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Sandia National Laboratories
Waste Isolation Pilot Plant

Defining Culebra Recharge through Geochemistry and Stable Isotope Analysis

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Acronym List	
δD	Deuterium
$\delta^{18}O$	Oxygen 18
^{14}C	Carbon 14
AR	Activity Ratio
CRA	Compliance Recertification Application
EDS	Energy Dispersion Spectroscopy
GMWL	Global Meteoric Water Line
^{3}H	Tritium
^{3}He	Helium 3
^{4}He	Helium 4
^{81}Kr	Krypton 81
LWB	Land Withdrawal Boundary
PA	Performance Assessment
RCHCM	Revised Culebra Hydrology Conceptual Model
SEM	Scanning Electron Microscope
SF6	Sulfur hexafluoride
^{234}U	Uranium 234
^{238}U	Uranium 238
WIPP	Waste Isolation Pilot Plant
XRD	X-Ray Diffraction

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Focal Area:

Groundwater studies at the WIPP site have focused on the Culebra Dolomite Member of the Rustler Formation because it is the most transmissive, continuously saturated unit above the repository and would provide the most likely groundwater transport pathway for radionuclides released from the repository by inadvertent human intrusion. This study aims to leverage groundwater geochemistry data to enhance the understanding of flow and recharge dynamics within the Culebra. By analyzing the geochemical signatures of groundwater, we can infer the sources and mixing processes that contribute to the current groundwater composition. The current understanding is that waters present in the Culebra are a result of mixing of water flowing into the study area from: ancient recharge from the north, primitive brines from the east, and relatively recent recharge from the southwest in Nash Draw (Beauheim et al., 2008).

Science Challenge:

The Waste Isolation Pilot Plant (WIPP) Performance Assessment (PA) is designed to address the requirements of 40 CFR section 191.13, and involves three basic entities: (1) models for both the physical processes that take place at the WIPP site and the estimation of potential radionuclide releases that may be associated with these processes, (2) a probabilistic characterization of the uncertainty in the models and parameters that underlie the WIPP PA (to account for epistemic uncertainty), and (3) a probabilistic characterization of different futures that could occur at the WIPP site over the next 10,000 years (to account for aleatory uncertainty) (U.S. DOE 2019: Appendix-PA). One component of the PA performed for the Compliance Recertification Application (CRA) for the WIPP is modeling the transport of radionuclides through the Culebra. Transport modeling in PA requires groundwater flow information including input parameter representations such as transmissivity fields (T-fields). Development and calibration of T-fields requires transmissivity (T), storativity (S), horizontal anisotropy (A), and vertical recharge (R) data. The geochemistry of the Culebra groundwater can be used as a tool to evaluate the various representations of recharge flow in the Culebra and whether these representations are realistic for modeling compliance calculations on a 10,000-year time frame. The rates and spatial distribution of vertical leakage to the Culebra are needed in order to understand the compliance and basin-scale models for WIPP. A more detailed understanding of the Culebra groundwater geochemistry can provide more information as to the plausibility of the occurrence and magnitude of recharge through vertical flow in the Rustler Formation and provide useful information regarding groundwater flow and particle tracking in the event of a repository intrusion.

The hydrological peer review conducted in 2008 (Burgess et al., 2008) found inadequacies relating to the understanding of recharge, groundwater flow, and the geochemical processes associated with the Culebra hydrology conceptual model. Agreement between water chemistry and flow direction indicators and sources must be made consistent with prescribed flow directed by calculated T-fields used in compliance recertification applications.

The proposed work seeks to acquire new data and interpretations to integrate with existing data that could connect groundwater flow, geochemistry, and regional recharge/discharge to provide a more complete picture of the Culebra conceptual model. A more detailed understanding of the geochemistry of the existing Culebra monitoring wells, local springs, and precipitation would

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provide additional clarity regarding variations in Culebra confinement, groundwater flow, as well as the potential location and extent of recharge. This work proposes to conduct groundwater analyses and sampling throughout the current WIPP monitoring network and the surrounding areas including Nash Draw. Samples will be analyzed for major cations and anions, isotopes such as ^{4}He, $^{238}U/^{234}U$, $\delta^{18}O$, δD and the young water tracers, tritium and SF6. In addition, XRD and SEM/EDS analysis will be conducted on available core samples (from the WIPP core library) to identify trace elements, levels of dissolution, and minerals participating in rock water interactions. Specific items regarding recharge and groundwater flow that need to be investigated include:

- The residence time and spatial variability of water chemistry in the Culebra
- Culebra confinement
- The preferential flow patterns of waters in the Culebra
- The locations and potential effects of Culebra discharge and recharge in the Nash Draw
- Fracture interconnectivity

Rationale:

The 2008 peer review (Burgess et al., 2008) concluded that without understanding the geochemistry surrounding the Culebra hydrogeology, there remains some uncertainty in the Revised Culebra Hydrology Conceptual Model (RCHCM) with the final report stating:

"The chemical data from wells in the WIPP Site cannot be completely reconciled with the RCHCM because the sources of the principal solutes (Ca, Na, SO_4 and Cl), whether from dissolution of evaporite minerals (gypsum, anhydrite, halite) within, above or below the Culebra, are not completely understood."

This weakness has gone unaddressed. In order to provide a better understanding of flow, vertical leakage, and general Culebra hydrogeology, more insight is needed into the recharge and discharge processes in the unit. For instance, vertical leakage from the shallow water table in Nash Draw has been identified as a potential contributor to water-level fluctuations. Additionally, fractures and karst features in Nash Draw may serve as hydraulic pathways to the Culebra (Powers et al., 2006). However, these hypotheses require validation through additional data collection. With the expansion of the additional waste panels to the WIPP towards the west, there is renewed concern regarding the uncertainties documented in the RCHCM.

The current limitations in recharge characterization are primarily attributed to insufficient spatial subsurface data resolution, absence of surface water samples (including precipitation and surface flow), and lack of regional geochemical analysis. Specific data needed are: 1) more extensive water analyses (both in space and in type of water); 2) new kinds of water analyses (age dating); and 3) core characterization (more and more detailed).

More extensive water chemistry analysis both spatially and in terms of additional components are needed in order to better understand the origin of recharge in Nash Draw and the potential impacts of flow to the Culebra hydrology. Precipitation data and additional groundwater samples from the Nash Draw area are needed in order to characterize recharge and discharge. In past groundwater chemistry analyses, some key components such as iron and bromide were not analyzed. These

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analytes are key to understanding recharge and how precipitation may affect the groundwater. The chemistry data from ongoing routine groundwater sampling events will allow for input into routine calculations for regulatory analyses as well as for the monitoring of groundwater quality changes through time. Analyses of major cations and anions along with trace elements would provide new insights into groundwater rock/water interactions and potential recharge events to the Rustler Formation. These data would provide some validation of the Culebra flow model and T-Fields used in PA for the WIPP.

Mean subsurface residence time determination using natural tracers offers insights into groundwater flow and recharge timescales. The work that has been done in this area has so far been inconclusive and not spatially extensive. The broad suite of residence time tracers we propose below are designed to work on a long range of timescales and capture the significant variation in water residence times that likely exists over the study area but has yet to be extensively examined in one study.

The use of groundwater geochemistry is most effectively applied when considered in conjunction with the host rock characteristics. Mineralogical analysis of WIPP cores is basic and very few of the existing cores in the WIPP core library have been analyzed in detail for trace minerology. Identifying gypsum-rich zones within fractures is crucial, as they significantly influence transmissivity and the current lack of data hinders comprehensive fracture network assessment. A better understanding of detailed core analysis from the monitoring network core (WIPP core library), would also provide additional understanding of solute contribution to the Culebra waters, a major unanswered question identified by the peer review.

Acquiring the described data would improve the understanding of the Culebra geochemistry, flow directionality, and rock water interactions, and provide insights into vertical leakage associated with recharge.

Narrative:

Optimization and re-evaluation of the Culebra well network has been ongoing since the CCA. Plans are currently underway to expand the WIPP waste panels towards the west. Kushnereit et al. (2020) evaluated the potential travel pathways and LWB impact times of hypothetical particles released into the Culebra above the additional panels (Bowman et al., 2023). Groundwater flow and particle tracking simulations were completed for a range of hypothetical release point locations. The proposed expansion of the underground facility raises the question of whether adequate well coverage exists in the western region of the monitoring network. Results of the Kushnereit study showed that particle flow/path-line direction was towards the south and southwest, towards Nash Draw with some of the particle tracks exiting the LWB on the western side, in a full mining scenario. For this reason, understanding the hydrology west of the WIPP site and in particular Nash Draw is important to ensure the safe operation of WIPP.

Water levels in Culebra wells in Nash Draw (Figure 1) respond more rapidly to precipitation events than other wells in the WIPP network (U.S. DOE 2014: Appendix T-FIELDS, 2014). This suggests reduced confinement in that area. However, the extent of recharge from Nash Draw to the Culebra remains unclear. Historical records indicate the existence of several springs of unknown origin in

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Nash Draw (Chapman, 1988; Powers et al., 2006). Analyzing the geochemical and stable isotope composition of these springs and the Culebra monitoring wells in Nash Draw could yield valuable insights into Culebra recharge and discharge dynamics, such as the determination of the origin of the springs and a better understanding of flow in Nash Draw.

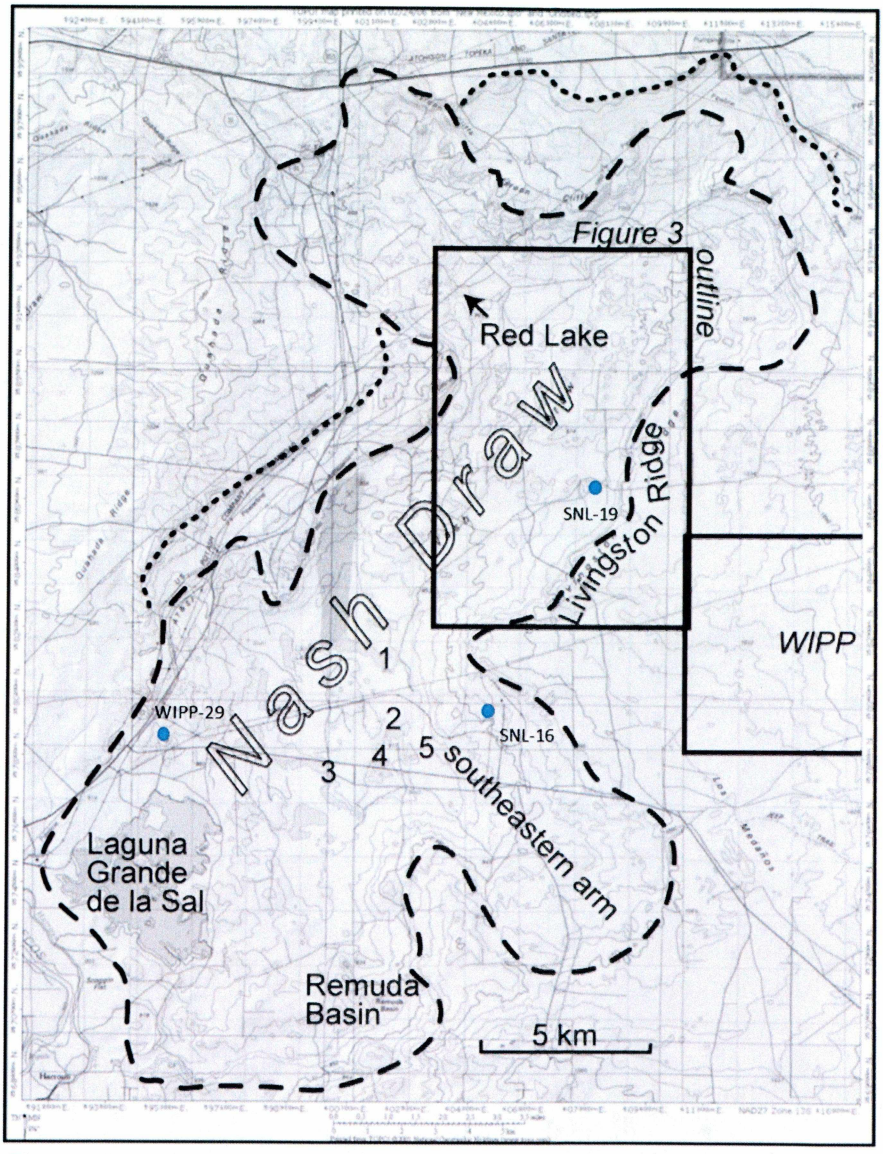


Figure 1 Nash Draw and Notable Features of Area (edited from Powers et al., 2006).

Figure 1 provides a general location map of Nash Draw with notable features identified. The numbers in the central portion of the figure refer to the brine lakes informally named Laguna Uno (1) through Cinco (5). A portion of the WIPP LWB is also included in relation to Nash Draw. The approximate locations of WIPP monitoring wells SNL-16, SNL-19, and WIPP-29 are also indicated on the figure. A notable feature in the map is the presence of the natural lake Laguna Grande de la Sal which is fed partly by brines from potash mine effluent (Powers et al., 2006).

Surface drainage basins can play a significant role in the determination of recharge location and the extent of recharge to an aquifer. In the region of Nash Draw, topographic maps, aerial

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photographs, and some field analyses were used to define separate surface drainage basin (U.S. DOE 2014; Appendix T-FIELD). Figure 2 shows the estimated drainage basins of the Nash Draw region in relation to the LWB. Several of the localized closed drainage basins represent potential recharge locations for the Rustler Formation.

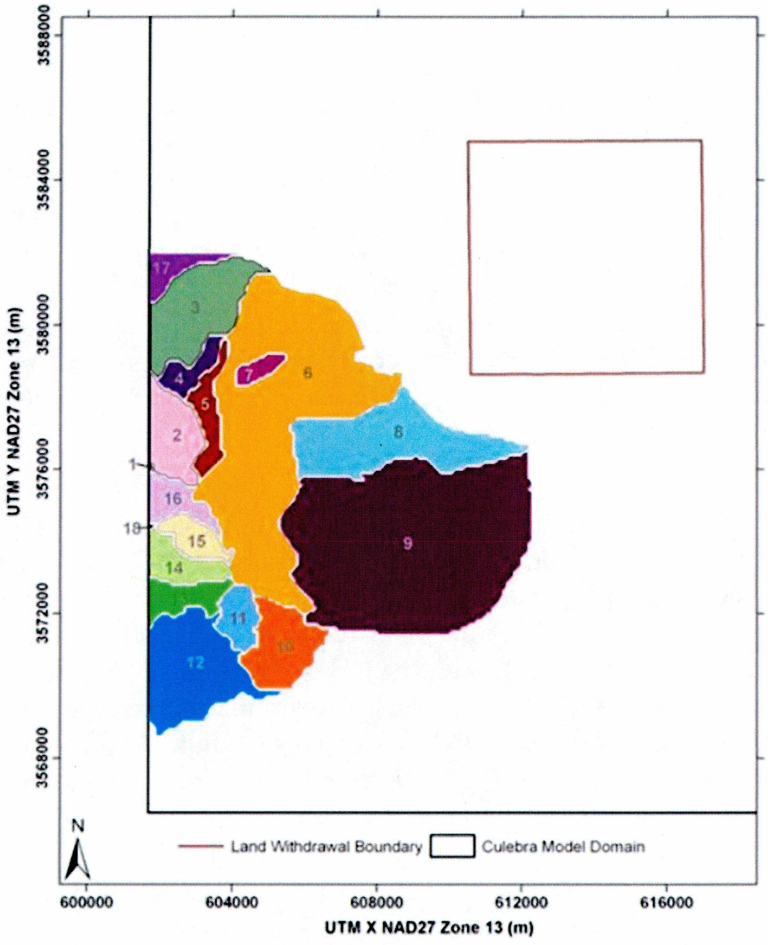


Figure 2 Mapped drainage basins in Nash Draw region (the square is the WIPP LWB) (U.S. DOE 2014. APPENDIX T-FIELDS))

Ground and Surface Water Geochemistry

Geochemistry data can be used as a tool to evaluate the variability in Culebra flow and confinement across the monitoring network as well as the potential vertical flow between the members in the Rustler Formation. Geochemical data will be used to characterize recharge waters, anomalous waters, and cement dissolution in fractures, and to determine potential flow regimes affecting transmissivity variability. Geochemistry data can be used to model groundwater evolution, mixing, and preferential flow paths by backward particle tracking using the MODPATH option of MODFLOW6 v 6.2.2. Previous studies have not employed modeling programs such as these. Understanding flow paths and mixing would provide information about the interconnectivity of fractures contributing to transmissivity variability and potential mixing of newer recharge waters with more ancient Culebra waters.

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Ground and Surface Water Isotope Geochemistry

Earlier investigations at WIPP have attempted to use ^{14}C, ^{81}Kr, stable water isotopes, and ^{3}H to estimate groundwater residence times, all of which have been either unsuccessful, inconclusive or had conflicting results. Among the currently available results from different age-dating methods associated with the Culebra, there remains an order of magnitude gap between derived estimates ages for ^{14}C and ^{81}Kr. (Sturchio et al., 2014, Lambert, 1987, Lambert and Harvey 1987). Other methods for estimating groundwater residence have not been used in the area, including ^{4}He and the young water tracers, $^{3}H/He$ and SF6. At its simplest, the measurement of young water tracers will help to pinpoint areas which are receiving modern recharge. However, in parts of the aquifer where the Culebra is suspected to be unconfined (i.e., near outcrops in Nash Draw), depth discrete sampling of young water tracers can also be used to estimate recharge rates. Where the Culebra is confined, both young and old tracers can be combined to better estimate horizontal groundwater flow velocities and delineate flow paths. Collecting and analyzing data for these tracers, alongside more extensive and precise water isotope data, could significantly enhance our understanding of groundwater ages, recharge dynamics, and mixing processes within the Culebra aquifer system.

Tritium and SF6

It is proposed that wells and springs around Nash Draw be sampled for young groundwater tracers to look for evidence of modern recharge impacting waters of the Culebra. $^{3}H/He$ and SF6 are both robust tracers of modern recharge because they rely on distinct and well-documented atmospheric inputs that serve as clear markers for groundwater recharged within the past few decades. $^{3}H/He$ dating involves the measurement of tritium (^{3}H) and helium-3 (^{3}He) concentrations in groundwater. Tritium is a radioactive isotope of hydrogen that is produced in the atmosphere by cosmic ray interactions and atmospheric nuclear weapons testing. Helium-3 is a stable isotope of helium that is produced through the decay of tritium. After water incorporating tritium has entered an aquifer, helium-3 will begin to accumulate. By measuring the ratio of tritium to helium-3 in groundwater samples, groundwater age can be estimated, particularly for groundwater recharged within the past 50 years (van Rooyen et al., 2021, Allen and Boutt, 2023, Okofo et al., 2022). If $^{3}He_{trit}$ is confined in the aquifer, the apparent $^{3}H/^{3}He$ age (in years) can be calculated using the equation (Schlosser et al., 1988 and 1989):

$$\tau = \frac{T_{1/2}}{ln2} ln\left[1 + \frac{^{3}He_{trit}}{^{3}H}\right]$$

where $T_{1/2}$ is the ^{3}H half-life. Chapman (1988) reported that a subset of Culebra waters were essentially tritium dead or the level of detection was not suitable for groundwater dating applications, in the area where the Culebra is well confined. This is not the case however for waters nearer to the surface and surrounding area (e.g. Ogalla, Nash Draw and High Plains Texas) (Lambert and Harvey 1987). Collecting new data for $^{3}H/^{3}He$ dating could provide a more comprehensive understanding of groundwater ages in areas where modern water inputs are hypothesized. Currently, it is not known the extent to which this modern water recharges the Culebra aquifer. This method will help identify modern recharge to the Culebra and can be used in conjunction with other tools like ^{4}He dating (for understanding residence time in older groundwater from horizontal flow – see below), providing a more comprehensive picture of water age.

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Similarly, SF6 dating involves the measurement of sulfur hexafluoride (SF6) concentrations in groundwater. SF6 is a synthetic, non-reactive gas that has been widely used in various industrial applications. Like $^{3}H/He$ dating, SF6 dating is particularly effective for dating modern recharge because SF6 has been released into the atmosphere only since the mid-20th century. SF6 is inert and does not react chemically with other substances in groundwater, making it an ideal tracer for tracking the movement of recent recharge (Allen and Boutt, 2023; Okofo et al., 2022).

SF6 dating is conducted by measuring the aqueous concentration by gas chromatography after the SF6 is stripped from the water sample. The value is then converted into air concentration using Henry's Law. This value can then be compared to the atmospheric concentration curve to estimate the year the sample was last in contact with the atmosphere (the recharge year) (Solomon and Gilmore, 2024). The tracer age is then calculated with the sample collection date minus the recharge year.

Helium

It is proposed that wells and springs around Nash Draw as well as other wells within the Culebra member be sampled for helium tracers to look for evidence of recharge impacting waters of the Culebra. The ^{4}He method is based on the fact that ^{4}He is produced and accumulates in the subsurface through the decay of naturally occurring uranium and thorium in aquifer materials (Clark, 2015). There are multiple advantages to using ^{4}He over or in addition to other tracers of groundwater residence time that have been investigated at WIPP. First, unlike carbon, helium is a noble gas and chemically inert. Once it is dissolved in groundwater, it remains relatively unaffected by chemical reactions or physical processes. Additionally, helium-4 dating can provide relatively accurate age estimates for groundwater ranging from thousands to millions of years, which notably encompasses the possible resolvable age ranges of both ^{14}C and ^{81}Kr. Groundwater age can be estimated as:

$$\tau = \frac{C_w}{GC_1(\frac{1}{n} - 1)}$$

where C_w is the concentration of radiogenic ^{4}He (μcm^3 STP m^{-3}), n is the fractional porosity (dimensionless), G is the rate at which radiogenic helium is generated in the aquifer over time, and C_1 is a conversion factor (3.7197×10^{-14} μcm^3 STP $atom^{-1}$) (Solomon, 2000).

The field sampling and measurement of helium-4 is more routine and simpler when compared to ^{81}Kr. Though there are uncertainties related to helium-4 age dating, given the extensive data available about WIPP, errors related to this method should be able to resolve the order of magnitude gap between ^{14}C and ^{81}Kr derived estimates. To date, no studies have attempted to use ^{4}He to estimate groundwater residence time in the area around WIPP. Several studies have proven to be successful in recent years in dating of groundwater using ^{4}He (Casillas-Trasvina et al., 2022, Trincero et al., 2019). These studies have been successful in evaluating the origin of groundwater and various mixing processes present in a groundwater system. This technique is especially effective when considered with multiple tracers.

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Mixing and Groundwater Age

Mixing between older and young groundwater is expected. The effect of mixing on tracer concentrations depends on the relationship between recharge time and tracer concentration. Tritium concentrations decrease with age, and thus mixed samples will be biased young. If the accumulation of ^{4}He is spatially constant across a flow path, however, then mixed samples will accurately reflect the mean age because it is an accumulating tracer. The impact of mixing on measured groundwater ages depends on how much mixing occurs. Since mixing affects each tracer differently, differences in the ages they indicate can show the extent of mixing. Tracer-tracer plots can help spot non-conservative tracer behavior and identify mixing, with multiple tracers leading to better constraints on mixing behavior.

Oxygen-18 and Deuterium ($\delta^{18}O$, δD)

It is proposed that wells, precipitation, springs around Nash Draw as well as other wells within the Culebra member be sampled for stable isotopes as additional tracers to help constrain ages derived by other age-dating methods and improve understanding of mixing behaviors and inter-basin groundwater flow. Oxygen-18 and deuterium are natural isotopes found in water molecules and act as nearly conservative tracers, except during evapoconcentration. Because of this, they have been widely used to understand groundwater processes (Clark and Fritz, 1997). While a direct age cannot be calculated using this technique, it can be used as a secondary tracer of age and will help determine recharge conditions which can be matched with calculated ages. Craig (1961) showed that there is a strong linear correlation between ^{18}O and deuterium in natural meteoric waters, the Global Meteoric Water Line (GMWL). The GMWL can be defined by;

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

where the relative abundance of stable isotopes is defined as;

$$\delta = \left(\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right) X\ 1000$$

and R refers to the isotopic ratio ($^{18}O/^{16}O$ or 2H/1H) and $\delta^{18}O$, δD are reported in per mil (‰) notation relative to the Standard Mean Ocean Water (SMOW; Craig, 1961).

^{18}O and deuterium ratios in groundwater are mainly controlled by the isotopic composition of the recharging precipitation. Equilibrium fractionation is highly dependent on temperature and humidity. Specifically, colder temperatures cause lower $\delta^{18}O/\delta D$ values and warmer more humid conditions cause higher $\delta^{18}O/\delta D$ values (Figure 3).

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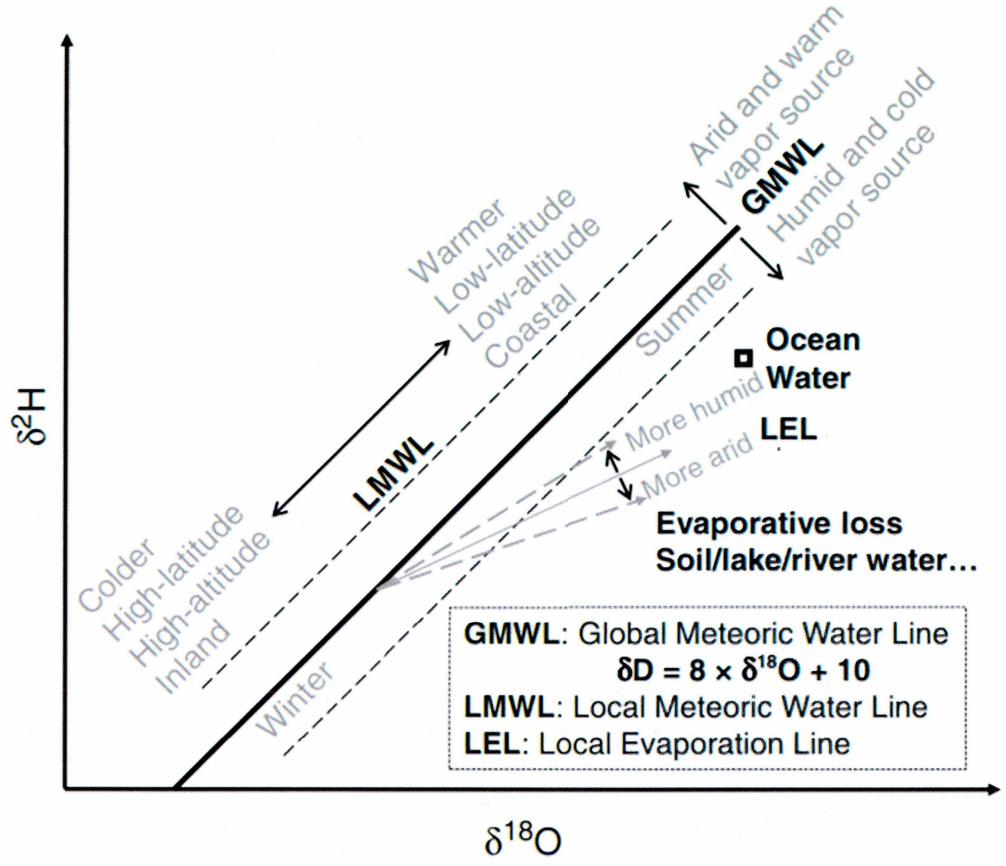


Figure 3 Schematic diagram of isotopic variations in hydrosphere (Xia and Yu, 2019)

Evaporation can also influence the isotopic composition of groundwater, especially in arid environments. Hence, by comparing the isotopic composition of precipitation to that of groundwater, the origin and timing of recharge can be inferred (Jasechko et al., 2014, Fryar et al., 2021, Mehta et al., 2000a, Mehta et al., 2000b).

Lambert and Harvey (1987) reported on the ^{18}O and deuterium data findings of 97 ground and surface waters collected from the Delaware Basin surrounding the WIPP facility. Based on data collected in the Lambert and Harvey study, it was shown that the waters above the Rustler/Salado contact are of meteoric origin. However, the study did not definitively determine whether this meteoric recharge is recent or ancient but it was estimated to be in excess of 10,000 years. Precision in the Lambert and Harvey 1987 study for ^{18}O and deuterium for highly saline samples was up to 4 percent. Modern day precision for ^{18}O and deuterium analysis is closer to 0.5 percent. Since 1987 (Lambert and Harvey study), the well network has been expanded significantly. Incorporation of new ^{18}O and deuterium data from the Culebra could help to further define Culebra groundwater origin and potential modern recharge events. Several new wells and locations (approximately 34) have been incorporated into the WIPP monitoring network since the Lambert and Harvey research was completed.

WIPP Core Petrographic Analysis

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Transmissivity of the Culebra is primarily controlled by the interconnectivity of the fractures and vugs present within the formation. Primary variability in the transmissivity of said fractures and vugs is due to the level of filling present by gypsum/anhydrite cements (Powers et al., 2003). Some preliminary mineralogical analysis was completed by Sewards et al. (1991) on 10 WIPP boreholes including: H-3, H-6, H-7, H-10, H-11, WIPP-12, WIPP-19, WIPP-25, WIPP-26, and WIPP-29. However, approximately 30 new cores have been drilled since then, which could provide new mineralogical information about the fracture systems that control hydrology, as well as information about water-rock interactions that control solute chemistry. Gaining a detailed understanding of the minerology in the cores in the Nash Draw region would assist in providing a deeper understanding of ancient recharge and potential dissolution events that may have caused or exacerbated subsidence in this region.

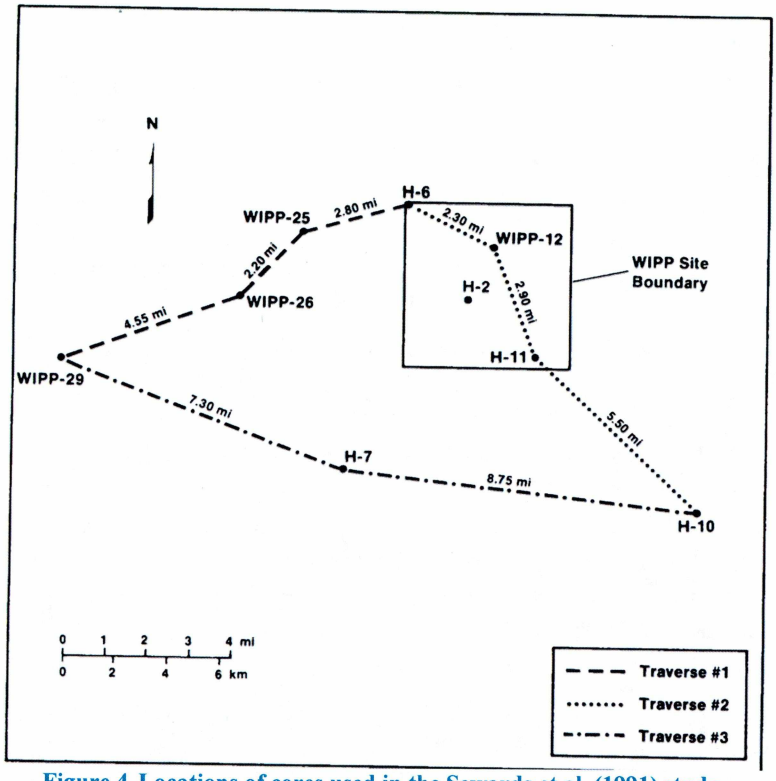


Figure 4 Locations of cores used in the Sewards et al. (1991) study

It is proposed that core samples be collected from relevant stored historical monitoring well core at various intervals within the core column, with a primary focus on the Culebra and lower Rustler Formation. Samples will be subjected to detailed analysis by XRF, XRD and SEM/EDS. XRF, XRD, and SEM/EDS would be used to better characterize the trace mineralogy associated with the various members of the Rustler Formation. Knowledge of the trace minerology could provide information about rock-water interactions, dissolution, rock age, and potential subsidence events. Minerology data obtained would be compared to ground and surface water chemistry to develop a complete picture of both groundwater and formation interactions.

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Conclusions

Age dating of water sources using natural tracers can be an effective tool for determining if recharge or vertical leakage from precipitation are directly contributing to recharge of underlying aquifers. The distribution of groundwater age at the WIPP site and Nash Draw can give valuable information about transit time in the flow-regime. Data requirements for chemical isotope analyses are independent of many of the physical factors required in flow modeling. Past attempts to determine the timing of meteoric recharge of Culebra groundwater in the vicinity of the WIPP site using atmospheric tracers have been largely unsuccessful. The current understanding of Culebra hydrology is that waters present in the Culebra are a result of mixing of water flowing into the study area from: ancient recharge from the north, primitive brines from the east, and relatively recent recharge from the southwest in Nash Draw (Beauheim et al., 2008). Results of the proposed analyses (age dating, water chemistry, and core fracture analyses) will be used to improve or support the conceptual model of the Culebra geochemistry and flow. In particular, the understanding of the relationship between the Culebra hydrology and recharge/discharge in Nash Draw will be improved. Groundwater flow patterns will be studied to establish a better understanding of hard data and the hydrology conceptual model.

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