September-October), and ‘cold season’ (November through March). As shown in Figure 5, we have plotted δDᵥ against
T (as recorded at the time and place of vapor collection) for each of these four groups. There is little to no correlation between daily fluctuations of $\delta D_v$ and $T$ regardless of season. The strongest $\delta D_v$ - $T$ correlation that does exist is a weak positive correlation within samples collected during flights in October and November.

One focus of previous vapor studies has been on the relationship between humidity and $\delta D_v$, though the observed association between these two variables is not consistent. White and Gedzelman (1984) found a positive correlation between $\delta D$ and $T_d$ from air samples taken in New York, but Lawrence and Gedzelman (2003) determined that a poor correlation exists between these variables in tropical water vapor. Both Lee et al. (2006) and Wen et al. (2010) found that the correlations between $\delta D_v$ and mixing ratio (w) varied throughout the year, with the weakest correlations occurring in the summer. As observed in a plot of $\delta D_v$ vs w (Figure 6), $\delta D_v$ and w exists are positively correlated in the spring and winter months, but virtually no correlation is evident during the summer and early fall. It is interesting to note that samples taken by aircraft over the summer months exhibit a stronger correlation between $\delta D_v$ and w than do the surface samples. Correlation coefficients by month and sample type are presented in Table 1.
Table 1

Correlation coefficients (r) between δD_v and simultaneous local mixing ratio (w) by month and sample type. ‘n’ indicates number of samples in each category. ‘All’ include samples taken from the roof, from flights, and from regional samples in AZ and eastern NM.

Above we have shown that relatively poor correlations exist between δD_v and humidity or temperature conditions at the time of the sample. However, if we include the seasonal cycle and compare the ranges of all monthly temperature and humidity values against δD_v, a different relationship emerges. From our weather station data, we have plotted the monthly variability of T and T_d (as recorded every 15 minutes) along with δD_v (Figure 7). From this it can be observed that a clear overall correlation exists between the monthly ranges of δD_v, δD_p, T, and T_d. In general, higher values of δD_v and δD_p are associated with elevated values of T and T_d in the summer, while lower δD_v and δD_p values are observed during periods of low T and T_d in the winter. A slight exception
to this is observed during the monsoon months of July and August, when the dew point increases to its annual peak but $\delta D_v$ stays relatively constant.

2.5 Relationship between precipitation and $\delta D_v$

With regards to the many existing studies on the isotopic composition of precipitation, it is desirable to determine if precipitation is in isotopic equilibrium with the surface-level vapor at any time. To do so, we compared the $\delta D$ values of collected precipitation ($\delta D_p$) with the values of $\delta D_v$ recorded prior (within eight hours) to the precipitation event. Within our 30-month dataset, we have 121 pairs of vapor-precipitation to compare. Using equilibrium fractionation factors (Majoube, 1971) and the recorded surface $T$ at the time of the precipitation event, we calculated the differences between $\delta D_v$ and $\delta D_p$ (Figure 8). Precipitation is rarely in equilibrium with vapor, with $\delta D_p$ values of individual events both heavier and lighter than expected equilibrium values. In general, $\delta D_p$ values tend to be heavier than the calculated equilibrium value, though during the winter and spring it is common to have $\delta D_p$ values lighter than equilibrium, with snow and hail almost always lighter than their equilibrium value with vapor.

If one takes a climatological approach and uses monthly averages of $T$, $\delta D_v$, and $\delta D_p$ rather than analyzing individual events, precipitation appears to be closer to equilibrium with surface vapor. As illustrated in Figure 8, monthly mean $\delta D_p$ values are higher than the calculated equilibrium value with $\delta D_v$ for all months except May, October,
November, and December. The largest deviation from equilibrium is in June, where $\delta D_p$ is 34 per mil heavier than the expected equilibrium value. This is also the month with the lowest average relative humidity (RH), suggesting that the heavy values of precipitation are due to a significant amount of evaporation during descent. Summaries of monthly $\delta D_v$, $\delta D_p$, $T$, and RH can be found in Table 2. For a more complete analysis of the relationship between $\delta D_p$ and $\delta D_v$, please see Chapter 3.

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**Table 2**

Tabulated values of monthly average values of $\delta D_v$, $\delta D_p$, $T$, and RH.

### 2.6 Causes of $\delta D_v$ variation

Variations in $\delta D_v$ are observed on timescales that range from diurnal to interannual, with the magnitude and frequency of variations dictated by atmospheric processes occurring at different timescales. We have identified several processes responsible for
causing variability in δD_V on diurnal to weekly timescales, including vertical mixing, horizontal advection, and alternating moisture sources. Synoptic-scale weather events such as cold fronts, warm fronts, midlatitude waves, easterly waves, and stagnant centers of high pressure can also dramatically affect δD_V values. Local contributions from evapotranspiration and recycled precipitation also can affect δD_V if the correct atmospheric conditions prevail. The relative importance of each of these mechanisms changes with the seasons. Since an exhaustive investigation of every variation of δD_V in our 30-month dataset is beyond the scope of this paper, we instead provide detailed analysis of excerpts from our dataset that are representative of different seasons.

Our goal in this section of the paper is to evaluate the causes behind the observed variations in δD_V at different times of the year. To do so, we compared fluctuations in δD_V with other locally measured meteorological variables such as humidity, air pressure, wind speed, etc. measured from our weather station as automatically logged every 15 minutes. In addition, we obtained GPS-derived integrated precipitable water data (stations ABQ1 and ZAB1, located in Albuquerque), also logged in 15-minute intervals, from the NOAA Earth System Research Laboratory (see Tregoning et al., 1998 for description of method). The side-by-side comparison of two humidity variables - dew point (T_d) from the sampling site and vertically integrated precipitable water (PW) over Albuquerque lets us distinguish between wetting or drying events that are affecting the entire atmosphere vs those only locally occurring at the surface. In general, these two humidity variables track each other quite well, so for the sake of convenience we focus our efforts on the relationship between δD_V and PW.
In addition to these local measurements, we also utilized plots of meteorological variables (such as geopotential height, absolute humidity, and omega) generated by the NOAA/ESRL Physical Sciences Division website (http://www.esrl.noaa.gov/psd/) using NCEP Reanalysis data (Kalnay et al., 1996). Archived infrared (IR) and water vapor images were obtained through the National Climatic Data Center (http://www.ncdc.noaa.gov/oa/satellite.html). Cloud-top temperature data for selected times were obtained from the Pueblo, CO office of the National Weather Service. Archived upper air soundings were obtained from the University of Wyoming (http://weather.uwyo.edu/upperair/sounding.html). Archived weather maps were obtained from Unisys (weather.unisys.com) and the Hydrometeorological Prediction Center (http://www.hpc.ncep.noaa.gov/dailywxmap/index.html). Langrangian trajectory analysis was performed using the online version of HYSPLIT (Hybrid Single Particle Langrangian Integrated Trajectory Model (Draxler and Hess, 1998) using the GDAS data set. Doppler radar data were obtained through NCDC and processed with the NOAA Weather and Climate Toolkit software (http://www.ncdc.noaa.gov/oa/wct/).

2.6.1 The Fall

We begin our analysis with observations made during the fall season. Late summer is a transition time between the summer monsoon circulation, with light and variable winds at the surface, to a drier regime with westerly winds that increase in speed with the progression of fall. Humid monsoonal air usually ceases in September, though its exact termination date is not easy to define nor consistent from year to year. To
illustrate the behavior of \( \delta D_v \) as we pass from late summer into fall, we show in Figure 9 a portion of our time series from September 1 to December 15 2005. On the monthly timescale, this period can be characterized as one of decreasing \( \delta D_v \) and PW with time, with notable day- to week-scale peaks and dips in \( \delta D_v \) that are usually correlated with PW.

In general, the increases and decreases of \( \delta D_v \) observed in Figure 9 occur due to variations in regional advection caused by the passing of midlatitude waves, which effectively change the source(s) of the moisture that is advected into NM. Geopotential height maps and 48-hr backward trajectories associated with periods of increased \( \delta D_v \) are shown in Figure 10, while similar maps showing examples of decreased \( \delta D_v \) are illustrated in Figure 11. Periods of elevated \( \delta D_v \) are usually associated with advection from relatively warm and humid regions, while episodes of relatively low \( \delta D_v \) occur during periods of advection from cool and dry areas; however, the source locations for these two pools of air change throughout the season. In the early fall, we see periods of elevated \( \delta D_v \) associated with advection from the southeast, while \( \delta D_v \) decreases are typically due to advection from the southwest. As the year progresses, advection from the east becomes less frequent as NM becomes increasingly under the influence of the Westerlies. Periods of elevated \( \delta D_v \) become associated instead with advection from the south/southwest, while decreases in \( \delta D_v \) become associated with that from the west/northwest. In late fall, the source for isotopically heavy moisture shifts to the west, while that for isotopically light moisture to a more northerly source. Examples of these scenarios are given below.
The time series in Figure 9 begins with a pulse of monsoonal moisture arriving in NM on September 1 and lasting until ~September 9 2005. Values of $\delta D_v$ are relatively high during this period, similar to those observed during July and August (see monsoon season section below). The occurrence of a high pressure center over the southern plain states is responsible for anticyclonic circulation that transports moisture from the Gulf of Mexico into the American Southwest. The prevailing lower atmospheric conditions for periods A-C are shown in Figure 10, panel A-C (hereafter referred to as Figure 10$_{AC}$). Figure 10$_{AC}$ consists of a 222-hr composite map of 700mb geopotential height (hereafter such maps are abbreviated as [z700]$_{222}$) with reverse trajectories of 500m 1500m, and 3000m above ground level (AGL). This circulation persists throughout times A, B, and C even though the behavior of $\delta D_v$ and PW is not the same in all three periods. Elevated $\delta D_v$ occurs at times A and C as the influx of moisture from the Gulf of Mexico increases both PW and $\delta D_v$. This decrease in $\delta D_v$ at time B is unique to other decreases in $\delta D_v$ observed in Figure 9 in that it is not associated with advection from a cool and dry airmass. Instead, the sharp decrease in $\delta D_v$ at B is due to the 'amount effect' as described in more detail in the monsoon section (see 'Type IV' activity in monsoon season below).

After time C, the aforementioned high pressure system moves eastward toward the southeastern US as a mid-latitude wave approaches the west coast. The wave creates a cutoff low (COL) that stalls off the coast for several days before moving inland. As the wave moves over the continent, it alters the general circulation pattern over the American Southwest. Advection into New Mexico shifts from southeasterly flow (at
time C) to southwesterly flow as the east side of the wave advances toward NM (Figure 11). Between times C and D, both PW and $\delta D_V$ decrease until the trough axis axes moves over NM, causing a minimum in PW and $\delta D_V$ at time D with subsiding air aloft. Once this wave continues eastward after time D, high pressure rapidly builds up again over the southern plains states. This causes the advection pattern to return to a southeasterly flow from the Gulf of Mexico (Figure 10E), similar to that of times A-C. This circulation causes both PW and $\delta D_V$ to increase until time E passes, when the high then weakens and a second midlatitude wave causes another COL to approach the west coast. With the high to the east and the COL to the west (Figure 11F), NM is under southwesterly flow, causing the dip in $\delta D_V$ and PW at point F.

For much of the fall, the theme is similar and repetitive: positive and negative excursions in PW and $\delta D_V$ result from a reoccurring center of high pressure to the east/southeast of NM that is periodically interrupted by midlatitude waves approaching from the west. At times A, C, E, and G, elevated values of PW and $\delta D_V$ consistently occur when anticyclonic advection around the high brings Gulf of MX moisture into NM from the southeast as a midlatitude wave approaches the west coast. At times I, J, L, N, and S, peaks in $\delta D_V$ and PW are due to advection from the southwest, as triggered by the approaching midlatitude waves. Although advection from the southwest is noted for low values of $\delta D_V$ and PW in the early fall, by later in the season this same moisture source provides air with relatively high $\delta D_V$ and PW compared to the colder and drier westerly/northwesterly flow more common later in the year. The 48-hr backward trajectories in Figures 10i, 10j, 10l, 10n, and 10s, imply a moisture source southwest of
NM, possibly in the Gulf of California or eastern Pacific. However, the contemporaneous high pressure centered to the east/southeast of NM in all of these cases (with the exception of time S, where the high is located directly to the south of NM) superimposes an anticyclonic rotation to the circulation pattern. The effect of this can be observed in most of the 48-hr backward trajectories, especially at the 500m AGL level (dotted lines in Figure 9). The anticyclonic rotation shown in the backward trajectories suggests that periods of elevated PW and δD_v may be due to the advection of some component of moisture derived from the Gulf of Mexico.

A period of elevated δD_v and PW that does not fit this pattern is time Q, where NM is in near-zonal flow conditions with a complete absence of either a nearby midlatitude wave or center of high pressure. In this case, the elevated δD_v and PW values are due to an incoming plume of tropical moisture originating from the ITCZ at approximately 150°W, which stretches across the western Pacific Ocean and hits the west coast of North America on 12/1/05. As observed in the satellite IR image in Figure 10Q, this moisture is directly over NM ~48 hours later, coinciding with the peak in δD_v and PW.

The rapid decreases in δD_v and PW within the fall time series (Figure 9), which become increasingly pronounced as the year progresses, are consistently associated with the passing of midlatitude waves. These waves may manifest themselves as troughs of low pressure (see Figures 10G, 10J, 10L) or as COLs that can stall off of the west coast for several days (10i, 10N). In either case, the nature of the waves changes with the progression of fall, with waves moving farther south, having colder cores, and
exhibiting stronger pressure gradients as the polar front moves gradually southward with the onset of winter. This can be observed in successive panels in Figure 11. Consequently, the minimums in $\delta D_V$ and PW values observed with each passing wave reflect these slowly changing conditions.

For example, the wave presented in Figure 11_D is relatively small, with warm central temperatures and a modest pressure gradient. During this event, $\delta D_V$ decreases to -164‰, PW decreases to 0.49 cm, and Td drops to -8.3°C during their minimum at time D. By comparison with the wave in Figure 11_O, the wave at time O is clearly stronger with colder central temperatures and a higher pressure gradient. During the event at time O, $\delta D_V$ drops to -225‰, PW to 0.15 cm, and Td falls to -18.9°C. The lower numbers for these three variables at time O vs time D probably reflect the colder and drier air in wave O. The core 700mb air temperature for each passing wave (shown in Figure 11 as shaded backgrounds) is roughly correlated with the relative depth of the $\delta D_V$ and PW decreases in Figure 9. Additionally, the stronger midlatitude waves common later in the year are responsible for more northerly flow into New Mexico (observable in the reverse trajectories in Figure 11), with stronger subsidence on the west side of the wave. Both of these characteristics contribute to stronger decreases in $\delta D_V$ and PW as the year progresses due to the cold, dry, and subsiding air with longer rainout history than that from a warmer and more humid source.

In summary, throughout the fall we observe episodes of elevated $\delta D_V$ and PW being caused by advection of air from regions relatively warm and humid compared to those
expected from the prevailing wind direction at the time. Conversely, episodes of depressed $\delta D_V$ and PW result from the advection of abnormally cold and dry airmasses. The moisture sources responsible for both the increases and decreases in $\delta D_V$ change as the year progresses. In the late summer and early fall, moisture from the Gulf of Mexico is relatively humid and enriched in isotopically heavy water vapor compared to the water vapor otherwise sourced by westerly winds from the Pacific. However, as the season progresses into late fall and winter, the lower tropospheric conditions shut off this potential moisture source. The polar jet moves farther south, bringing with it colder and drier air from the north/northwest. During this time, the Pacific-derived moisture is now relatively humid with higher $\delta D_V$ values compared to the drier and colder polar air. The passing of midlatitude waves, which become stronger, colder, and dip further to the south as the season progresses, are largely responsible for major shifts in advection that change the effective source of moisture for NM.

2.6.2 The Winter

The behavior of $\delta D_V$ during the winter is, for the most part, a continuation of the same activity observed in the late fall. The second half of January 2006 is presented in Figure 12 as an example of wintertime behavior. The passing of mid-latitude waves causes the circulation to alternate between uplift and advection of air from a relatively warm and humid source (typically the Eastern Pacific) to that of a relatively cold and dry one (typically the subpolar region) with accompanying subsidence. These passing waves along with their succeeding centers of high pressure give rise to highly variable $\delta D_V$ as
illustrated in Figure 12. Periods of anomalously high and low δDν values are explored in more detail below.

During this time of year, wave axes exhibit a positive tilt (to the northeast), which causes southwesterly flow on the upwind side of the wave as shown in Figures 13b and 13d. The influx of this moisture from the eastern Pacific provides relatively high δDν and PW values compared to that from the subpolar and continental airmasses common for this time of year. Consequently, the δDν and PW peaks at times B and D result from the influx of eastern Pacific moisture while NM is upwind of approaching midlatitude waves.

The other two periods of elevated δDν values within Figure 12 - times A and G - are the result of a circulation around a high pressure ridge in the region. Time A, a period of modest δDν values, is contemporaneous with a building ridge of high pressure behind a cold front that passed through NM a day earlier. Although reverse trajectory analysis does not show anything particularly meaningful (due to the low wind speeds), a matrix of forward trajectories (Figure 13a) shows subtle anticyclonic rotation over central Mexico. This suggests that at least a small amount of Gulf of MX moisture may be entering southern NM, giving rise to the increased δDν and PW.

A more obvious scenario involving advection from the Gulf of MX occurs at time G, where a high pressure centered to the southeast of NM exists concurrently with the arrival of a trough of low pressure centered over Baja California (Figure 13c). This is the same configuration of the lower atmosphere that we showed for periods of elevated δDν and PW in the fall analysis (above). The results here are similar, with a
southeasterly flow bringing Gulf of MX moisture into NM, increasing $\delta D_v$ and PW.

Additionally, the sampling area received 2mm of precipitation, which further increases Td and $\delta D_v$.

Decreases in $\delta D_v$ in Figure 12 are associated with the western side of midlatitude troughs as they pass over NM, causing advection from the north/northwest and subsidence of dry air aloft, leading to temporary decreases in $\delta D_v$ and PW as shown at times C and E. The northeast-trending wave axes cause advection that is more northerly in origin than what is observed during the fall seasons (for example, compare the orientation of the reverse trajectories in Figure 13c with any of those in Figure 11). This fact, along with the fact that midlatitude waves during the winter have the coldest cores and are at the lowest latitudes among waves throughout the year, contributes to relatively low $\delta D_v$ values (-255‰ at point C, -245‰ at point E). These effects can be noticed in the 30-month dataset of Figure 2, where the lowest $\delta D_v$ and PW values tend to occur during the winter months.

The low PW and $\delta D_v$ values at time F is a bit unusual in that NM is saddled between a strong midlatitude wave approaching New England and a COL centered off of the coast of Baja. Although there is some ambiguity in the source for the dry air at time E, trajectory analysis suggests that it is derived from the descending air westward of the trough. It is possible that the $\delta D_v$ minimum at time E may also be partly caused by the development of the cut-off low itself. COLs contain air that originates at high latitudes and retains its high potential vorticity as it is displaced to lower latitudes (Palmen and
Newton, 1969). The troposphere within the COL is destabilized, which can lead to deep convection (Hoskins et al., 1985). COLs have been shown to be effective at bringing dry upper tropospheric (or even stratospheric) air down to the surface, a process documented by Bamber et al. (1984), World Meteorological Organization (1986), Vaughan and Price (1989), Ebel et al. (1991), and Price and Vaughan (1993). Three proposed mechanisms through which this might happen include convection erosion, turbulent mixing near the jet stream, and tropopause folding (Prince and Vaughan, 1993). In the case of time E, the COL centered off the coast of southern California/northern Baja stalled for over 48 hours before moving inland. While trajectory analysis implies that advection of polar air is occurring prior to the depletion at time E, we cannot rule out the addition of D-depleted moisture from the approaching COL itself.

A more direct example of COL-caused D depletion occurs almost exactly a year later on January 21, 2007 (Figure 14). In this event, two COLs are formed and pass over NM within a 72 hour period, leading to two subsequent minima of $\delta D_V$ values. The time series in Figure 14 starts with the passing of a midlatitude wave, shown over the Great Basin in Figure 14A. The elevated $\delta D_V$ and PW values at time A are due to southerly advection ahead of the midlatitude wave. $\delta D_V$ and PW values drop off due to northerly advection as the wave passes to the east of NM (Figure 14b). Presumably, $\delta D_V$ reaches a minimum between times B and C, but we do not have enough $\delta D_V$ data from that period to detect it.
As the wave in Figure 14b moves eastward, a COL detaches from the wave and settles over northern Baja (Figure 14c). At the same time, a plume of subtropical moisture originating from the ITCZ moves northeast over MX and into NM. The position of the COL and the adjacent cloud bank can be seen in the IR satellite image of 1-18-07 9Z (Figure 14). A dry air intrusion from the COL modifies the subtropical moisture plume, a process that can be seen in the IR image of 1-19-07 21Z (Figure 14). As the COL approaches NM, $\delta D_v$ values plummet while both humidity variables increase at time D. Although the backward trajectories in Figure 14d are difficult to interpret, it is very likely that moisture at time D is derived from the COL, which is nearly overhead at this time. Radiosonde soundings from Albuquerque confirm that the subtropical cloud bank was of high altitude (8000m ASL or higher). Thus it is likely that moisture from the high altitude clouds, which should be strongly depleted in D, was brought down to the surface by the COL. This resulted in a strong minimum in $\delta D_v$ values ($\delta D_v = -255\%$) during a period of otherwise modest humidity.

Although we cannot be certain that tropospheric folding was occurring during time F (Figure 14), there is a limited amount of evidence that suggests such an event was probably taking place. High tropopause pressures (greater than 400hpa) are generally associated with tropospheric folding (Phil Schumacher, personal communication). In maps of tropospheric height (Figure 15), values very close to 400hpa are observed in the center of the COL. Upper air soundings from Flagstaff AZ (Figure 15) also show a tropopause near the 400 hpa level.
As the COL in Figure 14e1 moves to the northeast, the advection returns to
northwesterly flow and $\delta D_v$ values rebound a bit (time E). The 700mb air temperature
map (shaded background, Figure 14e1) shows a pool of particularly cold air over UT/NV.
This is the precursor to a second COL, which starts to form over AZ only 6 hours later
(Figure 14e2). When this second COL approaches NM (Figure 14f), $\delta D_v$ plummets once
again, though similar decreases are not observed in either of the humidity variables. In
fact, the $\delta D_v$ minimum at time F represents the lowest $\delta D_v$ value recorded in the 30-
month study. The isotopically light moisture at time F may be related to the core
temperature of the COL, which is colder than that of the previous COL in Figure 14c.
The difference can be seen in a comparison of the 700mb core air temperatures
between that of Figure 14c and 14f. The latter COL stalls for several days over
northwest MX, and is still present at time G (Figure 14g), when a building ridge of high
pressure to the north of the COL eventually causes northerly flow into NM, leading to a
rise in $\delta D_v$ and PW.

As we observed in the fall, the passing midlatitude wave is the first-order influence
on controlling $\delta D_v$ and PW. The northeast-leaning wave axes tend to promote
advection from the southwest as the wave approaches NM, and north/northwest
advection as the wave continues to the east. Such waves have colder cores, higher
pressure gradients, and lower latitudes than similar waves in the fall, leading to more
pronounced decreases in $\delta D_v$ and PW. In addition, the role of COLs in contributing to
severe $\delta D_v$ depletions becomes important in the winter, mostly likely because of their
ability to transport moisture vertically down from high altitudes.
2.6.3 The Spring

2.6.3.1 Early Spring

As previously illustrated in Figure 4, among all seasons the highest daily variance in $\delta D_V$ is observed during the spring. An example of this variability can be observed in a portion of the timeseries from early March 2006 (Figure 16). Within a single week, $\delta D_V$ values exhibit two excursions of 100$\%$ or more, plus multiple swings of smaller (but still substantial) magnitudes. We attribute this high variability to a combination of low humidity, atmospheric synoptic-scale dynamics common in the spring, and the occurrence of subcloud evaporation. The low humidity of the lower troposphere allows for the possibility of large fluctuations in $\delta D_V$, as nearly any contribution of water vapor to the atmosphere has the potential to strongly control the overall $\delta D_V$ value from simple mass balance considerations.

In Figure 17 we illustrate how rapid variations in $\delta D_V$ are possible in the spring from day-scale changes in the lower troposphere. At time A, NM is situated between a high pressure centered over the Gulf of Mexico and midlatitude cyclone approaching the Pacific Northwest (Figure 17A1). This causes advection from the southwest, which transports eastern Pacific/Gulf of California moisture into NM, elevating both $\delta D_V$ and PW. At this time there may also be a component of advection from the Gulf of Mexico, as the lowest-level (500m AGL) backward trajectory shows an eastern origin with anticyclonic rotation (Figure 17A1). At the same time, subsidence is occurring southeast of the center of the low due to the negative relative vorticity advection from a
decreasing pressure gradient south of the jet axis. This subsidence can be observed on a map of omega, where positive values of dP/dt exist over the eastern Pacific and most of California and Nevada (Figure 17A2). The large pool of dry air from this subsidence is observable in the 700mb specific humidity map (shaded background) of Figure 17A1, where it is approaching (but not yet over) New Mexico.

Approximately 24 hours later (time B), the high pressure ridge previously over the Gulf of Mexico builds westward over NM and northern MX, shutting off any possible flow from the Gulf of Mexico. Advection is now entirely from the southwest with subsidence aloft. The dry air previously over California and the eastern Pacific (from Figure 17A1) is advected over NM (Figure 17B), causing δDv and PW to subsequently plummet. Atmospheric soundings from El Paso, Flagstaff, Phoenix, and Tucson (not shown) confirm a widespread deep layer of very dry air in the lower troposphere. This interval of extremely low δDv and PW is interrupted by a small pulse of moisture that dramatically increases δDv (time C). Although the trajectories have not changed appreciably (see Figure 17C), the large rise in δDv would be consistent to the complete evaporation of extremely small amounts of precipitation (virga). Although there is no record of precipitation hitting the ground at this time, Doppler RADAR echoes over the general Albuquerque area coincide with the timing of the peak in δDv values as shown in Figure 18. The contemporaneous upper air sounding from the Albuquerque airport (Figure 18, time C) shows extremely dry atmosphere below cloudbase, conditions favorable to virga formation. The evaporation of even a trivial amount of rain or snow
into the dry lower atmosphere would dramatically increase $\delta D_V$ values due to the fractionated (D-enriched) nature of precipitation.

During the following day (time D), advection maintains a southwesterly flow as the ridge of high pressure moves to the east and an incoming trough of low pressure approaches the west coast. A band of subtropical moisture, which can be seen as a plume of high specific humidity in Figure 17_D, is responsible for the rise in PW on the morning of 3/7/06. A cold front then passes through ~24 hrs later as the trough propagates across NM, initiating convective cells common with unstable air. Although no precipitation was received at the collection location, Doppler Radar echoes again suggest light scattered precipitation, with virga being a likely possibility in the dry lower atmosphere (Figure 18, time E). The large but short-lived peaks in $\delta D_V$ and PW at time E are consistent with such an event, where the spike in both PW and $\delta D_V$ occur from the complete evaporation of a small amount of precipitation.

As the trough of low pressure passes to the east of NM, the advection shifts to a northerly flow. The dry polar air moves in behind the cold front, causing a significant decrease in $\delta D_V$ and PW at time F (Figure 17_F). These low values are rather short-lived, as a second trough approaching the west coast causes advection to shift back to a southwesterly flow (Figure 17_G). This second trough moves relatively slowly and is responsible for consistent advection from the southwest for the remaining ~72 hours of the time series in Figure 16. Despite the nearly unchanging atmospheric conditions, there is considerable variability in $\delta D_V$ and PW during this period. This can be attributed
to intermittent precipitation and virga. The two $\delta D_V$ peaks at time G coincide with contemporaneous Doppler Radar echoes but are not associated with any recorded precipitation on the ground - a scenario analogous to times C and E (Figure 18). Finally, snow starts to fall at time H with over 1 cm of accumulation by the morning of 3/12/06. This event elevates $\delta D_V$, and appears to buffer the $\delta D_V$ value for a period after the moist air moves out of the area (note the $\delta D_V$, $T_d$, and PW activity in the last 24 hrs of Figure 16).

2.6.3.2 Late Spring

Prior to the onset of the summer monsoonal flow, the atmosphere over NM is quite dry though temperatures are high. As with the early spring, high variation in $\delta D_V$ is observed, most likely due to the exceptionally low humidity. Late spring retains characteristics of the cold season, as midlatitude waves continue to influence the direction of advection and hence the moisture sources influencing NM. Additionally, we witness harbingers of summer circulation, including easterly waves that begin to propagate into the Gulf of Mexico and close to the US/MX border.

A time series of $\delta D_V$ and PW representing the late spring is shown in Figure 19, which starts on 6/10/05 and extends to the end of the month. Two midlatitude waves pass in the first few days of this sequence, giving rise to the variations in $\delta D_V$ and PW at times A, B, and C. However, the circulation over NM is complicated by the simultaneous arrival of an easterly wave in the Gulf of Mexico. As the first midlatitude wave approaches NM, advection is from the west, causing low values of $\delta D_V$ and PW (Figure 20A). However, as
the second midlatitude wave approaches at time B, an easterly wave simultaneously moves ashore over the southern gulf states. While the midlatitude wave’s axis is located over NM, high pressure associated with the easterly wave train is briefly over eastern Texas (Figure 20b). This superimposes a anticyclonic circulation on the backward trajectories, which likely brings a pulse of Gulf of MX moisture into NM. Unfortunately, we did not have the sampling resolution at that time to capture the $\delta D_V$ values for this pulse of moisture, but most likely there would have been a peak in $\delta D_V$ values at time B, contemporaneous with observed peak in moisture. As the midlatitude passes to the east, advection from the north (Figure 20c) brings dry and D-depleted air into NM, resulting in the low values of $\delta D_V$ and PW at time C in Figure 19.

With the passage of the midlatitude wave after time C, a high pressure begins to build over Texas. Anticyclonic advection around the high transports moisture from the Gulf of Mexico into NM (Figure 20d). This causes $\delta D_V$ and PW to increase over a period of several days, culminating in the peaks of these values at time D before the high shifts further west. This forces advection back to a source in the Pacific, causing $\delta D_V$ and PW values to decrease (Figure 20e). After a few days, the high shifts back toward the east, and advection from the Gulf of Mexico resumes (Figure 20f), increasing $\delta D_V$ and PW values once again.

Following time F is an extended period of unusually high $\delta D_V$ and PW values. For the most part, this is caused by the continued advection from the Gulf of Mexico due to the high pressure east of NM. However, this time is remarkable in that the highest $\delta D_V$
values found in our 30-month study occur at this time. More specifically, at Time H we record a $\delta D_V$ value of -55‰, which coincides with a local maximum of PW and $T_d$. There are other occasions where PW and $T_d$ exceed the values at Time H, but nowhere else in our dataset do we see $\delta D_V$ values this high. In addition to these surface observations, air samples taken from an airplane at 6/26/05 12Z reveal that this D-enriched moisture extends over 1km AGL (Chapter 1; Strong et al., 2007).

These anomalously high $\delta D_V$ values occur as (a) a high pressure over the south/southeastern US prevails for several days, suppressing convection over a wide region including Texas and NM, and (b) a new easterly wave train moves into the Gulf of Mexico. At time G, subsidence is occurring over much of the southeastern US and the northern Gulf of Mexico from the combined effects of the high pressure centered over Arkansas and the western extension of the Bermuda High over Florida. This subsidence can be seen as positive values of Omega (shaded background) in Figure 20G1. An easterly wave can be seen forming over the Caribbean at this time, visible in the 700mb geopotential height map in Figure 20G1. The regional circulation, illustrated by a matrix of 24-hr forward trajectories in Figure 20G2, shows easterly flow across the Gulf of Mexico and into Texas/eastern NM. By time H, the subsidence over Texas has strengthened due to the ongoing ridge of high pressure, while subsidence in the northeastern Gulf of Mexico is now enhanced by the easterly wave (Figure 20H1). As shown in Figure 20H2, the regional circulation is still similar to that of time G in that easterly flow prevails in the region. Consequently, for several days the circulation regime forces air to be transported westward across the northern Gulf of Mexico and
into Texas/NM. During this time, ongoing subsidence along the path of transport severely limits the mixing between the boundary layer and the free atmosphere. This subsidence also prevents fractionation of the water vapor due to rainout by suppressing convective activity. It is likely that the moisture in the lower ~1km measured in NM at time H represents water vapor from the Gulf of Mexico that has undergone very little fractionation or mixing, hence the elevated $\delta D_V$ values. Vapor sampling at Corpus Christi, TX, during May of 2007 yielded $\delta D_V$ values of -71‰, which while not as D-enriched as our heaviest sample at time H ($\delta D_V = -55‰$), is similar to the values collected during this anomalous period of high $\delta D_V$ values.

After time H, the variations in $\delta D_V$ and PW values are due to the drifting high pressure system over the southeastern US. At time I, the high pressure migrates westward until the western extension of the high forces advection from the southwest (Figure 20i), thereby lowering $\delta D_V$ and PW values. A midlatitude wave moving ashore at time J causes the ridge to move further east, triggering southeasterly flow from the Gulf of Mexico (Figure 20j). As the midlatitude wave moves to the northeast, the high pressure rebuilds and migrates back to the west, returning southwesterly flow to NM (Figure 20k).

In summary, the spring is a time of great variability in $\delta D_V$ (figure 7). The low humidity allows small contributions of water vapor to make disproportionate change in $\delta D_V$ through simple mass balance considerations. In addition, the low relative humidity of the lower atmosphere is conducive to the formation of virga during convective
activity. This allows fractionated liquid water to be returned to the boundary layer, giving rise to large positive excursions in δD_v. Midlatitude waves are still common during this time of year as well as a recurring area of high pressure to the southeast (usually over the Gulf of MX). In the late spring, atmospheric conditions are slowly changing to those akin to the summer monsoon, where easterly waves begin to advect moisture in from the Gulf of MX. Anomalously heavy δD_v values during the spring appear to be the result of direct advection of Gulf of MX moisture into NM during regional subsidence.

2.6.1 The Summer (monsoon season)

As described in previous sections of this paper, the relationship between δD_v and PW is usually correlative, with advective direction (and hence ultimately the moisture source) being the principal control on δD_v and PW. However, the winds during NM’s monsoon season are light and variable, with no dominant advective direction for the majority of the summer. Reverse trajectory analysis tools (i.e., HYSPLIT) are not particularly useful in determining the causes of δD_v variations in the summer, as there is often very little or no wind and consequently no distinctive wind direction(s) that would indicate major changes in moisture source location. Midlatitude waves, a major mechanism for controlling advection other times of the year, are not prominent during the summer as they typically pass to the north of NM this time of year.

Based on data collected through three consecutive monsoon seasons (Figure 21), we have identified four categories of δD_v-PW relationships that occur over time spans of
several days: increasing $\delta D_V$ with increasing PW ["Type I"], decreasing $\delta D_V$ with decreasing PW ["Type II"], increasing $\delta D_V$ with decreasing PW ["Type III"], and regions of symmetrically anticorrelated $\delta D_V$ and PW ["Type IV"]. Examples of these four types of activity are shown in Figure 21 and are explained in future sections. In addition to these multi-day trends, there are short-term (~24-48 hour) periods of anomalous $\delta D_V$ activity. Below we present examples of each type of $\delta D_V$-PW relationship. Here we introduce the use of composite maps that show the atmospheric conditions averaged over several days in an effort to understand the multiday trends in $\delta D_V$ and PW. We often superimpose trajectory analysis over these composite maps to demonstrate an example of the circulation pattern at a particular time, though the two products are not representing the same exact time span.

2.6.1.1 [Type I] - Increasing $\delta D_V$, Increasing PW

A regularly occurring feature of the North American Monsoon is a center of high pressure that separates the westerlies (to the north) from the easterlies (to the south). This so-called "Monsoon High" typically builds over North America during the summer months, usually staying in a particular region for days at a time. As this high pressure system slowly shifts its position, the resulting changes in circulation can dramatically alter the behavior of $\delta D_V$ and PW observed in NM.

Type I activity denotes conditions of increasing values of absolute humidity, represented here as PW, and $\delta D_V$. Most commonly this is due to advection of Gulf of MX moisture directly into NM along a relatively short and direct route. One mechanism
responsible for this is the occurrence of the Monsoon High to the northeast of NM; anticyclonic circulation around the high will pump moist air from the Gulf of MX into NM, resulting in increased local PW and $\delta D_V$ values. This scenario is very similar to that of elevated $\delta D_V$ and PW periods explored in other seasons. Segment $I_8$ (Figure 21) is an example of such activity; the $[z700]_{90}$ map shown in Figure 22$_8$ illustrates the presence of this high centered over northeast OK. A matrix of 24-hr forward trajectories (beginning midway through this composite time period and superimposed on the $[z700]_{90}$ map as dashed lines) shows advection from the Gulf of MX directly into NM, resulting in the pronounced increase in PW and $\delta D_V$ values. Over time, the high's center moves toward New England and eventually east over the Atlantic sea, but the western extension of the high remains over the central southern states, promoting this circulation pattern for ~7 consecutive days. As a result, PW and $\delta D_V$ values increase for about a week, though the increase in PW is more dramatic than that of $\delta D_V$.

A second mechanism to directly import Gulf of MX moisture into NM is from the cyclonic circulation around a center of low pressure situated to the southeast of NM. This may happen if an easterly wave stalls over the northwestern Gulf Coast, as is the case in segment $I_c$ (Figure 21). The $[z700]_{90}$ map (Figure 22$_c$) shows the low centered over the TX/MX border, with an accompanying high situated over southern Florida. The resulting circulation pattern from this stalled easterly wave causes advection from the Gulf of MX, around the northern nose of the low pressure system, and into New Mexico. This creates a period of Type I activity that lasts ~6 consecutive days.
During the summer months, easterly waves regularly propagate across the Gulf of Mexico and into mainland MX. Occasionally the position of the Monsoon High over the continental US will be juxtaposed against components of an easterly wave, the components of which may work together to promote advection of subtropical moisture into New Mexico. During segment I_A (Figure 21), the Monsoon High is in a position similar to that of I_B, but has been elongated in an E-W direction as shown on \([z700]\) map in Figure 22_A. A contemporaneous easterly wave train sets up centers of low pressure over northern Mexico and the southeastern US. Cyclonic advection around the low with anticyclonic advection around the Monsoon High results in the advection of moist Gulf of Mexico air into NM. As with the previous two examples, this third example of Type I activity lasted ~6 days.

2.6.1.2 [Type II] - Decreasing \(\delta D_V\), Decreasing PW

Although the Monsoon High normally resides over the southeastern part of the US, it does occasionally migrate over the southwestern states. When this happens, southern source(s) of moisture are blocked while advection is from the north/northwest with subsidence aloft. This serves to dry NM's atmosphere while transporting relatively dry and D-depleted moisture from an area northwest of Albuquerque - quite possibly the Pacific Northwest. One example of this is illustrated with segment II_A (Figure 21). In this case, the \([z700]\) map (Figure 23_A) shows a center of high pressure lingering over the CA/MX border region while an intense center of low pressure (Hurricane Katrina) moves ashore in the southern Gulf States. Trajectories show advection from the north due to
NM's position east of the high's center, creating a ~6-day period of increasing PW and \( \delta D_V \) values.

In the second example of Type II activity, (segment II\textsubscript{B}, Figure 21), a persistent high pressure system wanders around the western portion of the US for most of July 2006, its location and strength being occasionally interrupted by easterly waves. By mid July, it settles over the AZ/NM/MX border region for several days. In the \([z700]_{90}\) map (Figure 23\textsubscript{B}), it can be seen that this center of high pressure is actually part of a larger ridge that extends out to the Bermuda High. In this case, the high remains centered over the southwestern states for ~6 days before being disturbed by an incoming easterly wave. During this time trajectories caused by the anticyclonic circulation around the high's center show advection is most likely from the eastern Pacific, which lowers PW and \( \delta D_V \) values.

2.6.1.3 [Type III] - Increasing \( \delta D_V \), Decreasing PW

The correlative \( \delta D_V \)-PW relationships described above for Type I and Type II periods are also observed during other times of the year, though the mechanism for producing such relationships during other seasons is usually the change in advection from passing midlatitude waves instead of stagnant centers of anomalous air pressure. By contrast, the anticorrelative behavior observed during the Type III and IV periods are unique to the summer months. Periods of increasing \( \delta D_V \) values with decreasing PW (Type III) often occur when the regional circulation pattern brings subtropical moisture into NM during periods of concurrent regional subsidence. The subsidence serves to (a) slowly
decrease absolute humidity as dry air aloft mixes downward, (b) suppress convective activity, preventing fractionation by precipitation, and (c) trap water vapor contributions from evapotranspiration (which tend to have relatively high $\delta D_V$ values) close to the surface. The result is a multiday drying of the atmosphere, while $\delta D_V$ values continue to increase.

In an earlier section, we showed that a high located to the northeast of NM can serve as a means to transport moisture directly into NM from the Gulf of MX, thereby producing Type I $\delta D_V$-PW behavior. In this section, we show that a high centered in roughly the same location can produce different results because of subtle differences in the position or subsidence strength. In our first example if Type III activity, consider the high pressure centered over the northern coast of the Gulf of MX in the $[z700]_{175}$ map in Figure 24C (segment IIIA). This high is positioned to the east of NM during segment IIIA (Figure 24A), which is slightly south of the high's position during segment IA (Figure 22A). The lower latitude during segment IIIA causes the anticyclonic circulation to advect moisture from the Gulf of MX across mainland MX into NM. This produces a longer trajectory path than that during segment IA. As time progresses during segment IIIA, the western edge of the high gradually pushes further westward, lengthening the trajectory path required to arrive in NM. This fact combined with the increasing subsidence from the approaching high causes the humidity to decrease over time during segment IIIA. Had this high been positioned slightly further north, most likely the drying effects in NM would have been greatly diminished or nonexistent.
A second example of Type III activity occurs when the Monsoon High is actually positioned in the same location as a previous Type I example, but with different subsidence characteristics. Segment III\textsubscript{C} (Figure 21) occurs as the high is positioned to the northeast of New Mexico as shown in the [z700]\textsubscript{126} map of Figure 24\textsubscript{C}. This is very similar in appearance to that shown in the [z700]\textsubscript{90} map in Figure 22\textsubscript{B} for Segment I\textsubscript{B}. As in the example of Segment I\textsubscript{B}, anticyclonic circulation around the high brings Gulf of MX moisture into NM. However, unlike Segment I\textsubscript{B}, the region of moisture transport is also under subsidence during the period of Segment III\textsubscript{B}. This can be observed in a side-by-side comparison of the two segments in question. Figure 25 shows the [z700]\textsubscript{126} maps of Segments III\textsubscript{C} and I\textsubscript{B} in addition to 700mb composite maps of omega over the same time periods. While the high pressure in both cases is centered over northeast OK, the difference between the two scenarios is that the composite map of III\textsubscript{C} shows an easterly wave approaching MX, while the segment I\textsubscript{B} map shows virtually no easterly wave component in that area. This creates a pressure gradient during III\textsubscript{C} that increases away from the center of the high toward the southwest, which in turn causes increasing positive vorticity southwest of the high’s center. On the omega maps (shaded backgrounds in Figure 25), the difference in degree of subsidence between these two time periods can be observed: during segment III\textsubscript{C}, subsidence over the region of vapor transport is considerably greater than that of I\textsubscript{B}. IR satellite images during the period of III\textsubscript{C} (not shown) confirm that convection over Texas was very subdued, with very little precipitation recorded. Therefore, we conclude that vapor was transported across TX and into NM largely unfractionated.
Our third example for Type III activity occurs when the Monsoon High is positioned directly over the 4-corners area. The high pressure system dominant throughout the IIIb period (Figure 24b) is reminiscent of those during segments IIa and IIb (Figure 23). However, there are two important differences between the lower atmospheric conditions of the IIIb segment and the Type II segments. First, the high during IIIb is smaller in areal extent, which causes the circulation to be more localized than around the larger high pressure centers of the Type II segments. Second, period IIIc features an easterly wave that moves ashore in MX, causing a center of low pressure to be stalled on the northern MX / southern TX for several days. Moisture is advected around the northern nose of the Mexican low and into the anticyclonic circulation stream over the 4-corners region. As with the previous two examples, the subsidence from the high serves to lower the humidity while preserving the $\delta D_V$ values of the moisture as it arrives from the Gulf of MX.

2.6.1.4 Type IV - Symmetrically anticorrelated $\delta D_V$ and PW

One unique feature of the summer time series (Figure 21) are the periods of roughly symmetrical anticorrelated PW and $\delta D_V$ activity. Although they occur every summer, they are particularly common during the 2006 monsoon season, one of the wettest monsoons on record. Type IV periods tend to occur during times when the sampling area is downwind of a region that has recently received a substantial amount of precipitation, and often follow periods of Type I activity. For example, segment IVa (Figure 21) occurs directly after segment Ii. In the case of segment IVa, the high
previously centered over northeast OK (from Figure 22_b) has moved toward the northeast, but the southwestern nose of the ridge continues to cause southeasterly flow into NM, with the additional feature of an easterly wave approaching MX (Figure 26_a). This extended circulation pattern (a total of ~8 days) creates a large area of high specific humidity that extends from northwest MX into nearly all of NM (Figure 26_b). This is responsible for the high PW we observe during the IV_a period (Figure 21).

The δD – PW anticorrelation of period IV_a begins at approximately 9/5/05 0z, so it is instructive to look at the history of the incoming moisture prior to this time. Figure 26_c shows a three-day cumulative modeled precipitation map from NCAR/NCEP reanalysis ending at 9/5/05 0z. Superimposed on this map are 72-hr reverse trajectories of the 500, 1500, and 3000m AGL parcels ending at 9/5/05 0z. This map shows that during the 72 hours leading up to period IV_a, areas in the advection path received tens of mm of precipitation. As this moisture moves into NM, PW increases but the water vapor becomes more depleted in D. We believe this is due to the 'amount effect' (Dansgaard, 1964), where deep convection removes isotopically-enriched water vapor from the air. This is further confirmed by very low cloud top temperature data available at the time. Figure 26_d shows a cloud top temperature map for 9-6-05 0Z, near the peak of segment IVa. Cloud top temperatures of -75°C are detected, while upper level backward trajectories (~4000m AGL) show this region to be a potential moisture source.

Segments IV_b and IV_c share similar characteristics with that of IV_a, with precipitation accumulations occurring directly in the path of advection just prior to the observed
anticorrelation event. We do not have cloud top temperature data for this period, but have reconstructed the conditions leading up to these events nonetheless. In both of these cases, northern MX is subject to simultaneous moisture transport from both the east and west directions, resulting in high humidity and rainfall near the MX/US border.

In the three days leading up to segment IV_B, a high pressure centered over Florida brought Gulf of MX moisture into NM/MX from the southeast while a strong center of low pressure off the west coast of MX (Tropical Storm Emilia) advected east Pacific / Gulf of CA moisture into NM/MX from the southwest (Figure 26_E, 26_G). This resulted in areas of high humidity and (modeled) precipitation over northern MX and east TX. As the anticorrelated period of IV_B begins, forward trajectories show southerly flow into NM directly from these regions of high humidity and precipitation.

In a similar manner, the three days preceding period IV_C were also marked by a high over the Gulf MX that pumped moisture into MX and TX, though the ridge was not nearly as strong as in the previous example. This circulation was also augmented by an easterly wave over MX (Figure 26_H). Additionally, anticyclonic circulation around a small center of high pressure in northwest MX drew in moisture westward from the Gulf of CA. Collectively this resulted in an area of high humidity similar to that in the previous example of IV_B, with a large center of (modeled) precipitation in northern MX (Figure 26_F). Although the 24-hr forward trajectories in Figure 26_F are not as straightforward as those in 26_E, they still show advection over MX and into southern NM. It is very likely that moisture moving into NM traveled through the shown area of high specific humidity and heavy precipitation, leading to the anticorrelation event of IV_C.
2.6.2 The $\delta D_V$ minimum of 7/23/07

The most dramatic example of 'amount effect' we witness in our dataset is the $\delta D_V$ minimum of 7-22-07 (Segment IVD). Although we classify this period as Type IV, it is missing the symmetric $\delta D_V$-PW anticorrelation pattern common to the other Type IV examples. This is due to a transitory ridge that briefly interrupts this $\delta D_V$-PW relationship midway through the event (at approximately 7-24-07 02). That aside, this occurrence of the amount effect is the strongest, with a $\delta D_V$ decrease of 70‰ from nearby days ($\delta D_V = -109‰$ at 7/20 drops to -179‰ on 7/23). It arguably also lasts the longest of all amount effect events - upwards of a week or so - though the exact start and end date of such events are difficult to define.

Since the minimum $\delta D_V$ value is reached on 7/23/07, we explore the conditions leading up to this event by examining maps of 700hpa geopotential height and specific humidity, 24-hr accumulated precipitation, and cloud top temperatures for ~4 days prior to 7/23. As with the previous Type IV examples, high pressure exists to the east/southeast of NM - usually centered over the Gulf of MX - which transports moisture from the Gulf of MX into eastern MX and TX. At the same time, an easterly wave over the Gulf of CA brings eastern Pacific moisture northward into western MX. Both of these circulation patterns persist for several days, increasing the absolute humidity over NM and northern MX. The effect of this can be seen in the specific humidity maps (shaded backgrounds) of Figures 27a, 27b, 27c, and 27d, where locations over NM and northern MX become more humid with time.
The (modeled) precipitation maps of Figures 27_{E}, 27_{F}, 27_{G}, and 27_{H} show persistent daily rain occurring along the MX/TX border. In addition, 24-hr forward trajectories show that advection into NM moves directly through these areas of precipitation. Cloud top temperature data confirms deep convection occurring in this area. Mesoscale convective activity occurs in roughly the same region for over four days, with cloud top temperatures reaching at least -70°C in all four days, and -75°C in three. This long-lived convective system is most likely responsible for the strong decrease in $\delta D_V$ values that we observe during period IV_D.

As part of an effort to answer questions regarding the areal extent of isotopic events, an effort was made to sample water vapor across the southwestern US. A brief summary of the results from this campaign are shown in Figure 28. Water vapor samples are labeled according to their location either in AZ (near the Gulf of CA along the AZ/MX border) or eastern NM (usually Roswell to Carlsbad). Samples from west Texas are included in the eastern NM group. These data show that the $\delta D_V$ minimum of 7/23 was detected in eastern NM, with even lower $\delta D_V$ values than measured in Albuquerque (Figure 28). This is consistent with the advective direction and precipitation patterns described above.

Relatively low $\delta D_V$ values downwind of strong convective activity have been observed by others. During a sampling campaign in southern MX, Lawrence et al (2004) observed that water vapor samples taken downwind of thunderstorms had lower $\delta D_V$ values than samples taken in otherwise similar conditions, with the $\delta D_V$ values decreasing as
convective systems became more organized. In general, deep convective systems are known to produce vapor and precipitation depleted in heavy isotopes, particularly in tropical storms and hurricanes [i.e., Lawrence et al (1996), Lawrence et al (1998), and Gedzelman et al (2003)] but even in more moderate mesoscale tropical systems (Bony et al 2008). Model-generated results from Gedzelman et al (2003) show that large convective systems start producing water vapor abnormally depleted in heavy isotopes ~24 hours after storm formation. With our Type IV periods of anticorrelated $\delta_{Dv-PW}$ data, we may be seeing the onset of the "amount effect" more common in the tropical latitudes.

### 2.6.3 Hurricanes and Gulf Surges

If certain conditions are met, hurricanes in the eastern Pacific can have dramatic effects on NM’s atmospheric moisture. Most Pacific hurricanes, which form just north of the ITCZ offshore of the southwest coast of MX, tend to propagate in a northwest direction toward open ocean, where they eventually dissipate over colder water far from any continent. On occasion though, these storms move northward along the west coast of MX and across the Baja Peninsula. From there they often get caught in the westerlies, which push them into northwest MX and possibly into southern AZ, NM or TX, potentially causing heavy local rainfall even after these storms have weakened below tropical depression status (Richie et al., 2011).

Hurricanes can have two main effects on the atmospheric water vapor in New Mexico. First, it is well documented that hurricane moisture is extremely depleted in
heavy isotopes [i.e., Lawrence et al (1996), Lawrence et al (1998), and Gedzelman et al (2003)], so we would expect that a pulse of such moisture into New Mexico should have high PW with unseasonably low $\delta D$ values. Second, hurricanes or smaller disturbances entering the mouth of the Gulf of CA often triggers a 'gulf surge' event, where low-level moisture over the Gulf of CA moves northward and enters AZ. Although gulf surge moisture is commonly measured in AZ (Stensrud et al., 1997), it remains uncertain if this moisture effectively reaches as far eastward as Albuquerque.

We report two instances of hurricane moisture reaching the Albuquerque sampling location: Hurricane John in 2006 and Hurricane Henriette in 2007. Hurricane Henriette (Figure 29) is the more straightforward example, with the hurricane entering the Gulf of CA (Figure 29A2) and causing a gulf surge that is clearly visible in the trajectories of Figure 29A1. This gulf surge moisture can be identified in Figure 21 (labeled) as an increase in PW, though the $\delta D$ values do not change much, remaining around -104‰. Once Henriette moves inland and over MX, it weakens substantially, with the moisture plume moving over NM and into TX. Although the arrival of the hurricane moisture in Albuquerque only results in partly cloudy skies, a small rise in PW, and no local precipitation, $\delta D$ values plummet immediately during the night of 9/5/07, eventually reaching a value of -198‰. Although the exact termination date of the anomalously low $\delta D$ period is difficult to determine given the high variability of the data, it appears that the hurricane moisture remained detectable in Albuquerque for about 7 days before $\delta D$ values returned to pre-hurricane levels.
A similar but slightly more complicated scenario evolved for Hurricane John in 2006. In this case, two hurricanes, Kristy (to the west), and John (to the east, identified by the arrow) formed at nearly the same time as shown in Figure 30A2. Kristy migrated to the northwest, while John moved northward and entered the Gulf of CA. The forward trajectories of Figure 30B1 imply that John's arrival in the Gulf of CA did not seem to trigger a gulf surge. However, a pulse of moisture does arrive ahead of the hurricane moisture (Figure 21), and wind direction from radiosonde soundings (Figure 31) indicate westerlies below the 500mb level as the moisture moves into Albuquerque. As John moved northward up the Gulf, it diminished in size, with the westerlies blowing its moisture eastward over southern NM as shown in Figure 27C2. Albuquerque only received a trace of precipitation as the hurricane moisture moved in, with the skies remaining mostly clear.

As with Henriette, the low $\delta D_V$ values associated with hurricane moisture lasted for 7-8 days before returning to pre-hurricane levels, though the arrival of a cold front immediately after the hurricane moisture complicates this observation. It is curious that during the $\delta D_V$ minimums from both hurricanes and the 'amount effect' event of 7-23-07 (segment IV_D), water vapor anomalously low in D continues to be detectable in our vapor samples up to 7-8 days after the initial decrease in $\delta D_V$ values. However, IR and water vapor imagery shows the moisture plumes moving out of the sampling area at least 4 days before the $\delta D_V$ values are completely back to pre-event levels. This may represent the residence time of water vapor in the boundary layer during the summer, when low-level winds are weak. Daily convective mixing between the boundary layer
and the free atmosphere may be what ultimately removes the low $\delta D$ vapor from the sampling area.

It has been known that easterly waves passing the Gulf of CA will tend to initiate gulf surges into AZ even if these waves don't propagate up the gulf of CA themselves (Stensrud et al., 1997; Fuller and Stensrud, 2000; Zehnder 2004). Higgins et al. (2004) have demonstrated that, on average, about three gulf surge events occur per month in AZ during the monsoon season from this phenomenon, though it has remained unknown whether any of this low-level moisture flows over the continental divide to reach Albuquerque.

Here we offer three examples of gulf surges (one from each year) triggered from tropical disturbances passing the mouth of the Gulf of CA that result in gulf surges. In the first, Hurricane Hilary passes by the Gulf of CA, triggering a gulf surge event that starts ~8/22/05 and lasts until about 8/25/05. As shown in Figure 32, the 500m AGL 24-hr forward trajectories not only show southerly flow into AZ, but also westerly/southwesterly flow into New Mexico. This surge event results in a rise in PW and $\delta D$ in Albuquerque, which peaks at a value of -94% at ~8/24/05 12z (Figure 21, "Gulf Surge Hilary").

In the second example, Hurricane Ileana passes by the Gulf almost exactly a year later, initiating gulf surge circulation on ~8/24/06 (Figure 32). As with the previous example, the forward trajectories show a westerly/southwesterly flow into NM. In this case, the $\delta D$ peaks at -98.5%, a higher value than any in the previous month (Figure
However, there is no accompanying pulse in PW, which instead shows a steady downward trend at this time. The different PW outcomes between these two surge events can be explained by different subsidence conditions over New Mexico. In a comparison of omega maps, the Ileana surge event (Figure 32_B2) occurred during a greater degree of subsidence over central New Mexico than the Hillary surge event (Figure 32_A2). In the case of Ileana, the gulf surge moisture reached Albuquerque, but subsidence aloft caused a simultaneous drying of the atmosphere. These conditions are in fact another example of the Type III activity described previously.

Our third example of a surge is triggered on 8/18/07 12Z by an easterly wave that did not grow large enough to become named. The disturbance passes by the gulf and quickly loses strength, but is successful in triggering a strong gulf surge that clearly impacts New Mexico, with a peak in δDV (-80‰) and a strong pulse in PW (Figure 21, "Gulf Surge 2007"). The strong signal in NM may be due to the fact that this gulf surge is amplified by an easterly wave that is situated over northern MX (Figure 32_C). This causes Gulf of MX moisture to advect over MX and then turn eastward, as shown by the forward trajectories in Figure 32_C. The high values in δDV and PW at this time may be a result of a combination of moisture from both the Gulf of MX and the Gulf of CA.

2.6.4 Anomalously high δDV values during the summer

In addition to the long-term trends in δDV and PW from Type I through IV conditions as well as the effects from hurricane and gulf surge moisture, there are short-term variations in δDV and PW that require further explanation. In some cases, the
increases/decreases in these variables are due to similar atmospheric conditions previously explained in the Type I through IV sections above but occurring in a shorter timeframe. At other times, midlatitude waves - rare but not impossible events during the Albuquerque summer - occasionally break up the monsoon circulation. Here we give three examples of short-lived pulses of isotopically "heavy" moisture, identified on Figure 21 as peaks in δD labeled "H."

A common situation that results in short-term increases of δD values is the occurrence of a COL centered over TX. Over the three summers there are several occasions where a COL stalls over TX for days at a time; over our study period this is especially common with monsoon onset, but can also happen during other parts of the summer. When this occurs, cyclonic rotation around the low advects moisture northward from the Gulf of Mexico. Whether any of the moisture reaches NM depends on other characteristics of the lower atmosphere in the region. The COL is usually accompanied by a high pressure system that is centered over the western states, and while the COL can remains stationary for over a week, the exact center and strength of the high pressure shifts daily. If the high is relatively close to NM, the moisture from the COL is usually shunted to the northeast. However, if the high weakens or migrates away from NM (usually to the west/northwest), then a pulse of Gulf of Mississippi moisture derived from the COL can reach NM. Two examples of this, exactly a year apart, are shown in Figures 33A and 33C. In the first example (from 2006) the COL, derived from an easterly wave, forms approximately 7/1/05, 3 days prior to the map shown in Figure 33A. At that time, a high pressure was centered over NM and AZ. As the high slowly retrogrades to a
position over southern NV (as shown in Figure 33A), moisture from the COL is able to reach NM before the high quickly returns ~24 hours later. This results in a short-lived peak in $\delta D_v$ (Figure 21, labeled "H_A") before conditions return to the previous circulation pattern.

In the second example (from 2007), the COL forms from a midlatitude wave over New England on ~ 7/1/07, migrates southwest and settles over TX on 7/3/07. Contemporaneous to the COL formation is a high centered over the 4-corners region. As with the previous example, Gulf of MX moisture is drawn northward and steered to the northeast by the combined circulatory effects of the COL and the high. This situation prevails until the center of the high migrates over northern NV, which allows a pulse of Gulf of MX moisture to move into NM as shown in Figure 33C. This is responsible for the peak of $\delta D_v$ labeled "H_B" in Figure 21. Eventually this COL dissipates and the high returns over the American Southwest.

Our third example of a short-level period of high $\delta D_v$ occurs as a result of reconfiguration of the Monsoon High itself. Prior to period "H_C", the high extended over most of the continental US; the $\delta D_v$ and Td depression observed ~24 hours prior to H_C (see Figure 21) are a result of this high extending down over NM. As the high begins to break down, its center migrates toward the pacific northwest while a portion of the ridge extends eastward over the middle of the country (Figure 33B). Anticyclonic circulation around this eastern extension of high pressure brings Gulf of MX moisture into NM as shown by the 24-hr forward trajectories in Figure 33B. This circulation is very
transient; once the high has reestablished itself over the Pacific Northwest and becomes more symmetrical, this circulation ceases.

2.6.5 Anomalously low $\delta D_v$ values during the summer

There are several sharp and distinct decreases in PW and $\delta D_v$ values during the summer months (Figure 21) where both variables are tightly positively correlated. Three examples of such periods with unseasonably isotopically light water vapor and low PW are labeled in Figure 21 as "L." Throughout most of the summer, a large pool of dry air exists over the Pacific Ocean due to persistent subsidence from the North Pacific High. On occasion, the circulation over North America allows a plume of this dry air to be brought over the continent. When this happens, both $\delta D_v$ and PW temporarily drop to unusually low values.

Here we show three examples of abnormally sharp decreases in PW and $\delta D_v$ values during the summer due to an influx of dry Pacific air. The first example ("LA" Figure 21) occurs at the end of segment II_b, itself a multiday period of decreasing PW and $\delta D_v$ values. As previously described in an earlier section, during II_b the American Southwest is under the influence of a high pressure system, the composite map of which was shown in Figure 23_b. During this time, high pressure is broad in areal extent, migrating east and west across the southwestern states. However, at the end of this period the center of high pressure becomes smaller, more symmetric, and is located directly over northern AZ (Figure 34_a). This allows anticyclonic circulation around the high, which advects dry air in from the western Pacific. This dry air can be seen in the 700hpa
specific humidity maps in Figure 34_A (48 hours prior to the dry event L_A) and 34_B (during the dry event L_A). A very similar situation is observed with dry event L_C in 2007 (Figure 21). As with the prior example (L_A), a relatively small high pressure centered over AZ draws in dry air from the Pacific. In Figure 34_E, the pool of dry air can be seen northwest of the high, caused by subsiding air south of the axis of zonal flow. This dry air is then drawn into New Mexico as shown in Figure 34_F, causing a substantial decrease in δD_V values for ~48 hours (longer for PW).

In our third example (L_B), a great mass of dry air exists out over the Pacific from subsidence southeast of the Pacific High (Figure 34_C). A midlatitude wave can be seen centered over Wyoming, the southernmost extent of which passes over NM. As the wave passes to the east of NM, cyclonic advection around the wave brings subsiding dry air into NM (Figure 34_D). As soon as the wave passes toward the northeast, high pressure rebuilds over the western states, which blocks any further dry air from entering NM. This dry event lasts approximately 48 hours, though it should be noted that the relative decrease in PW is greater than either the δD_V or Td. This implies that the dry air aloft did not mix down as efficiently as it did in the previous two examples.

2.7 Mixing vs Rayleigh fractionation processes

We have shown in the previous sections that the water vapor over NM originates from a variety of sources, which can change on seasonal to daily timescales. However, other processes undoubtedly contribute to the δD_V value of the water vapor at any given day. Most importantly, vertical mixing and rainout (Rayleigh distillation) are two
processes that probably have a significant impact on the $\delta D_V$ values recorded in Albuquerque. It is of interest then to determine whether our range of $\delta D_V$ values can be modeled as a simple mixing process between two endmembers (a moist source and a dry source), as a simple Rayleigh fractionation process, or a mix of these two processes.

In this section we examine our data in a plot of $\delta D_V$ vs Q (specific humidity) to find evidence of these processes. In the plot of vapor samples taken from Albuquerque, Arizona, eastern NM, and TX (Figure 35), it can be seen that water vapor from various times of the year occupy different areas in $\delta D_V$ vs Q space. Spring, winter, and fall samples plot in the main cluster of points on the left side of the diagram, while water vapor from the monsoon season plots along the upper/central portion of the graph. Samples containing hurricane moisture and those taken during 'amount effect' depletion events plot in a unique area below the main body of monsoon data. Samples collected in AZ (red) mostly fall within the main body of monsoon season samples, though gulf surge events plot on the periphery of this body of data. For example, the gulf surge event of 8/15/07 (sampled in southern AZ) plots slightly higher than main monsoon body, while the gulf surge event of 8/1/07 plots slightly lower and further to the right. Samples taken from Houston and McAllen, TX during the summer months plot even further to the upper right. For comparison purposes, we include tropical water vapor data from Puerto Escondido, MX as reported by Lawrence et al. (2004); these samples plot farther to the right (i.e. higher q values) than any of our samples. For clarity purposes, we have only included four of their samples, representative of the
spread of reported $\delta D_V$ compositions along with a calculated average value of their 63 samples.

To evaluate possible mixing processes, we used a sample from 12/8/05 for our dry endmember, which has a $\delta D_V$ of -242‰ and a specific humidity (q) of 0.00080 kg/kg. Mixing curves (shown in Figure 31 as orange lines) were generated between this sample and three possible moisture sources. The most representative sample of moisture from the Gulf of MX in our dataset is that collected at Corpus Christi, TX on 5/15/07 (hereafter referred to as sample CCTX). A mixing curve constructed between the CCTX sample and our dry endmember forms the upper boundary (minus a few outliers) for our dataset on Figure 35 (solid orange line). A second possible moisture source for NM is that from the Gulf of CA. We have multiple samples of gulf surge moisture taken from southern AZ in 2007. In one instance, the gulf surge moisture (8/15/07) is not particularly different from that of CCTX, as they both share roughly equivalent $\delta D_V$ values and would produce similar mixing curves. However, the gulf surge moisture of 8/1/07 has lower $\delta D_V$ values, which produces a mixing curve that cuts through the monsoon data (Figure 35, dashed orange line). Other gulf surge samples plot within the cloud of monsoon data. Roughly 2/3 of our monsoon season data falls between the CCTX curve and the 8/1 gulf surge curve. If these two humid endmembers are truly representative of their respective sources, then Figure 35 shows that dry upper level air mixed with either a Gulf of MX or a Gulf of CA moisture source could explain some, but not all, of the variability observed in summer monsoon samples.
Admittedly we do not know the full range of δDv values for moisture coming from either of these two regions. Other samples taken from southeast TX later in the summer consistently plot in the upper right field (Figure 35, blue points), but the full range of isotopic compositions from the Gulf of MX is not known. Likewise, our gulf surge data show that considerable variability exists within Gulf of CA moisture, but the full range of possible compositions are not known. It is quite possible that water vapor from either gulf could occasionally have lower δDv values than observed due to the 'amount effect' if convection was particularly active over the water. If we use moisture from the 7/23/07 depletion (sampled in Albuquerque) as a possible source, we get a mixing curve that easily bounds the lower end of our monsoon dataset (Figure 35, dotted yellow line). It is possible that all of the variability observed in our monsoon data is simply due to different degrees of the 'amount effect' in either gulf.

Although mixing between two or more possible humid endmembers with dry air may explain the majority of our monsoon dataset within δDv-q space, simple mixing does not explain the majority of the samples during the remainder of the year. Further variation in dDv-q space may be due to Rayleigh fractionation, an idealized process in which liquid condensate is immediately removed from a cooling system. Rayleigh (1902) mathematically described this process as

\[ \left( \frac{R}{R_i} \right) = f^{x-1} \] 2.2
where \( R \) and \( R_i \) represents the heavy/light ratios of the system and initial reservoir, respectively. \( F \) is the fraction of the initial system remaining, and alpha is the equilibrium fractionation factor; Rayleigh fractionation assumes equilibrium fractionation at the moment of condensation. This equation can be converted into delta notation as

\[
\frac{1000 + \delta_l}{1000 + \delta_{l,i}} = f^{\alpha_l - \nu - 1} \tag{2.3}
\]

for the liquid phase, and

\[
\frac{1000 + \delta_v}{1000 + \delta_{v,i}} = f^{\alpha_v - \nu - 1} \tag{2.4}
\]

for the vapor phase. In our model, our starting temperature is the dew point of the collected air sample. From there, the temperature is decremented by steps of 0.1 degrees C. In each temperature step, the mass of liquid in excess of saturation is calculated. The equilibrium fractionation factor is then calculated based on the temperature-dependent fractionation factors from Merlivat and Nief (1967) and Majoube (1971). This fractionation factor is used to calculate the isotopic composition of the liquid excess. This liquid excess is then removed from the system, and the temperature is decremented another step of 0.1 degrees C.
Sample CCTX produces a Rayleigh curve that intersects the main body of data points (Figure 35, green solid line) while the Rayleigh curve from the gulf surge moisture of 8/1/07 roughly outlines the lower boundary of the dataset (Figure 35, green dashed line). Therefore the non-monsoon samples are bound between a mixing curve with the CCTX moisture on the upper end, and a Rayleigh fractionation curve with gulf surge 8/1 moisture on the lower end. Clearly, many cold season samples may not have a component of either Gulf of CA or Gulf of MX moisture, so these curves serve as theoretical endmember processes.

An alternative to direct mixing, especially in drier air, is proposed by Galewky and Hurley (2010). Isentropic mixing between airmasses of different properties could form trajectories in $\delta D_V$ - q space that follow different paths than simple mixing. As shown in Figure 36, isentropic mixing will result in samples that have very little change in $\delta D_V$ but can span a relatively wide range in specific humidity. This may help explain the spread of cold season data points in the lower left portion of the $\delta D_V$-q diagram (Figures 35 and 36).

**2.8 Conclusions**

New Mexico’s geographical location is well-suited for a comprehensive study of the relationship between the stable isotope composition of water vapor and concurrent weather conditions. NM’s latitude is sufficiently poleward to be under the influence of midlatitude waves in the winter, but equatorward enough to be under the influence of tropical easterly waves during the summer. NM’s location to the east (generally
downwind) of the Pacific Ocean, as well as halfway between the Gulf of CA and the Gulf of MX, gives it three potential moisture sources. Westerly wind patterns during most of the year give way to light and variable flow from the east, southeast, or southwest during the summertime North American Monsoon season. The Monsoon High, which separates the westerly flow to the north from the easterly flow to the south, moves around the continent slowly and often influences NM’s weather during the summer. And finally, NM is in a position to receive the remnants of Pacific hurricanes that move parallel to Baja California and into the American Southwest.

In this paper we have shown that the stable isotopic composition of water vapor is profoundly dependent on synoptic-scale weather patterns that determine moisture transport pathways. The weather regime relevant to the regional circulation and observed variations in $\delta D_V$ is dependent on the time of year. During fall, winter, and spring, midlatitude waves in westerly mean flow are responsible for the majority of $\delta D_V$ variations, while stagnant centers of anomalously high or low pressure with occasional interruption by easterly waves are primarily responsible for the summertime variations. Although there is not an appreciable correlation between $\delta D_V$ and temperature on short (daily to weekly) timescales, there is an overall correlation with temperature on the seasonal timescale.

Midlatitude waves are an important mechanism for large $\delta D_V$ variations that can occur on a daily timescale. The approaching wave tends to cause southerly flow that can range from the southeast to southwest, resulting in higher PW and $\delta D_V$ values.
Usually the approaching wave is complemented by a high pressure system over the Gulf of MX, which provides some anticyclonic rotation to the advection. As the wave passes over NM, advection shifts to a flow that can range from westerly to northerly. This change in advection, along with the subsidence common to the upwind side of passing midlatitude waves, is responsible for a sharp decrease in PW and \( \delta D_v \) values. Midlatitude waves can affect NM in all seasons, but influence NM the most during the cold season. During the winter, midlatitude waves have colder core temperatures, higher pressure gradients, and generally follow a track shifted toward lower latitudes. These features, along with the fact that the wave axes are tilted to the northeast during the winter, cause minimum values of in PW and \( \delta D_v \) values that lower than other times of the year. Cut-off lows (COLs) during the winter are associated with the lowest \( \delta D_v \) values observed during the 30-month study, probably due to their ability to bring air down from the upper troposphere or lower stratosphere (tropospheric folding).

The largest variance in daily \( \delta D_v \) values is observed in the spring. This is largely due to the extremely dry state of the lower atmosphere this time of year, where even the smallest contributions of water vapor from any source can disproportionately sway the \( \delta D_v \) values. Additionally, 100% recycled precipitation (virga) can introduce bursts of isotopically heavy vapor into the lower atmosphere, causing large and rapid increases in \( \delta D_v \) values. Midlatitude waves are still prevalent throughout the spring, and by late spring easterly waves start to influence circulation in the region.
By the beginning of monsoon season (early July), midlatitude waves are mostly passing to the north, leaving NM unaffected with only a few interruptions throughout the summer. The Monsoon High, a high pressure system that separates the westerlies to the north from the easterlies to the south, wanders over the continental US the Gulf of Mexico, sometimes spending over a week in a single location. The exact location of the Monsoon High is critical to the behavior of recorded surfaces $\delta D_V$ values in Albuquerque. If the high is positioned slightly to the northeast of NM (e.g., Oklahoma), the high serves as a moisture pump, in which anticyclonic rotation around the high advects moisture from the Gulf of MX directly into NM. This will raise both PW and $\delta D_V$ values [Type I activity]. If the Monsoon High is directly over NM or to the northwest of NM, subsidence and advection from the Pacific Ocean will cause both PW and $\delta D_V$ values to decrease [Type II activity]. If the high is located such that moisture is being advected into NM while subsidence is occurring either overhead or in the path of transport, then $\delta D_V$ values increase while PW decreases [Type III activity].

Periods of anticorrelated $\delta D_V$-PW behavior [Type IV activity] occur when NM is downwind of active convection. We believe this is a manifestation of the "amount effect" as originally described by Dansgaard (1964). In the most extreme example, the $\delta D_V$ minimum event of 7/23/07 was caused when NM was downwind of a mesoscale convective system that existed for over 4 days with cloud top temperatures of -70°C or colder. Unseasonably low values of $\delta D_V$ in the summer also occur due to the influx of hurricane moisture, as was the case with Hurricanes John in 2006 and Henriette in 2007. Hurricane moisture can be considered as an extreme example of "amount effect," while
the more modest anticorrelated Type IV events we have reported are likely the result of the beginnings of this process.

The stable isotopes of water vapor have the potential to be a useful tool for understanding atmospheric processes. Although there are many factors that contribute to the stable isotope composition of water vapor, we have shown that synoptic-scale weather processes have a first-order influence on $\delta D_V$ values. For this reason, stable isotopes may be helpful in diagnosing moisture transport pathways, especially if used in conjunction with traditional meteorological data. While there have been attempts to use stable isotopes alone as tracers to solve meteorological problems (e.g., Yamanaka et al, 2002; Anker et al., 2007; Tian et al., 2007), this technique has only has limited application as long as other meteorological variables are not taken into account. We suggest that while stable isotopes have great potential for diagnosing atmospheric processes, it is critically important for future work in this field to take the synoptic-scale meteorological conditions into careful consideration.

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2.9 Figures

Figure 1 - Location Map

Location Map of study area. All precipitation and most water vapor samples were collected in Albuquerque; additional water vapor was collected at locations shown (black dots).
Figure 2 - Caption

Time series of $\delta D_v$ (red, scale to left), and PW (blue, scale to right). Precipitation ($\delta D_p$) events are yello-filled stars, plotted with an scale shown to the left (black).
Figure 3 (part A) - same as Figure 2, but expanded over several pages
Figure 3 (part B) - same as Figure 2, but expanded over several pages
Figure 3 (part C) - same as Figure 2, but expanded over several pages
Figure 3 (part D) - same as Figure 2, but expanded over several pages
Figure 3 (part E) - same as Figure 2, but expanded over several pages
Boxplots showing monthly δD values of vapor (dark boxes) and precipitation (light boxes). Whiskers represent the 5th and 95th percentiles, while outliers are represented as dots (vapor) or stars (precip). Numbers next to the columns indicate total number of samples analyzed. The average monthly temperature as obtained from the Albuquerque airport. Vapor samples were collected between March 2005 and October 2007. Precipitation values include samples collected between 2002 - 2007.
Figure 5

Relationship between $\delta D_v$ and temperature at the time of sample. Unless otherwise noted, data are collected from the rooftop in Albuquerque, with “region” samples collected in AZ or eastern NM. For the most part, no observable association exists between $\delta D_v$ and temperature, though flights in October and November do show a weak correlation between these variables.
Figure 6
Relationship between δDν and mixing ratio (w) at the time of sample. Unless otherwise noted, data are collected from the rooftop in Albuquerque, with “region” samples collected in AZ or eastern NM.
Boxplots showing monthly values of \( \delta D_v \) (dark boxes) and \( \delta D_p \) (gray boxes). White and striped boxes show \( T \) and \( T_d \), respectively. Whiskers represent the 5th and 95th percentiles. In general, heavier \( \delta D_v \) and \( \delta D_p \) correlate with higher \( T \) and \( T_d \).

Precipitation includes samples collected three years prior to the start of the vapor collection.
**Figure 8 - Caption next page**

- **Measured $\delta D$ value of precipitation**
- **Expected $\delta D$ value of precipitation based on measured $\delta D_v$ values (vapor) and surface temperature**
- Difference between monthly mean $\delta D_p$ (measured) and the expected $\delta D_p$ equilibrium value from monthly means of $\delta D_v$ (measured) and temperature.
Comparison of δD values between vapor and precipitation of samples collected closely in time. Stars represent δD values of collected precipitation samples. Open squares represent the expected δD value of precipitation if the precipitation was in equilibrium with the surface-level water vapor at the surface temperature. The difference between the collected and expected equilibrium value is represented in either solid or dashed lines, showing that collected precipitation is isotopically lighter or heavier than the equilibrium composition, respectively. The gray bars at the top of the diagram represent the average difference between actual and equilibrium precipitation values over all samples collected in monthly bins.
Figure 9 - caption

Time series of $\delta_{DV}$, PW, and $T_d$ from 9/1/05 to 12/15/05 as an example of fall season variability. Letters refer to time periods described in the text and detailed in Figures 10 and 11. $\delta_{DV}$ from individual air samples are plotted as open circles with scale to the left; $\delta D$ values of precipitation (stars) are plotted on an offset scale, shown on the left (inset). Dew Point °C (recorded at sampling location) is plotted as a thin black line (scale on inner right); Vertically Integrated Precipitable Water (measured in Albuquerque, cm) is plotted as the grey line with the scale to the outer right.
700hpa geopotential height maps of periods of relatively high $\delta D_V$ during the fall time series, with letters corresponding to the designated times in Figure 9. Each map is a 6-hr composite that ends at the date given, with the exception of the first panel, which is a 222-hr composite. Contour intervals are 10 meters. Superimposed on the height maps are 48-hr backward trajectories that end at the given date. Dotted trajectories are 500m AGL, dashed are 1500m AGL, and solid are 3000m AGL.
Figure 10 (part B)

Caption next page
700hpa geopotential height maps of periods of elevated $\delta D_v$ during the fall time series (continued), with letters corresponding to the designated times in Figure 9. Each map is a 6-hr composite that ends at the date given, with the exception of the first panel, which is a 222-hr composite. Contour intervals are 10 meters. Superimposed on the height maps are 48-hr backward trajectories that end at the given date. Dotted trajectories are 500m AGL, dashed are 1500m AGL, and solid are 3000m AGL. Panel q shows backward trajectories superimposed over an IR satellite image from the given time. Panel q shows backward trajectories superimposed over an IR satellite image from the given time.
Figure 11 (part A) - Fall

700hpa geopotential height maps corresponding to periods of relatively low δDv values during the fall time series (Figure 9). Each map is a 6-hr composite that ends at the date given. Contour interval is 12 meters. Superimposed on the height maps are 48-hr backward trajectories that end at the given date. Dotted trajectories are 500m AGL, dashed are 1500m AGL, and solid are 3000m AGL. Shaded backgrounds are 700mb air temperatures. Letters d-r refer to specified events on Figure 9.
Figure 11 (part B) - Fall

700hpa geopotential height maps corresponding to periods of relatively low $\delta V$ values during the fall time series (continued). Each map is a 6-hr composite that ends at the date given. Contour interval is 12 meters. Superimposed on the height maps are 48-hr backward trajectories that end at the given date. Dotted trajectories are 500m AGL, dashed are 1500m AGL, and solid are 3000m AGL. Shaded backgrounds are 700mb air temperatures. Letters d-r refer to specified events on Figure 9.
Time series of $\delta D_V$, PW, and $T_d$ from 1/12/06 to 1/30/06 as an example of winter activity. Letters refer to time periods described in the text and detailed in Figure 13.

$\delta D_V$ from individual air samples are plotted as open circles with scale to the left; the single $\delta D$ value of precipitation is labeled (star), not at scale with the vapor measurements. Dew Point °C (recorded at sampling location) is plotted as a thin black line (scale on inner right); Vertically Integrated Precipitable Water (measured in Albuquerque, cm) is plotted as the grey line with the scale to the outer right.
Figure 13 (part A)

700hpa geopotential height maps for selected periods within the winter time series of Figure 12. Each map is a 6-hr composite ending at the noted time. Geopotential height contours are 12 meters. With the exception of panel A, 24-hr backward trajectories are superimposed on the pressure maps, ending at the noted time. Dotted lines, dashed lines, and solid lines are 500m, 1500m, and 3000m AGL, respectively. Panel A consists of a matrix of 24-hr forward trajectories, all of which are at 500m AGL.
700hpa geopotential height maps for selected periods within the winter time series of Figure 12 (continued). Each map is a 6-hr composite ending at the noted time. Geopotential height contours are 12 meters. With the exception of Panel F, 24-hr backward trajectories are superimposed on the pressure maps, ending at the noted time. Dotted lines, dashed lines, and solid lines are 500m, 1500m, and 3000m AGL, respectively. Panel F shows 48-hr reverse trajectories.
Figure 14 (part A) - Caption on next page
Figure 14 (part A) caption

Short time series from January 2007. All contour maps represent 700hpa geopotential height over a 6-hr period ending in the date shown. Geopotential height contour interval is 12 meters. Superimposed on the height maps as white thick lines are 48-hr reverse trajectories at 500m (dotted), 1500m (dashed), and 3000m (solid) AGL. Background shading represents air temperature at the 700hpa level. Darker shades indicate colder temperatures; scale on bottom.
Figure 14 (part B) - Caption on next page
Figure 14 (part B) caption

Top two panels are IR images from GOES 11 captured at the dates shown. All contour maps represent 700hpa geopotential height over a 6-hr period ending in the date shown. Geopotential height contour interval is 12 meters. Superimposed on the height maps as white thick lines are 48-hr reverse trajectories at 500m (dotted), 1500m (dashed), and 3000m (solid) AGL. Background shading represents air temperature at the 700hpa level. Darker shades indicate colder temperatures; scale on bottom.

Satellite IR images are from the dates listed.
Some of the evidence showing a low tropopause during the COL. The colored figures to the left map out the pressure level of the tropopause, showing a minimum heights near 400hpa at the center of the COL. Soundings from Flagstaff AZ around this time also show a tropopause near the 400 hpa level.
Figure 16 - Caption on next page
Figure 16 caption

Time series of $\delta D_V$, PW, and $T_d$ from 3/3/06 to 3/13/06 as an example of early spring activity. Letters refer to time periods described in the text and are detailed in Figure 17. $\delta D_V$ from individual air samples are plotted as open circles with scale to the left; $\delta D$ values of precipitation (stars) are plotted on an offset scale, shown on the left (inset). Dew Point (recorded at sampling location, °C) is plotted as a thin black line (scale on inner right); Vertically Integrated Precipitable Water (measured in Albuquerque, cm) is plotted as the grey line with the scale to the outer right.
Figure 17 (part A) - Caption on next page
Figure 17 (part A) - Caption

Times of interest in the "early spring" time series of Figure 16. 700hpa geopotential height maps at the given dates are shown contoured with intervals of 14m. 24-hr reverse trajectories that end at the given date are plotted as thick white lines, with 500m (dotted), 1500m (dashed), and 3000m (solid) AGL. Shaded background represents 700hpa specific humidity; lighter shades are more humid (scale on the bottom). Panel a2 is a 700hpa omega map for time A; lighter shades represented subsiding air while darker shades represent areas of uplift.
Figure 17 (part B) - Caption

Times of interest in the "early spring" time series of Figure 16. 700hpa geopotential height maps at the given dates are shown contoured with intervals of 14m. 24-hr reverse trajectories that end at the given date are plotted as thick white lines, with 500m (dotted), 1500m (dashed), and 3000m (solid) AGL. Shaded background represents 700hpa specific humidity; lighter shades are more humid (scale on the bottom).
Times of interest in the "early spring" time series of Figure 16. 700hpa geopotential height maps at the given dates are shown contoured with intervals of 14m. 24-hr reverse trajectories that end at the given date are plotted as thick white lines, with 500m (dotted), 1500m (dashed), and 3000m (solid) AGL. Shaded background represents 700hpa specific humidity; lighter shades are more humid (scale on the bottom).
Figure 18 (part A) - Caption on next page
Figure 18 (part A) - Caption

Doppler RADAR image (top) and upper air sounding (bottom) corresponding to 3/7/2006 5:02Z and 3/7/2006 12Z respectively. This corresponds to the peak of $\delta D_V$ values at time "C" on Figure 17. Sampling area in the RADAR image is denoted with the "X." Doppler RADAR image is derived from a 16-layer composite. Upper air sounding taken from Albuquerque airport shows a cloud layer at ~550 hpa with a dry atmosphere below cloud base.
Figure 18 (part B) - Caption

Doppler RADAR image (top) and upper air sounding (bottom) corresponding to 3/7/2006 21:57Z and 3/8/2006 0Z respectively. Sampling area in the radar image is denoted with the "X." Doppler RADAR image is derived from a 16-layer composite. Upper air sounding taken from Albuquerque airport shows a cloud layer at ~600 hpa with a dry atmosphere below cloud base.
Figure 19 - caption on next page
Figure 19- caption

Time series of δD_V, PW, and T_d from 6/10/05 to 6/30/05 as an example of late spring activity. Letters refer to time periods described in the text and detailed in Figures 9 and 10. δD_V from individual air samples are plotted as open circles with scale to the left; δD values of precipitation (stars) are plotted on an offset scale, shown on the left (inset). Dew Point (recorded at sampling location, °C) is plotted as a thin black line (scale on inner right); Vertically Integrated Precipitable Water (measured in Albuquerque, cm) is plotted as the grey line with the scale to the outer right.
Times of interest in the early spring time series of Figure 18. 700 hpa geopotential height maps at the given dates are shown contoured with intervals of 14 meters. 24-hr reverse trajectories that end at the given date are plotted as thick black lines, with 500m (dotted), 1500m (dashed), and 3000m (solid) AGL.
Figure 20 (part B) - caption next page
Figure 20 (part B) - caption

Times of interest in the early spring time series of Figure 18. 700hpa geopotential height maps at the given dates are shown contoured with intervals of 14 meters. Panels g₂ and h₂ show 24-hr forward trajectories at 500m AGL (dashed lines). Shaded backgrounds in g₁ and h₁ represents 700hpa omega values; lighter colors represent areas of subsidence while darker colors represent areas of uplift.
Figure 20 (part C)

Times of interest in the early spring time series of Figure 16. 700mb geopotential height maps at the given dates are shown contoured with intervals of 14mbar. 24-hr reverse trajectories that end at the given date are plotted as thick black lines, with 500m (dotted), 1500m (dashed), and 3000m (solid) AGL.
Figure 21 - caption

Three consecutive monsoon seasons showing $\delta D_V$, PW, and $T_D$ along with precipitation. Examples of types I, II, III, and IV activity are labeled and are referred to in the following diagrams. Letters refer to time periods described in the text and are detailed in the following figures. $\delta D_V$ from individual air samples are plotted as open circles with scale to the left; $\delta D$ values of precipitation (stars) are plotted on an offset scale, shown on the left (inset). Dew Point (recorded at sampling location, °C) is plotted as a thin black line (scale on inner right); Vertically Integrated Precipitable Water (measured in Albuquerque, cm) is plotted as the grey line with the scale to the outer right.
Figure 22 - Caption

Three examples of Type I activity. Each 700hpa geopotential height map is a composite of the dates listed, with contour intervals of 5m. Superimposed on the maps are a matrix of 24-hr forward trajectories (500m AGL, dashed lines) that begin at the date listed.
Two examples of Type II activity. Each 700hpa geopotential height map is a composite of the dates listed, with contour intervals of 5m. Superimposed on the maps are a matrix of 24-hr forward trajectories (500m AGL, dashed lines) that begin at the date listed.
Figure 24 - caption next page
Figure 24 - Caption

Three examples of Type III activity. Each 700hpa geopotential height map is a composite of the dates listed, with contour intervals of 5m. Superimposed on the maps are a matrix of 24-hr forward trajectories (500m AGL, dashed lines) that begin at the date listed.
Figure 25 - caption

Side-by-side comparison of segments IIIc and Iб. Although the geopotential height map for the high pressure looks similar in both images, during segment IIIc the high is accompanied by an easterly wave to the south. The resulting pressure gradient causes stronger subsidence (shown as lighter shading) than in the case of Iб.
Examples of times of interest surrounding (and usually preceding) Type IV activity.

Panels a,b,c, and d are relevant to the anticorrelated event of segment IV_a. Panel A: composite 700hpa geopotential map for dates shown; 24-hr forward trajectories at 500m AGL starting at time shown. Panel B: Composite map of specific humidity for time shown; lighter shades are more humid (scale at bottom). Panel C: 72-hr precipitation totals (contoured) prior to the IV_a event. Panel D: cloud top temperatures (C) for given time. Panels E+F: 72-hr precipitation accumulations (contoured) and 24-hr forward trajectories (500m AGL) prior to events IV_b and IV_c. Panels G and H: composite 700mbar geopotential height maps for times shown, with composite specific humidity (shaded) in background.
Figure 27 - Caption on next page
Events leading up to the $\delta D_V$ minimum of 7-23-07. Panels A through D show cloud top temperatures (C) at the given times. Panels E through H show 24-hr precipitation accumulations (modeled), overlain with 24-hr forward trajectories (500m AGL) starting at the given time.
Figure 28

$\delta D_V$ values for air samples taken in Albuquerque (solid line) compared with samples taken in southern AZ ('x's) and eastern NM/TX (stars).

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Figure 29

Evolution of Hurricane Henriette. Panels A₁ and B₁ show the 700mbar geopotential height (5mbar contour intervals) with superimposed 24-hr forward trajectories (500m AGL). Panels A₂ and B₂ are IR images from the given date; the white arrow shows the location of Hurricane Henriette moisture.
Figure 30 - caption on next page
Figure 30 - caption

Evolution of Hurricane John. Panels A$_1$, B$_1$, and C$_1$ show 700mbar geopotential height maps (5mbar contour interval) for the given times with overlain 24-hr forward trajectories (500m AGL) starting at the given times. Panels A$_2$, B$_2$, and C$_2$ are IR satellite images taken at the given date. Hurricane John moisture is indicated by the white arrow.
Figure 31

Radiosonde sounding showing the first arrival of moisture from Hurricane John with westerlies dominant.
Figure 32 - Caption next page
Figure 32 - caption

Three different gulf surges due to the passing of easterly waves. In Panel A, B, and C, 700hpa geopotential height is mapped (with 5mbar contour intervals) with overlying 24-hr forward trajectories (500m AGL) starting at the given times. Panels A and B are maps of omega (dp/dt) showing areas of subsidence (lightly shaded areas) and subsidence (dark areas) at the given times.
Figure 33 - caption next page
Figure 33 - caption

Three examples of conditions leading to anomalously high $\delta D_V$ values. 700hpa geopotential height maps for the dates shown are contoured with 7 meter height intervals. 24-hr forward trajectories (500m AGL) are superimposed over the maps.
Example of low $\delta D_V$ values associated with dry air. Maps showing 700hpa geopotential height (contoured, 5 meter height interval) with 700hpa specific humidity in background (shaded, darker colors are drier, scale on bottom). Top panel show conditions immediately before the dry events, while bottom panel shows conditions during the dry events.
Figure 34 (part B) - caption next page
Example of low $\delta D_v$ values associated with dry air. Maps showing 700hpa geopotential height (contoured, 5 meter height interval) with 700hpa specific humidity in background (shaded, darker colors are drier, scale on bottom). Left panels show conditions immediately before the dry events, while right panels show conditions during the dry events.
Figure 34 (part C) - caption next page
Figure 34 (part C) - caption

Example of low $\delta D_V$ values associated with dry air. Maps showing 700hpa geopotential height (contoured, 5 meter height interval) with 700hpa specific humidity in background (shaded, darker colors are drier, scale on bottom). Left panels show conditions immediately before the dry events, while right panels show conditions during the dry events.
Figure 35 - caption

Plot of $\delta D_V$ vs specific humidity ($q$) for water vapor samples analyzed in this study.

Samples from Albuquerque are identified by month, with legend shown in the lower right. Samples from southern AZ (2007) are colored in solid red, with each sampling trip represented by a different symbol. Samples collected in eastern NM (2007) are solid gray circles, while those from TX (2007) are black circles. Mixing curves between each of the three potential humid endmembers and the dry endmember of 12/8/05 are shown as tan lines. Rayleigh distillation curves from each of the same three possible humid endmembers are shown as green curves. Representative tropical water vapor data from Lawrence et al., 2004 are shown as red stars (upper right).
Plot of $\delta D_\nu$ vs specific humidity ($q$) for water vapor samples analyzed in this study with $\delta D_\nu$-$Q$ trajectories from Galewsky and Hurley 2010. Mixing along isentropic surfaces can move compositions roughly along the horizontal axis in this figure, while simple mixing produces steeper mixing curves (Figure 35).
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Chapter 3: Investigations into deuterium excess of water vapor and precipitation in the American Southwest

ABSTRACT

We present stable isotope analyses of 106 samples of surface water vapor and 40 samples of precipitation from the southwestern US. Water vapor was sampled in Albuquerque, New Mexico (NM) as well as in southern Arizona (AZ), eastern NM, and in western Texas (TX). Precipitation samples were exclusively collected in Albuquerque. The deuterium excess ($d$) of Albuquerque’s vapor samples are remarkably consistent, especially when compared to reported values of $d$ from other studies of water vapor. Our water vapor samples plot parallel to the Global Meteoric Water Line with an average $d$ of 13.5‰, while higher values of $d$ (up to 24‰) are observed in water vapor from AZ and eastern NM. Episodes of elevated $d$ are attributed to advection of moisture from areas of subsiding air over either the Gulf of Mexico or the Gulf of California. Ten pairs of water vapor and precipitation samples collected closely in time (less than 24 hours apart) were tested for isotopic equilibrium. Half of these sample pairs were found to be reasonably close to equilibrium, while the other half could be related by simple atmospheric processes such as Rayleigh fractionation and evaporation. Highly variable $d$ is observed in precipitation samples; this variability is due to evaporation during precipitation events and is not related to variations of the $d$ of the source vapor.
3.1 Introduction

The mass of an individual water molecule depends on the combination of different possible isotopes of H and O. Isotopically "heavy" water molecules, relatively rare in the hydrosphere, include isotopologues HD\(^{16}\)O and H\(_2\)\(^{18}\)O, whereas the overwhelming majority of water molecules are the "light" isotopologue H\(_2\)\(^{16}\)O. Stable isotope ratios (R) of HD\(^{16}\)O:H\(_2\)\(^{16}\)O or H\(_2\)\(^{18}\)O:H\(_2\)O measure the relative abundance of heavy isotopes within a body of water. Isotopic ratios are commonly expressed in delta notation (\(\delta\)) as a departure from standard mean ocean water (R\(_{SMOW}\)) and are written as:

\[
\delta = \left[ \frac{R_X - R_{SMOW}}{R_{SMOW}} \right] \times 1000
\]

When heavy isotopes are preferentially segregated into one phase (A) over the other (B), the fractionation factor (\(\alpha\)) is expressed mathematically as:

\[
\alpha_{A-B} = \frac{R_A}{R_B}
\]

For mathematical reasons, it often convenient to express this fractionation factor as

\[1000\ln(\alpha_{A-B}).\]
Stable isotopic ratios of hydrogen (D/H) and oxygen ($^{18}$O/$^{16}$O) have been used to study various aspects of the water cycle ever since the groundbreaking work of Dansgaard (1953), Epstein and Mayeda (1953), and Friedman (1953). Although there have been countless studies of precipitation, groundwater, surface water, and ice cores using either D/H or $^{18}$O/$^{16}$O, studies that look at both isotopic systems within the same suite of samples are more rare. However, the combination of both isotopic systems provides additional information that one cannot obtain from either system alone.

In an environment where two phases of water are present (such as liquid and vapor), there are two fundamental processes - equilibrium fractionation and disequilibrium kinetic effects - that contribute to the distribution of isotopomers between the two phases. The best understood of these processes is equilibrium fractionation, which requires atmospheric conditions of 100% relative humidity (RH). In equilibrium fractionation, heavier isotopomers are concentrated in the liquid or solid phase relative to the vapor phase during partial phase changes. This is due to the different vapor saturation pressures of the isotopomers - a result of the different bonding energies of the molecules involved. This process is temperature dependent, with higher fractionation between isotopomers occurring at lower temperatures. In the case of a cloud, the temperature at which condensation occurs will affect the isotopic composition of the condensate. In addition, an increasing degree of rainout, described as a variety of empirical "effects" by Dansgaard (1964), results in precipitation with a lesser proportion of heavy isotopes.
Disequilibrium fractionation occurs during evaporation in environments of less than 100% RH. Because of the different masses of isotopomers HD\textsuperscript{16}O (mass = 19), and H\textsubscript{2}\textsuperscript{18}O (mass = 20), the lighter HD\textsuperscript{16}O molecule will have the higher rate of diffusion. During evaporation into dry air, there will be an anomalously high concentration of HD\textsuperscript{16}O over what would otherwise be expected at a given concentration of H\textsubscript{2}\textsuperscript{18}O. This is referred to as deuterium excess (d), which is defined as

\[ d = \delta D - 8\delta^{18}O \]  

(Dansgaard, 1964). Changes in d in water vapor are interpreted to reflect conditions of the water vapor source, particularly relative humidity (Craig and Gordon, 1965) but to a lesser extent water temperature and wind speed (Merlivat and Jouzel 1979; Johnsen et al., 1989).

If precipitation samples are analyzed for both isotopic systems (\(\delta D\) and \(\delta^{18}O\)), it is traditional to express these data on a plot of \(\delta D\) vs \(\delta^{18}O\). When plotted in this manner, precipitation samples from around the world tend to fall on a linear trend with a slope of 8 in \(\delta D\) vs \(\delta^{18}O\) space, known as the "global meteoric water line" or GMWL (Craig, 1961). On average, worldwide precipitation tends to have d values of \(~10\). This is thought to be due to the average relative humidity conditions over the world's oceans. Local deviations from the GMWL are possible and are thought to be related to the climate of the region (Kendall and Coplen, 2001).
The transport and fractionation of stable isotopes in water vapor have been simulated in models with a wide range in complexity. Isotope models fall into two categories. The first type are dynamically simple models that deal with isolated air masses and the isotopic fractionation processes that are occurring within that airmass. Generally, this type of model uses some form of Rayleigh distillation, such as that used by Dansgaard (1964) and then later refined by Friedman et al. (1964), Taylor (1972), Siegenthaler and Matter (1983), and Jouzel and Merlivat (1984). These models can explain many of the observations of stable isotopes in precipitation, but do not simulate all of the complex processes involved in the formation of precipitation, especially over a broad spatial domain (Ciais and Jouzel, 1994).

This inherent deficiency in isolated air mass models eventually led to the incorporation of isotope physics into atmospheric general circulation models (GCMs), the second major category of models used to simulate isotopes in the water cycle. The first successful isotope-enabled GCM is credited to Joussaume et al. (1984) and Jouzel et al., (1987), who incorporated isotope physics into the Goddard Institute for Space Studies General Circulation Model (GISS), a three-dimensional GCM first described by Hansen et al. (1983). Isotope physics were then embedded into the European Centre Hamburg Model (ECHAM) (Hoffman et al., 1998). Both the isotope-enabled GISS and ECHAM models were considered successful in generating the main features observed in global precipitation patterns. Mathieu et al. (2002) incorporated isotope tracers into the Global Environmental and Ecological Simulation of Interactive Systems (GENESIS 2.0 GCM as first described by Pollard and Thompson, 1994); the GENESIS model claimed to
have a more sophisticated parameterization of interactions between precipitation and atmospheric water vapor than previous GCMs. Additional work with GCMs was completed by Noone and Simmonds (2002) who added isotope parameterizations to the Melbourne University GCM (MUGCM), a spectral primitive equation model based on Bourke et al. (1977) and McAvaney et al. (1978).

In the past ~10 years, isotope-enabled models have become more realistic with the incorporation of forcing/nudging techniques from observed data or reanalysis products. For example, Vuille et al. (2003) added sea surface temperature (SST) forcing with observed data to both the GISS and ECHAM GMC models. Yoshimura et al. (2003) used gridded reanalysis data sets (NCAR and ECMWF) with Rayleigh equations to create a model considered to be intermediate between the Rayleigh-type and isotope-enabled GCMs. This model was then expanded by Yoshimura et al., (2004) to enable longer timeframes and then subsequently by Yoshimura et al. (2008) to include spectral nudging. Similarly, Risi et al. (2010) used a nudging technique with reanalysis data and the LMDZ4 GCM. Improved representation of physical processes in models through better parameterization in isotope-enabled GCMs is ongoing (e.g., Lee and Fung, 2008; Bony and Emanuel, 2001; Smith et al., 2006; Lee et al., 2009; Wright et al., 2009).

While GCMs have been a useful tool to help interpret global patterns in stable isotopic ratios of precipitation and vapor, isotope-enabled GCMs have been used to diagnose more specific scientific problems in atmospheric dynamics. For example, Schmidt et al. (2005) used a version of the GISS model to study the exchange of water
vapor between the stratosphere and troposphere. Lee et al. (2009) used the isotope-enabled NCAR-CAM2 GCM to investigate deuterium excess during the last glacial maximum. In other instances scaled-down, simplified, or customized process models other than full GCMs have been run to address specific problems. Ciais and Jouzel (1994) created a one-dimensional model to simulate the physics of mixed clouds (ice and liquid) and the resulting isotopic fractionation. Dessler and Sherwood (2003) studied HDO in the tropical tropopause layer by combining Rayleigh distillation with a convective model utilizing the Emanuel parameterization. Likewise, Bony et al. (2008) developed a one-dimensional model utilizing Emanuel parameterization to investigate the role of tropical convection in the transport of water to the upper troposphere and lower stratosphere. Blossey et al. (2010) developed cloud-resolving simulations of an idealized equatorial Walker circulation to investigate the tropical tropopause layer. Galewsky and Hurley (2010) created an advection-condensation model to diagnose the maintenance of subtropical water vapor. These models each provide a different quantitative framework to address the isotopic ratios of water vapor at various locations in the atmosphere.

Although there has been a substantial investment in developing quantitative theoretical frameworks for interpreting $d$, there are relatively few measurements of $d$ of water vapor. Most $d$ analyses come from ice core studies (e.g., Vimeux et al., 1999, 2001, 2002; Uemura et al., 2004; Masson-Delmotte et al., 2005; Jouzel et al., 2007), paleoclimate studies utilizing groundwater (e.g., Wassenaar et al., 2009) or precipitation (e.g., Rozanski et al., 1993; Gat, 1996; Araguas-Araguas et al., 2000; Harvey, 2001). In
the case of ice and ancient groundwater, $d$ values are regarded as proxies of palaeoclimate conditions. However, there is very little water vapor data to provide ground truth for the existing models. Consequently, there have been field campaigns to determine $d$ of marine water vapor (e.g., Craig and Gordon, 1965; Gat et al., 2003; Lawrence et al., 2004; Uemura et al., 2008). In Europe, Schoch-Fischer et al. (1984) reported $d$ of water vapor captured in 24-hr increments over a ~8-year period in Germany. Dirican et al., (2005) reported $d$ in water vapor samples taken intermittently during a ~1-year field campaign in Turkey. Araguas-Araguas (2005) reported $\delta^{18}O$ in water vapor captured in Spain, though $d$ values were not reported on or investigated by the author. Similarly, Carreira (2005) reported $\delta^{18}O$ values from water vapor samples collected in Portugal, but provided no discussion about $d$. In recent years, more studies of $d$ in water vapor have begun to appear in the literature with the advent of tuned laser diode cavity wavelength-scanned cavity ringdown spectroscopy (Lee et al., 2005; Crosson, 2008; Brand et al., 2009; Gupta et al., 2009). Wen et al. (2010) have reported $d$ values for a continuous one-year study of surface water vapor in Beijing, China, showing that $d$ values there are generally lower and have less scatter in the summer. Galewsky et al. (2011) have reported $d$ values from a continuous ~2-month study from the Chajnantor Plateau in Chile, showing a correlation between $d$ and heavy isotopic enrichment.

While studies investigating the stable isotope composition of water vapor are few compared to the relatively vast number of precipitation studies, the number of papers that examine the relationship between the isotopic covariability of water vapor and
precipitation is smaller still. Jacob and Sonntag (1991) report that, during their 8-year field program in Germany, individual precipitation events and concurrent water vapor were usually not in isotopic equilibrium, though the monthly means of each were close to equilibrium. Similarly, isotopic surveys of water vapor and precipitation on the Iberian Peninsula (Carreira et al., 2005; Araguas-Araguas et al., 2005) show that long-term averages are approximately in equilibrium although the relationship between vapor and individual precipitation events is unclear. Wen et al. (2010) reported that the $d$ departure from equilibrium of vapor-precipitation pairs sampled in Beijing is negatively correlated with relative humidity.

In this paper we present a ~1-year study in which water vapor and precipitation were collected and analyzed for $\delta^D$ and $\delta^{18}$O in a semi-arid continental setting (the American Southwest). We examine the vapor data in $\delta^D - \delta^{18}$O space to compare against the GMWL as well as local precipitation. We investigate the relationship between the isotopic compositions of precipitation events and contemporaneous water vapor (pairs of samples taken within 24 hours) in an effort to determine if isotopic equilibrium exists between the surface-level water vapor and collected precipitation. Atmospheric processes involving precipitation formation, evaporation, and exchange with water vapor are simulated with simple models, while meteorological conditions at the time of sample collection are examined to evaluate the proposed models.
3.1.1 Study Area

Water vapor and precipitation samples were collected primarily in Albuquerque, NM. Additional vapor samples were collected sporadically at various sites in Arizona (AZ), Eastern NM, and Texas (TX) (Figure 1). The Albuquerque site, with an altitude of 1620 m, is located in an urban environment surrounded by arid desert with 215 mm of average annual rainfall. Approximately half of the yearly precipitation falls in July-August-September with the arrival of monsoonal moisture from the south. NM lies in the northern portion of the North American Monsoon System (NAMS), a convective circulation system that is centered in northwest Mexico (MX) but greatly affects the US states of AZ and NM (Douglas et al., 1993; Adams and Comrie, 1997). NM occasionally receives precipitation from the remnants of Pacific cyclones in late summer (Etheredge et al., 2004; Ritchie et al., 2011) while midlatitude storms originating over the Pacific Ocean provide sporadic precipitation during the remainder of the year (Tuan et al., 1973).

3.2 Methods

Water vapor was trapped cryogenically in a system of two concentric glass tubes shown in Figure 2. Moist air is drawn into the larger tube via a vacuum pump at a rate of 1-2 L/min. Ice precipitates on the walls of the glass tubes and particularly on the nichrome wire coil. Strategically placed dents in the outer glass tube prevent ice from
accumulating in one spot, which would otherwise form a blockage. The bottom of the outer tube is expanded into a bulb shape while the inner tube is elevated ~2 cm from the bottom. This allows falling ice crystals to accumulate in the bottom without being sucked out of the system. Dry air ultimately exits the small tube. In the field, air is pumped through the system until approximately 1 mL of water is obtained, which takes ~20 minutes to ~2 hours depending on the local dew point. After pumping is completed, the inner tube is pulled up a few cm, cut to a slightly shorter length than the outer tube, dropped down into the outer tube, and the entire sample is sealed with a stopper or wax. The sample stays in this tube until the extraction process at a later time.

In the laboratory, samples were extracted on a vacuum line and transferred to a glass vial. Hydrogen gas was generated with chromium reduction on a Finnegan HDevice and measured on a Finnigan Mat 252 mass spectrometer. Oxygen isotope values were determined using CO$_2$ equilibration [Epstein and Mayeda, 1953] with analysis on a Finnigan Delta Plus mass spectrometer. Analytical precision is +/- 1‰ for hydrogen and +/- 0.1‰ for oxygen. Data are reported relative to SMOW, defined such that IAEA water standards VSMOW and SLAP have $\delta^D$ values of 0.00 and -428.00‰ while $\delta^{18}O$ have values of 0.0 and -55.50‰, respectively.

To verify that our cryogenic system was working and capturing ~100% of the water vapor moving through the system, we compared $\delta^D$ values of cryogenic samples with $\delta^D$
values of concurrent water vapor samples taken with glass flasks as described in Strong et al. (2007). Water vapor samples gathered by flasks (which capture water vapor nearly instantaneously) were taken before and after the cryogenic sample. The δD values from cryogenically trapped water samples were identical (within analytical error) or between the δD values from water vapor collected by the flasks. This experiment was repeated over several weeks at different dew points until we were convinced that the cryogenic system was working properly.

The majority of the water vapor samples were collected on the roof of Northrop Hall, the 3-story Earth and Planetary Sciences (EPS) building at the University of New Mexico (central Albuquerque). The majority of the sampling occurred between April 2007 and October 2007, with a few samples taken in the winter months. Water vapor samples taken in locations other than EPS were taken 0.5 to 1.5 meters above the ground. Precipitation was also collected during the study period by trapping hydrometeors from individual storm events under mineral oil. Samples were collected on the EPS roof, the same location as vapor sampling. Stable isotope compositions were determined by chromium reduction (for δD) and CO₂ equilibration (for δ¹⁸O) as described above. Weather conditions were recorded every 15 minutes with a Davis Weather Station, also mounted on the EPS roof. In total, 106 vapor samples and 40 precipitation samples were collected and analyzed for δD and δ¹⁸O.
3.3 Data

The isotopic compositions of water vapor and precipitation samples are presented in Figure 3. Very broadly, isotopically depleted water vapor is common in the winter while summer water vapor is isotopically enriched, as discussed in detail in Chapter 2. Beyond these seasonal trends, however, it is difficult to discern any clear pattern between isotopic composition and air temperature or collection date. For example, there are examples of anomalously light vapor occurring in July (7-22, 7-24, 7-26) and anomalously heavy vapor occurring in the spring (e.g., 5-19, 5-25). Water vapor with notably low $\delta^D$ values were collected in Albuquerque on 9-6, concurrent with arrival of moisture from Hurricane Henriette (Chapter 2).

In $\delta^D - \delta^{18}O$ space, most Albuquerque water vapor samples plot to the left of and parallel to the GMWL, with an average $d$ value of 13.5‰ with a standard deviation of 10.4‰ (Figure 3). Vapor samples taken in AZ and TX tend to also plot along this trend, though some samples, particularly from AZ (e.g., 7-21), have higher values of $d$ than samples taken in Albuquerque. The highest $d$ value observed was 25.2‰ and was captured in southern Arizona on 7/21/07. We also have negative $d$ values that range down to -52.9‰, but it is not known if these negative values are actually representative of collected water vapor or an artifact of an analysis gone awry. By comparison, precipitation samples have more scatter than the vapor samples, with most (but not all) samples plotting to the right of the GMWL.
3.4 Relationship between precipitation and vapor

Our goal in this section is to evaluate whether any meaningful relationship exists between the vapor and precipitation samples collected closely in time. In particular, we investigate whether the water vapor collected at the surface could be a source for the subsequent precipitation. Within the dataset presented here, there are 10 instances of precipitation occurring within 24 hours after a vapor sample was collected. The vapor-precipitation pairs are plotted in δD - δ¹⁸O space in Figure 4 along with the collection times and size of precipitation events. A cursory check for equilibrium between vapor and subsequent precipitation samples indicates that the relationship between each of the 10 water vapor - precipitation pairs is not the same. We have plotted the 10 vapor-precipitation pairs in 1000In(α) space along with equilibrium curves based on fractionation factors from Majoube (1971) for liquid-vapor and Merivat and Nief (1967) for ice-vapor. As illustrated in Figure 5, five of the vapor-precipitation pairs (5, 7, 8, 10, and 2) lie near the equilibrium curve at temperatures that are reasonably close to observed surface temperatures (with the possible exception of point 2 which requires a temperature close to 37°C). The precipitation values from these five pairs plot relatively near the GMWL in Figure 3. The other five pairs plot distinctly away from the equilibrium curves in Figure 5, and are more distant from the GMWL in Figure 4.

The known equilibrium fractionation factors for liquid-vapor and ice-vapor illustrate that it is impossible for a rain composition to the right of the GMWL to be in isotopic equilibrium with vapor plotting to the left. Figure 6 illustrates this with water vapor
collected 11am on 8/26/07 followed by precipitation from a thunderstorm at 9pm on the same day. Liquid-vapor fractionation factors (Majoube 1971) require that any rain in equilibrium with the 8-26 water vapor will lie along the “liquid” line in Figure 6, which increasingly deviates from the GMWL with decreasing temperature. Ice-vapor fractionation factors (Majoube, 1970; Merlivat and Nief, 1967) predict that ice will similarly fall to the left of the GMWL, albeit at higher delta values. The “supercooled liquid” line was generated using the supercooled water fractionation factor published for hydrogen (Merlivat and Nief, 1967); without similarly published values for oxygen, an average between ice (Majoube 1970) and liquid (Majoube 1971) was used. As with the liquid and ice curves, the supercooled liquid line also plots to the left of the GMWL.

All of the equilibrium fractionation curves show that any liquid in equilibrium with our 8/26/07 vapor sample must fall to the left of the GMWL. The location of the 8/26/07 precipitation to the right of the GMWL indicates that the vapor and precipitation are not in isotopic equilibrium.

While condensation within a cloud is an equilibrium process, the continuous removal of precipitation changes the isotopic composition of both the precipitation and the residual vapor in the system. This process can be modeled as Rayleigh distillation, an idealized process that was described mathematically as

$$\left( \frac{R}{R_i} \right) = f^{\alpha - 1}$$

where R and R_i represent the heavy/light ratios of the system and initial reservoir, respectively. F is the fraction of the initial system remaining, and alpha is the
equilibrium fractionation factor; Rayleigh fractionation assumes equilibrium fractionation at the moment of condensation. This equation can be converted into delta notation as

\[
\frac{1000 + \delta_l}{1000 + \delta_{l'}} = f^{\alpha_{l-v}-1}
\]

for the liquid phase, and

\[
\frac{1000 + \delta_v}{1000 + \delta_{v'}} = f^{\alpha_{l-v}-1}
\]

for the vapor phase. Here we use the Rayleigh fractionation model to explore isotopic variations between pairs of vapor and precipitation collected closely in time.

First, we model the effect of simple Rayleigh distillation on cumulative precipitation. Our starting temperature is the dew point of the collected air sample on 8/26/07. From there, the temperature is decremented in steps of 0.1 degrees C. In each temperature step, the mass of liquid in excess of saturation is calculated. The equilibrium fractionation factors for oxygen and hydrogen are then calculated based on the temperature-dependent fractionation factors from Merlivat and Nief (1967), Majoube (1970), and Majoube (1971). These fractionation factors are used to calculate the isotopic composition of the liquid excess. This liquid excess is then removed from the system, and the temperature is decremented another step of 0.1 degrees C. The isotopic composition of the cumulative precipitation from this process is shown in Figure 7; the trajectory of the bulk precipitation parallels the GMWL as does the residual vapor.
Thus Rayleigh distillation itself does not change the $d$ value under the conditions modeled here.

Raindrops descending through an air column can undergo significant changes in isotopic composition due to evaporation and/or exchange processes (Stewart 1975). The evolution of the rain’s isotopic composition depends on the relative humidity and the isotopic composition of the water vapor in the air column. The $R$ value of a falling drop changes according to:

$$ R_w = (f^u)(R_{wi} - R_s^i) + R_s^i $$

where $R_w$ is the instantaneous $R$ of remaining water drop, $R_{wi}$ is the initial $R$ of water drop, and $f$ is the fraction of the water drop remaining (Criss, 1999). The exponent $u$ above is defined as:

$$ u = \frac{1 - \alpha_{evap}^o (1 - h)}{\alpha_{evap}^o (1 - h)} $$

where $\alpha_{evap}^o$ is the fractionation factor for evaporation into a vacuum, and $h$ is relative humidity (0 to 1). The term $R_s^i$ in equation 3.6 is defined as:

$$ R_s^i = \frac{\alpha_{eq} h R_v}{1 - \alpha_{evap}^o (1 - h)} $$

where $\alpha_{evap}^o$ is the fractionation factor for evaporation into a vacuum (Craig et al., 1963; Criss, 1999), $\alpha_{eq}$ is the equilibrium fractionation factor for liquid-vapor (Merlivat and
Nief 1967; Majoube 1971), $R_v$ is the R value of the atmosphere, and $h$ is the relative humidity (0 to 1). This $R_w$ term represents the R value that the liquid will approach over time. At 100% RH, exchange reactions between the raindrop and the water vapor in the atmosphere will drive the isotopic composition of the drop toward a value in equilibrium with the atmosphere. At zero percent humidity, the isotopic composition of the evaporating drop will follow a Rayleigh distillation curve. At values of RH less than 100%, a combination of evaporation and exchange reactions will cause the drop to approach an isotopic composition between the two values dictated by fractionation factors $\alpha_{evap}$ and $\alpha_{eq}$ (Criss, 1999).

To evaluate the potential relationship between pairs of collected precipitation and vapor, we combine the Rayleigh condensation model with the above equations for a falling raindrop through an air column. For simplicity, in our model the air column below cloudbase is homogenous in both RH and isotopic composition. Condensate is formed in equilibrium with the vapor and then removed from the system by the Rayleigh condensation model described above. The Rayleigh process continues until a predetermined percentage of initial vapor has been condensed into liquid. The cumulative condensate is then used as a starting composition for subsequent evaporation and exchange reactions with the air column. We performed many model runs varying (a) the percentage of initial condensate from Rayleigh fractionation, (b) different relative humidities of the lower atmosphere, and (c) varying fractions of evaporation for each of the vapor-precipitation pairs presented in Figure 4. Examples of model outputs for four of our vapor-precipitation pairs are shown in Figure 8. For most
of the vapor-precipitation pairs, the precipitation can be derived from the vapor by
removal of 10-40% of the water from the vapor via Rayleigh condensation followed by
evaporation of 10-30% of the drops as they fall through air of 10-50% RH. This degree of
rainout is consistent with precipitation efficiency of thunderstorms as reported by
Fankhauser (1988).

If our model is correct, then we should expect to see an inverse relationship between
lower atmospheric RH and the precipitation \( \delta \) value’s distance from the GMWL.
Atmospheric soundings from weather balloons released from Albuquerque International
Airport (~7km south of the EPS collection site) were used to assess the precipitation
samples. Precipitating clouds in Albuquerque's desert climate often occur in an
environment with a deep dry subcloud layer where RH is much less than 100%.
Although the temporal resolution of atmospheric soundings (12 hours) does not permit
validation with every collected precipitation sample, there does appear to be an overall
trend between the RH of the air column and the sample’s distance from the GMWL
(Figure 9). Air columns with exceptionally low RH are usually associated with
precipitation samples farthest to the right of the GMWL (e.g., Figure 9, May 13th
sounding). Moderately dry air columns are associated with precipitation samples closer
to - but still to the right of - the GMWL (e.g., Figure 9, Sept 23rd sounding). Precipitation
samples that are found to the left of the GMWL are associated with deep columns of
humid air (e.g., Figure 9, May 02). Presumably, precipitation at the surface below a
near-saturated air column are the most likely to represent cloud water with little
evaporation (though exchange with the humid air column cannot be ruled out).
3.5 Analysis of deuterium excess values

One of the most striking features about our Albuquerque vapor samples is their relatively constant $d$, causing them to plot nearly parallel to the GMWL. Assuming that this is telling of some atmospheric process at work, we investigate the possible processes responsible for this pattern and compare our data to other published vapor data.

The $d$ of water vapor is set by conditions at the source - particularly from relative humidity and wind speed (Merlivat and Coantic, 1975; Vogt, 1976; Merlivat and Jouzel, 1979). During evaporation, the lighter and more diffusive HD$^{16}$O will be overrepresented compared to the heavier H$_2^{18}$O, causing an excess of deuterium in the water vapor over what would be expected for equilibrium conditions (Dansgaard, 1964; Craig and Gordon, 1965). This effect increases with drier air at the water/air interface, with the maximum theoretical $d$ occurring during evaporation into air of zero humidity (Craig et al., 1963). Over time, a buildup of water vapor in the boundary layer will begin to favor equilibrium exchange, and the deuterium excess within the vapor will be lessened with continued exchange with the seawater (Craig and Gordon, 1965; Gat et al., 2003). Removal of the boundary layer in windy conditions will help preserve a layer of dry air at the surface, maintaining elevated levels of $d$. An air mass suspended above a body of water for a sustained time should eventually reduce its $d$ as the RH of the air mass increases from continued marine interaction (e.g., Gat et al., 2003).
Once an air mass leaves the marine environment and moves over the continent, there are relatively few mechanisms to change $d$ values. As previously illustrated in Figure 7, Rayleigh distillation does not appreciably change $d$ values and instead produces trajectories of isotopic composition nearly parallel to the GMWL. Collection of precipitation samples as airmasses move inland over a continent have shown that $d$ values stay relatively constant as the degree of rainout increases (Yurtsever and Gat, 1981; Sonntag et al., 1983; Schoch-Fischer et al., 1984). Instead, a seasonal cycle in $d$ values is observed in precipitation at subtropical and higher latitudes as the temperature and RH conditions of the moisture source changes throughout the year (Rozanski, 1993; Gat, 1996).

Equilibrium condensation and Rayleigh fractionation aside, there are still ways that the $d$ values of water vapor might change after it leaves its marine source. Experimentally derived equilibrium fractionation factors for ice at very low temperatures show deviation from the GMWL (Majoube, 1970, 1971). Additionally, ice formation and removal under supersaturated conditions should result in residual water vapor with higher $d$ due to kinetic effects (Jouzel and Merlivat, 1984; Galewsky et al., 2011). Under the conditions of low RH and high surface winds, evaporation from soil or surface water could contribute water vapor of increased $d$, though it is unlikely that enough moisture could be added to the atmosphere in this manner to measurably change the $d$ of the airmass (Strong et al., 2007). Probably the most significant process available to change $d$ is the partial evaporation of raindrops as they descend through the air column. As explained in the previous section, raindrops will evolve toward lower
$d$ values, moving them to the right of the GMWL. From mass balance requirements, the air column must then increase in $d$ from the contributions of evaporating drops. While partial evaporation of raindrops is evidently occurring, the constant $d$ in our water vapor samples suggests that the amount of recycled water vapor from partial evaporation of raindrops is trivial compared to the initial reservoir of vapor in the atmosphere.

A handful of other vapor studies provide useful comparisons for our dataset. Gat (2003) collected water vapor over the Mediterranean Sea from both the mast and deck of a ship. In general, the Mediterranean samples are isotopically heavier than our vapor samples, with higher (and more variable) $d$ (Figure 10). The high $d$ is interpreted to be caused by dry continental air from Africa or Europe interacting with warm seawater, resulting in episodes of intensive evaporation. We have also compared our data to that of Lawrence et al. (2004), who collected tropical water vapor from Puerto Escondido during the summer of 1998. Compared to our data, the tropical samples tend to be isotopically enriched (with the exception of a cluster of isotopically light samples associated with Tropical Storm Celia) and exhibit more variability in $d$ values (Figure 10). In general, our data overlap with both Gat (2003) and Lawrence et al. (2004), but differ in that the scatter in $d$ values is not nearly as large as reported in either of those two datasets.

Galewsky et al. (2011) measured upper tropospheric water vapor from Chajnantor Plateau in Chile using cavity ringdown spectroscopy during July and August 2010. Their data is shown in Figure 11, along with Rayleigh distillation curves under ice
supersaturation. Our data barely overlap with isotopically heaviest values from Galewsky et al. (2011), but appear continuous with the isotopically heaviest end of their dataset (blue points, Figure 11). This suggests that ice formation or sublimation under supersaturated conditions is probably not an important process that contributes to the overall isotopic composition of water vapor that we are measuring at the surface.

Instead, the present results seem more consistent with the processes of mixing and Rayleigh fractionation.

3.6 Evaluating source conditions

To evaluate possible source conditions for our water vapor samples, it is a useful exercise to compare our data with δD and δ18O values expected from marine water vapor. Although water vapor above the ocean is never truly in isotopic equilibrium with the ocean, the system does reach a steady state where the isotopic composition of the water vapor is relative constant. The evaporation process has been modeled from diffusion theory by Ehhalt and Knott (1965) while a derivation from kinetic theory is provided by Criss (1999). Both approaches lead to similar results for the fractionation of heavy isotopes between the ocean and marine water vapor. From Criss (1999), the fractionation factor for net evaporation from a body of water can be modeled as:

\[ \alpha_{evap} = \frac{R_w}{R_E} = \frac{\alpha_{evap}^o(1-h)}{1-\alpha_{eq}h R_v/R_w} \]  

3.10
where $R_E$ is the isotopic ratio of water being lost to the atmosphere at any instant, which itself is a net weighted difference between the incoming and outgoing water fluxes. $R_W$ is the isotopic ratio of the ocean, $R_v$ is the isotopic value of the water vapor above the ocean, $\alpha^{\text{evap}}$ is the fractionation factor for evaporation into a vacuum, $\alpha_{\text{eq}}$ is the equilibrium fractionation factor (at 100% relative humidity), and $h$ is the relative humidity (0-1). Craig and Gordon (1965) estimated that the average value of $\delta^D$ and $\delta^{18}$O for precipitation on Earth is -26‰ and -4.5‰ respectively, which gives $\alpha_{\text{evap}}$ values of 1.0267 and 1.0045 respectively.

Using these values for $\alpha_{\text{evap}}$, the temperature-dependent fractionation factors for equilibrium $[\alpha_{\text{eq}}]$ (Merlivat and Nief 1967; Majoube 1971) and evaporation into a vacuum $[\alpha^{\text{evap}}]$ (Craig et al., 1963; Criss, 1999) we calculated the steady state isotopic compositions of marine water vapor expected at different values of SST and RH. Fields of water vapor compositions expected above marine environments as predicted by equation 3.10 are plotted on Figure 10 according to SST and RH. Approximately half of our Albuquerque vapor samples, including all winter and fall but also a fair proportion of spring and summer samples, are too depleted in heavy isotopes to plot within any SST/RH field as predicted by the steady-state model. The other half, which are exclusively summer and spring samples, fall within fields corresponding to source water SSTs of 0 - 30°C and RH values of 80 - 90%. Of these, the overwhelming majority fall within SST fields below 20°C. Summer water vapor in NM likely originates from the Gulf of Mexico and/or the Gulf of California, which have SSTs from ~20°C to 30°C during the spring and summer season (Mitchell et al., 2002). This suggests that Albuquerque vapor
samples are mostly not in equilibrium with their marine sources, and are likely depleted in heavy isotopes from rainout, amount effect, and/or mixing over the continent.

Vapor samples collected in AZ, Eastern NM, and TX follow similar trends to the Albuquerque samples, though slightly more variability in $d$ is noted. Southern AZ samples, which were usually collected during summer Gulf Surge events (Stensrud et al., 1997), are geographically close (<100 km) to their moisture source in the Gulf of California. While a few samples do plot in marine vapor fields reasonably close to observed SSTs, most are too isotopically depleted to reasonably be in steady state with gulf marine water. This may indicate that air has not resided over the Gulf of California long enough for thorough exchange to take place. However, the overall lack of exceptionally high $d$ values (e.g., Gat et al., 2003) implies that this is not the case, suggesting that either rainout or the 'amount effect' (Dansgaard, 1964; Risi et al., 2008) may be the cause for the depleted isotopic values.

### 3.7 High $d$ value samples

Although our vapor samples from Albuquerque have relatively constant $d$ values, there are a few samples from AZ and eastern NM with higher $d$ values that plot noticeably farther from the GMWL than the rest of our vapor samples. To southwest of ABQ, the water vapor samples with the highest $d$ values - up to 24‰ - were collected in southern AZ during the Gulf Surge event of 7/21/07 (labeled in Figure 3). In the days prior to the Gulf Surge, high pressure centered over the 4-corners region extended southward over the Gulf of CA. This high persisted for several days as shown in the 3-
day composite map of 700hpa geopotential height in Figure 12A. A passing easterly wave, shown in Figure 12B, sets up the Gulf Surge event that moves Gulf of CA moisture northward into AZ as shown in the 24-hr forward trajectories in Figure 12B (dotted lines). The high $d$ values for this moisture are likely due to the interaction of dry descending air from the high pressure preceding the surge event. Just prior to the gulf surge event, marine water was evaporating into descending dry air, creating anomalously high $d$ values over the Gulf of CA. At the time this vapor was sampled, moisture was being advected into AZ by the easterly wave.

A similar situation exists for the Gulf Surge sample collected 9/5/07. Although its $d$ value is not as high as the previous example ($d = 21\%$), it still plots notably farther from the GMWL than the surrounding samples (see Figure 3). Prior to the Gulf Surge event of 9/5/07, a high pressure system was persistent in the 4-corners region for about 7 days before a Gulf Surge, initiated by Hurricane Henriette, pushed gulf moisture into southern AZ. Although subsidence from this high pressure region did not extend as far south as the previous example, the elevated $d$ in the 9/5/07 sample suggests that there was a high flux of dry air interacting with the surface of the Gulf of CA. A similar situation also existed for the vapors collected in southern AZ on 5/29/07. In this third example, high pressure over the Gulf of CA persisted several days before the arrival of an easterly wave across central MX. Southerly flow from the gulf brought moisture into southern AZ, which was measured to have $d$ values of 19‰.
With regards to sampling done to the southeast of ABQ, most of the water vapors collected in eastern NM and/or TX do show d values similar to those collected in Albuquerque. Our most direct samples of Gulf of Mexico moisture were collected at Corpus Christi on May 15th. With an average d value of 18.2‰, these samples are only slightly higher than our dataset average value of 13.5‰. These samples are the isotopically heaviest within our dataset, and plot within the marine vapor fields at temperatures slightly warmer than the local SST of 28°C. They also plot within the range of marine vapor samples collected by Craig and Gordon (1965) over the Pacific Ocean.

One sample from southeastern NM that does have an anomalously high d value (21‰) was collected on 8/6/07 (Figure 3). The atmospheric conditions responsible for the generation of this water vapor are similar to the previous examples of high d vapor from the Gulf of CA, except that in this situation the vapor originated over the Gulf of MX. Several days prior to the collection date, a ridge of high pressure over the east coast of MX and the northeastern portion of the Gulf of MX caused prolonged subsidence, bringing dry air aloft over this portion of the gulf. The subsidence can be seen in the 3-day composite map of Omega (dp/dt) at the 700hpa level (shaded background, Figure 13B). At the time of sample collection, anticyclonic circulation around a High centered over eastern OK and cyclonic circulation around a Low centered over western TX (Figure 13A) transported moisture from the northwestern part of the Gulf of MX into southeastern NM (see 24-hr forward trajectories, Figure 13B). This sample was collected in SE New Mexico, directly in the path of the trajectories shown in Figure 13B.
The only samples with anomalously high $d$ values in our entire dataset were collected in either southern AZ or eastern NM. By comparison, the $d$ values of water vapor collected in ABQ are relatively constant. Most likely the reason for this is the geographical location of Albuquerque in central New Mexico, which prevents vapors of high $d$ from reaching the collection site. Vapors with high $d$ could be generated over either the Gulf of CA or Gulf of MX if vigorous subsidence were occurring over either body of water. Although several conditions could lead to subsidence, a large area of sinking air lasting several days would almost certainly require a significant High pressure system to build over the source vapor region. While High pressure systems do occasionally build over the Gulf of CA and are very common over the Gulf of MX, the very existence of High pressure in either location causes circulation patterns that deflect this moisture from central NM. For example, while a strong High pressure may be generating vapor with high $d$ values over the Gulf of MX, anticyclonic circulation around that High would advect this moisture to the eastern states, away from NM.

An illustration of this can be seen in the days immediately following the high $d$ sample of 8/4/07 (discussed above). This sample was taken in southeastern NM at a time when a high pressure system was migrating westward over the Gulf of NM (the western extension of which can be seen in Figure 13A). Although atmospheric conditions at 8/4/07 0z allow for the transport of moisture from the northwestern Gulf of MX into NM, the building ridge of high pressure (seen in Figure 13C) quickly shifts advection to the northeast (as shown in the 24-hr forward trajectories of Figure 13D). At the same time, the Omega map (shaded background in Figure 13D) shows an increase
in subsidence over that shown in Figure 13B, due to the increased influence of the building high pressure. So while $d$ values of water vapor from the northwestern Gulf of MX probably increase after our sample of 8/4/07 was taken, advection carries this moisture to the northeast and away from New Mexico.

In a similar manner, stationary High pressure over the northern Baja Peninsula would be conducive to the generation of water vapor with high $d$ values. However, if this were to occur, the resulting vapor would be advected anticyclonically around the high and likely transported southwest over the Pacific Ocean instead of toward Albuquerque. Thus the few samples of elevated $d$ that we did collect are representative of special circumstances (such as a high pressure system interrupted by an easterly wave) and sampling in the correct geographic locations.

### 3.8 Conclusions

New Mexico is uniquely situated in that it is roughly equidistant between three potential moisture sources: The eastern Pacific Ocean, the Gulf of CA, and the Gulf of MX. Because of this, NM seems well-suited as a testing ground to search for variations of water vapor $d$ in a continental setting. However, despite the numerous sources of moisture affecting NM, we find that the $d$ is relatively constant, especially when compared to similar studies of marine vapor.

The generation of water vapor with high $d$ is generally thought to be the consequence of dry (low RH) air impinging on bodies of surface water. This usually
requires subsidence of dry air aloft, a feature normally associated with areas of high air pressure. Such ridges of high pressure are common in the region, especially over the Gulf of MX. These conditions seem ripe for the generation of water vapor with elevated values of \( d \), but high values of \( d \) are not observed in Albuquerque. Instead, vapor samples in our dataset with the highest values of \( d \) were collected in southern AZ and southeastern NM. In these instances, subsidence was occurring over the source body of water several days before a change of atmospheric conditions advected this moisture onto the continent.

Our samples of elevated \( d \) were captured during transient events in the atmosphere; areas of subsidence were interrupted in such a way that moisture from these regions may have been advected inland a short distance, though not to Albuquerque. In general though, large scale subsidence over either gulf will not result in the advection of moisture into NM due to the anticyclonic circulation around centers of high pressure. If marine water vapor with high \( d \) values are being generated within an intense anticyclone over the Gulf of MX, those air parcels would be transported over the southeastern US and miss NM completely. High pressure centers over the northern Gulf of CA are rare, but when they occur moisture will be advected southwest over the Pacific Ocean. For these reasons, high \( d \) values are not expected in central NM.

Despite the relatively constant values of \( d \) observed in Albuquerque's water vapor, we observe much more variability of \( d \) in our precipitation samples. From ten pairs of stable isotope measurements of water vapor and precipitation related closely in time,
we observed that half of these samples are roughly in isotopic equilibrium while half are not. Of the half that are not, it can be shown that the precipitation compositions can be derived from the vapor compositions through simple combinations of Rayleigh fractionation and evaporation processes. Raindrops falling through the lower atmosphere are subject to evaporation and exchange reactions with water vapor in the lower atmosphere, thereby altering their isotopic composition. The $d$ of precipitation varies inversely to the RH in the lower atmosphere.

The reconstruction of past climates from records such as ice cores depend on the interpretation of variations in $d$. We offer two insights into the variability of $d$ that should be considered, especially in the interpretation of continental ice cores. First, we have shown that the $d$ of precipitation is highly dependent on the conditions of the lower atmosphere. Extremely low values of $d$ in precipitation are not associated with water vapor of low initial $d$, but instead are caused by evaporation of falling hydrometeors through lower tropospheric air of low RH. Precipitation in isotopic equilibrium with water vapor is only possible when the air column is saturated (100% RH). Second, we have illustrated that geographic location is an important consideration in interpreting variations in $d$ (or the lack thereof). In the case of New Mexico, its location naturally acts as a low-pass $d$ filter, as meteorologic conditions that should create vapor with high $d$ also serve to deflect these vapors from NM. Interpretation of continental ice cores should consider these same processes when interpreting variations in $d$. 
3.9 Figures

Figure 1 - Location Map

Location Map of study area. All precipitation and most water vapor samples were collected in Albuquerque; additional water vapor was collected at locations shown (black dots).
Figure 2 - Cryogenic Trap

Schematic diagram of cryogenic device used to trap water vapor for $\delta$D and $\delta^{18}$O analysis. Air enters the glass outer tube, which is submerged in a dry ice/ethanol slurry.

Ice crystallizes on the nichrome wire and around the dents.
Figure 3 - caption next page
Figure 3 - caption

Water vapor and precipitation data plotted in $\delta D - \delta^{18}O$ space. Deuterium excess ($d$) is represented as a vertical distance on this plot. The global meteoric water line (GMWL) has a $d$ of 10‰; our vapor samples have an average $d$ value of 13.5‰. All dates are in 2007. Solid black dots represent water vapor captured in Albuquerque, green triangles represent precipitation collected in Albuquerque. Red squares are vapor samples collected from southern AZ while blue circles are vapor samples from southeast NM or western TX.
Pairs of vapor samples with precipitation collected less than 24 hours afterward. Vapor samples are underlined; precipitation samples are not. See table (inset) for collection times.
Figure 5 - vapor-precip pairs in 1000ln(\alpha) space

Water vapor – precipitation pairs plotted in 1000ln(\alpha) space. The black line illustrates the range of isotopic compositions that would be in equilibrium at the temperatures shown. Sample numbers are from Figure 4.
Figure 6 - Equilibrium Fractionation

Plots of possible liquid and ice compositions that would be in equilibrium with the 8/26/07 surface-level water vapor. Fractionation is temperature dependent as shown.
Using the 8/26/07 vapor as a starting point, Rayleigh fractionation would produce cumulative liquid compositions as shown on the solid black arrow. Numbers along the arrow represent percentages of condensate from the initial vapor. As condensation increases, the isotopic values for the bulk precipitation and residual vapor both decrease. However, d does not change in this process.
Figure 8 (part A) - caption next page
Figure 8 (Part A) - Caption

Vapor-precipitation sample pair for vapor collected on 8-26-07 (11am) and precipitation collected on 8-26-07 (9pm) are shown. The vapor composition is used as a starting point for Rayleigh fractionation. The cumulative condensate composition is shown parallel to the GMWL; numbers next to this line represent percentages of condensate from the original air mass. Dotted lines emanating from the Rayleigh line are trajectories of evaporation at different values of relative humidity (shown as 'h'). Larger dots along these evaporation trajectories denote percentages of raindrop evaporation.

The isotopic composition of the precipitation can be achieved with a relatively small amount of condensation (~10%) that then loses ~20% of its volume through evaporation through the subcloud layer.
Figure 8 (Part B) - caption next page
Figure 8 (Part B) - Caption

Vapor-precipitation sample pair for vapor collected on 7-14-07 (2pm) and precipitation collected on 7-15-07 (5pm) are shown. The vapor composition is used as a starting point for Rayleigh fractionation. The cumulative condensate composition is shown parallel to the GMWL; numbers next to this line represent percentages of condensate from the original air mass. Dotted lines emanating from the Rayleigh line are trajectories of evaporation at different values of relative humidity (shown as 'h'). Larger dots along these evaporation trajectories denote percentages of raindrop evaporation. The isotopic composition of the precipitation can be achieved with a moderate amount of condensation (~50%) that then loses ~25% of its volume through evaporation through the subcloud layer.
Figure 8 (Part C) - caption next page.

- δD vs. δ¹⁸O plot showing data points and trend lines.
- Labeled axes: δD, δ¹⁸O.
- Annotations: vapor: 7-24-07 11:30am, Residual Vapor, precip: 7-24-07 2:20pm 0.1".
-标注了不同百分比的凝结和雨滴蒸发的线。
Figure 8 (Part C) - Caption

Vapor-precipitation sample pair for vapor collected on 7-24-07 (11:30 am) and precipitation collected on 7-24-07 (2:20 pm) are shown. The vapor composition is used as a starting point for Rayleigh fractionation. The cumulative condensate composition is shown parallel to the GMWL; numbers next to this line represent percentages of condensate from the original air mass. Dotted lines emanating from the Rayleigh line are trajectories of evaporation at different values of relative humidity (shown as ‘h’).

Larger dots along these evaporation trajectories denote percentages of raindrop evaporation. The isotopic composition of the precipitation can be achieved with a small amount of condensation (~10%) that then loses ~20% of its volume through evaporation through the subcloud layer.
Figure 8 (Part D) - caption next page
Figure 8 (Part D) - Caption

Vapor-precipitation sample pair for vapor collected on 7-19-07 (9pm) and precipitation collected on 7-20-07 (1am) are shown. The vapor composition is used as a starting point for Rayleigh fractionation. The cumulative condensate composition is shown parallel to the GMWL; numbers next to this line represent percentages of condensate from the original air mass. Dotted lines emanating from the Rayleigh line are trajectories of evaporation at different values of relative humidity (shown as 'h'). Larger dots along these evaporation trajectories denote percentages of raindrop evaporation. The isotopic composition of the precipitation can be achieved with a moderate amount of condensation (~40%) that then loses ~15% of its volume through evaporation through the subcloud layer.
Figure 9 - caption next page
Comparison of atmospheric soundings (inset) with $d$ of precipitation samples. Solid triangles are precipitation samples while open circles are vapor samples from 2007. All soundings are simplified skew-T plots with pressure on the vertical axis and temperature on the horizontal axis. Solid lines are temperature while dotted lines are dew point; the horizontal distance between these two lines increases with decreasing RH. The sounding of 5/2/07 12Z shows nearly 100% RH throughout the entire air column; this corresponds to precipitation samples to the left of the GMWL. Drier air columns (9/23/07 12z and 5/13/07 0z) correspond to precipitation samples with lower $d$ values due to increased evaporation below cloud base.
Figure 10 - caption on next page
Our data [solid circles from Albuquerque; solid squares from AZ/TX/Eastern NM] compared to that of Gat (2003) ['M' and 'D'], Lawrence et al. (2004) ['T'], and Craig and Gordon (1965) [crossed or dotted circles]. Dotted lines indicate fields of water vapor compositions predicted by the Craig and Gordon (1965) model. SST and relative humidity parameters for this model are shown. In this subset of our data (winter values are not shown), there is much overlap between our water vapor values and those of other workers. However, water vapor sample from marine sources tends to show more scatter in $d$ than what we have measured in the American Southwest.
Figure 11 - Caption

Water vapor data from this study (blue dots) compared to that from Figure 3 in Galewsky et al. (2011) (black dots). Red dashed line is a mixing curve; solid thick black line is a Rayleigh distillation curve for liquid saturation. Light dashed and solid lines represent Rayleigh distillation under ice supersaturation (RH for % of supersaturation scenarios given).
**Figure 12 - caption**

Illustration of conditions leading to water vapor with high $d$ values. Panel A: 3-day composite map of 700hpa geopotential height 7/15/07 - 7/18/07. During this time, a high pressure is centered over the 4-corners region, extending south over the Gulf of CA. Subsidence from this high allowed water vapor with high $d$ to be generated in the northern Gulf of CA. Panel B: 700hpa geopotential height 7/19/07 00Z. An easterly wave disrupts the high and causes southerly flow into AZ; these vapors were captured in southern AZ and have anomalously high $d$ values. 24-hr forward trajectories (500m AGL) starting at the time shown are illustrated as dashed lines in Panel B. Geopotential height contour interval is 5mb.
Panels A and C show 700mb geopotential height (m) for the dates shown. Panels B and D show composite omega maps for the times shown (shaded backgrounds, lighter shades indicate stronger subsidence) overlain with 24-hr forward trajectories (500m AGL) plotted in dashed lines for the times shown. Vapor with high d values was generated by the conditions shown in Panel B and collected at the time shown in Panel A. Although subsidence increases between Panels B and D, the trajectories in D shift this moisture away from New Mexico due to the growing influence of the high pressure over the Gulf of MX. Thus while vapor with high d is likely being generated in Panel D, it is transported away from New Mexico.
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