EEG-35 DOE/AL/10752-35

STABLE ISOTOPES IN SOUTHEASTERN NEW MEXICO GROUNDWATER: IMPLICATIONS FOR DATING RECHARGE IN THE WIPP AREA

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October 1986

FOREWORD

The purpose of the Environmental Evaluation Group (EEG) is to conduct an independent technical evaluation of the potential radiation exposure to people from the proposed Federal Radioactive Waste Isolation Pilot Plant (WIPP) near Carlsbad, in order to protect the public health and safety and ensure that there is minimal environmental degradation. The EEG is part of the Environmental Improvement Division, a component of the New Mexico Health and Environment Department -- the agency charged with the primary responsibility for protecting the health of the citizens of New Mexico.

The Group is neither a proponent nor an opponent of WIPP.

Analyses are conducted of available data concerning the proposed site. the design of the repository. its planned operation, and its long-term stability. These analyses include assessments of reports issued by the U.S. Department of Energy (DOE) and its contractors, other Federal agencies and organizations, as they relate to the potential health, safety and environmental impacts from WIPP.

The project is funded entirely by the U.S. Department of Energy through Contract DE-AC04-79AL10752 with the New Mexico Health and Environment Department.

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ACKNOWLEDGMENTS

Comments on this report while in draft were graciously provided by Lokesh Chaturvedi. William Foege, Regina Hunter, Fred Phillips, and G. W. Gross. The report benefited greatly from their reviews and the author is grateful for their comments. The report relies heavily on stable isotope data generated by Steve Lambert of Sandia National Labs. Steve Lambert introduced the author to the application of stable isotopes to the WIPP project and Fred Phillips suggested using G. W. Gross' stable-isotope and tritium data from the Roswell area to expand the data base. EEG's collection and analysis of precipitation and groundwater samples was arranged by Peter Spiegler and Dan Ramey. The author also gratefully acknowledges the word processing and formatting of the manuscript provided by Teresa Ortiz.

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EXECUTIVE SUMMARY

The first geologic repository for nuclear waste in the United States, the Waste Isolation Pilot Plant (WIPP), is being excavated at a depth of 2150 ft below ground surface in the Salado Formation in southeastern New Mexico. If a breach of the repository occurs, the water-bearing zones of the Rustler Formation, overlying the Salado. are considered to be the most likely pathways for the transport of radionuclides to the biosphere. A thorough characterization of the hydrology of the Rustler Formation is crucial to the evaluation of the consequences of a breach of the WIPP repository.

The Department of Energy is currently conducting studies of the Rustler Formation (many at the request of the State of New Mexico) that should significantly improve knowledge about the radionuclide contaminant transport ability of the Rustler. One recently completed study examined stable isotope data from Rustler groundwater and concluded that Rustler groundwater in the vicinity of the WIPP Site is not receiving significant modern meteoric recharge (Lambert, 1986). In addition, Lambert (1986) concludes that the stable isotope data reveal an hydraulic isolation of two possible discharge areas (well WIPP-29 and Surprise Spring) from the Rustler Formation elsewhere in Nash Draw and near the site. The conclusions of Lambert's

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(1986) stable isotope study allow longer residence time of water in the Rustler Formation and reduce the calculated consequences of a breach of the WIPP repository.

The present study compiles stable isotope data from throughout southeastern New Mexico and compares them to data from the WIPP area. The stable isotopic compositions of most samples of groundwater from the Rustler Formation are similar to the composition of other, verifiably young, groundwater in the area. Though the stable-isotope data cannot indicate ages for water in the various aquifers, neither do the data show any distinction between most Rustler groundwater and verifiably young groundwater.

A small number of samples, primarily from the Rustler/Salado contact east of Nash Draw, have isotopic compositions that are not characteristic of recently recharged meteoric water. These waters' enrichment in heavy isotopes may be due to mixing with deeper groundwater (supported by the stable isotopic composition of Salado fluid inclusions and Castile brine) or to exchange between the groundwater and hydrous minerals.

A comparison of the heavy isotope enrichment observed in evaporating waters and the composition of the water at WIPP-29 and Surprise Spring shows that the isotopic composition of these

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Nash Draw waters could be derived by evaporating Rustler groundwater. Based on stable isotopes, both WIPP-29 and Surprise Spring could be discharge areas for Rustler groundwater moving from elsewhere in Nash Draw and the east.

The enrichment in heavy isotopes found in water from pools in Carlsbad Caverns was used by Lambert (1986) as evidence that the relatively depleted Rustler water was recharged during a past, more pluvial, time. However, the uniqueness of the isotopic composition of water in the Caverns' pools suggests that rather than representing the composition of recent recharge, the heavy isotopes are enriched by evaporation and equilibrium isotope exchange in the humid cave environment. Recharge in the extreme karst environment near the cavern may also favor isotopically heavy precipitation.

The age of water in the Rustler Formation and the presence or absence of modern recharge cannot be determined on the basis of stable isotopic composition alone. Physical measurements of the flow system of the Rustler are the best way to locate and quantify recharge to the Rustler. Regional hydrologic testing of the Rustler fluid-bearing zones has begun and will provide data on the transmissivity and degree of fracture connection.

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Additional water-level measurements in more locations are needed to refine potentiometric surface maps and determine the location of recharge and discharge areas and groundwater divides. Unsaturated zone studies of infiltration in suspected recharge areas are also needed.

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STABLE ISOTOPES IN SOUTHEASTERN NEW MEXICO GROUNDWATER: IMPLICATIONS FOR DATING RECHARGE IN THE WIPP AREA

STATEMENT OF PROBLEM

The first geologic repository for nuclear waste in the United States, the Waste Isolation Pilot Plant (WIPP), relies on geologic isolation to separate the waste from the biosphere. The water-bearing zones in the Rustler Formation, overlying the Salado Formation salt, are generally considered the most likely pathways by which waste could be transported to the biosphere. Therefore, a thorough characterization of the hydrology of the Rustler Formation is crucial to the proper evaluation of the consequence of a radionuclide release from the WIPP.

A recent evaluation of stable isotope data from Rustler groundwater (Lambert, 1986) concludes that "...Rustler groundwater in most of Nash Draw and at the WIPP site is not receiving significant modern meteoric recharge." The implications of this conclusion are suggested by Lambert (1986) 1) the Rustler may contain fossil water (relic of former to be: recharge conditions) that is being removed without replacement at Malaga Bend, resulting in a large change in storage; and 2) the Rustler may contain stagnant fossil water entrapped during an episode of permeability reduction. Both of these scenarios result in reduced discharge, and eventually no natural discharge, from the Rustler, with corresponding increased residence time of water in the aquifer. The impact of this characterization of the Rustler hydrology on radionucliderelease consequence analysis is obvious and significant.

In addition to the conclusions concerning recharge to the Rustler, Lambert (1986) also concludes that the isotopic data reveal an hydraulic isolation of well WIPP-29 and Surprise Spring, both in Nash Draw, from the rest of the Rustler. The implication of this conclusion is that Surprise Spring and the area around WIPP-29 are not discharge points for Rustler groundwater. All discharge from the Rustler is concluded to occur near Malaga Bend and release scenarios can take credit for this longer flow path before radionuclides are released to the environment.

Lambert's (1986) basis for concluding that the Rustler is not receiving significant amounts of modern meteoric recharge is a difference between the stable isotopic composition of water in pools in Carlsbad Caverns and of groundwater in the Rustler Formation. Lambert considers Carlsbad Caverns water as being typical of modern recharge. Lambert's evidence for the lack of discharge is the difference between isotopic data from Surprise Spring and WIPP-29 and the majority of Rustler isotopic compositions. He attributes this difference to hydraulic isolation. The data used in Lambert (1986), as well as additional isotopic data published for southeastern New Mexico, are used here to examine the timing of recharge to the waterbearing zones of the Rustler and the possibility of discharge at WIPP-29 and Surprise Spring.

HYDROGEOLOGIC SETTING

The focus of this study, the WIPP site and vicinity, is located in the northern Delaware Basin of southeastern New Mexico (Figure 1). The stratigraphy and water-bearing properties of units in the Delaware Basin are discussed below to acquaint the reader with the hydrogeology of the area. In addition to the data from the vicinity of the WIPP site, isotopic data from the Roswell Underground Water Basin are also presented. The hydrogeology of the Roswell Basin will be briefly described following the discussion of the northern Delaware Basin.

Delaware Basin

The term "Delaware Basin" refers to the area in Southeast New Mexico and West Texas where vast amounts of clastic sediments and evaporites were accumulated in a slowly sinking shallow sea during late Paleozoic time. The basin is bounded by, and includes, the Capitan Reef. The following discussion is based on these investigations of water-bearing zones in the Delaware Basin: Hiss (1975), the Capitan Aquifer: Nicholson and Clebsch (1961), groundwater in southern Lea County: Hendrickson and Jones (1952), groundwater in Eddy County: and Mercer (1983), groundwater in the WIPP area.

The Delaware Basin consists of the arcuate Capitan Limestone reef complex and up to 13,000 feet of limestone, shale, and evaporites. The basin was tilted to the east and the Guadalupe Mountains uplifted during the Cenozoic. The reef and waterbearing formations above the Salado are the primary consideration in this study (Table 1 and Figure 2). The limited data available from deeper aquifers suggest that water-rock reactions have altered the isotopic composition of the groundwater (Lambert, 1978), reducing these water's relevance to a discussion of recent meteoric recharge.

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Figure 1. Map of New Mexico showing counties in southeastern New Mexico and the location of the Delaware Structural Basin and the Roswell Groundwater Basin.

TABLE 1

Delaware Basin Post-Ochoan Stratigraphy

PERIOD	FORMATION	LITHOLOGY				
Quaternary	Alluvium and surficial sand	gravel, sand, clay				
Quaternary	Mescalero caliche	caliche				
Quaternary	Gatuna	gravel, sand, clay				
Tertiary	Ogallala	calcareous sand, minor clay and gravel				
Cretaceous	Scattered outcrops	limestone and re- worked sediments				
Triassic	Dockum Group (Chinle and Santa Rosa)	mudstone, siltstone, and sandstone with conglomerate				
Permian	Dewey Lake	red beds of mudstone siltstone, minor sandstone				
Permian	Rustler	anhydrite, dolomite, halite, siltstone				
Permian	Salado	halite, anhydrite. clay, polyhalite, potash minerals				
Permian	Capitan Limestone	limestone reef				

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Capitan Limestone

The Capitan Limestone aquifer is a productive and important aquifer in southeastern New Mexico and western Texas, supplying groundwater for municipal and industrial use. The aquifer has high porosity and permeability developed along solution features, though permeability is lower in the vicinity of submarine canyons and in areas where the calcium carbonate content is relatively low (Hiss, 1975). In the western part of the basin, water enters the Capitan in the Guadalupe Mountains and flows through the karstic system to discharge points at springs along the Pecos River at Carlsbad. Leakage from adjacent shelf and basin aquifers and infiltration of water on Capitan outcrops in the Glass Mountains of Texas provide water to the aquifer east of the Pecos River. Discharge occurs by leakage into shelf aquifers to the east and by pumping.

Carlsbad Caverns

Water in Carlsbad Caverns is part of an isolated, perched hydrologic system within the Capitan Reef (Hendrickson and Jones, 1952). The Caverns extend from the surface to a depth of 900 feet, with the most extensive caves developed between the depths of 600 and 800 feet below the surface. Though the caves were formed by circulating groundwater, and the cave levels were probably controlled by past, higher, water tables, the caves are above the Capitan water table today and no streams or springs flow in the explored part of the caverns. The relatively small amount of groundwater that enters the caverns is discharged by evaporation (Hendrickson and Jones, 1952; Ron Kerbo, National Park Service at Carlsbad Caverns, personal comm., 1986). For instance, one of the larger cavern pools, the "Lake of Clouds", located at the lowest known point of the caverns, has no apparent drainage and its level remains nearly constant

(Barnett, 1980). Though the relative humidity in the cave is high, the evaporation surface is large and changes in barometric pressure result in active air circulation.

Rustler Formation

The primary water-bearing zones in the Rustler Formation are the Rustler/Salado contact zone, the Culebra Dolomite, and the Magenta Dolomite (from stratigraphically lowest to highest). The Rustler/Salado contact water-bearing zone is composed of clay with interlayered gypsum and sandstone and is considered to be the result of the dissolution of clay-bearing halite and other evaporites. The Rustler/Salado contact aquifer was formerly assumed to be confined to the dissolution/collapse feature of Nash Draw, but "...data from WIPP boreholes shows that the aquifer extends east of Livingston Ridge on to the WIPP site and is not confined by the physiographic depression of Nash Draw" (Chaturvedi and Channell, 1985). Water in all zones of the Rustler Formation in Nash Draw may have experienced contamination by introduced water. Disposal of oil-field brines and effluent from potash mining operations may have altered the original water chemistry in Nash Draw.

Water in the Rustler fluid-bearing zones is generally considered to discharge at Malaga Bend on the Pecos River, and possibly at Laguna Grande de la Sal in Nash Draw (Figure 3). Potentiometric levels in wells show the water movement in the Magenta to be primarily to the west, and to the southwest in the Culebra and Rustler/Salado contact (Figures A-1, A-2, and A-3 in the Appendix). The proposed recharge area for these aquifers in Clayton Basin (Mercer, 1983) has recently been questioned due to an apparent groundwater divide immediately south of Clayton Basin (Hunter, 1985). Other potential recharge areas exist in



Figure 3. Location of geographic features in the vicinity of the WIPP site.

the Laguna Plata and San Simon Swale areas of eastern Lea County (Figure 3). though a groundwater divide may separate the San Simon region from the WIPP site (Nicholson and Clebsch, 1961; Hunter, 1985). The potential for recharge to the Rustler through the overlying Dewey Lake Redbeds remains unknown. Also unknown are the hydrogeologic conditions in the Rustler immediately to the east of the WIPP site.

Dewey Lake Redbeds

The Dewey Lake Redbeds Formation overlies the Rustler Formation and locally contains perched water within lenticular sand units. Recharge may take place through local dune sands and along fractures or bedding planes in the mudstone and siltstone. Movement of water in the Dewey Lake is considered to be restricted due to the overall low permeability of the formation (Mercer, 1983).

Santa Rosa Sandstone

The Triassic Santa Rosa Sandstone is the principle aquifer in the western third of southern Lea County. The Santa Rosa is recharged by precipitation and runoff directly on the outcrop and through sand dunes in Lea and Eddy Counties (Nicholson and Clebsch, 1961). Recharge probably also occurs by groundwater flow through the Ogallala Formation where the Ogallala overlies the Santa Rosa. Groundwater in western Lea County moves to the south and southwest in the Santa Rosa Formation, toward Laguna Plata (Figure 3). Discharge may occur in this area from the Santa Rosa to Permian units through zones of increased permeability due to collapse (Nicholson and Clebsch, 1961). Elsewhere in southwestern Lea County, flow in the Santa Rosa is strongly influenced by San Simon Swale. The Triassic Chinle Formation also contains water in Lea County, but no isotope data are available from that unit.

Ogallala Formation

The Ogallala Formation is a large and very productive aquifer across the High Plains of the United States. In southeastern New Mexico, the Ogallala represents a continuous and productive unit only east of the Pecos River. The recharge of the Ogallala is due entirely to precipitation. Water movement is predominantly southeastward, though in the area of Mescalero Ridge (Figure 3), some water moves southwestward across the ridge and into the Santa Rosa Sandstone (Nicholson and Clebsch, 1961). The water that moves southeast is eventually either intercepted by wells or discharges along the eastern edge of the Llano Estacado.

Quaternary Deposits

Quaternary deposits, including the Gatuna Formation, playa deposits, and alluvium, contain localized water in the Delaware Basin. Recharge to these units occurs by infiltration of precipitation, streams, canals, and irrigation return water. Leakage from the Capitan aquifer also contributes water to the alluvium west of the Pecos River. Alluvium associated with the Pecos River contains a productive aquifer yielding water to irrigation wells. The Gatuna Formation is reported to yield water (Cooper and Glanzman, 1971), but the discontinuous nature of the unit restricts water movement and the quantity of water is small (Mercer, 1983). Where the Gatuna overlies the Santa Rosa Sandstone, it probably contributes recharge to the Santa Rosa. Elsewhere, discharge probably occurs by transpiration. The occurrence of water in other Quaternary deposits is variable and localized.

Roswell Basin

The following discussion of the Roswell Basin is derived primarily from Hoy and Gross (1982) and Welder (1983). The term

"basin" here refers to a groundwater basin (an area containing a large aquifer and any related aquifers), rather than a structural basin like the Delaware Basin. The Roswell Groundwater Basin covers approximately 6000 square miles in southeastern New Mexico (Figure 1). It contains an eastwarddipping limestone aquifer which consists of the San Andres and Grayburg Formations (Table 2), overlain in the east by the leaky confining beds of the Artesia Group and an alluvial water-table aquifer. Water in the carbonate aquifer is unconfined in the western part of the basin and confined to the east. Along the Pecos River between Roswell and Artesia, flowing artesian conditions were encountered in wells completed in the limestone, prior to the extensive use of irrigation for farming.

Water movement in the Roswell Basin is generally eastward to the Pecos River, with an additional southward component in some areas. Recharge to the limestone aquifer occurs as infiltration of precipitation and streamflow to the karstic San Andres outcrops and as upward leakage from underlying sedimentary beds. The underlying beds (Glorieta sandstone and Yeso Formation), are recharged at their exposures in the Sacramento Mountains. Recharge to the alluvial aquifer occurs by infiltration of precipitation, surface runoff, and irrigation return flow. Under pre-irrigation conditions, the alluvial aquifer also received recharge through the leaky confining layer from the limestone aquifer. Since the onset of irrigation, however, the flow is reversed during periods of large withdrawals from the carbonate aquifer, and the alluvial aquifer recharges the carbonate aquifer during these periods. The major discharge from all units in the basin is by pumping for irrigation water. Additional discharge occurs from both the alluvial and the carbonate aquifers to the Pecos River.

TABLE 2

Roswell Groundwater Basin Stratigraphy

PERIOD	FORMATION	LITHOLOGY				
Quaternary	Alluvium and surficial sand	caliche, gravel, sand, clay				
Quaternary	Gatuna	gravel, sand, clay				
Permian	Artesia Group: Tansill Yates Seven Rivers Queen Grayburg	Upper portion: clay, sand, evaporites Lower portion: clay, sand, carbonates				
Permian	San Andres	Upper portion: evaporites, sand, carbonate Lower portion: carbonate, shale, sand (Glorieta Sandstone)				
Permian	Yeso	Shale, carbonate				

(See Figure 2 for stratigraphic relationship with Delaware Basin Formations)

STABLE ISOTOPES AND HYDROGEOLOGY

Interpretation of stable isotope ratios in water is an established method of supplementing information derived from conventional hydrogeologic techniques. Detailed information on the theory and application of stable isotope studies to hydrogeology can be found in Gat and Gonfiantini (1981) and Faure (1977). Hoy and Gross (1982) also discuss the stable isotope approach to hydrology, with special emphasis on applications to the Roswell Basin. The isotopic data are represented as the relative difference in the ratio of the heavy isotope to the light isotope with respect to a reference, using the δ -notation:

<u>R sample - R reference</u>

R reference

5 =

with R as the ¹⁸O/¹⁶O or D/H isotope concentration ratio. The reference is usually Standard Mean Ocean Water (SMOW). The 5-values are presented as per mil [δ (%) = δ X 1000]. Discussions of the δ -notation can be found in the references given above.

The usefulness of stable isotope ratios lies in the fact that because of the mass differences between oxygen-16 and oxygen-18 and between protium and deuterium, the thermodynamic properties are different between water molecules of varying isotopic composition. This difference results in isotopic fractionation during many reactions. The fractionation which results during physical processes such as evaporation and condensation, and fractionation which results from exchange reactions such as between water and limestone, are of primary concern to this discussion.

Isotopic Fractionation During Condensation

The isotopic composition of precipitation has been related to temperature, amount of precipitation, latitude, distance from the ocean, and altitude. The most important factor is the temperature of condensation (Yurtsever and Gat, 1981). A strong linear relationship exists between δ D and δ^{18} O values of precipitation worldwide. This relationship is often referred to as the Meteoric Water Line (MWL) (Figure 4), and can be described by the equation:

$$\delta D = 8\delta^{10}O + 10$$

(Craig, 1961).

The $\delta D - \delta^{18}O$ relationship for a given region can differ from the global equation, usually in the value of the D-axis intercept (deuterium excess). Water with relatively low values of δD and $\delta^{18}O$ indicate that they condensed at relatively cool temperatures. Conversely, higher values of δD and $\delta^{18}O$ indicate condensation in warm temperatures.

The impact of latitude, distance from the ocean, and altitude on the isotopic composition of precipitation is related both to the relationship with temperature of these variables, and to the "rain-out" effect. As water vapor in an air mass moves away from the point of evaporation, the heavy isotopes condense first and are said to be "rained-out" of the cloud. Subsequent precipitation becomes isotopically lighter as the cloud becomes successively depleted in the heavy isotopes. The same process relates to the amount of precipitation in a single event. The initial precipitation will be relatively isotopically heavy, but as more water condenses, the rain becomes depleted in heavy isotopes. Therefore, large-volume rainfall events are characterized by relatively light isotopic compositions.



Figure 4. Plot of δD vs δ 0 showing the observed range in isotopic paths (evaporation "window") traced by a residual water as it undergoes evaporation. See text for a discussion of the factors that determine which evaporation-line slope a water will follow.

The impact of altitude on the isotopic composition of precipitation is pertinent to this discussion because some of the recharge to the Roswell Basin occurs in the Sacramento Mountains. The question is whether the isotopic composition of groundwater that receives part of its recharge from precipitation at high altitudes in the Roswell Basin can be compared to groundwater in the Rustler Formation which probably receives most of its recharge at lower elevations. Hoy and Gross (1982) attempted to identify the relative contribution of recharge from higher and lower elevations to the Roswell Basin limestone aquifer on the basis of isotopic composition. Thev found that the groundwater data, irrespective of altitude, fell in a tight cluster within the range of the isotopic composition of precipitation at lower to intermediate elevations in the They concluded that in this semi-arid, continental basin. environment, the temperature effect due to altitude is masked by the large, rapid temperature fluctuations that occur at all elevations across the basin. Nevertheless, caution is taken here to use data only from low to intermediate elevations in the Roswell Basin and the potential impact of high-elevation recharge is recognized.

Isotopic Fractionation During Evaporation

Evaporation of water, whether from a surface-water body or from the unsaturated zone, leaves the residual water enriched in the heavier isotopes of oxygen and hydrogen (Figure 4). The isotopic path traced by the residual water as successively more water is evaporated is characterized by a slope of less than 8 in $\mathcal{5}D-\mathcal{5}^{18}O$ space. The lower slope reflects the greater fractionation of oxygen, compared to hydrogen, during the evaporation process. The slope of the evaporation path depends upon the relative humidity of the air, the fractionation factor, the excess separation factor (amount of isotopic fractionation

in excess of the appropriate equilibrium process), and the ratio of the isotopic compositions of the air and liquid. The relative humidity and fractionation factor are both temperature dependent. Lower slopes indicate evaporation under conditions of lower relative humidity and higher slopes indicate evaporation in relatively high humidity environments.

Gat (1981) reported that most observed slopes are within the range of 3.5 to 6. Lloyd (1966) reported a somewhat larger range of 2.5 to 6 for evaporating seawater. Allison (1982) reported evaporation line slopes between 2 and 4.7 for the condition of evaporation in the unsaturated zone of sand columns. The lower slopes of unsaturated zone evaporation are attributed to the greater role of kinetic fractionation during vapour-phase movement through the dry surface layer. In addition to the controlling factors for surface-water evaporation slopes listed above, the slope for evaporation in the unsaturated zone probably also depends on the thickness of the zone of vapour-phase transport (Allison, 1982). The range of evaporation-line slopes is traced in $\delta D - \delta^{18}$ O space on Figure 4.

Isotopic Fractionation During Exchange Reactions The isotopic composition of water can also be modified by exchange reactions. The typical case of isotopic exchange involves hydrothermal systems in which high temperatures increase the rate of isotopic exchange between groundwater and rocks. In lower temperature environments, isotopic exchange reactions generally require long periods of water-rock contact (i.e., slow-moving groundwater systems) and a large rock-towater ratio. Isotopic exchange between water and carbonates results in an oxygen-18 enrichment of the groundwater. This shift is the result of the oxygen-18 enriched nature of

carbonates (+20% to +30% for limestone. slightly higher for dolomite). Both the deuterium and oxygen-18 content can be affected in a water that reacts with hydrous minerals such as gypsum. All of these rock-water reactions result in an oxygen-18 enriched water. plotting to the right of the Meteoric Water Line in $\delta D - \delta^{18}O$ space.

The isotopic composition of water that has exchanged isotopes with rock may mimic that of water that has undergone evaporation. In practice, however, the environment in which the sample is collected (surface water, shallow groundwater, or deep formation water removed from atmospheric contact) dictates which fractionation scenario is more likely. The interpretation is more difficult in the case of a remnant evaporitic brine that subsequently undergoes rock-water reactions.

Stable Isotopes and Fossil Water

Stable isotopes can be used in hydrogeologic investigations to help identify the presence of fossil water (paleowater) in aquifers. However, no simple correlation exists between variations in the stable isotope content of precipitation and past climatic patterns. Paleoclimatic interpretations of isotopic data in the absence of groundwater-age measurements are risky because of the number of variables affecting the isotopic composition of precipitation (e.g. isotopic content of vapor sources, precipitation history of the air mass, humidity, and temperature profiles in the lower atmosphere). For instance, groundwater recharged by rain during polar front occlusions could be depleted in heavy isotopes and misinterpreted as paleowater if no tritium or carbon-14 measurements are available (Fontes, 1981).

Paleowater investigations usually rely on the popular concept that the glacial episodes during the Quaternary were characterized by low temperatures, low evaporation, and/or high rainfall in the mid-latitudes. Presumably, this would result in precipitation during glacial periods having a lighter stableisotope content. Successful applications of stable isotopes to investigations of paleowaters have shown that a given aquifer may have a much lower deuterium and oxygen-18 content than present-day precipitation and often a different deuterium-excess value. The use of hydrogeologic evidence and carbon-14 dates to support the hypothesis is a consistent feature of valid paleoclimate studies.

STABLE ISOTOPE DATA FROM SOUTHEASTERN NEW MEXICO

The data used in this report are presented in Table 3. The three primary sources for published stable-isotope data for aquifers in southeastern New Mexico are Lambert (1986), Lambert (1978). and Hoy and Gross (1982). Isotopic data are also presented graphically in Lambert (1983), but the identity of wells is not listed. Popielak and others (1983), O'Neil and others (1986), and Knauth and Beeunas (1986) present isotope data from the Salado and Castile Formations. Additional data from rainfall samples and WIPP-area groundwater have been obtained by the EEG.

On some samples, Hoy and Gross (1982) have reported only the oxygen-18 analysis and the Ogallala data in Lambert (1986) consist only of deuterium analyses. To facilitate presentation, the other isotope for these data is calculated by using the local meteoric water line determined by Hoy and Gross (1982) for the Roswell Basin. The local line is based on data from aquifers, springs, snow, and surface water, and three years of precipitation and is expressed by the following equation:

 $\delta D = 7.27 (\pm 0.38) \delta^{18}0 + 5.36 (\pm 1.25)$ (Hoy and Gross, 1982).

The potential error introduced by calculating a δ^{18} O or δ D value is small because the samples involved are generally accepted as recent. unaltered meteoric water by virtue of either their tritium contents or their location in shallow aquifers. The exception to this is the data point from the Pecos River at Artesia (sample number S-13. Hoy and Gross, 1982) which probably should plot to the right of the meteoric water line due to evaporation. The meteoric water line will be discussed further in the section on the isotopic composition of precipitation. surface water, and groundwater in southeastern New Mexico.

TABLE 3

Stable Isotopic Data and Tritium Values of Water from Southeastern New Mexico

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FORMATION	MOMER	WELL.	DATE	<i>5</i> 0–18	<i>5</i> D	т.U.	SOURCE
Capitan		Carlsbad	pre-1977	-7.9	-54		Lambert, 1978
Capitan		Middleton	**	-7.5	-55		**
Capitan		Hackberry	**	-6.5	-46		+1
Capitan	Caverns		**	-3.6	-24		**
Capitan	Caverns		**	-4.3	-28		**
Capitan	Caverns		**	-4.2	-29		**
Capitan	Caverns		*	-3.0	-20		**
S Rustler	?	Duval Mine	**	-6.4	-48		**
Rustler	?	James Ranch	++	-5.0	-40		**
Rustler	?	Fairview	**	-7.1	-53		**
Rustler	?	Indian	**	-6.3	-46		**
Rustler	?	Mobley		-6.9	-44		**
Bustler	?	Mobley #3	**	-5.9	-44		**
Rustler	Magenta	H-1	**	-6.8	-48		**
Rustler	Culebra	H-1	**	-7.0	-50		**
Rustler	Magenta	Н-З	**	-7.3	-53		**
Rustler	Culebra	н-3	**	-7.0	-53		**
Santa Rosa		Smith L.R.	**	-7.2	-52		**
Salado		Duval Mine	**	+3.0	-10		**
Salado		Duval Mine	**	+2.6	-12		**
Morrow		Todd State	**	+2.7	-15		**
Morrow		Todd Federal	**	+9.2	-18		**
Bell Canyon		Todd Federal	**	+2.2	-13		**
Castile		ERDA-6	**	+10.3	0		**
Weighted Mean	ppt		pre-1982	-6.0	-38*		Hoy & Gross, 198
Snow	location:	Sierra Blanca	1-16-79	-21.2	-146		
Snow	location:	Sierra Blanca	1-14-79	-21.8	-158		**
Snow	location:	Sierra Blanca	1-14-79	-15.4	-102		**

FORMATION	MEMBER	WELL	DATE	<i>5</i> 0-18	<i>5</i> D	T.U.	SOURCE	
Rain	location: Ros	well	4-76	-10.0	-71		Hoy & Gross,	1982
Rain	location: Ros	swell	7 & 8-76	-4.8	-35		**	
Rain	location: Ros	well	9 & 10-76	-6.2	-50		54	
Rain	location: Ros	swell	3 & 4-77	-6.4	-44		**	
Rain	location: Ros	well	7-77	-0.8	-5		**	
Rain	location: Ros	swell	10-77	-6.4	-28		**	
Rain	location: Ros	well	9-78	-5.2	-37		**	
Alluvial Aquifer	Hagerman-Arte	esia mean		-7.15	-47*		**	
Pecos River @ Art	esia	S-13	4-1-78	-5.5	-35*	36.0	**	
Pecos River @ Ros	swell	S-10	4-1-78	-12.6	-86*	40.7	**	
Glorieta/Yeso		07	77-78	-7.4	-48*	12	**	
Glorieta/Yeso		08	77~78	-8.2	-56	33	**	
San Andres		WR5	78	-9.2	-64	16	*	
San Andres		WP14	mean	-6.5	-42*	7	**	
San Andres		WP14	4-78	-7.3	-42.6		**	
San Andres		WP14	4-79	-7.9	-48.6		**	
San Andres		WP16	7-77	-7.5	-48.4	16.4	**	
Alluvium/Gatuna		WA10	75-78	-7.1	-46*	6.3	**	
Alluvium/Gatuna		WA11	77	-7.2	-51.1	6.8	**	
San Andres		WP4	76-78	-7.1	-46*	7.3	**	
San Andres		WP2	4-79	-7.7	-55.4	10.4	**	
San Andres		WR14	5-77	-7.2	-47.3	9.1	**	
Spring		F 5	77-78	-2.7	-34.3	36.9	**	
Bitter Lakes		S23	78	-4.1	-29.5		**	
Bitter Lakes		S2 3	78	±0.6	-6.0		**	
Rustler	Magenta	W-25	84?	-6.2	-43.5		Lambert, 198	36
Rustler	Culebra	W-25	**	-6.4	-43.5		••	
Rustler	R/S	W-25	**	-7.1	-52		**	
Rustler	Culebra	W-26	**	-6.5	-43.5		**	
Rustler	R/S	W-26	**	-6.7	-46.5		**	
Rustler	Magenta	W-27	••	-6.3	-46.5		**	
Rustler	Oulebra	W-27	**	-6.1	-45.5		**	
Rustler	R/S	W-27	**	-7.0	-48.5		**	
Rustler	Culebra	W-28	**	-6.6	-46		**	
Rustler	R/S	W-28	39	-8.0	-57.5		**	
Bustler	Gulebra	W-29	**	-0.45	-27		**	
FORMATION	MEMBER	WELL.	DATE	<i>5</i> 0– 1 8	δD	т.U.	SOURCE	
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Bustler	B/S	w-29	**	-7.0	-47.5		Lambert	1986
Bustler	Magenta	W-30	**	-6.5	-42		•	1000
Bustler	Gulebra	W-30	**	-7.1	-50		**	
Bustler	B/S	W-30	**	-7.1	-52		**	
Surprise Spring	, -		**	-2.4	-30.5		**	
Canitan	Caverns		•	-4	-37		••	
Canitan	Caverns		**	-4	-31.5		••	
Capitan	Caverns		**	-3.5	-23.5		**	
?-San Simon Sink		W-15	**	-4.5	-38.5		**	
Summer rain			••	-2.3	-19		**	
Ogallala		Eastern New Mexico	pre-1986		-39 to -41		**	
Pecos River			June	-3.5	-36		**	
Dewey Lake (?)			pre-1980?	-5	-40		**	
Bustler	R/S	HI	**	+1.8	-28		**	
[∧] Austler	R/S	нз	**	+0.2	-38		**	
Bustler	R/S	H2		-2.7	-41		**	
Rustler	R/S	HS	**	-1.7	-44		••	
Bustler	R/S	HB	**	-4.8	-52		**	
Rustler	R/S	H4	**	-4	-57		**	
Rustler	R/S	P14	**	-9	-63		Lambert,	1986
Bustler	Culebra	H1	+	-7.2	-49			
Bustler	Culebra	HЗ	**	-6.5	-49		**	
Rustler	Culebra	P15	••	-7.2	-52		**	
Rustler	Culebra	P17	**	-5.8	-50		**	
Rustler	Culebra	P18	17	-4.5	-46		**	
Rustler	Magenta	H1	**	-6.8	-47		**	
Bustler	Magenta	H3	**	-6.1	-48		**	
Capitan	Caverns		••	-1.6	-17		••	
Capitan	Caverns		**	-3	-20		••	
Capitan	Caverns		**	-3.5	-24		**	
Capitan	Caverns		**	-4.2	-28		50	
Capitan	Caverns		**	-4.0	-29		**	
Capitan	Caverns		**	-4.3	-30		**	
Capitan	Caverns		**	-5	-33		**	
Canitan	Caverns		**	-6.1	-32		**	
oup our					00			

FORMATION	MEMBER	WELL.	DATE	<i>5</i> 0-18	<i>5</i> D	Τ.υ.	SOURCE
Rustler	Culebra	DOE-2	1985	-7.07	-55		EFG, 1985
Rustler	Culebra	н-3	**	-6.76	-55		**
rain	location: C	arlsbad	11-24-84	-14.06	-97		\$*
rain	location: W	IPP site	12-04-84	-5.12	-25		**
rain	location: W	IFP site	12-18-84	-4.36	-31		79
snow	location: C	arlsbad	1-01-85	-22.54	-162		**
snow	location: W	IPP site	1-31-85	-10.95	-71		**
snow (?)	location: C	arlsbad	2-24-85	-15.95	-122		**
rain	location: W	IFP site	2-28-85	-6.22	-52.5		**
rain	location: W	IPP site	3-19-85	-7.59	-62		**
rain	location: W	IPP site	8-85	-3.6	-19		**
rain	location: W	IFP site	7-85	-3.1	-13		**
Castile		ERDA-6	1982	+9.51	- 5		Popielak, et al, 1983
Castile		WIPP-12	1982	+10.45	-0.8		
v Salado		ERDA-9	1983	+3.4	-21		O'Neil , et al, 1986
Salado		ERDA-9	**	+1.2	-28		f a
Salado		ERDA-9	**	+8.4	-14		**
Salado		ERDA-9	**	+8.0	-10		**
Salado		ERDA-9	**	+5.8	-14		**
Salado		ERDA-9	**	+9.9	- 2		**
Sal.ado		ERDA-9	**	+7.5	- 8		**
Salado		ERDA-9	**	+8.1	- 4		*
Salado		ERDA-9	**	+9.5	- 5		**
Salado		WIPP Mine	1985	+4.7	- 9		Knauth & Beeunas, 1986
Salado		WIPP Mine	**	+3.5	- 6		**
Salado		WIPP Mine	**	+2.9	- 7		**
Salado		WIPP Mine	**	+3.2	- 9		**
Salado		WIPP Mine	*	+3.7	- 5		m
Salado		WIFP Mine	**	+2.9	- 5		**

*denotes values calculated from $\delta D=7.3 \ \beta^{18}O+10$ (Hoy & Gross, 1982) **EEG analyses performed by Global Geochemistry Corp., Canoga Park, California

Only selected data from Hoy and Gross (1982) are presented here. The selection is based on tritium values higher than 4 Tritium Units (TU) to include only water which has been recharged in the last thirty years, and based on locations as geographically and topographically similar to the Carlsbad area as possible. Only lower altitude wells in the Roswell Basin are used in this study (<5000 ft msl). The impact of potentially higher elevation recharge to some of the Hoy and Gross wells is discussed in the section on "Isotopic Fractionation During Condensation." The Roswell Basin. Carlsbad Caverns. and the WIPP area are all located in the Southeastern Plains of New Mexico and experience fairly uniform climatic conditions. For instance, the towns of both Roswell and Carlsbad receive 13 inches of average annual precipitation, with virtually the same seasonal distribution (Figure 5) (Tuan et al, 1973).

The tritium values of the Hoy and Gross (1982) groundwater samples reported here range from 5 to 33 Tritium Units (TU). The last precipitation before extensive atmospheric tests of nuclear bombs occurred in 1951 and the natural activity (between 4 and 20 TU) of this precipitation will have decayed down to about 1 to 4 TU in the 1980's. Therefore, groundwaters recharged and removed from contact with the atmosphere before 1951 will now have tritium values of less than or equal to 1 to 4 TU (Fontes, 1983). There are difficulties in using tritium data to obtain quantitative ages because mixing with older groundwater, hydrodynamic dispersion, and variation in the amount of tritium in rainfall complicate the analysis. However, any groundwater with a tritium level over 4 TU has had contact with the atmosphere (the tritium source) within the last 30 years. establishing a recent meteoric connection for the Roswell Basin samples reported here.



Figure 5. Monthly average precipitation recorded at weather stations in the towns of Roswell and Carlsbad. Modified from Tuan and others (1973).

Mixing may have affected the tritium results from the Roswell Basin limestone-aquifer wells reported here (denoted by "WP" in Table 3). The presence of more than 4 TU tritium documents recent recharge, but this recharge may have mixed with older groundwater in the limestone aquifer (Hoy and Gross, 1982; Gross et al, 1976). However, the "older" groundwater in the limestone aquifer is believed to have an age of one hundred to several hundred years (Gross, pers. comm., 1985), a time period too short to encompass the large scale climatic changes necessary to dramatically alter the isotopic composition of precipitation. Water from the alluvial aquifer wells ("WA" wells) and the observation wells ("O" wells) may be affected by mixing with irrigation returns from Pecos River water and from well water from the limestone aquifer. However, water levels in the observation wells responded rapidly to runoff events in nearby stream courses, indicating that recharge from surface water is important in the system (Hoy and Gross, 1982). Hoy and Gross (1982, p. 70) have concluded that "Groundwaters in the Roswell Basin, therefore, represent present climatic conditions".

In addition to the numerical data obtained for this analysis. sixteen points have been taken from a graph presented in Lambert (1986, Figure 3). These are presumably the same data shown in Lambert (1983) in which the identity of the individual data points is not listed. The numbers assigned to these points may be slightly in error since they were interpreted from the graph.

Data Presentation

The isotopic data used in this study are presented in Table 3. The sample locations in southeastern New Mexico are shown on Figure 6. with a more-detailed map of wells in the WIPP vicinity presented in Figure 7. The large quantity of data is presented in a series of graphs for clarity. Maps modified from Mercer



Figure 6. Location of wells (exclusive of the WIPP area) and surface water samples for which stable isotope data are available.







Figure 7. Location of wells in the WIPP area for which stable isotope data are available.

(1983), showing potentiometric contours of the Rustler waterbearing units are included as Appendix A for easy reference.

STABLE ISOTOPES IN RUSTLER FORMATION GROUNDWATER

Figure 8 displays two groups of $5D-5^{18}O$ compositions. There is a group of Rustler data points paralleling the meteoric water line and a group of additional Rustler points (primarily from the Rustler/Salado contact) that stretch from the light end of the meteoric water line toward oxygen-18 and deuterium enriched values. The slight offset from Craig's (1961) meteoric water line exhibited by the first Rustler group could be the expression of a local meteoric water line. As discussed more fully in the next section, data from the Roswell basin indicate that the local meteoric water line does not differ significantly from the global line defined by Craig (1961). It is probable that the offset from the meteoric water line reflects partial evaporation of water either as it falls through the atmosphere. or as it infiltrates through the unsaturated zone.

The group of Rustler points (Group A) outlined near the meteoric water line (MWL) in Figure 8 contains all of the Magenta samples, almost all of the Culebra samples, and Rustler/Salado Interface zone samples that were collected from wells located in Nash Draw. The trend of this group along and close to the MWL indicates that none of these samples have undergone extensive isotopic exchange with the aquifer matrix. There is also no obvious isotopic distinction marking Nash Draw water that has been contaminated by oil-field brine or potash-mine effluent. Most potash-refining water is imported from the Ogallala Formation in the vicinity of Hobbs, New Mexico. Water from the



Figure 8. Plot of δD vs $\delta^{18}0$ for groundwater from units in the Rustler Formation. Two groups are identified: Group A near the meteoric water line, and Group B enriched in heavy isotopes relative to the meteoric water line. A hypothetical evaporation line from Group A to WIPP-29 is also shown. The data are listed in Table 3.

Ogallala in southeastern New Mexico is not drastically different in isotopic composition from Rustler groundwater (Ogallala $\delta D = -39$ to -41 and most Group A Rustler values of -42 to -50), making the identification of contamination difficult. In the case of oil-field brine, there is no heavy-isotope enrichment indicating significant contamination of Nash Draw water by enriched oil-field brine (Figure 9). Isotopic analysis of brine from the major hydrocarbon-producing unit in the area, the Pennsylvanian Morrow Formation, revealed 5^{18} O values in excess of +2 per mil (Lambert, 1978).

The Rustler/Salado Interface East of Nash Draw

The trend of the Rustler/Salado Interface data that plot far from the meteoric water line suggests four possibilities: 1) the aquifer is composed of reactive materials that are exchanging oxygen-18 and deuterium. 2) the residence time of water is substantially longer in this aquifer, as compared to the Culebra and Magenta, allowing more time for water-rock reactions, 3) evaporation is occurring during the recharge process, or 4) mixing is occurring with remnant, evaporitic brines. All of the enriched samples were collected east of Nash Draw and therefore are not expected to be affected by contamination from introduced water. The four possibilities for the isotopic enrichment are discussed below. The offset of these points from the meteoric water line has also been discussed by Lambert (1983). He relates the heavy-isotope enrichment to a reduced water-to-rock ratio and well production rates and concludes that interaction of rock and water involving the exchange of both hydrogen and oxygen accounts for the enrichment.

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Figure 9. Plot of δD vs $\delta^{18}O$ for groundwater from the Rustler Formation and deeper formations in the Delaware Basin. The least-squares linear regression line was calculated using the data shown in open symbols. A range is used for seawater composition to account for melting of ice sheets during the Permian. The data are listed in Tables 3.

Isotopic Exchange Between Water and Rock

The Rustler/Salado Interface matrix is a layer of primarily fine-grained clastic material with smaller amounts of anhydrite. halite. and polyhalite. The lack of limestone and dolomite precludes 0-18 enrichment by exchange between water and carbonates. Exchange between the groundwater and petroleum hydrocarbons or hydrogen sulfide could affect the deuterium concentration, but not oxygen (Clayton et al, 1986). Exchange with hydroxide-bearing clay minerals could conceivably alter both the hydrogen and oxygen isotopic compositions (Clayton et al, 1966; Taylor, 1974) and is consistent with the mineralogy of the matrix.

O'Neil and Kharaka (1976) observed rapid hydrogen isotope exchange between clay minerals and water in the laboratory and concluded that this must be an active process in nature even at low temperatures. They also concluded that the mechanism of oxygen isotope exchange between minerals and waters usually involves a solution/redeposition step, and therefore, oxygen isotope exchange between clays and water at low temperatures is negligible under most conditions. Appreciable exchange of both oxygen and hydrogen was observed in montmorillonite clays where the presence of interlayer water facilitates isotopic exchange (O'Neil and Kharaka, 1976). However, most clays in the world's modern ocean basins have not reached isotopic equilibrium with the marine environment in hundreds of thousands of years, but rather the clays continue to reflect their detrital origin (Savin, 1980).

Aside from reaction kinetics, a major problem with invoking isotopic exchange between clay minerals and water to account for

the enriched nature of the eastern Rustler/Salado Interface samples is the original isotopic composition of the clay. No isotopic measurements are available from minerals in the Interface matrix, so published values for clay minerals (principally kaolinite, illite, montorillonite, and gibbsite) must be used. Though enriched in 0-18 relative to meteoric water, published values for clays show a depletion in the minerals' deuterium content (Savin and Epstein, 1970; Taylor, 1974; O'Neil and Kharaka, 1976). Fractionation factors for kaolinite and montmorillonite reveal that the mineral is about 27 per mil enriched in 0-18 and about 30 per mil depleted in deuterium relative to the coexisting meteoric water (Taylor, 1974). All of the clay minerals analyzed by Savin and Epstein (1970) were depleted in deuterium with respect to sea water, including those which apparently formed in isotopic equilibrium Most of their clay samples had δD values with the ocean. between -50 and -80 per mil and 5^{18} 0 values between +13 and +29 per mil (Savin and Epstein, 1970).

Even if exchange between Rustler/Salado Interface groundwater and clay minerals occurs, it is not a guaranteed mechanism to account for the enriched water compositions. Given the range in published values for clays, equilibrium fractionation between clay and groundwater could leave the water depleted in oxygen -18 and only slightly enriched in deuterium, relative to the water's original composition. It is possible that clays deposited in an evaporitic brine are enriched in heavy isotopes and that exchange with such clays could enrich the coexisting water. Exchange with other hydrous minerals, such as polyhalite, is another possible enrichment mechanism. However, relying on exchange between minerals and water to explain the Rustler/Salado Interface isotopic composition will remain tenuous until the isotopic composition of the matrix minerals is determined.

Residence Time

The rate of water movement through the Rustler/Salado Interface has been interpreted as being extremely slow, especially in the eastern area where the enriched isotopic compositions occur (Mercer. 1983). Therefore, the period of contact between the water and the matrix minerals could be long enough for isotopic exchange to occur, even at relatively low temperatures. However, as discussed in the previous section, there are no isotope exchange reactions consistent with the Rustler/Salado Interface mineralogy that will assuredly enrich the water in both oxygen-18 and deuterium.

There is a rough correlation between Rustler/Salado potentiometric contours and stable isotope content. The heaviest group. including the data from H1, H2, H3, and H5 (Figure 8), all fall up-gradient from the 3100 foot contour on Mercer's (1983) map (Figure A-1 in Appendix A). A more meaningful correlation is the coincidence between all of the Rustler/Salado points that fall on the meteoric water line on Figure 8 (P14, W-25, 26, 27, 28, 29, and 30) and the zone of "active circulation" on Mercer's (1983) water-quality map (Figure 10). Mercer's boundary between the more-developed flow system to the west and the less-developed to the east is given strong support by the isotopic data.

Evaporation During Recharge

Water that has undergone evaporation exhibits a similar oxygen-18 and deuterium enrichment as displayed by some of the groundwater from the Rustler/Salado Interface. The trend away from the meteoric water line may reflect evaporation of recharging water as it moves through the unsaturated zone. If evaporation is the explanation for the heavy-isotope enrichment, this implies either a different recharge area or different



Figure 10. Stable isotope interpretations superimposed on Mercer's (1983) division of the Rustler/Salado Interface groundwater flow system. Adapted from Mercer (1983).

recharge conditions (perhaps temporally controlled) for the eastern Rustler/Salado Interface groundwater compared to the non-enriched Rustler samples. A different recharge area need not be a great distance away: slight differences in geomorphology and sediment type can have a large impact on the isotopic characteristics of recharge (Allison et al. 1985; Stephens, 1985).

Though evaporation of recharging water could account for the heavy-isotope enrichment of the eastern Rustler/Salado Interface brines, it is difficult to infer a recent meteoric origin for these samples. Though the trend of these data back toward the meteoric water line suggests a meteoric origin, the least-squares best-fit line through the Rustler/Salado Interface heavy-isotope enriched points leads to a source water on the meteoric water line with an approximate composition of δD =-74 and δ^{18} 0 = -10 (Please note that the best-fit line shown on Figure 9 includes data in addition to that from the Rustler/Salado Interface). This source composition is within the range of presently observed precipitation (discussed in a following section), but it is considerably more depleted in heavy isotopes than the Rustler groundwater that is clustered about the meteoric water line.

The lighter source water could be explained by recharge either during the cooler season or from heavy rainfalls depleted in heavy isotopes, but this explanation seems contradictory to the evaporation during recharge needed to account for the deviation from the meteoric water line. The most simple explanation is that these waters were recharged at some time in the past when the mean isotopic composition of rainfall was more depleted in the heavy isotopes of oxygen and hydrogen than today, and that the water has had a long residence time during which its

isotopic composition has changed either due to rock/water interaction or mixing of different waters.

Mixing With Heavy-Isotope Enriched Water

Mixing with a remnant evaporitic brine could produce a water enriched in heavy isotopes. However, the Rustler/Salado Interface samples do not lie on a mixing line between the nonenriched Rustler groundwater and an evaporation window leading from a range of the isotopic composition of seawater (Figure 9). A range of seawater is shown on Figure 9 because Permian seawater may have been slightly depleted in heavy isotopes relative to modern seawater due to melting of the polar ice caps. Complete melting of all ice sheets could lower the δ^{16} O value of seawater to -1‰ and the δ D to -10‰ (Taylor, 1974). The maximum evaporative enrichment of seawater in δ^{16} O is probably near +6‰, limited by back exchange between the brine and atmospheric water vapor (Lloyd, 1966).

The remnant evaporitic brine would not necessarily have to be a simple evaporated seawater brine. Based on the isotopic composition of fluid inclusions from the Permian-age San Andres salt in the Palo Duro Basin, Knauth and Beeunas (1985 and 1986) concluded that the salt precipitated from a mixed meteoricmarine evaporative brine. A modern example of such a mixed continental/oceanic system in the coastal salt pans of the Salina Ometepec, Baja California, contains brines with similar isotopic compositions to the Palo Duro Basin fluid inclusions (Knauth and Beeunas, 1985; Kreitler et al, 1984). Mixing between the meteoric Rustler water and remnant brine with a mixed meteoric-marine evaporative isotopic composition could produce enriched brines similar to the eastern Rustler/Salado Interface brines. However, water in the Rustler/Salado Interface probably does not represent anything approaching pure Permian water. The nature of the Interface (a contact residuum

from the dissolution of evaporites) and the trend of these data back toward the meteoric water line suggests that flushing of original fluids has occurred.

The trajectory of the enriched Interface samples points through the isotopic composition of fluid inclusions from the Salado Formation (O'Neil et al, 1986) toward the very enriched brine samples collected from brine reservoirs in the Castile Formation (Figure 9). This trend has been discussed by Roedder (1984) and O'Neil and others (1986), though the trend now appears stronger with the addition of Lambert's (1986) data. O'Neil and others (1986) conclude that the isotopic trend reflects mixing between evaporated Permian seawater (perhaps in the form of gypsum dehydration water) and later meteoric water possibly introduced during salt recrystallization. Though Roedder (1984) agrees that mixing is one interpretation of the data. he suggests that the trend in the Salado fluid inclusion data may represent deposition in a mixed meteoric/marine Permian environment, such as postulated by Knauth and Beeunas (1985 and 1986) for the Palo Duro Basin.

The trajectory of the Rustler/Salado Interface data on Figure 9 cannot be due simply to deposition in a mixed meteoric/marine Permian environment because the interface is the result of post-Permian dissolution of salt by meteoric water. The trend indicates that either the Rustler/Salado Interface water has mixed with a Castile-like brine or that the Interface water is undergoing a similar isotopic evolution as the deeper brines. Both of these hypotheses are complicated by the radically different major ion chemistries (particularly SO₄, Mg, and K) in the Rustler/Salado Interface and the Castile (Table 4). However, mineral precipitation/solution might account for the ion discrepancies in the mixing model, and the isotopic and

Table 4

Formation Castile Castile Castile R/S R/S R/S R/S R/S R/S R/S WIII-12 нı H2 1#1 н£ HБ Well EFIDA-6 нß P14 EFIDA-6 313,000 TIDS (mg/L) 321,000 330,000 328,000 325,000 311,000 326,000 320,000 411,000 315,000 C1 (mg/L) 186,100 200,000 210,000 210,000 290,000 200,000 170,000 180,000 178,000 210,000 504 (mg/L) 16,000 16,000 18,000 1,400 2,000 520 1,300 370 2,000 10,000 HICG_ (mg/L) Ca⁺⁺ (mg/L) 1,310 2,600 2,700 199 467 300 675 1 ---220 130 **49**0 350 13,000 9,200 18,000 8,300 2,100 4,200 570 ¹∼ Mg⁺⁺ (mg/L.) 350 450 1,600 30,000 25,000 25,000 27,000 82,000 21,000 1,200 Na⁺(mg/L) 112,000 112,000 138,000 56,000 66,000 59,000 66,000 14,000 80,000 120,000 κ⁺ (mg/L) 5,100 3,800 2,900 17,000 9,100 14,000 8,600 21,000 8,000 13,000 Ropielak, '83 Ropielak '83 Source Lanbert '78 Mercer '83 Salado fluid

Chemical Analyses of Oroundwater from the Castile Formation and the Rustler/Salado Interface Fast of Livingston Ridge

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major solute evolution paths do not have to be identical in the evolution model. Considering the large uncertainty in the cause of the isotopic enrichment of the Castile brine (O'Neil et al, 1986; Popielak et al, 1983; Lambert, 1978) and the lack of application of some of the Castile-enrichment hypotheses to the Rustler/Salado Interface (e.g. gypsum hydration water), the mixing of deeper brine and meteoric water seems the best explanation for the Rustler/Salado Interface isotopic compositions. The mechanism of this mixing could be related to the slow movement of water through approximately two thousand feet of low-permeability evaporites, or to a major salt recrystallization event, or to a tectonic event that produced conduits for flow in the form of fractures. It should be noted that the isotopic composition of Salado fluid inclusions analyzed by Knauth and Beeunas (1986) do not plot on the Rustler/Salado Interface-Castile brine mixing line. There are apparently at least two types of isotopically distinct water in inclusions, perhaps related to the two groups of fluid inclusions identified by Stein and Krumhansl (1986) on the basis of major ion composition.

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Isotopic exchange between minerals and water (coupled with a long residence time), evaporation during recharge, and mixing with enriched brine could all produce the heavy-isotope enrichment observed in some of the Rustler/Salado Interface samples. Given the lack of a well-defined recharge area and the low permeabilities encountered in the eastern part of the Rustler/Salado Interface (Mercer, 1983), exchange and mixing seem more likely to be the cause of the enrichment than evaporation. Whatever the cause of the enrichment in heavy isotopes, the Rustler/Salado groundwater from the eastern part of the study area does not seem to be closely related to modern meteoric water in the area.

The Culebra and Magenta Dolomites

Of the water from the Culebra and Magenta dolomites, only the groundwater from the Culebra in wells P-18 and W-29 plot outside the area defining the typical non-enriched Rustler isotopic composition. The measured hydraulic properties in the Culebra, which identify P-18 as having the lowest transmissivity, and the dolomite composition of the Culebra, suggest that the isotopic deviation of P-18 is probably due to water-rock interaction. Considering the aquifer matrix, oxygen-isotope exchange between the groundwater and dolomite is the most reasonable reaction. Both P-17 and P-18 are within Mercer's (1983) zone of restricted circulation in the Culebra (Figure 11). Well P-17 shows a slight oxygen-18 enrichment, and it may be that P-17 belongs outside the typical Rustler group. There are not enough isotopic data to either support or deny Mercer's (1983) division of the Culebra flow system. However, as discussed by Chaturvedi and Channell (1985, p. 37), recent hydrologic tests have revealed high transmissivities within the "zone of restricted circulation", indicating that the previous division of the flow system is not valid.

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Well WIPP-29

The location of WIPP-29 within the zone of active circulation in Nash Draw and the very shallow water level measured in this well (8.2 ft below the surface, Mercer, 1983), indicate that evaporation is a probable cause for this sample's deviation from the MWL. Though the top of the Culebra dolomite is actually four feet below the water level, the loss of core in the limestone above the Culebra indicates that the overlying limestone is fractured (SNL and USGS, 1979), and the Culebra and overlying units probably behave as a single hydrologic unit in the WIPP-29 area (Chaturvedi and Channell, 1985). As discussed earlier, evaporation-line slopes usually vary between 2.5 and 6 for surface water (Gat, 1981; Lloyd, 1966) and have been



Figure 11. Stable isotope interpretations superimposed on Mercer's (1983) division of the Culebra flow system. Recent hydrologic tests have revealed high transmissivities within the "zone of restricted circulation", indicating that the division of the flow system is not valid. Adapted from Mercer (1983).

observed to be slightly lower for evaporation in the unsaturated zone (Allison, 1982). A postulated evaporation line leading from the Rustler grouping to WIPP-29 has a slope of 3.7, which lies in the smaller end of the range of usually observed evaporation-line slopes reported by Gat (1981) (Figures 4 and 8). The low slope is indicative of evaporation in a lowhumidity, continental environment, such as is found in Nash Draw, and is consistent with the lower slopes observed for unsaturated-zone evaporation (Allison, 1982). The isotopic composition of WIPP-29 must be interpreted with caution due to the possibility of contamination of the Nash Draw area with potash-refining effluent and oil-field brine. Most of the water used for potash refining comes from the Ogallala Aquifer near Hobbs and would not cause an enriched heavy-isotope composition. Mixing between Rustler water and enriched oil-field brine similar to the samples from the Morrow Formation (Figure 9) could result in an isotopically heavy water; however, the dissolved solids in the mix would not be as high as the dissolved solids reported in the Culebra at WIPP-29 (Table 5).

Lambert (1986) believes that the WIPP-29 isotopic composition is evidence of a "profound hydraulic isolation of WIPP-29 from the rest of the Culebra." Though Lambert (1986) states that the isotopic composition of WIPP-29 can be derived by evaporating water with an isotopic composition representative of the Culebra, he discounts the evaporation mechanism because "...the high transmissivity of the Culebra at WIPP-29 (1000 feet squared per day; Gonzalez, 1983) together with the little enrichment in solutes relative to the rest of the Culebra (Lambert and Robinson, 1984) shows that water is in quantity much greater than that probably necessary to offset loss by evaporation" (Lambert, 1986). Though the water must be abundant

Table 5

Total dissolved solids content of groundwater in the Culebra member in WIFF-area wells and groundwater from the hydrocarbon-producing Morrow Formation in southeastern New Mexico

	Rustler	Formation	Well	H1	H2	H3	194	H5
	Culebra	Menher	1106 (mg/L)	97,300	8900	51,600	18,200	144,000
	Austler	Formation	Well	HS	H7	BB	89	H10
	Culebra	Member	TDS (mg/L)	52,000	3200	3000	3300	66,000
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	Rustler	Formation	Well	P14	P15	P17	P18	W25
	Culebra	Member	TD6 (mg/L)	33,700	23,700	92,500	118,000	17,000
	Bustler	Formation	Well	W26	W27	W28	W29	W 30
	Culebra	Member	TD6 (mg/L)	16,000	126,000	56,000	239,000	109,000
	MORTOW 1	Formation	Well	Todd State	: Todd	Federal		
			TTTC (met (T)	35 600		2 400		
				ູບບູບບູບ	3	4, TUU		

enough to offset loss by evaporation (otherwise the water table would be dropping), that does not preclude evaporation-induced enrichment of the heavy isotopes in the residual water. The situation of water flowing in the Culebra from an unknown recharge point to the area around WIPP-29 where partial evaporation takes place, and then on to its ultimate discharge at Laguna Grande de la Sal, can be modeled as a constant volume lake with both inflow and outflow. In this model:

$$\delta_{L}^{SS} = \delta_{in} - \frac{F_{in}}{F_{out}} - \frac{F_{in}}{F_{out}}$$
(Gat, 1981)

with δ_L^{SS} = the steady state isotopic composition of the lake $\overline{\delta}_{in}$ = the mean isotopic composition of the inflow $\overline{\delta}_E$ = the mean isotopic composition of evaporation F_{in}, F_{out} = the amount of flow in and out E = the amount of evaporation

If evaporation is negligible, the steady state isotopic composition of the lake approaches that of the inflow and no enrichment in heavy isotopes occurs. However, as evaporation becomes more important than outflow $(E > F_{out})$, the steady state isotopic composition of the lake is increasingly modified from that of the inflow. Therefore, though the lake volume remains constant (with adequate inflow to offset evaporation loss), and there is outflow from the lake, the lake can become enriched in the heavy isotopes due to evaporation.

Applying this model to WIPP-29 reveals that the abundance of water noted at WIPP-29 does not contradict heavy-isotope enrichment by evaporation. The large dissolved solids content

at WIPP-29 Culebra, relative to the rest of the Culebra, also supports an evaporation hypothesis (Table 5). Given the shallow depth to groundwater at WIPP-29, partial evaporation in the unsaturated zone is the most likely cause of the observed isotopic enrichment. The stable isotope content of groundwater from WIPP-29 is consistent with the existence of a hydraulic connection between the Culebra at WIPP-29 and the Culebra elsewhere in Nash Draw and to the east.

Summary

The Rustler Formation groundwater shown in Figure 8 falls into two distinct groups of water. There is a group that closely parallels the MWL, collected from active flow systems in the Rustler Formation. The second group deviates substantially from the MWL. being enriched in oxygen-18 and deuterium. The enriched samples come from areas of restricted circulation or high evaporation and presumably reflect mixing with enriched brine, interaction between the water and rocks, or evaporation of water in the unsaturated zone. The isotopic compositions of the Rustler samples that plot along the meteoric water line do not indicate a long residence time for the water, as would be indicated if there was an enrichment in the heavy isotopes due to exchange with the aquifer matrix. Considering that the matrix is dolomite, enrichment of the water in oxgen-18 would be expected if there were long residence times and a large rock-towater ratio. The lack of enrichment does not prove, however. that the water was recharged under current climatic conditions. Modern precipitation and verifiably young groundwater in the area must be examined to evaluate if the isotopic composition of Rustler groundwaters could be derived from modern meteoric recharge.

STABLE ISOTOPES IN PRECIPITATION, SURFACE WATER, AND OTHER GROUNDWATER IN THE AREA

Precipitation

The isotopic composition of samples of precipitation in southeastern New Mexico is presented in Figure 12. The samples from the WIPP site and from Carlsbad are grab samples from individual storm events. Likewise, the snow samples from Sierra Blanca (on the western border of the Roswell Basin) are also grab samples (Hoy and Gross, 1982). The Roswell precipitation data are monthly or bimonthly composites collected at the Roswell National Oceanographic and Atmospheric Administration weather station (Hoy and Gross, 1982).

The data plotted from Hoy and Gross (1982) include only those samples for which both oxygen-18 and deuterium measurements were made. In addition to these data, Hoy and Gross (1982) analyzed oxygen-18 for monthly composites of precipitation for three years. These data were weighted according to volume of precipitation and a weighted mean 50-18 composition for precipitation at Roswell was computed (Hoy and Gross, 1982). This weighted mean is also plotted on Figure 12, estimating the corresponding 5D value from the local meteoric water line.

The weighted mean isotopic composition for precipitation at Roswell is relatively enriched in the heavy isotopes compared to the range of values. This reflects the season of maximum rainfall (Figure 5). Moisture in southeastern New Mexico originates in both the Pacific and the Gulf of Mexico; however, the isotopically heavier Gulf moisture predominates in the summer months, when the majority of rainfall occurs (Tuan et al. 1973).



Figure 12. Plot of δD vs $\delta^{18}O$ for precipitation at Carlsbad, the WIPP Site, and in the Roswell Basin. Hoy and Gross (1982) calculated the local meteoric water line for the Roswell Basin and the weighted mean precipitation value for the town of Roswell. Data are listed in Table 3.

The isotopic composition of isolated precipitation events in Carlsbad and at the WIPP site falls in a range that coincides well with observed rains and snows in the Roswell Basin. The snow samples collected in Carlsbad exhibit the same extreme depletion in heavy isotopes that is seen in the snow samples from Sierra Blanca, while the summer rain is enriched in heavy isotopes similar to the summer rain in Roswell.

The global meteoric water line shown on Figure 12 was established by Craig (1961) on the basis of about 400 meteoric water samples collected worldwide. The line is defined by: $\delta D=8\delta^{18}0 + 10$ (Craig, 1961). Since the global line was identified, it has been noted that different areas of the world have unique δD -axis intercepts and occasionally different slopes than the global meteoric water line. The meteoric water line in North America is defined by a line with a slope similar to the global line, but with an intercept of 6 ± 3 rather than 10 (Yurtsever and Gat, 1981).

Using data from precipitation, groundwater, and surface water in the Roswell Basin, Hoy and Gross (1982) identified a local meteoric water line described by:

 $\delta D = 7.27 (\pm 0.38) \delta^{18}0 + 5.36 (\pm 1.25).$ According to Hoy and Gross (1982), the difference between Craig's (1961) line and the Roswell data may not be statistically significant. If significant, the minor departure of the Roswell Basin data from the global meteoric water line may be due to a slight evaporation effect. A least-squares linear regression through the data from the random precipitation sampling in the Delaware Basin (Carlsbad and the WIPP site) gives a line defined by:

$$\delta D = 7.54 \ \delta^{18} 0 + 5.07$$

with a correlation coefficient of 0.989. Though not based on a

statistically sound sample distribution, there appears to be a similarity in the $\delta D/\delta^{18}$ O relationship between meteoric water in the Delaware and Roswell Basins. This suggests that if there is any slight evaporation effect on the isotopic composition of rainfall, it is similar in both basins.

Groundwater

In many areas, the isotopic composition of meteoric groundwater approximates the mean composition of precipitation over the recharge area (Gat, 1981). However, some groundwater is either more enriched or more depleted in heavy isotopes than the mean composition of local rainfall. Such differences are often larger under more arid conditions and are usually the result of the recharge process (Gat, 1981). In order to determine the isotopic composition of water that actually infiltrates to recharge aquifers in arid areas, it is useful to sample shallow groundwater that can be proven to receive modern recharge. The presence of modern recharge can be determined by radiometric age dating (principally using tritium). or by observing fluctuating water-table levels with variations in rainfall. Unfortunately. no indisputably young groundwater has been identified in the immediate WIPP area. However, groundwater in the Roswell Basin has been dated with tritium and can be documented as receiving recharge within the last thirty years (Hoy and Gross, 1982). In addition, water found in pools in Carlsbad Caverns is generally considered to come from the infiltration of modern precipitation on outcrops (Lambert, 1986).

Roswell Basin

The isotopic compositions of groundwater and surface water in southeastern New Mexico are plotted on Figure 13, along with the outline of the non-deviated Rustler samples and the weighted mean precipitation point from Hoy and Gross (1982). The



Figure 13. Plot of δD vs $\delta^{18}O$ for groundwater and surface water in southeastern New Mexico. Rustler Formation water is not shown, but the area occupied by most Rustler groundwater is shaded. The Roswell Basin groundwater has been dated with tritium as receiving recharge within the last thirty years. The data are listed in Table 3.

coincidence between the isotopic composition of the verifiably young Roswell Basin groundwater and the composition of the Rustler water is striking (Figures 8 and 13).

The isotopic composition of the weighted mean precipitation in the Roswell Basin is somewhat enriched in heavy isotopes compared to groundwater from both the Roswell and Delaware The lighter composition of the groundwater relative to Basins. the weighted mean precipitation could be related to either, or both. of the following processes. First, though the majority of rainfall may occur in the summer, this is also the time of the highest evapotranspiration rate. Because of cooler temperatures. lower evaporation, and reduced plant activity, recharge from isotopically lighter winter precipitation may be favored over recharge from summer rain. A second possibility is that recharge in this arid area may occur primarily from intense, infrequent storms. Rainfall events with high total precipitation volumes are characterized by lighter isotopic compositions (Gat and Gonfiantini, 1981; Vogel, 1963). Therefore. the lighter isotopic composition of groundwater relative to the composition of weighted mean precipitation could be due to either a seasonal or an amount effect.

A similar discrepancy between the isotopic composition of groundwater and of the mean precipitation has been noted in the Kalahari Desert in southern Africa. Vogel and others (1963) found that groundwater in South Africa contained considerably less deuterium than either the area rain or river water. After confirming that low deuterium concentrations were associated with heavy precipitation, they concluded that the groundwater supply was not being continuously replenished by precipitation, but was recharged primarily from occasional heavy downpours

(Vogel et al., 1963). The possibility that the depleted Kalahari groundwater was recharged in a previous climatic regime by rain of a different isotopic composition than present was contradicted by the C-14 ages of the groundwater (Mazor et al., 1974).

Carlsbad Caverns

The isotopic composition of water from pools in Carlsbad Caverns is markedly enriched in the heavy isotopes relative to the composition of groundwater in units of the Rustler Formation (Figure 13). This difference between the isotopic content of water from the Caverns and groundwater from the Rustler is the basis for Lambert's (1986) conclusion that the Rustler is not receiving recent meteoric recharge. Lambert (1986) assumes that the relatively heavy content of the Caverns' water is representative of modern meteoric recharge in southeastern New Mexico. However, the Caverns' water is more enriched than both the mean precipitation and verifiably young groundwater in the Roswell Basin, and therefore is not representative of all young groundwater in the area.

The difference between the isotopic composition of the Roswell Basin water and the Caverns' water could be attributed to the influence of isotopically lighter high-altitude recharge in the Roswell Basin. However, as discussed previously in greater detail, Roswell Basin groundwater has an isotopic content consistent with that of precipitation at low to intermediate elevations in the basin. In addition, some of the data, particularly from the alluvial aquifer in the Artesia area, are from aquifers that receive major portions of their recharge by direct infiltration of precipitation at low elevations and these groundwaters are also substantially lighter isotopically than the Caverns' water.

The heavy-isotope enriched nature of the Carlsbad Caverns' water may be related to the Caverns' unique hydrologic environment. in which recharge occurs on a karstic terrain and discharge is almost entirely by evaporation from seeps along the walls and from pools (Hendrickson and Jones, 1952). The recharge mechanism for the Caverns may favor isotopically heavy water. presumably by allowing the infiltration of more summer precipitation. National Park Service personnel at Carlsbad Caverns have observed increased dripping in the Caverns in the summer months. relative to the rest of the year, and have noted an increase in drip rate in the Big Room within a few weeks of large, sustained storms (Ron Kerbo, National Park Service, personal communication, 1986). The extreme karst conditions at the Caverns may allow rapid infiltration of all precipitation, whereas infiltration elsewhere in southeastern New Mexico may favor recharge during cooler months when evaporation is less effective or only during heavy storms.

The enrichment in heavy isotopes in water in Carlsbad Caverns could also be explained by evaporation from pools in the humid environment of the cave. Evaporation could also occur as the water moves through the 600 feet of unsaturated zone and as water slowly drips from and along speleothems. The humid environment of the cave (usually at 96% relative humidity in the main body of the cave; Ron Kerbo, National Park Service. personal communication, 1986) would result in a higher evaporation-line slope, leading back to an original isotopic composition for the water approximating that of the value for Indeed, an evaporation "window" weighted mean precipitation. leading from the value for weighted mean precipitation and outlined by evaporation-line slopes between 2.5 and 6. encompasses almost all of the Caverns' data (Figure 14). The data cluster about the higher slope (6) and are not markedly



Figure 14. Plot of δD vs $\delta^{18}0$ for water from pools in Carlsbad Caverns, overlain by an evaporation window leading from the weighted mean composition of precipitation. The clustering of data about the higher slope is consistent with evaporation in the humid cave environment.

offset from the local meteoric water line observed by Hoy and Gross (1982) (with a slope of approximately 7.3). This lack of notable deviation from the meteoric water line reflects the fact that when the relative humidity approaches 100%, an equilibrium isotopic fractionation (exchange reaction) occurs between the atmospheric moisture and the liquid (Gat. 1981). An equilibrium isotopic exchange reaction between atmospheric moisture and the liquid also occurs under lower relative humidity conditions. but it is masked by the kinetic separation (non-equilibrium component) resulting from fractionation during evaporation.

Ogallala Formation

Data from other groundwater in southeastern New Mexico are also presented in Figure 13, though none of these waters have been documented as receiving recent recharge. The isotopic data from the Ogallala and the Dewey Lake (?) fall between the areas defined by the Caverns and Rustler isotopic compositions. The Ogallala point represents the composition of nine municipal water systems in southeastern New Mexico that draw from the Ogallala. The Ogallala receives recharge by direct infiltration of precipitation and probably represents recent recharge. The lighter isotopic composition of the Ogallala, compared to that of water found in Carlsbad Caverns, further demonstrates that the Caverns are not isotopically representative of all young groundwater in southeastern New Mexico.

Dewey Lake Redbeds

The Dewey Lake (?) sample (question mark notation is from Lambert, 1986) has unclear origins. Lambert (1978) reported groundwater from the Rustler Formation (member unidentified), collected from a well on the James Ranch, that had an isotopic composition identical to the Dewey Lake (?) point (collected from a well on the James Ranch) reported in Lambert (1986).
Presumably, the data reported for the James Ranch well in Lambert (1978) and Lambert (1986) are identical. The zone of completion of the James Ranch wells has been a matter of speculation, though a recent investigation concluded that rather than being completed in the Rustler, as previously thought, the wells were possibly completed in the Dewey Lake (Mercer, 1983).

The uncertainty of the sampled interval necessitates caution in using the Dewey Lake (?) data. The data plot toward the heavier end of the space between the Rustler and Caverns fields. If the water is from the Rustler, the distinction between the Rustler and Caverns isotopic compositions is much less distinct than interpreted by Lambert (1986). If the point is from the Dewey Lake, the age and history of the water are still uncertain. Because of its low permeability, the Dewey Lake is not known to contain significant amounts of groundwater and has no detected continuous zone of saturation (Mercer, 1983). The presence of moist cuttings was usually the only indication of groundwater in the Dewey Lake during drilling for WIPP-site hydrogeologic investigations (Mercer, 1983).

Santa Rosa Sandstone

The other aquifers in southeast New Mexico for which isotopic data are available are the Santa Rosa Aquifer and the Capitan Aquifer. The isotopic compositions of water from both of these units plot within the Rustler field on Figure 13. The Santa Rosa receives recharge directly from precipitation and possibly by groundwater flow from the overlying Ogallala Formation. The water in the Santa Rosa probably represents modern recharge, as does water in the Ogallala, and is similar isotopically to water in the Rustler.

Capitan Limestone

The data from the Capitan Aquifer also coincide with the composition range found for the Rustler groundwater and are lighter than Caverns' water. Lambert (1986) concluded that modern recharge is inhibited within the Capitan, just as he postulates recharge is inhibited in the Rustler. Though highly permeable, the recharge conditions to the Capitan east of the Pecos River are not well understood. However, one of the Capitan points is from Carlsbad City Well #7 (Lambert. 1978), located west of the Pecos River. The Capitan flow system west of the Pecos is well-developed in highly karstic limestone, receiving recharge on outcrops along the Guadalupe Mountains and discharging at large springs in the Pecos River (Hiss, 1975).

Surface Water

The isotopic composition of most of the surface water data (from lakes. springs. and the Pecos River) shows the effect of evaporation. The greater degree of oxygen-18 enrichment seen in the surface waters as compared to water from Carlsbad Caverns is due to the surface waters' evaporation in the semi-arid desert environment. resulting in a lower evaporation-line slope. Overlaying the evaporation "window" shown on Figure 4 onto the surface water points presented in Figure 13 results in evaporation lines for these river and spring points leading back to isotopic compositions that fall in the Rustler groundwater group.

Surprise Spring

It should be noted that the isotopic composition of the water from Surprise Spring could be obtained by the evaporation of Rustler groundwater (Figure 13). Therefore, based on the stable isotopes, Surprise Spring could be a discharge point for Rustler groundwater. Lambert (1986) has asserted that Surprise Spring

could not be derived isotopically from Rustler groundwater and that oxygen isotope shift (presumably due to water/rock reactions) may be responsible for the spring's composition. Given the spring's surface exposure, the aridity of the area, and the ability to draw reasonable evaporation lines from the Rustler isotopic composition to the Surprise Spring isotopic composition, evaporation of Rustler groundwater seems a more likely method of deriving the enriched isotopic composition of Surprise Spring than water/rock reactions. As discussed earlier, such water/rock isotopic exchange would be extremely slow at the relatively low temperatures encountered outside of geothermal areas.

Summary

It is clear from Figures 8 and 13 that most of the isotopic compositions of groundwater in southeastern New Mexico fall in the same range as that observed in the Rustler aquifers. It is important to note that the Roswell Basin waters have been dated. proving that they were recharged during current climatic conditions, and that these waters have the same range of stable isotopic compositions as the water from the Rustler Formation. The Roswell Basin water, as well as undated groundwater from the Ogallala, Santa Rosa, and Capitan Formations, all have isotopic compositions consistent with those measured in groundwater from the Rustler Formation. No groundwater in southeastern New Mexico has been found that has an isotopic composition within the range defined by water from Carlsbad Caverns. The Caverns' water appears to be closely related isotopically to surface water in the area. Both the Caverns' water and surface water has undergone evaporation, but the surface water exhibits more deviation from the meteoric water line because of evaporation in a lower relative-humidity environment.

CONCLUSIONS AND RECOMMENDATIONS

The isotopic compositions of most of the samples of groundwater from the Magenta and Culebra aquifers, and for the Rustler/Salado Interface Zone west of the WIPP site, are similar to that of other groundwater in southeastern New Mexico. The isotopic compositions of recently recharged, dated groundwater in the Roswell Basin, of water in the shallow, active Ogallala and Santa Rosa aquifers east of the WIPP site. and of the Capitan and Rustler aquifers in the Carlsbad area, are all lighter than the isotopic composition of water found in Carlsbad Caverns. The isotopic similarity between the aquifers indicates that all of the systems were recharged by isotopically similar waters produced by similar climatic conditions. Though the stable-isotope data in no way indicate absolute ages for water in the various aquifers, neither do they show any distinction between most Rustler groundwater and verifiably young groundwater.

Some groundwater samples can be argued to be part of relatively old, slow-moving groundwater systems. This distinction is based on an observed shift away from the meteoric water line and toward enrichment in the heavy isotopes. Most of the shifted samples are from the Rustler/Salado contact east of Nash Draw. and their positions agree favorably with Mercer's (1983) distinction between more- and less-developed flow systems in the contact. The waters' enrichment in heavy isotopes may be due to mixing with deeper groundwater (supported by the stable isotopic composition of Salado fluid inclusions and Castile brine) or to exchange between the groundwater and hydrous minerals. In contrast, it is significant that most of the Culebra and Magenta waters do not exhibit an oxygen-18 excess, indicating that the waters' residence time has not been long enough for isotopic exchange between the water and dolomite.

The isotopic compositions of water from WIPP-29 and from Surprise Spring can be derived by partially evaporating a water with an isotopic composition representative of water found in the Rustler aquifers. Therefore, the stable isotope data are consistent with the concept of discharge from the Rustler by evaporation in the unsaturated zone in the area of WIPP-29 and discharge by direct evaporation from Surprise Spring outflow.

The stable isotope data from water in southeastern New Mexico indicates that water from Carlsbad Caverns is not isotopically representative of groundwater recharge in the area. The isotopic composition of the Caverns' water is more similar to that of surface water in the area rather than groundwater. There are two possible explanations for the unique, heavy, composition of the Caverns' water. First, evaporation and equilibrium isotopic exchange in the humid environment of the cave could produce the Caverns' isotopic composition from a starting fluid with approximately the same isotopic composition as the area's weighted mean precipitation. Second, the Caverns may receive disproportionately more recharge from isotopically heavy summer rains than the aquifers in the area, perhaps due to the unique hydrologic system imposed by the extreme karst conditions.

There is currently no basis for concluding that the Rustler aquifers are not receiving significant amounts of modern meteoric recharge. The concept that the Rustler contains slowmoving, fossil water is not supported by the isotopic data except in the eastern part of the Rustler/Salado Interface. In fact, the isotopic similarity between the Rustler water and verifiably young groundwater in the area, and the lack of isotopic exchange between Culebra and Magenta water and the carbonate matrix, imply that there is a good possibility that the Rustler is currently receiving recharge.

Stable isotopes, though valuable tools in interpretive hydrology, are best applied in situations where the basic hydrology of the system is understood, but refinement of interpretations is desired. However, there are many uncertainties remaining concerning the physical hydrology of Rustler flow systems, especially in relation to recharge. Unfortunately, the question of recharge cannot be answered on the basis of stable isotopes alone.

Additional data on the isotopic composition of precipitation at the WIPP, of infiltrating precipitation, and of shallow, young groundwater in the area will certainly aid in the interpretation of the current data base. However, actual physical measurements of the flow system of the Rustler are probably the only way the amount and location of recharge to the Rustler can be defined. Such studies have been recommended and outlined by Hunter (1985) and include water-level measurements and sampling to determine the location of groundwater divides and measurements of infiltration in the unsaturated zone of suspected recharge areas. These studies should be conducted.

REFERENCES

- Allison, G.B., 1982, The Relationship Between O-18 and Deuterium in Water in Sand Columns Undergoing Evaporation, Journal of Hydrology, Vol. 55, pp. 163-169.
- Allison, G.B., Stone, W.J., and Hughes, M.W., 1985, Recharge in karst and dune elements of a semi-arid landscape as indicated by natural isotopes and chloride. Journal of Hydrology, Vol. 76. pp. 1-25.
- Barnett, J., 1980, Carlsbad Caverns, Silent Chambers, Timeless Beauty, Carlsbad Caverns Natural History Association, Carlsbad, New Mexico, 31p.
- Chaturvedi, L. and Channell, J.K., 1985, The Rustler Formation as a Transport Medium For Contaminated Groundwater, Environmental Evaluation Group Report EEG-32, 85 p.
- Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F., and Shimp, N.F., 1966, The Origin of Saline Formation Waters, Journal of Geophysical Research, Vol. 71, no. 16, pp. 3869-3882.
- Cooper, J.B., and Glanzman, V.M., 1971, Geohydrology of the Project Gnome Site, Eddy County, New Mexico, U.S. Geological Survey Professional Paper 712-A, 24p.
- Craig, H., 1961, Isotopic variations in meteoric waters, Science, v.133, pp. 1702-1703.
- Faure. G., 1977. Principles of Isotope Geology. John Wiley and Sons. New York, 464p.

- Fontes, J.Ch., 1981, Palaeowaters, <u>in</u> Gat, J.R., and Gonfiantini, R. (eds.), Stable Isotope Hydrology, International Atomic Energy Agency, Technical Report Series, No. 210, pp. 273-302.
- Fontes, J.Ch., 1983, Dating of Groundwater, <u>in</u> Guidebook on Nuclear Techniques in Hydrology, International Atomic Energy Agency, Technical Report Series No. 91, pp. 285-317.
- Gat, J.R., 1981, Isotopic Fractionation, <u>in</u> Gat, J.R., and Gonfiantini. R. (eds.), Stable Isotope Hydrology, International Atomic Energy Agency, Technical Report Series, No. 210, pp. 21-33.
- Gat, J.R., and Gonfiantini, R., 1981, Stable Isotope Hydrology, Deuterium and Oxygen-18 in the Water Cycle, International Atomic Energy Agency, Technical Report Series No. 210, Vienna, 337p.
- Gonzalez, D.D., 1983, Groundwater Flow in the Rustler Formation Waste Isolation Pilot Plant (WIPP), Southeast New Mexico (SENM): Interim Report, Sandia National Laboratories, SAND 82-1012.
- Gross. G.W., Hoy, R.N., and Duffy. C.J., 1976, Application of Environmental Tritium in the Measurement of Recharge and Aquifer Parameters in a Semi-Arid Limestone Terrain, New Mexico Water Resources Research Institute, Report No. 60, 212p.
- Hendrickson, G.E., and Jones, R.S., 1952, Geology and Ground-Water Resources of Eddy County, New Mexico, State Bureau of Mines and Mineral Resources, Ground-Water Report 3, 169p.

- Hiss. W.L., 1975, Stratigraphy and Ground-Water Hydrology of the Capitan Aquifer. Southeastern New Mexico and Western Texas, University of Colorado, Ph.D. dissertation, 396p.
- Hoy, R.N., and Gross, G.W., 1982, A Baseline Study of Oxygen 18 and Deuterium in the Roswell, New Mexico, Groundwater Basin, New Mexico Water Resources Research Institute, Report No. 144, 95p.
- Hunter, R.L., 1985. A Preliminary Regional Water Balance for the WIPP Site and Surrounding Area. Sandia National Laboratories. SAND84-2233, 98p.
- Knauth, L.P., and Beeunas, M.A., 1985, Origin of Fluid Inclusion Water in Bedded Salt Deposits, Palo Duro Basin. Texas, Office of Nuclear Waste Isolation, Battelle Memorial Institute, BMI/ONWI-569, 59p.
- Knauth, L.P. and Beeunas, M.A., 1986, Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters, Geochimica et Cosmochimica Acta, Vol. 50, pp. 419-433.
- Kreitler, C.W., Chapman, J.B., and Knauth, L.P., 1984, Chemical and Isotopic Composition of Waters from the Salina Ometepec, Baja California. The University of Texas at Austin. Bureau of Economic Geology. Open-file Report OF-WTWI-1984-41. Austin, Texas, 13p.

- Lambert, S.J., 1978, Geochemistry of Delaware Basin Groundwaters, <u>in</u> Austin, G.S. (ed.), Geology and Mineral Deposits of Ochoan Rocks in Delaware Basin and Adjacent Areas, New Mexico Bureau of Mines and Mineral Resources, Circular 159, pp. 33-38.
- Lambert, S.J., 1983, Dissolution of Evaporites in and Around the Delaware Basin, Southeastern New Mexico and Texas, Sandia National Laboratories, SAND82-0461, 96p.
- Lambert. S.J., 1986, Stable-Isotope Studies of Groundwaters in Southeastern New Mexico, (SAND85-1978C), in Chaturvedi, L. (ed.), The Rustler Formation at the WIPP Site, Environmental Evaluation Group Report, EEG-34.
- Lambert, S.J., and Robinson, K.L., 1984, Field Geochemical Studies of Groundwaters in Nash Draw, Southeastern New Mexico, Sandia National Laboratories, SAND83-1122, 38p.
- Lloyd, R.M., 1966, Oxygen isotope enrichment of sea water by evaporation, Geochimica et Cosmochimica Acta, Vol. 30, pp. 801-814.
- Mazor, E., Verhagen, B.T., Sellschop, J.P.F., Robins, N.S., and Hutton, L.G., 1974, Kalahari Groundwaters: Their Hydrogen, Carbon and Oxygen Isotopes, <u>in</u> Isotope Techniques in Groundwater Hydrology 1974, Vol. 1, International Atomic Energy Agency, Vienna, Austria, pp. 203-225.
- Mercer, J.W., 1983, Geohydrology of the Proposed Waste Isolation Pilot Plant Site, Los Medanos Area, Southeastern New Mexico, U.S. Geological Survey Water-Resources Investigations Report 83-4016, 113p.

- Nicholson, Jr., A., and Clebsch, Jr., A., 1961, Geology and Ground-Water Conditions in Southern Lea County, New Mexico, State Bureau of Mines and Mineral Resources. Ground-Water Report 6, 123p.
- O'Neil, J.R. and Kharaka, Y.K., 1976, Hydrogen and Oxygen Isotope Exchange Reactions Between Clay Minerals and Water, Geochimica et Cosmochimica Acta. Vol. 40, pp. 241-246.
- O'Neil, J.R., Johnson, C.M., White, L.D., and Roedder, E, 1986, The Origin of Fluids in the Salt Beds of the Delaware Basin, New Mexico and Texas, Journal of Applied Geochemistry, Vol. 1. no. 2. pp. 265-271.
- Popielak, R.S. Beauheim, R.L., Black, S.R., Coons, W.E., Ellingson, C.T., and Olsen, R.L., 1983, Brine Reservoirs in the Castile Formation. Waste Isolation Pilot Plant (WIPP) Project, Southeastern New Mexico, Department of Energy, TME 3153.
- Roedder. E., 1984, The Fluids in Salt, American Mineralogist, Vol. 69, pp. 413-439.
- Sandia National Laboratories and U.S. Geological Survey, 1979, Basic Data Report for Drillhole WIPP 29 (Waste Isolation Pilot Plant ~ WIPP), Sandia National Laboratories, SAND79-0283, 19p. + appendices.
- Savin. S.M., 1980. Oxygen and Hydrogen Isotope Effects in Low-Temperature Mineral-Water Interactions, <u>in</u> Fritz, P. and Fontes, J.Ch. (eds.), Handbook of Environmental Isotope Geochemistry, Vol. 1, The Terrestrial Environment, Elsevier Scientific Publishing Company, pp. 282-327.

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- Savin, S.M. and Epstein, S., 1970, The Oxygen and Hydrogen Isotope Geochemistry of Clay Minerals, Geochimica et Cosmochimica Acta, Vol. 34, pp. 25-42.
- Stein. C.L. and Krumhansl, J.L., 1986, Chemistry of brines in salt from the Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico: A Preliminary Investigation, Sandia National Laboratory, SAND85-0897, 37p.
- Stephens, D.B., 1985, Ground Water Recharge Mechanisms in a Semi-Arid Terrain of New Mexico, <u>in</u> Joint Proceedings of Fifth Annual AGU Front Range Branch Hydrology Days and Fourteenth Annual Rocky Mountain Groundwater Conference. Hydrology Days Publications. Fort Collins, Colorado, pp. 213-224.
- Taylor Jr., H.P., 1974, The Application of Oxygen and Hydrogen Isotope Studies to Problems of Hydrothermal Alteration and Ore Deposition, Economic Geology, Vol. 69, pp. 843-883.
- Tuan, Y., C.E. Everard, J.G. Widdison, and I. Bennett, 1973, <u>The</u> <u>Climate of New Mexico</u>, State Planning Office, Santa Fe, New Mexico, 197p.
- U. S. Department of Energy (DOE), 1984, Waste Isolation Pilot Plant Safety Analysis Report, variable paging.
- Vogel, J.C., Ehhalt, D. and Roether, W., 1963, A Survey of the Natural Isotopes of Water in South Africa, <u>in</u> Radioisotopes in Hydrology, International Atomic Energy Agency, Vienna, Austria, pp. 407-415.

- Welder, G.E., 1983, Geohydrologic Framework of the Roswell Ground-Water Basin, Chavez and Eddy Counties, New Mexico, New Mexico State Engineer, Technical Report 42, 28p.
- Yurtsever, Y., and J.R. Gat, 1981, Atmospheric Waters. <u>in</u> Gat, J.R. and Gonfiantini, R. (eds.). Stable Isotope Hydrology, International Atomic Energy Agency, Technical Report Series, No. 210, pp.103-142.

APPENDIX A

Potentiometric Surface Maps (freshwater heads) for water-bearing zones in the Rustler (modified from Mercer, 1983).

- A-1. Rustler-Salado Interface
- A-2. Culebra Dolomite
- A-3. Magenta Dolomite



Figure A-1. Adjusted potentiometric contours of the Rustler/Salado contact residuum (modified from Mercer, 1983).



Figure A-2. Adjusted potentiometric contours of the Culebra Dolomite Member of the Rustler Formation (Modified from Mercer, 1983).



Figure A-3. Adjusted potentiometric contours of the Magenta Dolomite Member of the Rustler Formation (modified from Mercer, 1983).