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CHEMICAL AND RADIOCHEMICAL CHARACTERISTICS OF GROUNDWATER
IN THE CULEBRA DOLOMITE, SOUTHEASTERN NEW MEXICO

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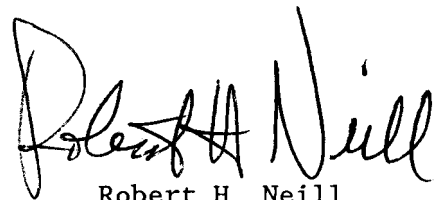
FOREWORD

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.

A handwritten signature in black ink, appearing to read "Robert H. Neill". The signature is stylized and cursive, with the first name "Robert" written in a smaller, more compact script than the last name "Neill".

Robert H. Neill

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EXECUTIVE SUMMARY

The nation's first geologic repository for radioactive waste is being excavated in southeastern New Mexico at the Waste Isolation Pilot Plant (WIPP). It is located in the northern part of the Delaware Basin, within the bedded halite of the Salado Formation. Post-closure radioactive release scenarios from WIPP often involve hydrologic transport of radionuclides through the overlying Rustler Formation, in the Culebra Dolomite Member. The Environmental Evaluation Group (EEG) has conducted an investigation of the chemistry of Culebra groundwater with several objectives. Major ion analyses provide geochemical data that can be used to help determine groundwater flow paths and reactions that occur along those flow paths. Radiochemical data establish a baseline of existing radionuclides in area groundwater prior to the arrival of waste at WIPP. Both stable and radioactive constituents provide information that can be used to help predict the behavior of the Culebra as a radionuclide transport pathway.

Salinities in Culebra groundwater generally increase from west to east, with a large decrease in the area south of NM Highway 128. The linear correlation between total dissolved solids and Cl, and the almost one-to-one molar correlation between Cl and Na, are strong evidence that the salinity increase is due to halite dissolution. The increase in K and Mg concentrations eastward across the WIPP site corresponds to an increase in Cl, probably due to the dissolution of evaporite minerals coexisting with the halite. There is no obvious reason to relate the high K and Mg concentrations to low aquifer transmissivity and long residence times (as concluded by Mercer, 1983).

Two chemical facies exist in Culebra groundwater, and one of these can be further subdivided. A Na-Cl type water dominates over most of the sampled area with a Ca-SO₄ type occurring in the southern to southwestern area. The Na-Cl water can be subdivided into a low Ca area to the east and a higher Ca area to the west.

As groundwater moves from north to south across the area, the Total Dissolved Solids (TDS) decrease by an order of magnitude and the major hydrochemical facies change from Na-Cl to Ca-SO₄. The only plausible mechanism to effect

this change is the influx of a large quantity of low TDS water. The possibility of recharge in the southern area is enhanced by the presence of solution and fill features such as the gypsum caves in the Forty-Niner Member of the Rustler near the Gnome site. These features could behave as conduits supplying fresher water to deeper Rustler units.

Exclusive of the low-salinity southern area, most wells located on the same general flow path have similar ion ratios. A few anomalies, especially in the area around wells H-1, H-2, and H-3 could be due to leakage of more saline water into the Culebra from underlying units. Abnormally high pressures in the Salado could provide a driving force for fluid movement upward. The possibility of such leakage is also indicated by the oxygen and hydrogen isotopic compositions that indicate mixing through the Rustler, Salado, and Castile formations.

The distribution of salinities and hydrochemical facies in Culebra groundwater corresponds to the amount of evaporite dissolution in the Rustler Formation. The southern area of low TDS values and Ca-SO_4 water corresponds to an area of complete removal of halite from the Rustler and widespread gypsification of anhydrite. Groundwater in the northeastern area, with TDS values greater than 100,000 mg/L and almost pure Na+K-Cl brine, occurs in the area where halite is found in the Rustler Formation. The western part of the WIPP Site and extending toward Nash Draw is geologically and chemically between the two extremes. Though all halite has been removed from the Rustler over most of this area, gypsification and dissolution of anhydrite have not progressed as far as they have in the southern area. The salinity distribution and uranium data suggest that the Culebra contains discrete flow paths interspersed with areas of slower water movement. This is consistent with the fracture and possibly karst-related flow system that occurs in the Culebra, which in turn is tied to dissolution of halite from the Rustler and underlying Salado.

The dissolved uranium content in Culebra groundwater is relatively high, indicating that the aquifer maintains uranium as an oxidized solute. Sources of uranium are suspected to be related to clastic beds in the Rustler and overlying formations. There is marked disequilibrium between U-238 and U-234 activities in Culebra groundwater. The highest disequilibrium occurs in water

from low transmissivity wells, which in turn are in areas lacking fractures and presumed to have slower groundwater velocities. The association of low transmissivity with low total uranium content and high disequilibrium can be explained by three processes related to the lack of fractures: 1) assumed longer groundwater residence time in the low transmissivity zones allows more adsorption of uranium onto the rock matrix than occurs in the fractured portions of the Culebra, 2) more reducing conditions may exist in tighter parts of the aquifer, and 3) uranium in the formation may occur primarily as linings on fracture surfaces and thus less uranium is available to go into solution in unfractured parts of the aquifer. The relative abundance of U-234 in these unfractured areas could be explained if the Culebra matrix has U-238 more tightly bound than is found on fracture surfaces and coatings. Therefore, the uranium in solution would be due primarily to U-234 that is loosened from its crystal sites by alpha recoil.

The radium isotopes, Ra-226 and Ra-228, are sometimes present in relatively large amounts. There is a strong, positive linear relationship between the radium isotopes and dissolved Cl content. This relationship is believed to reflect the greater radium mobility in higher chloride water. The balancing complement of cations in high chloride brines compete for adsorption sites with radium. Radium concentration correlates well with the hydrochemical facies with high radium contents in the northern Na-Cl brine area and lower radium contents south of NM 128 in the Ca-SO₄ area. In the Ca-SO₄ type southern area, saturation with gypsum and relatively low chloride contents may combine to create a suitable environment for effective removal of radium by coprecipitation. A similar process may be at work to a lesser extent in the western WIPP area where chloride content is intermediate and calcium is a relatively more abundant cation.

Surprisingly, Th-228 was detected in samples from 5 wells. Thorium is not usually carried extensively in solution in ordinary geochemical environments because it occurs in an insoluble +4 oxidation state. The high TDS in parts of Culebra groundwater may explain thorium's presence in solution. Thorium may be kept mobile as thorium chloride and thorium sulfate complexes.

Analyses were performed for the waste nuclides Am-241, Pu-238 and Pu-239+240 and H-3 in order to establish pre-operational levels in the WIPP area. No values above the minimum detectable level were obtained for any of these radionuclides. Analyses for Cs-137 revealed detectable activities in several samples. However, the Cs-137 reported is believed to be an artifact of the analysis of water with a high potassium content. The analysis of Cs-137 is performed by chemical separation and beta counting and there is a possibility for some interference from other beta-gamma emitters in the Group 1A elements separated by chloro-platinate precipitation. The three samples where Cs-137 was reported also have high potassium content. Analysis of a surface water sample supports the interference hypothesis, as beta counting detected Cs-137 while a gamma spectroscopy analysis did not.

Radionuclide analyses should continue on Culebra groundwater. Differences between interpreted controlling factors of radium concentration in this study and previous work highlight the need for continued investigations of the processes controlling the distribution of naturally occurring radionuclides in the Culebra. The high chloride contents, coupled with relatively oxidizing conditions appear to be contributing factors to the high concentrations of radium and uranium. The mobility of other waste nuclides, or naturally occurring analogs, should be carefully analyzed for the Culebra geochemical environment. Variations in radium concentrations in water from wells sampled a year apart emphasizes the importance of repeat sampling to provide a better statistical data base.

Major ion analyses should be performed for additional water samples from the area south of NM 128 and in the transition zone between the hydrochemical facies to help quantify and locate the apparent fresh water recharge responsible for the chemical changes. Wells at H-5 also require additional investigation because conflicting data interpretations suggest both very old and very young water in this area. Accurate knowledge of the Culebra chemical environment is vital to understanding groundwater flow paths and evaluating radionuclide migration.

ACKNOWLEDGEMENTS

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IN THE CULEBRA DOLOMITE, SOUTHEASTERN NEW MEXICO**

INTRODUCTION

The nation's first geologic repository for radioactive waste is being excavated in southeastern New Mexico at the Waste Isolation Pilot Plant (WIPP). It is located in the northern part of the Delaware Basin, within the bedded halite of the Salado Formation. Post-closure radioactive release scenarios from WIPP often involve hydrologic transport of radionuclides through the overlying Rustler Formation, in the Culebra Dolomite Member. In order to help characterize the radionuclide transport properties of the Culebra, the Environmental Evaluation Group (EEG) has conducted an investigation of the chemistry of Culebra groundwater as part of the State of New Mexico's independent environmental monitoring effort. EEG's program is coordinated with groundwater sampling conducted by the U. S. Department of Energy (DOE).

The DOE began a major groundwater sampling effort in 1985 to obtain representative and repeatable groundwater quality data in the WIPP area (Colton and Morse, 1985). This continuing effort consists of several rigorous samplings of 23 wells near WIPP. The sampling plan and procedures are described in detail by Colton and Morse (1985), with field data and laboratory analytical results presented in Uhland and Randall (1986) and Uhland et al. (1987). Splits of the groundwater samples are provided to the EEG for independent analysis.

This report presents the results and interpretations of EEG's groundwater chemistry program. EEG has several objectives for water-sample analysis. Major ion analyses are performed to provide geochemical data that can be used to help determine groundwater flow paths and reactions that occur along those flow paths. Radiochemical data are gathered to establish a baseline of existing radionuclides in area groundwater prior to the arrival of waste at WIPP. Both stable and radioactive constituents provide information that can be used to help predict the behavior of the Culebra as a radionuclide transport pathway.

SAMPLE COLLECTION AND ANALYSIS

The DOE sampling program includes a mobile laboratory at the well-head to serially analyze key parameters (Colton and Morse, 1985). A final sample is taken after the key parameters stabilize. When final samples are collected by the DOE sampling team, EEG sample bottles are also filled. The State's samples are then sent to independent laboratories for analysis. The data are presented in the appendix.

Dissolved ionic constituents were determined by the New Mexico Bureau of Mines and Mineral Resources under the supervision of Ms. Lynn Brandvold. Cations were determined by atomic absorption spectrometry, chloride by mercuric nitrate titration, sulfate by barium chloride gravimetry, and fluoride by ion specific electrode.

Radiochemical analyses were performed by Accu-Labs Research, Inc., of Wheat Ridge, Colorado, under the supervision of Mr. Bud Summers. Gross alpha and gross beta are determined using proportional counters. All other analyses were preceded by chemical separation. Ra-226 is precipitated with barium then determined by radon emanation. Ra-228 is determined by proportional counting. Sr-90 and Cs-137 are also determined with proportional counting. An alpha spectrometer using internal tracers is used for the isotopic determination of Pu-238, Pu-239+240, Th-232, Th-230, Th-228, U-238, U-235, U-233+234, and Am-241. Tritium is analyzed by liquid scintillation spectrometry.

The radiochemical analyses are presented in the appendix along with a counting error and minimum detectable level (MDL) for each analysis. The counting error represents the variability of the radioactive disintegration process at the 95% confidence level, 1.96σ . This report assumes that the MDL of radionuclides in water samples is:

$$\text{MDL} = 1.96 \left[\sigma_{\text{S+B}}^2 + \sigma_{\text{B}}^2 \right]^{1/2}$$

where $\sigma_{\text{S+B}}$ and σ_{B} are the standard deviations of the counting errors of the sample plus background (S+B) and the background (B). This procedure is used rather than other methods that relate lower limits of detection to σ_{B} only, because the reported values of $\sigma_{\text{S+B}}$ are much greater than those of σ_{B} .

Sample Identification

Most of the analyses discussed in this report are from water samples collected from wells drilled as part of characterization of the WIPP site (Fig. 1). Many of the wells at WIPP were drilled on hydropads usually consisting of three wells completed in differing hydrologic units. The actual wells are denoted by suffixes to the well name, e.g., H-2A, H-2B, and H-2C. For simplicity in this report, only the general well name is usually given (e.g., H-2), though the exact well identification is given in the data tables. Unless otherwise stated, all data are from water samples collected from the Culebra Dolomite Member of the Rustler Formation. The Culebra is a 25 to 30 ft. thick vuggy, fractured, gypsiferous dolomite (Fig. 2).

MAJOR ION CHEMISTRY

Previous Work

A large number of chemical analyses of WIPP groundwater have been performed by the U. S. Geological Survey and are reported in Mercer and Orr (1979) and Mercer (1983). These analyses are compiled in Ramey (1985). The low productivity and uncertain history of some of the WIPP wells (especially regarding steps taken to prevent loss of drilling fluid in the karst depression of Nash Draw) led to concern about the quality of these samples (Lambert and Robinson, 1984). This concern, as well as data needs for aquifer chemistry and environmental monitoring programs, led to the current sampling effort. Field and laboratory results obtained by DOE contractors during the current Water Quality Sampling Program are available in Uhland and Randall (1986) and Uhland et al. (1987). Data from Culebra groundwater gathered by the EEG are presented here, while a complete presentation of all EEG environmental data can be found in Kenney et al. (in prep.). Robinson (1988) presents a detailed comparison of WIPP water chemistry data with an analysis of the data quality.

Mercer (1983) noted increasing salinity in the Culebra from west to east across the WIPP area. He related an increase in potassium and magnesium to the east with a decrease in transmissivity. Neill et al. (1983) identified two major

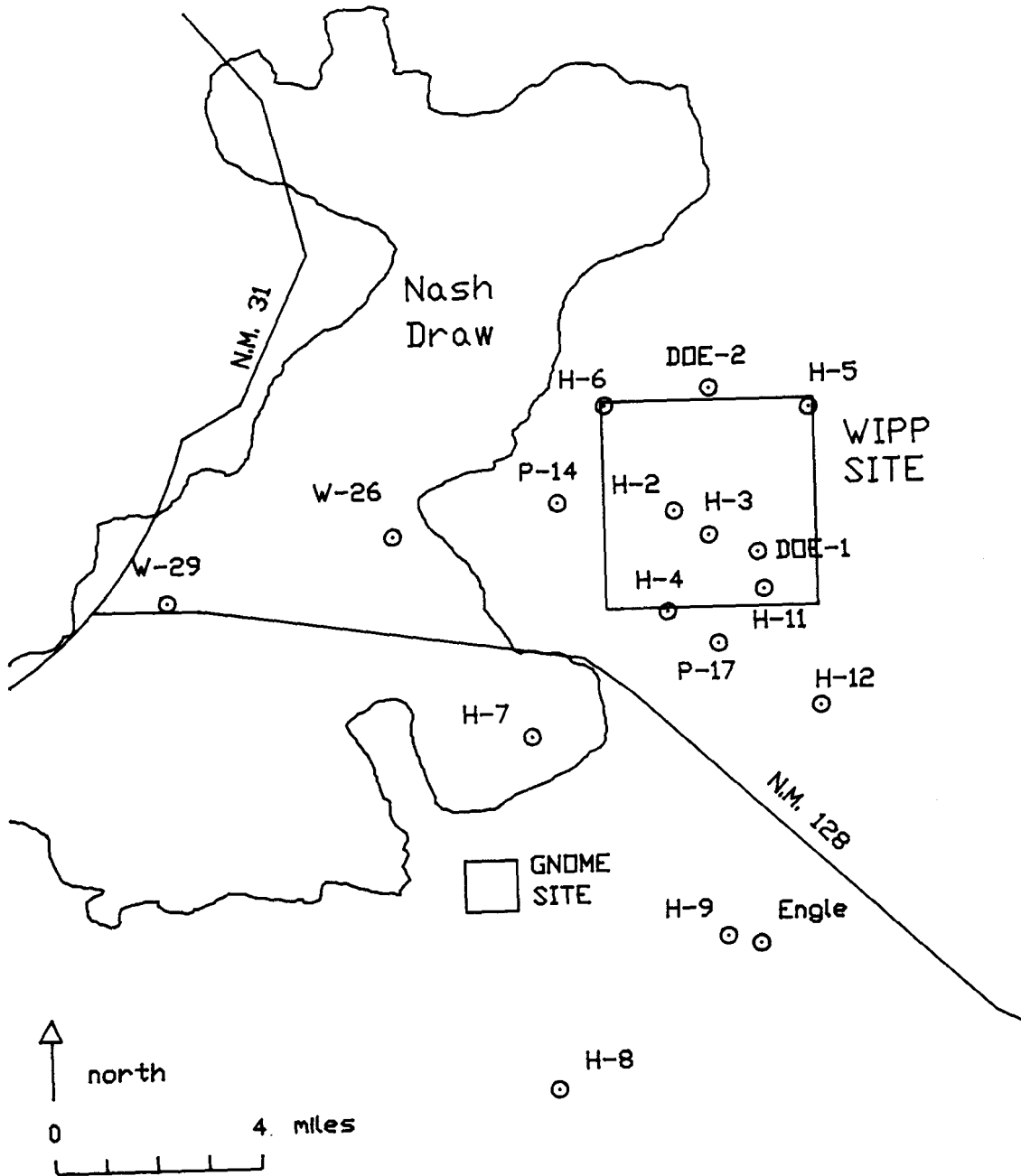


Figure 1. Location map showing the WIPP and Gnome sites and wells referred to in this study.

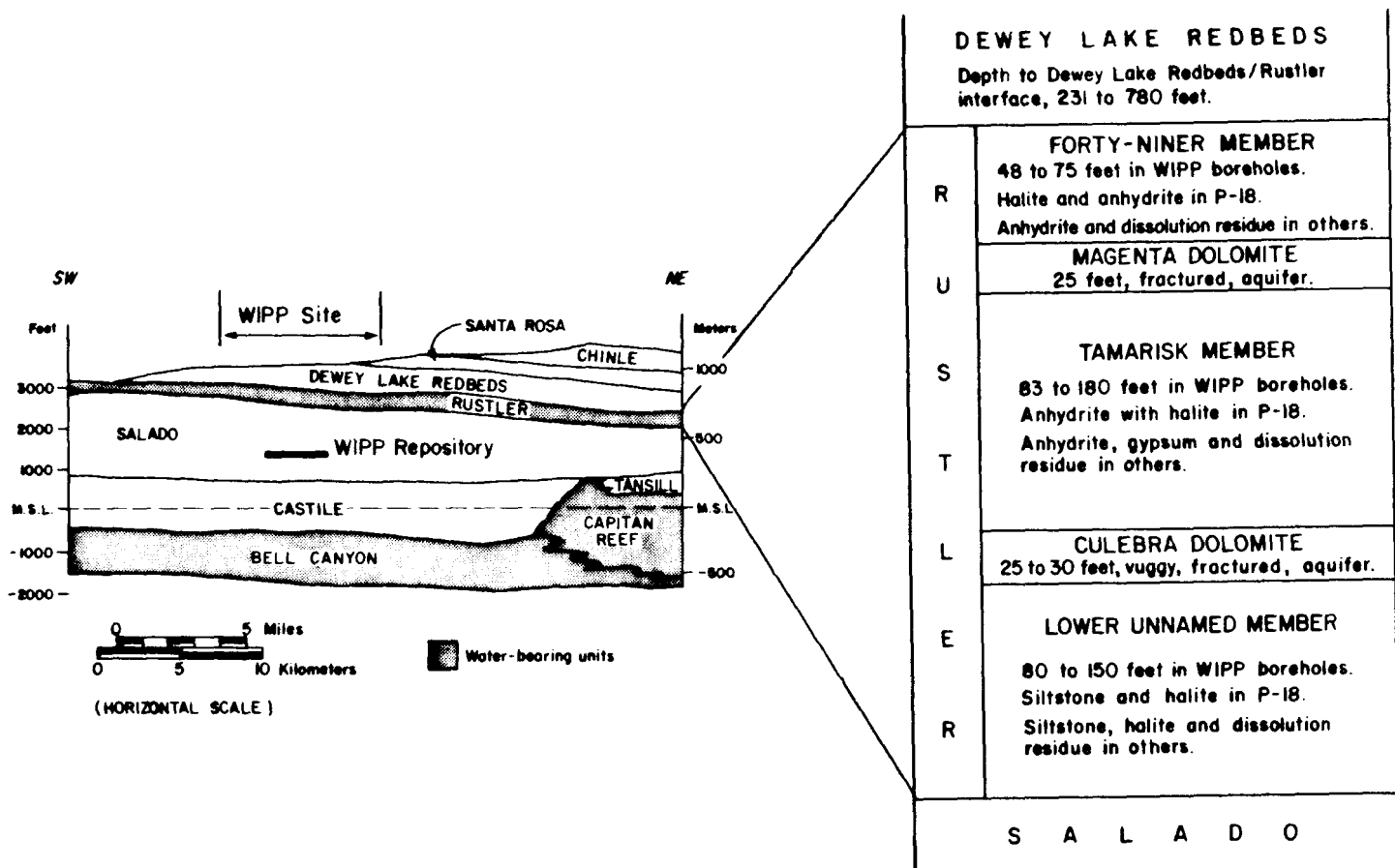


Figure 2. Generalized stratigraphy at the WIPP site, emphasizing the five members of the Rustler Formation.

hydrochemical facies in the Culebra in the WIPP area: a northern area, including the actual site, containing a Na-Cl type water and a southern area containing a Ca-Mg-SO₄ water. Ramey (1985) refined this hydrochemical characterization by dividing the northern area into an eastern part containing high concentrations of K and Mg, and a western part with relatively lower K and Mg content.

Salinity Patterns

The recent analyses confirm the presence of generally increasing salinities from west to east (Fig. 3), and a large decrease in salinity in the southern area (south of NM Highway 128). The linear correlation between total dissolved solids (TDS) and Cl, and the almost one-to-one molar correlation between Cl and Na, are strong evidence that the salinity increase is due to halite dissolution (Fig. 4). K, Mg, and SO₄ contents all increase with increasing Cl (Fig. 5). No obvious relationship is found between Cl content and Ca, U, F, and Li content in Culebra groundwater (Fig. 6). Considering the major Culebra mineralogy (dolomite with anhydrite/gypsum fracture and vug fillings, Lowenstein, 1987), the calcium content is likely controlled by carbonate and sulfate mineral equilibria.

The most saline Culebra groundwater sample is from well W-29, located in southern Nash Draw. The chemical composition of water from this well is anomalous compared to the others, both in its extreme TDS value (266,000 mg/L) and in its very high K content (20,800 mg/L). Data from W-29 are plotted in Figs. 4a and 4b, but are excluded from other plots because of the relatively unusual chemical composition. The oxygen and hydrogen isotopic composition of groundwater from W-29 reveals an enrichment in heavy isotopes and deviation from the meteoric water line that suggest evaporation has occurred (Chapman, 1986). The shallow depth to the Culebra (12 feet) and location close to a saline lake, Laguna Grande de la Sal, also support the possibility of evaporative effects on Culebra groundwater in that area. The large water discharges from nearby potash mines and high K content suggest that the W-29 composition may also be affected by local potash mining activity.

The increase in K and Mg concentrations eastward across the WIPP site corresponds to an increase in Cl, probably due to the dissolution of evaporite minerals coexisting with the halite. The dissolution of polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$)

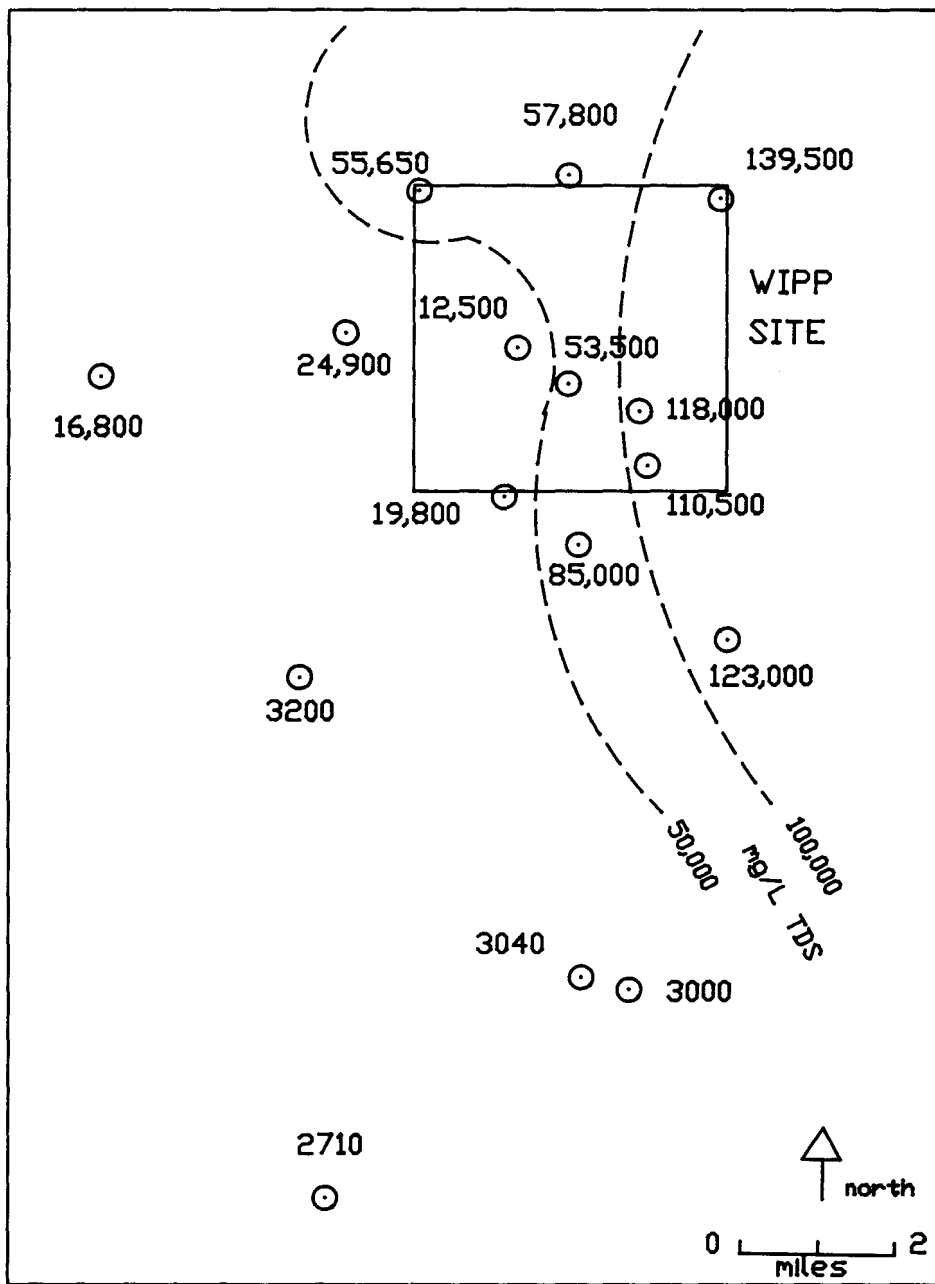


Figure 3. Total dissolved solids content in Culebra groundwater, mg/L.

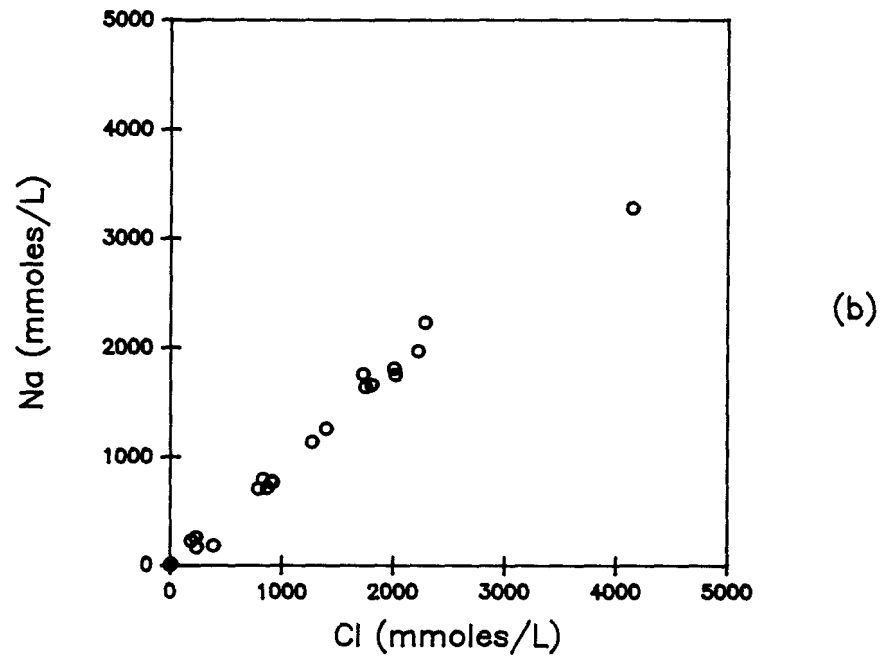
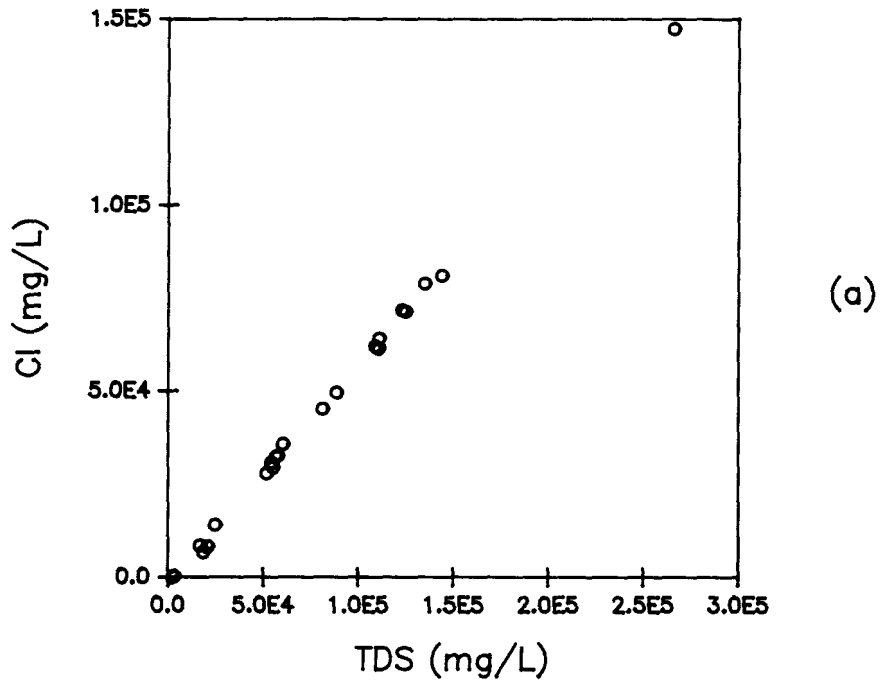
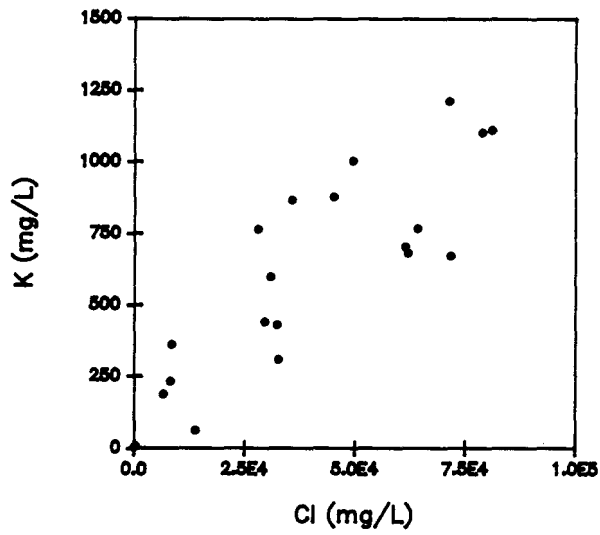
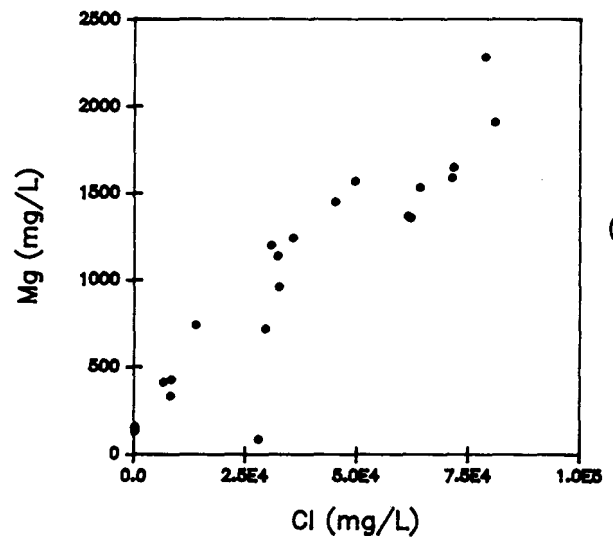


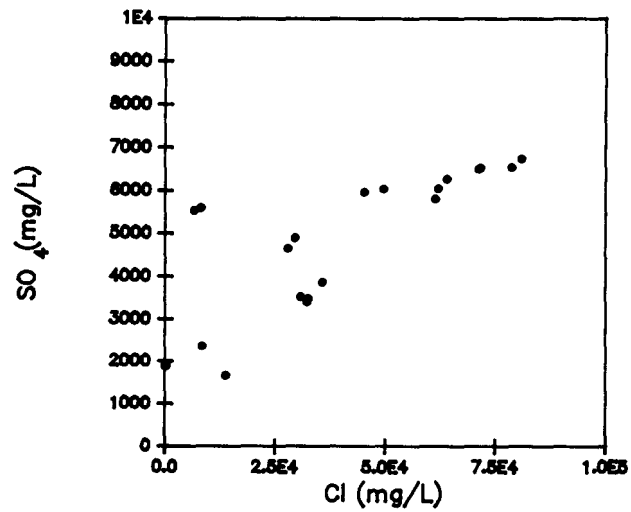
Figure 4(a) Cl content versus total dissolved solids.
 Figure 4(b) Na versus Cl, in millimoles per liter.



(a)

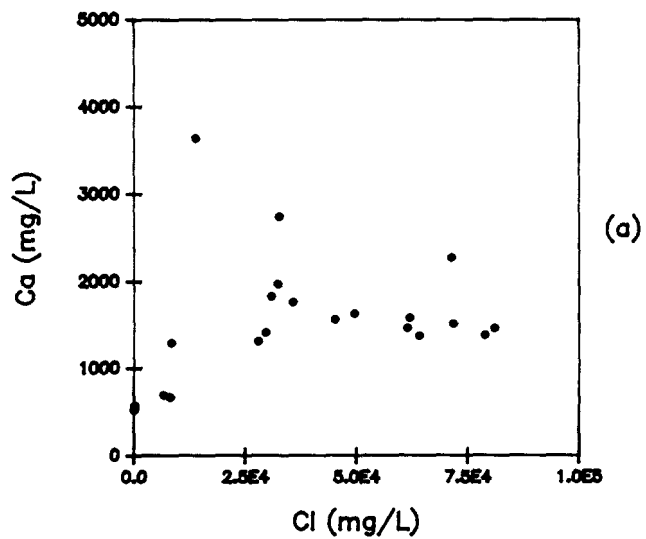


(b)

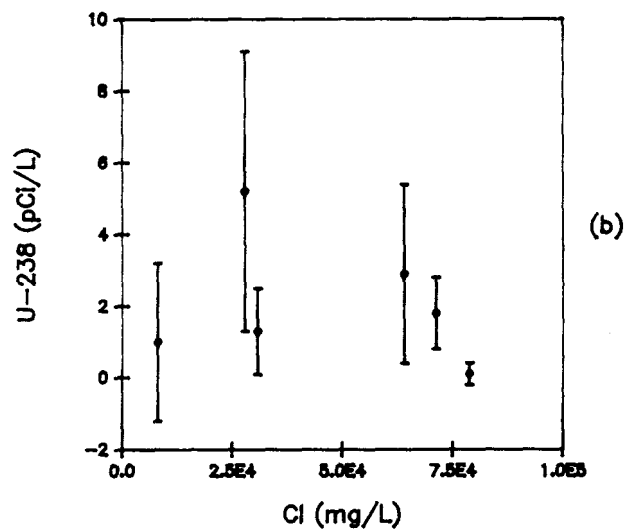


(c)

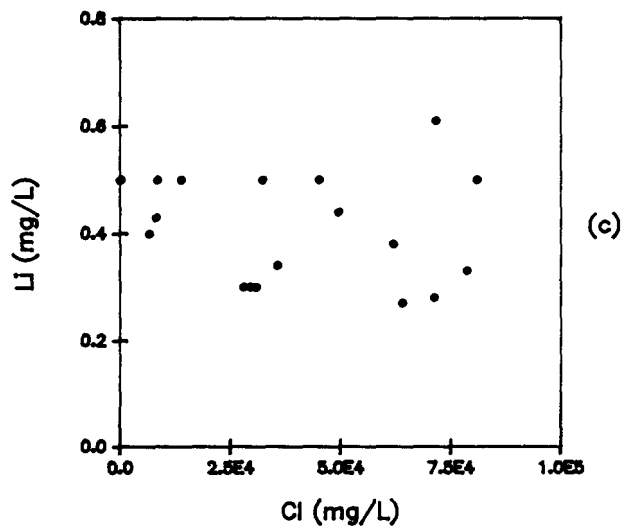
Figure 5(a) K versus Cl.
 Figure 5(b) Mg versus Cl.
 Figure 5(c) SO₄ versus Cl.



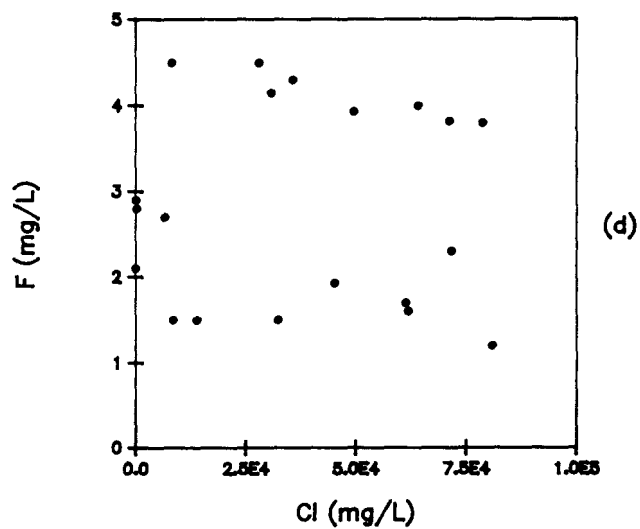
(a)



(b)



(c)



(d)

Figure 6(a) Ca versus Cl.
Figure 6(c) Li versus Cl.

Figure 6(b) U-238 versus Cl.
Figure 6(d) F versus Cl.

could increase both K and Mg, though a subsequent process would be needed to remove Ca from solution, such as gypsum precipitation and de-dolomitization. Whatever the reactions involved, there is no obvious reason to relate the increase in K and Mg concentrations to low aquifer transmissivity and long residence times as concluded by Mercer (1983). Indeed, samples from two wells in the eastern part of the site, unavailable to Mercer (1983), have high salinities and K and Mg contents, but are also relatively transmissive (DOE-1, $T=33 \text{ ft}^2/\text{day}$; H-11, $T = 10 \text{ ft}^2/\text{day}$, Haug et al., 1986).

There is a definite trend of decreasing concentration among Cl, Na, K, and Mg toward the west and south. The major ions also change from Na and Cl in the north to Ca and SO_4 in the south. There is some reversal of the salinity trend in Nash Draw, in particular at well W-29, with high salinities possibly related to evaporite dissolution and potash mining.

Hydrochemical Facies

The division of the Culebra into two major hydrochemical facies (Neill et al., 1983) is supported by the new data. The facies definitions follow divisions of the Piper trilinear diagram as suggested by Back (1961) and discussed in Freeze and Cherry (1979). The facies used in this report are based on the anion and cation triangles and are shown in Fig. 7. Based on these divisions, two major chemical facies exist, and one of these can be further subdivided (Fig. 8). A Na-Cl type water dominates over most of the sampled area with a Ca- SO_4 type occurring in the southern to southwestern area (Fig. 9). The Na-Cl water can be subdivided into a low Ca area to the east and a higher Ca area to the west (greater than 10% meq/L Ca compared to total Ca, Mg and Na+K). A chemical mixing line can be drawn between an almost pure Na-K-Cl endmember and a Ca-Mg- SO_4 endmember.

Not reflected on the Piper diagram are the large changes in salinity that accompany the chemical facies changes. The eastern Na-Cl type water is characterized by TDS contents greater than 100,000 mg/L (Fig. 3). The Na-Cl with increased Ca-type water has lower salinities, ranging from 17,000 to 56,000 mg/L TDS. The Ca- SO_4 water has low TDS values around 3000 mg/L.

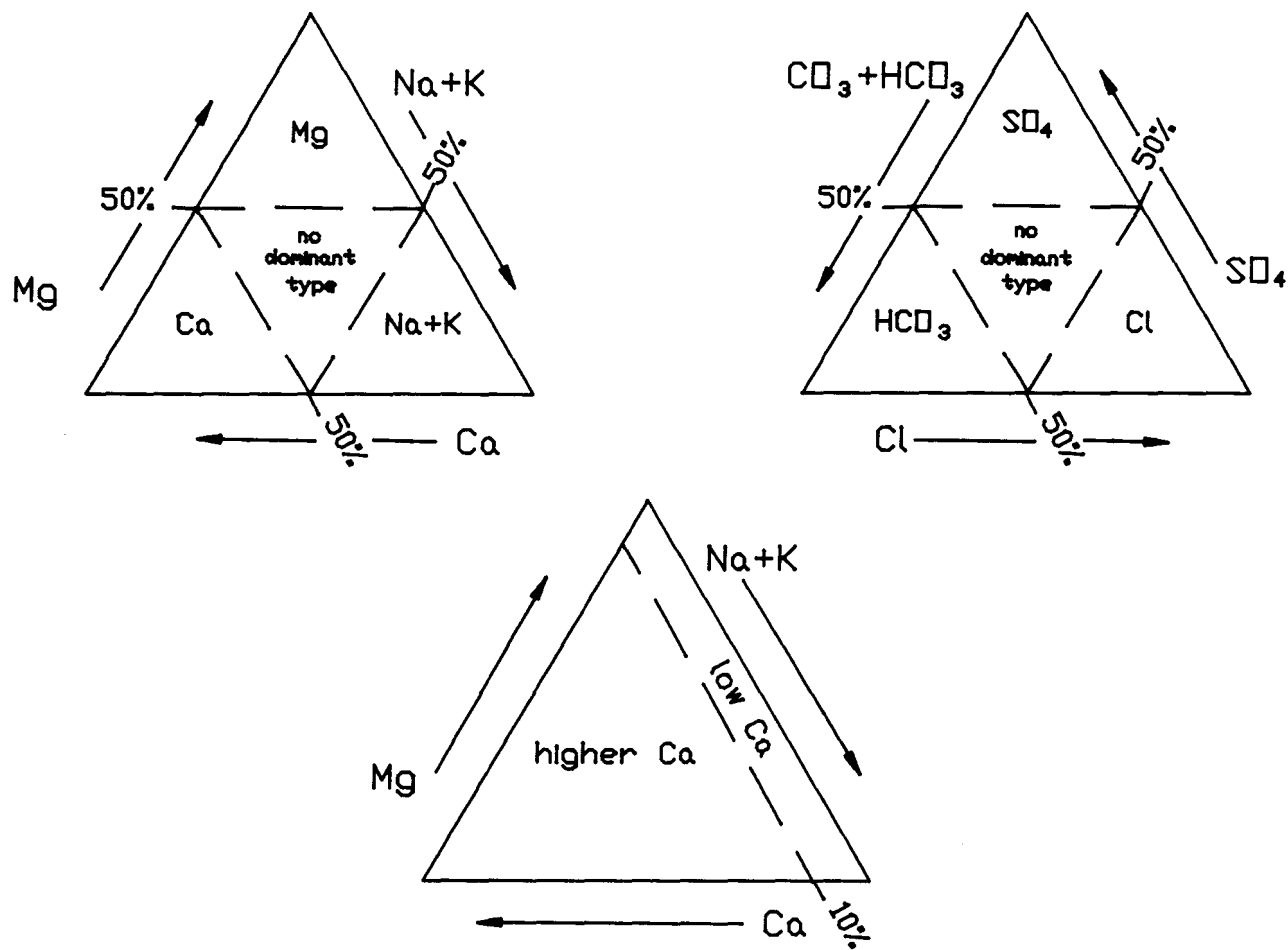


Figure 7. Facies divisions based on the anion and cation triangles of the Piper trilinear diagram. Units on the triangles are milliequivalents per liter.

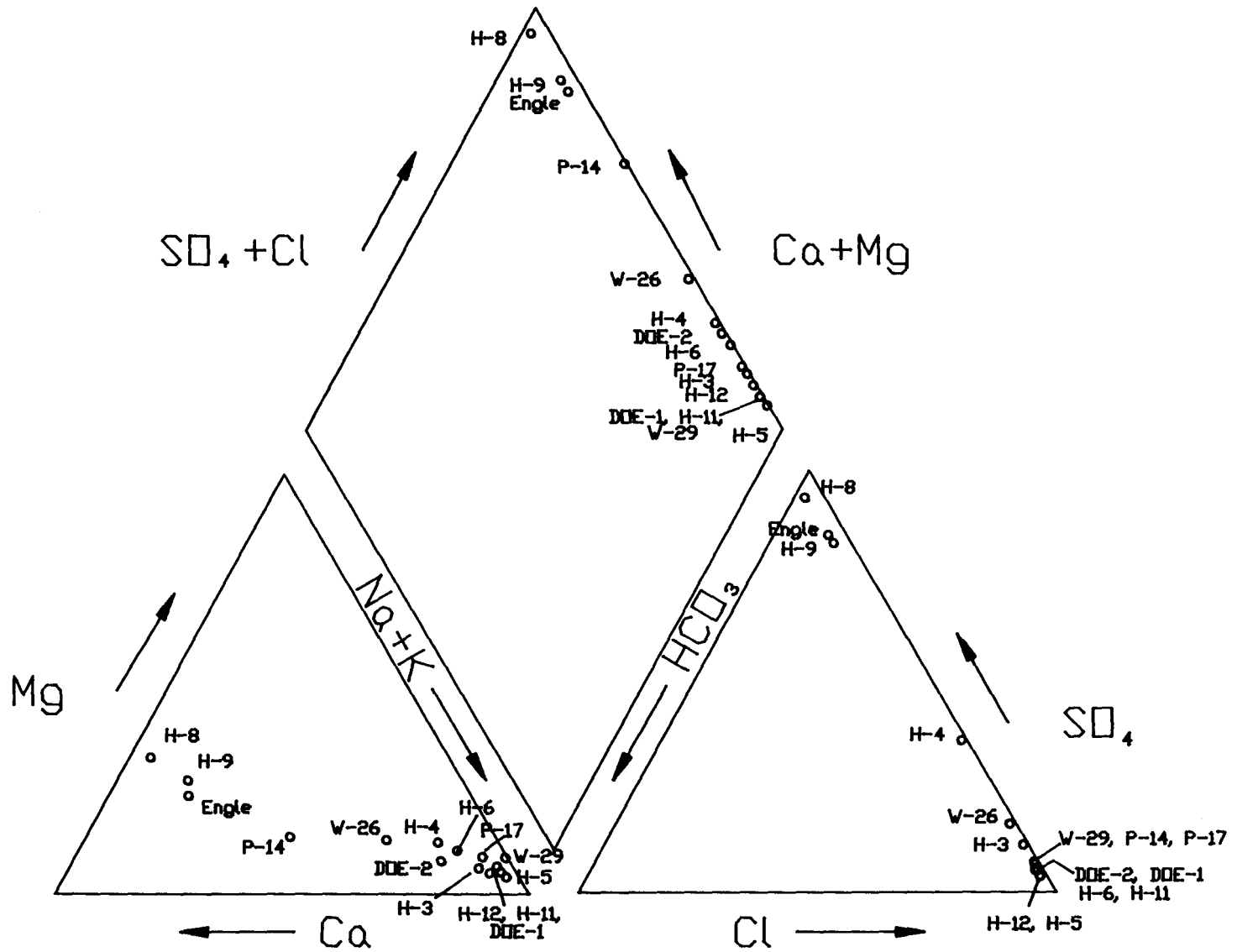


Figure 8. Culobra groundwater data plotted on a Piper trilinear diagram. Axes range from 0 to 100% milliequivalents per liter, increasing in the direction of the arrows. Facies definitions are shown in Figure 7.

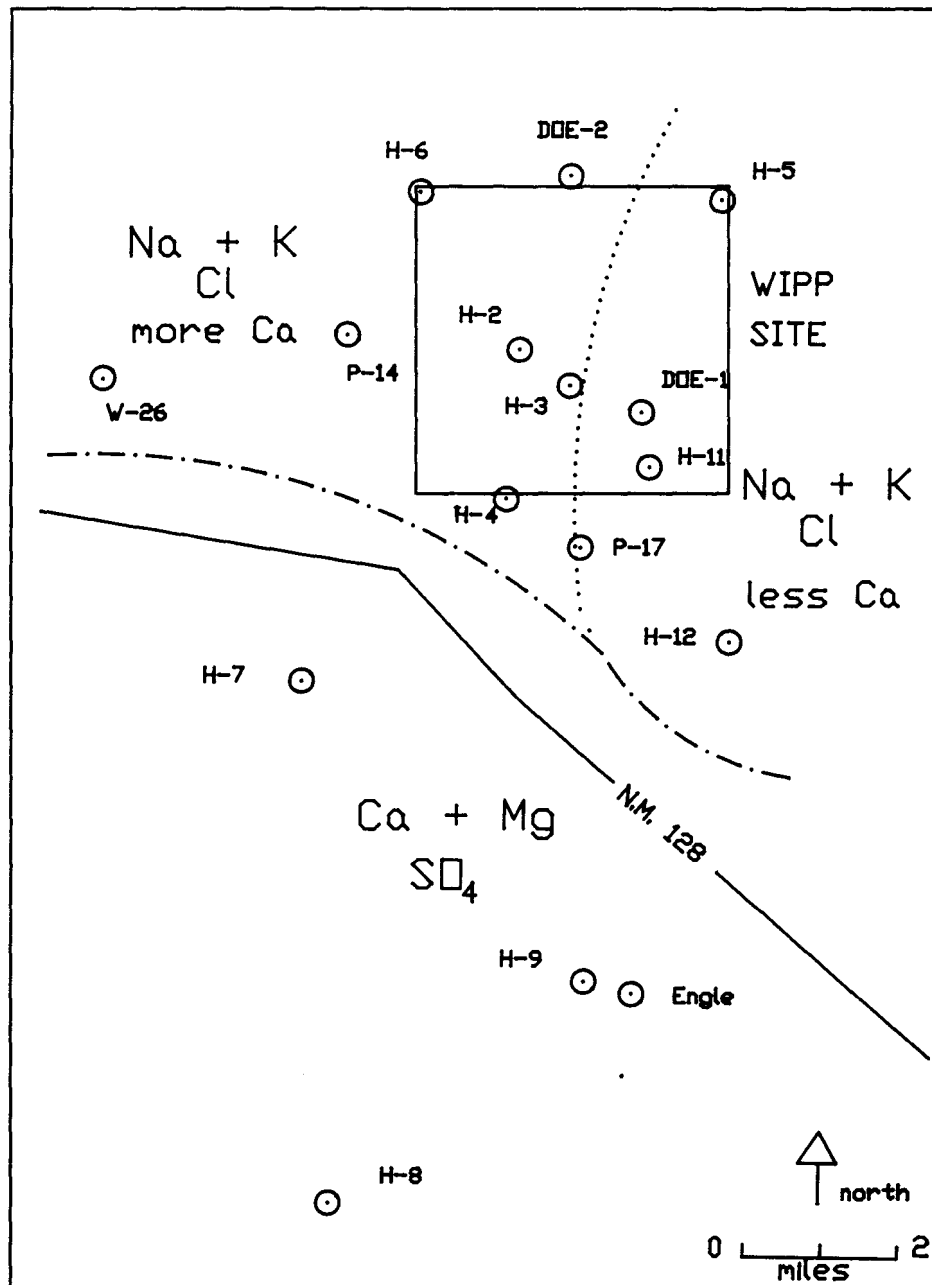


Figure 9. Hydrochemical facies map for groundwater in the Culebra Dolomite. The main division is into a Na-Cl area to the north and Ca+Mg-SO₄ area to the south. The northern area can be further subdivided into a low Ca area to the east and higher Ca area to the west (>10% meq/L Ca compared to all cations). For corresponding TDS variations, see Fig. 3.

The hydrochemical facies and their interpretation in relation to groundwater flow paths are analyzed in the "Discussion" section.

RADIOCHEMISTRY

Both natural and anthropogenic radionuclides were analyzed in WIPP groundwater. Naturally occurring analytes included members of the uranium and thorium decay series. Man-made nuclides were chosen on the basis of their presence in the WIPP radioactive waste inventory. In addition, gross alpha and beta counts were performed on many samples. The radiochemical analyses are presented in the appendix along with a counting error and Minimum Detectable Level (MDL) for each analysis. An analyte is considered to not be detected if the reported value falls below the MDL. The calculation of the MDL is discussed in the earlier section on "Sample Collection and Analysis." The \pm values given in the text after a concentration number represent the counting error at the 95% confidence level, 1.96σ .

Previous Work

Radiochemical analyses were reported for Culebra groundwater as part of the site investigations for the Gnome Project (Cooper and Glanzman, 1971). These included Gross alpha and beta, uranium, Ra-226, and Sr-90, and are from wells located 7 miles south-southwest of WIPP (Fig. 1). Mercer (1983) summarized radiochemical analyses performed by the U. S. Geological Survey on samples from wells drilled for WIPP. These analyses also include gross alpha and beta, uranium, and Ra-226. Simpson et al. (1985) performed a wide variety of radionuclide analyses on waters in the Delaware Basin in a field investigation of the mobility of radionuclides in high-chloride environments. Lambert and Carter (1987) have discussed uranium isotope disequilibrium in regard to Rustler water.

Uranium Decay Series

Analyses of dissolved uranium performed early in the program suggested very high uranium contents in Culebra groundwater (20 - 60 μ g/L). These analyses are not supported by either the earlier reported analyses (Cooper and Glanzman, 1971; Mercer, 1983; Lambert and Carter, 1987) or the uranium isotope concentrations

determined for later samples (Table 1). The dissolved uranium data are believed to be affected by analytical interference from other dissolved species (Mr. B. Summers, pers. comm.). The uranium content based on U-238 activity ranges from below detection to 22 $\mu\text{g/L}$. The uranium content of natural waters is usually between 0.1 and 10 $\mu\text{g/L}$, with higher amounts unusual (Hem, 1982).

TABLE 1

| <u>WELL</u> | <u>U($\mu\text{g/L}$)</u> | <u>U-238(p/Ci/L)</u> | <u>$\mu\text{ g/L}$ Calculated from U-238</u> | <u>U-234/U-238 A.R.</u> |
|-------------|--------------------------------------|----------------------|--|-------------------------|
| H3-B3 | 35 | 5.2 \pm 3.9 | 15.6 | 1.46 |
| Engle | 20 | -- | -- | -- |
| DOE-2 | 53 | 5.2 \pm 1.2 | 15.6 | 3.65 |
| H-4B | 53 | 1.0 \pm 2.2 | 3.0 | 14.0 |
| H-5B | 53 | 0.1 \pm 0.3 | 0.3 | 18.0 |
| H-12 | 39 | -- | -- | -- |
| H-11B3 | 60 | 2.9 \pm 2.5 | 8.7 | 4.14 |
| H-6B | 56 | 1.3 \pm 1.2 | 3.9 | 5.46 |
| DOE-1 | 59 | 1.8 \pm 1.0 | 5.4 | 4.17 |
| H-7B | -- | 7.4 \pm 3.4 | 22.0 | 1.49 |
| H-2A | -- | 1.8 \pm 0.8 | 5.4 | 9.44 |

Uranium content is closely related to the oxidation-reduction potential in an aquifer because uranium in the +6 state is more mobile than uranium in the +4 state. Field Eh values for Rustler groundwater are available in Uhland and Randall (1986). Fig. 10 shows a relationship in Culebra groundwater between increasing Eh value and increasing U-238 activity. However, all of the Culebra waters with the exceptions of those from H-2 and H-5 are relatively oxidizing (Eh > 100 mv relative to a hydrogen electrode). Though increasing Eh appears to be associated with an increase in uranium content, there is no identified "reducing zone" in which uranium transport in the Culebra is severely retarded. Some models of uranium geochemistry in groundwater rely on the presence of a reducing barrier where most uranium in solution is precipitated (as described in Osmond and Cowart, 1976). Despite the depth (500-700 ft.) and confined nature of the Culebra, the aquifer apparently maintains uranium as an oxidized solute.

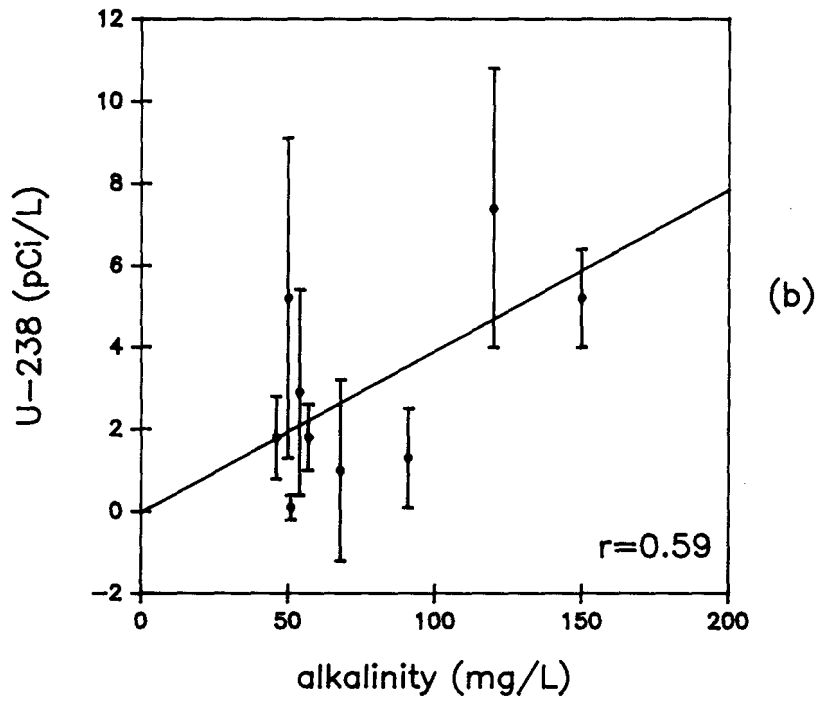
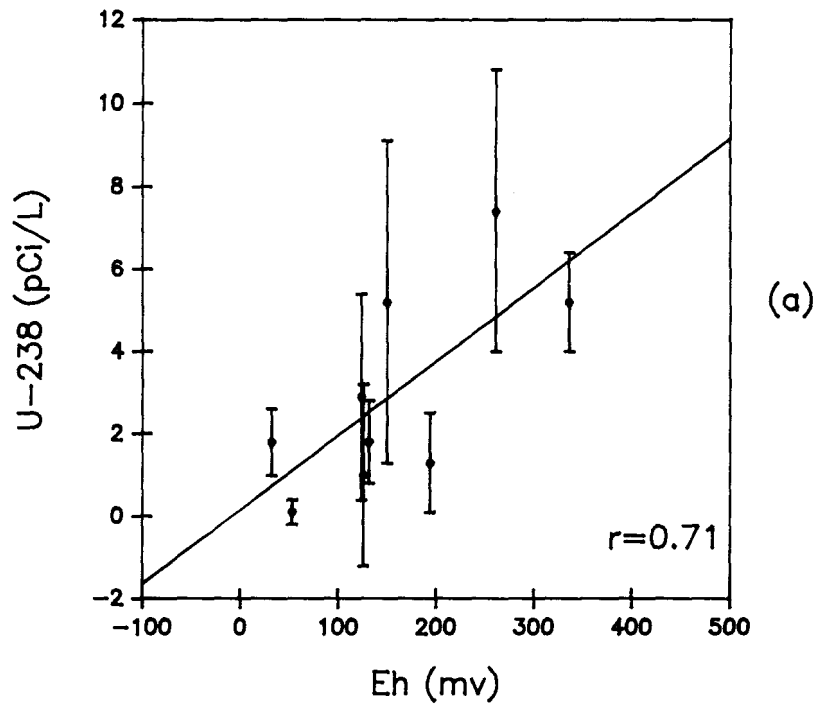


Figure 10(a) U-238 versus Eh.
 Figure 10(b) U-238 versus alkalinity.

Uranium content in some groundwater systems has been related to total dissolved solids and bicarbonate content (Barker and Scott, 1958). As shown in Fig. 6, there is little correlation between Cl and U in Culebra groundwater. Fig. 10 shows a positive relationship, albeit weak, between HCO_3 and uranium, suggesting that uranyl-carbonate complexes are important, as noted by Barker and Scott, (1958). However, the wide range in U-238 content among waters clustered about 50 mg/L HCO_3 indicates that carbonate complexing is not the only process controlling uranium transport in the Culebra. In addition to TDS and HCO_3 , dissolved uranium could be affected by the rate of supply, the presence of highly sorptive materials such as organic matter, clays, and oxyhydroxides of Fe^{+3} and Mn. There are no data about the variability of the above factors in the Culebra, so their importance in controlling uranium content cannot be evaluated.

Uranium content is not closely tied to transmissivity values (Fig. 11). The low transmissivity wells ($<1 \text{ ft}^2/\text{day}$) have low U-238 content, but among the higher transmissivity wells, there is not clear trend of uranium with transmissivity.

Source of Dissolved Uranium

Sources of dissolved uranium are uncertain, but may be related to clastic beds in the Rustler and overlying formations. If there is leakage of fluids through the underlying evaporites to the Culebra, then the Salado and Castile could also be sources. Most of the information on uranium occurrence in the WIPP area is related to economic interest. Siemers et al. (1978), in their evaluation of the mineral potential of the WIPP site, found no evidence of economic or subeconomic concentrations of uranium in the Dewey Lake Redbeds Formation at WIPP. A spectral gamma ray log in ERDA-9 indicates that most of the gamma-ray activity in the section from the surface through the Salado Formation is due to K-40, not members of the uranium or thorium decay series. Throughout the Santa Rosa (Triassic Dockum Group), Dewey Lake Redbeds, and Rustler, the spectral gamma ray log indicates uniformly low uranium concentrations of less than 13 ppm (Siemers et al., 1978).

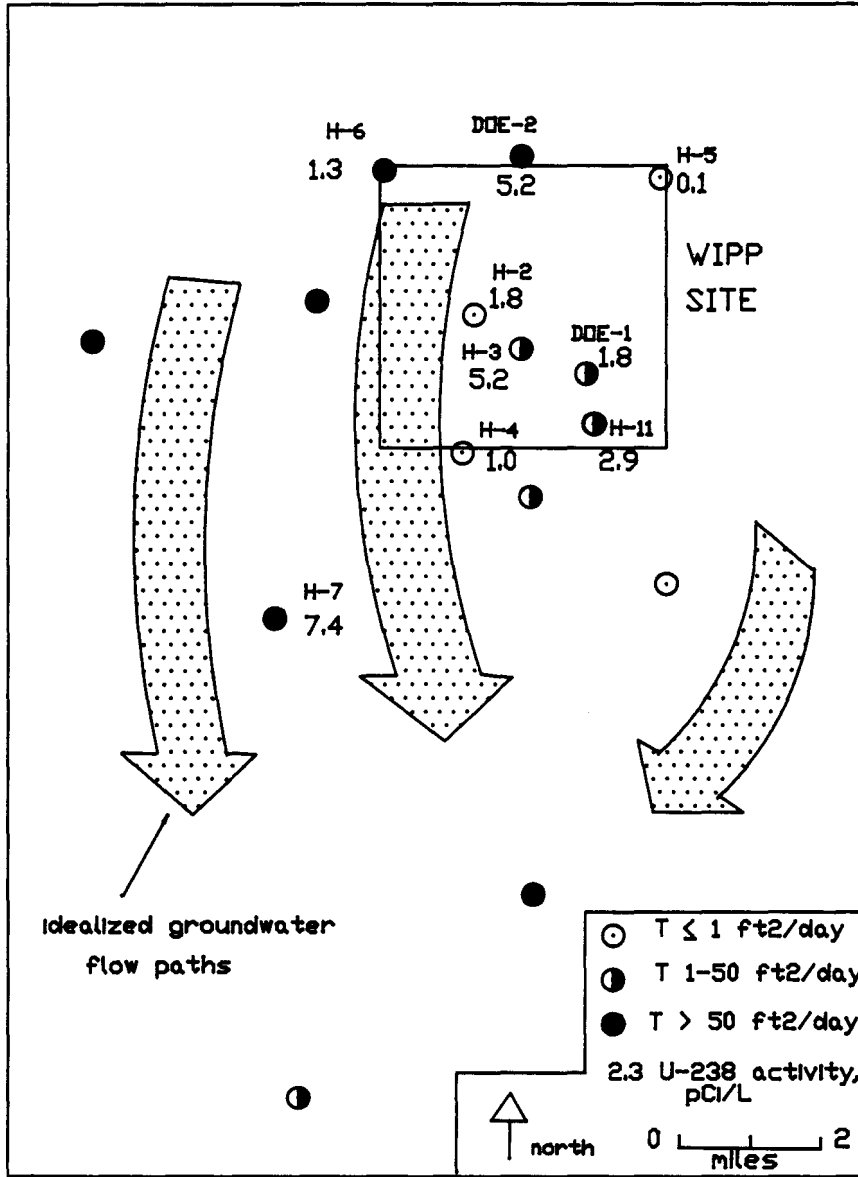


Figure 11. U-238 content, with well transmissivity values and idealized groundwater flow directions depicted. Transmissivity data and flow directions from Haug et al. (1987).

Subeconomic deposits of uranium are found in both the Santa Rosa Sandstone and Gatuna Formation elsewhere in New Mexico (Siemers et al., 1978). Test holes in Chaves and Lea Counties (including one approximately 20 miles southeast of WIPP) have identified anomalous concentrations of uranium in the Dockum Group. Anomalous radioactivity has also been detected in dark-red gypsiferous sandy clay of the Gatuna Formation, exposed in oil-field drilling-mud pits. One occurrence in Lea County, about 25 miles northeast of WIPP, contained 60 ppm U_3O_8 and visible specks of carnotite (Waltman, 1954, as reported by Finch, 1972). In addition, Pearlette volcanic ash beds of Pleistocene age, scattered throughout the region, are noticeably radioactive, containing 20-40 ppm U_3O_8 . A volcanic ash bed is present near the top of the Gatuna Formation on the east side of Nash Draw (Bachman, 1984).

Concentrations of other, shorter-lived, members of the decay chains (such as Ra-226) indicate that the Culebra must be a uranium and thorium source, in addition to overlying clastic units. This is also indicated by the down-gradient increase in U-238, suggesting continued dissolution of uranium along the flow path (Fig. 11). Carbonates and evaporites are not generally known for high uranium and thorium contents (Durrance, 1986), but high concentrations are not needed if a large volume of rock is dissolved. Lambert and Carter (1987) report bulk uranium concentrations from 0.54 to 0.97×10^{-6} g/g in the Culebra dolomite. Though gamma logs run through the Rustler did not usually show any areas of high radioactivity, a high gamma count was recorded during initial logging of the Culebra in well P-15 (Mercer and Orr, 1979). A subsequently run Spectralog attributed the activity to uranium. It may be that the Culebra contains pockets of uranium-rich material that have only been encountered once during WIPP drilling. If such accumulations exist, they may be related to variations in groundwater oxidation state or lateral variations in clay content. It is also possible that uranium and thorium in the Culebra occur mainly as coatings on grain or fracture surfaces. If so, the amount of uranium and thorium available to go into solution could be larger than that indicated by whole-rock analysis.

Uranium Isotopic Disequilibrium

Marked disequilibrium exists between U-238 and U-234 activities in Culebra groundwater. Cherdyntsev et al. (1955) were the first to discuss the observation

that rather than secular equilibrium between radioactive parent (U-238) and radioactive daughter (U-234), some natural systems (particularly groundwater) experience large variations in their U-234/U-238 activity ratios. Proposed mechanisms of uranium isotope fractionation include: 1) movement of the atom across the solid/liquid boundary by alpha recoil during U-238 decay, 2) increased vulnerability of U-234 to solution due to either recoil displacement or oxidation from U^{+4} to U^{+6} , and 3) chemical fractionation of the intermediate daughter, Th-234 (Osmond and Cowart, 1976). Observed 234/238 activity ratios in Culebra groundwater range from 1.5 to 18.

Uranium 234/238 disequilibrium covaries with aquifer transmissivities. The very highest U-234/U-238 activity ratios (greater than 6) are associated with the lowest transmissivities ($<1 \text{ ft}^2/\text{day}$) (Fig. 12). Among the higher transmissivity wells, there is a weak pattern of increasing activity ratio (AR) with increasing transmissivity. There is also a general trend of decreasing A.R. with increasing uranium content (based on U-238 activity) (Fig. 12).

The rate of groundwater movement is related to the hydraulic conductivity and hydraulic gradient. Though steeper hydraulic gradients are found to the east of the WIPP site and more gradual gradients occur south of the site and in Nash Draw, the "Best Estimate of Undisturbed Freshwater Heads" calculated by Haug et al. (1987) shows a fairly regular gradient across the site itself (Fig. 13). There is uncertainty associated with any interpretation of a Culebra freshwater head map because flow directions are not necessarily perpendicular to potentiometric contours due to fracture flow conditions. However, given the apparent regular gradient across the site, relatively constant thickness of the Culebra and assumed constant porosity, groundwater velocities are certainly lower in the low transmissivity areas as compared to the high transmissivity areas. This is also supported by the fact that the high transmissivity zones are characterized as having fracture flow. The build-up of excess U-234 therefore seems linked to possibly long groundwater residence times, allowing for both more U-238 decay and leaching of U-234.

Lower transmissivity wells also have low total uranium content, and of this uranium, the majority of the activity is from U-234. There are three possible explanations for the low total uranium content and they relate to the observation

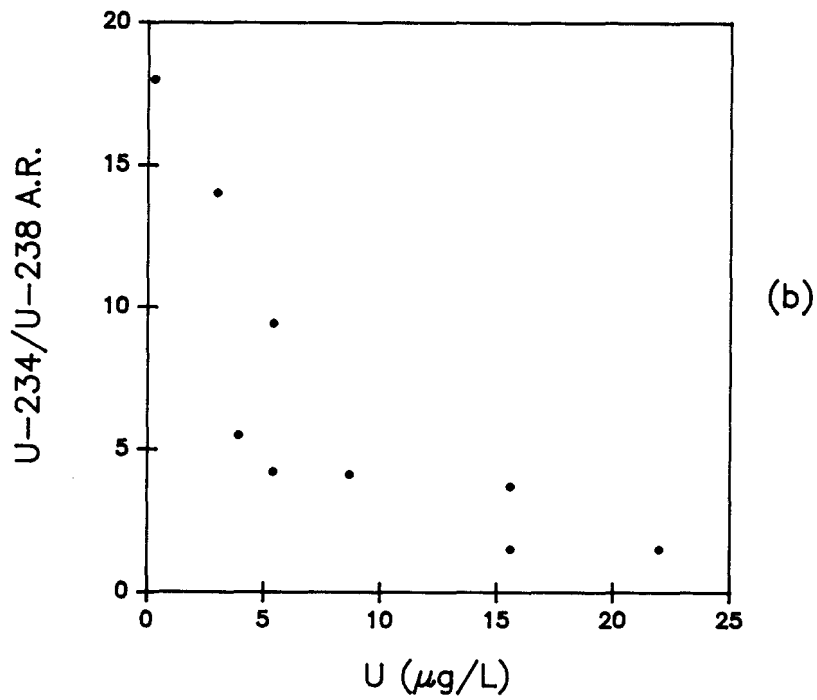
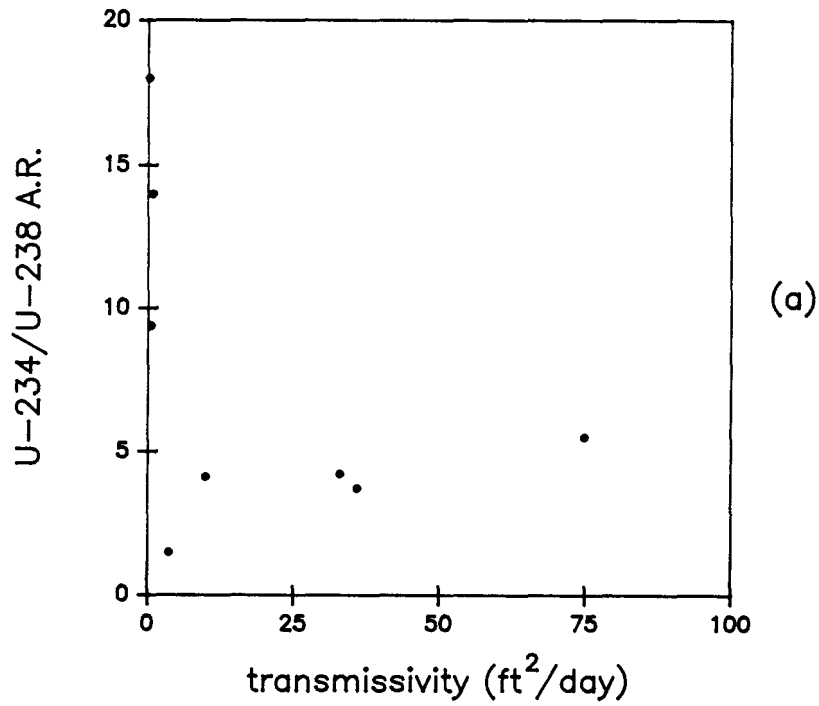


Figure 12(a) U-234/U-238 activity ratio versus aquifer transmissivity.

Figure 12(b) U-234/U-238 activity ratio versus uranium content. The uranium content is calculated from U-238 activity.

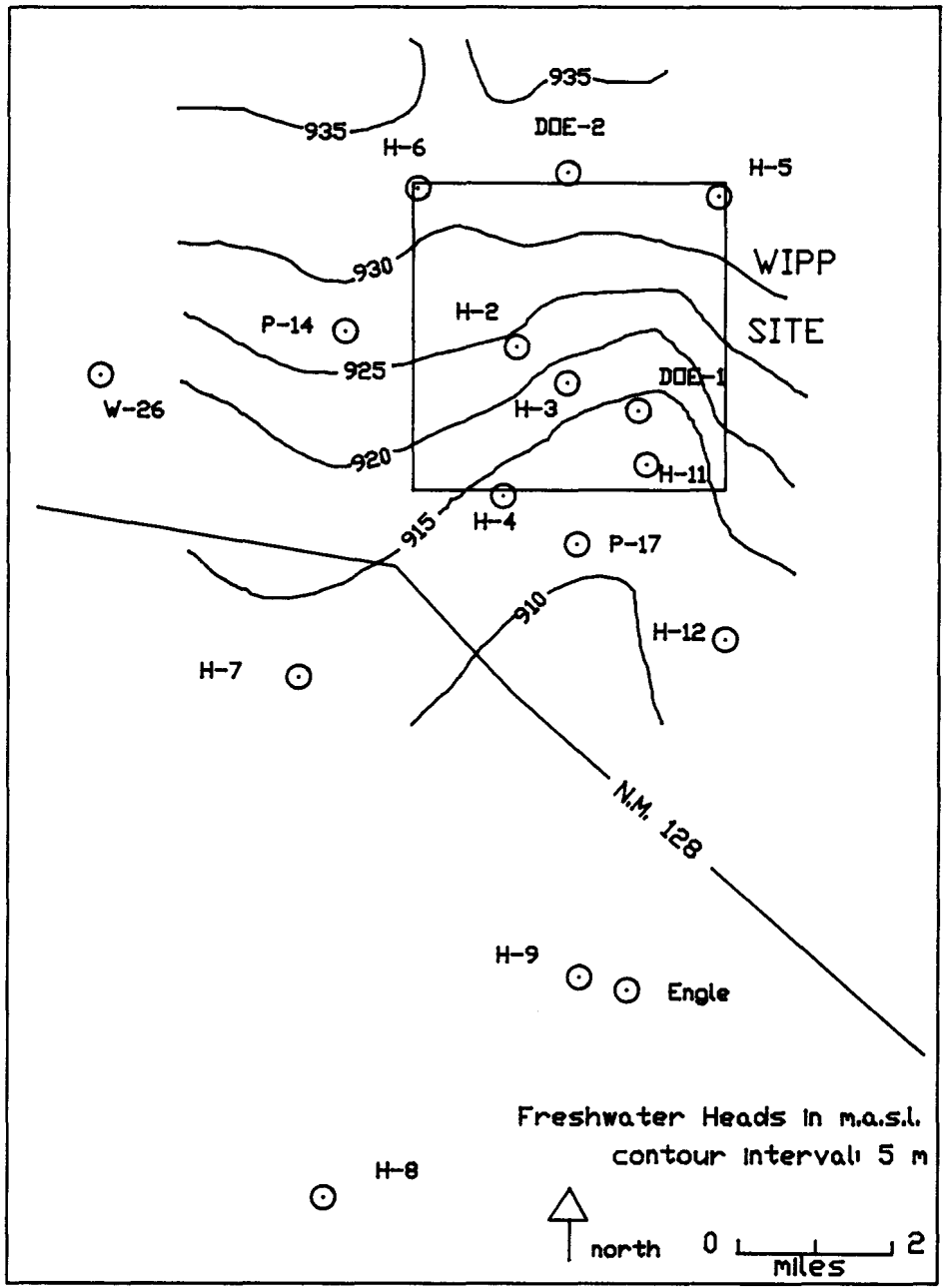


Figure 13. "Best estimate" of undisturbed freshwater heads in the Culebra Dolomite, adapted from Haug et al. (1987).

that the low-T zones are characterized hydrologically as lacking fractures. First, an assumed longer groundwater residence time in the low-T zones may allow more adsorption of uranium onto the rock matrix than occurs in the fractured portions of the Culebra. Second, more reducing conditions may exist in tighter parts of the aquifer. Third, uranium may occur in the formation primarily as linings on fracture surfaces, and thus less uranium is available to go into solution in unfractured parts of the aquifer. The relative abundance of U-234 in these unfractured areas could be explained if the Culebra matrix has U-238 more tightly bound than is found on fracture surfaces and coatings. Therefore, the uranium in solution would be due primarily to U-234 that is loosened from its crystal sites by alpha recoil.

Radium-226

The immediate decay product of U-234, Th-230, was detected just at the MDL in the first sample collected from H-6, but was not above the MDL in the next H-6 sample nor in any other Culebra groundwater sample. However, the next nuclide in the decay chain, Ra-226, is sometimes present in relatively large amounts. Ra-226 varies from less than the MDL at well H-8 to 280 pCi/L at well H-12. Relatively large variations in Ra-226 content have been noted in 3 out of the 7 wells that have been sampled twice. The Ra-226 concentration in water from H-5 and DOE-1 decreased from 1985 to 1986, while it doubled during the same period in well H-4. Wells H-4 and H-5 are low transmissivity wells and the variability may be related to different degrees of purging at low discharge rates. DOE-1 has a relatively high transmissivity, so well purging should not be a problem. The difference between analyses at DOE-1 is on the order of 30% and is unexplained. Future analyses may help reveal the cause of the variation. However, some analytical variation is often encountered when determining the quantity of trace elements. Temporal variation related to recharge conditions cannot be ruled out, but seems unlikely as the confined nature of the aquifer suggests a distant recharge point and other wells in the area did not exhibit significant Ra-226 variations from 1985 to 1986.

The radium source is probably Th-230 in the solid phase in the Culebra. Carbon-14 dates on a few WIPP groundwater samples range from 2000 to 17,000 years (Lambert, 1987; F. Phillips, written communication). Most samples are dated to

be at least 10,000 years since removed from atmospheric contact, which is long enough for substantial decay of any radium picked up during recharge through overlying formations.

There is a positive linear relationship between Ra-226 and Cl, with a correlation coefficient of 0.85 (Fig. 14). No similar relationship with chloride is obvious for the distant Ra-226 precursors U-234 and U-238, nor between the uranium isotopes and Ra-226. Three physical processes could account for the Ra-226 and Cl relationship: 1) the source of the chloride is also the source of the radium, 2) radium is more mobile in higher chloride water, or 3) an unidentified solute covaries with chloride and this other solute affects radium concentration. The first process seems rather unlikely. The major source of chloride in the Culebra is halite dissolution. Evaporites in general do not have high uranium contents and spectral gamma ray logs at the WIPP site indicate that radioactivity in the halite sections is primarily from K-40. The second process, increased mobility of radium in chloride-rich brine is likely to be a contributing factor for the association of high Ra-226 with high Cl and will be discussed below. The third possibility is difficult to analyze due to the unidentified nature of the other solutes, but undoubtedly radium concentration is affected by the presence of solutes in addition to chloride.

The association of high Cl and high Ra was attributed by Tanner (1964) to the balancing complement of cations in high chloride brines, which compete for adsorption sites with Ra-226. Bloch and Key (1981) have noted that many oil-field brines have anomalously high radium contents, though these brines are often of a Ca-Cl type. Cech et al. (1987) reported an association of radium and radon in groundwater with proximity to salt domes in the Houston area, but they attributed this to either uranium deposits associated with the domes or brine leaking up around the domes. The lack of an increase in uranium with increasing chloride in Culebra brine supports the hypothesis that in the Culebra, Ra-226 is simply more mobile in high-Cl environments, not that Cl-rich brines are associated with the radium source.

There is no strong relationship between Ra-226 and transmissivity (Fig. 14). The highest transmissivity wells (greater than 1000 ft²/day) are all characterized by low Ra-226 contents, but they also have low chloride contents (with the exception

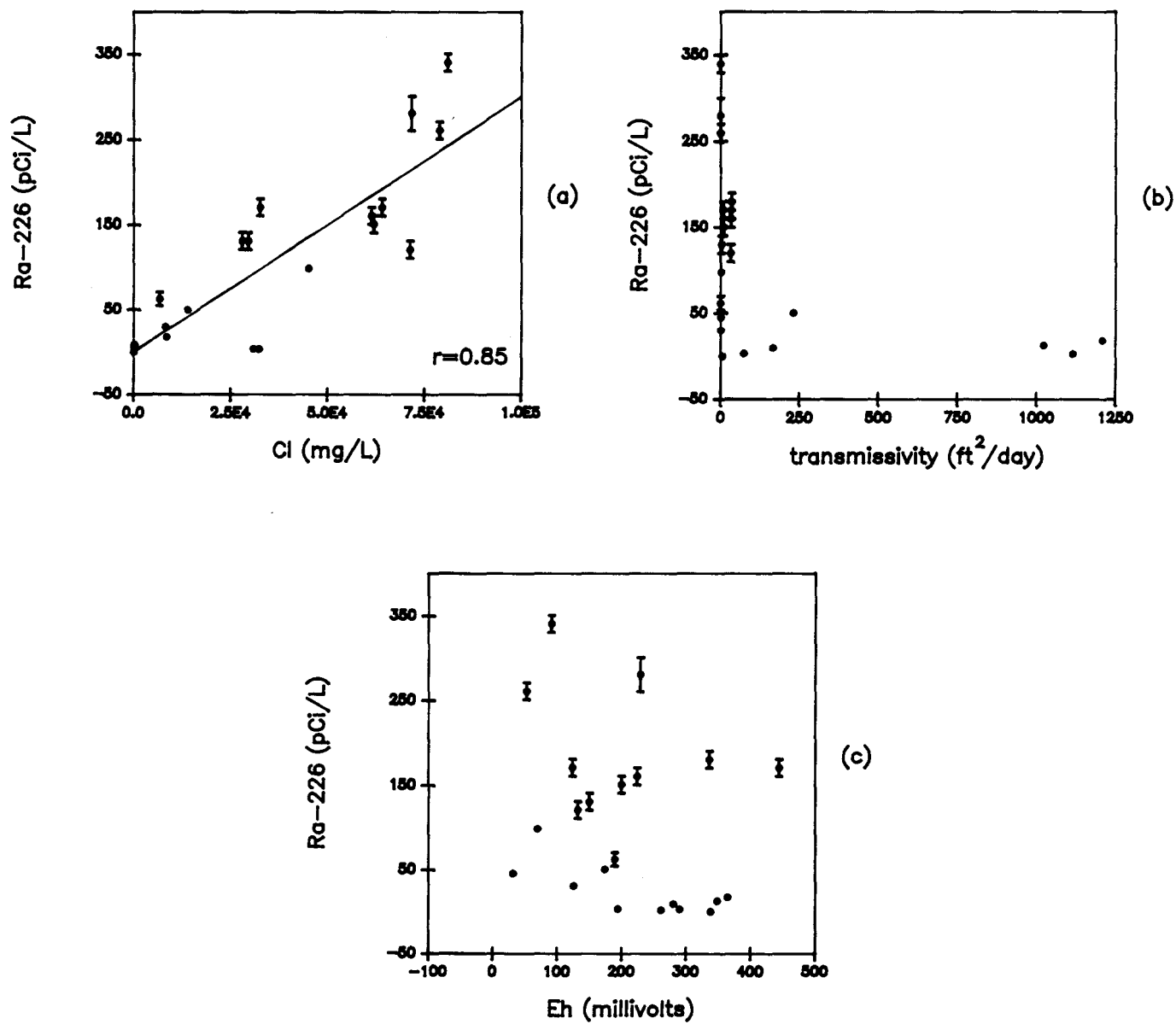


Figure 14(a) Ra-226 versus Cl.
 Figure 14(b) Ra-226 versus aquifer transmissivity.
 Figure 14(c) Ra-226 versus field Eh values.

of W-29). The highest Ra-226 waters are from wells with transmissivities less than $1 \text{ ft}^2/\text{day}$ (H-5 and H-12), but these wells also have relatively high chloride contents. Good examples of the lack of control of transmissivity on radium are wells H-2 and H-4. Both of these wells have transmissivity values less than $1 \text{ ft}^2/\text{day}$, but also have relatively low Ra-226 contents ($<100 \text{ pCi/L}$).

There are two exceptions to the Cl/Ra-226 relationship. Well W-29 is the largest exception with a very high chloride content, but a Ra-226 level of only 12 pCi/L (it is not plotted on Fig.14). Lambert and Harvey (1987) have argued that W-29 is not representative of Culebra groundwater because it may be affected by surface processes given the shallow depth to the Culebra (12 ft., Mercer, 1983). The other anomalous Cl/Ra-226 relationship is at H-6, where the Ra-226 content is less than 3 pCi/L , but the Cl is over $30,000 \text{ mg/L}$. If the hypothesis for W-29 is correct, then H-6 may also be influenced by surface processes (for instance, recharge) despite the Culebra's depth (600') and confined nature (Mercer, 1983). Additional support for the concept of recharge in the H-6 area is the proximity to Well W-33. Drilled into a large surface depression located less than a mile from H-6, W-33 encountered cavernous areas of dissolution in the Rustler Formation.

Szabo and Zapezca (1987) identified Eh as an important control on Ra-226 concentration in New Jersey groundwater. The observed increase in Ra-226 activity with decrease in Eh was attributed to the Eh control on iron and manganese hydroxide coatings on grains and Eh control on sulfate activity. In relatively reducing environments (between Eh values of -100 and $+200 \text{ mv}$; Hem, 1982), iron and manganese hydroxides are soluble and less abundant for radium adsorption. The reduction of sulfate to sulfide prevents the coprecipitation of radium with sulfate minerals.

There is no trend between Ra-226 and Eh in Culebra groundwater (Fig. 14). Calcium sulfate precipitation may be the primary mechanism of radium removal from solution, particularly in the southern area dominated by Ca-SO_4 water (Fig. 15). Higher sulfate contents are found in other parts of the Culebra, but are coupled with high chloride content. In the Ca-SO_4 type southern area, saturation with gypsum and relatively low chloride contents may combine to create a suitable environment for effective removal of radium by coprecipitation. A similar

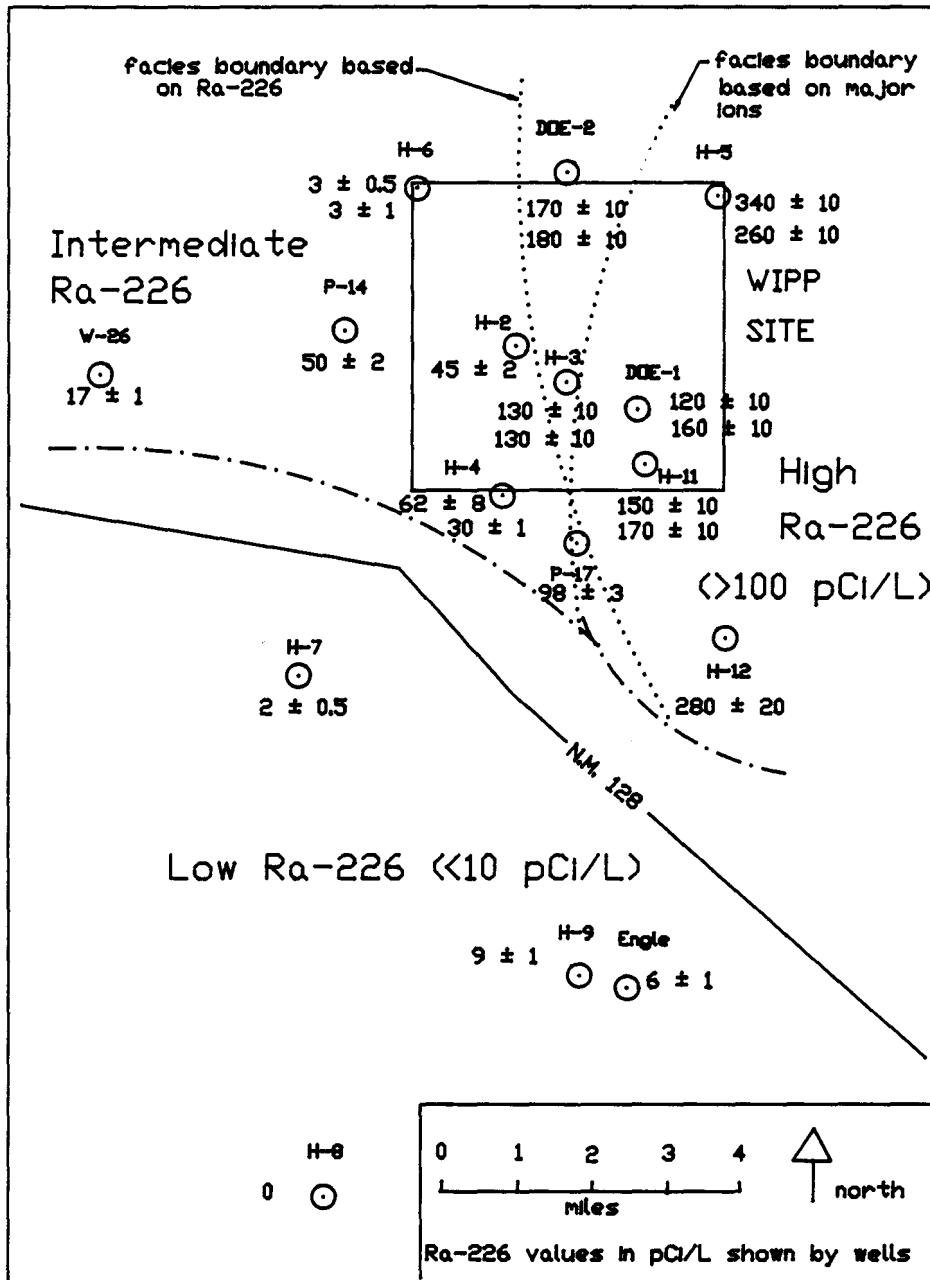


Figure 15. Ra-226 values superimposed on the hydrochemical facies map (Fig. 9). Areas of differing radium concentration correspond well with the hydrochemical facies, with low Ra-226 values in the southern Ca-SO₄ area and higher values in the northern Na-Cl area.

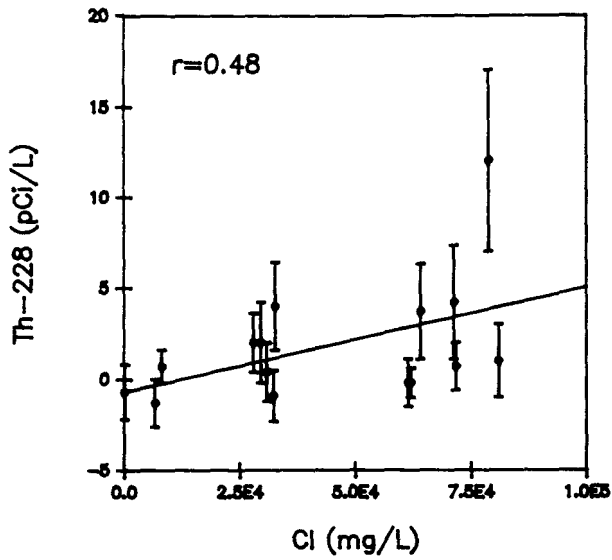
process may be at work to a lesser extent in the western WIPP area where the chloride content is intermediate and calcium is a relatively more abundant cation.

Thorium Decay Series

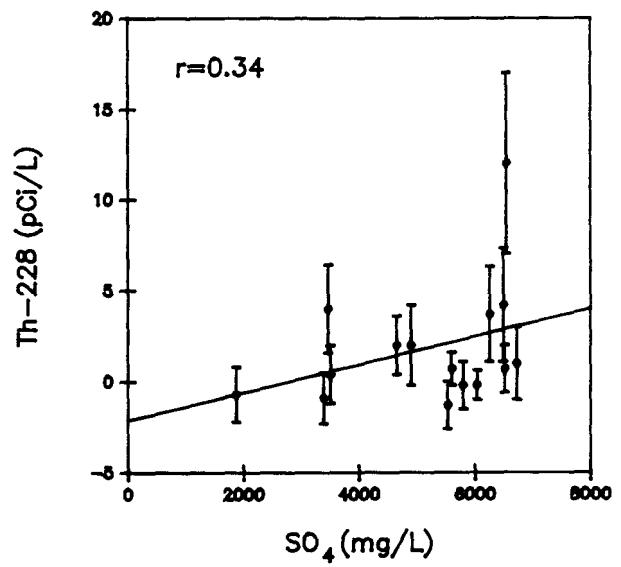
The parent of the thorium decay series, Th-232, was not detected in any groundwater samples, indicating that it is in the solid phase. Two members of the thorium decay series have been measured at levels above the MDL in Culebra groundwater: Ra-228 and Th-228. The Th-228 is not present in large amounts, but is found at levels above the MDL in one out of the two samples analyzed from wells DOE-2, DOE-1, H-3, H-5, and H-11. The most notable occurrence is at H-5 where 12 ± 5 pCi/L of Th-228 were found. Simpson et al. (1985) also noted the presence of Th-228 in Delaware Basin groundwater. Radium-228 is present at significant levels in many samples, with the highest activity of 25 ± 2 pCi/L also occurring at H-5.

In ordinary geochemical environments, thorium is not carried extensively in solution because it occurs in the insoluble +4 oxidation state (Hem, 1982 and Durrance, 1986). Because of the very low solubility of Th at typical water pH, chemical precipitates such as limestone and dolomite were characterized by Michel and Cothorn (1986) as having very low thorium contents. However, the high Ra-228 content in Culebra groundwater, coupled with Ra-228's short half-life of 5.75 years, indicates that the Culebra dolomite contains Th-232 to act as a source for Ra-228.

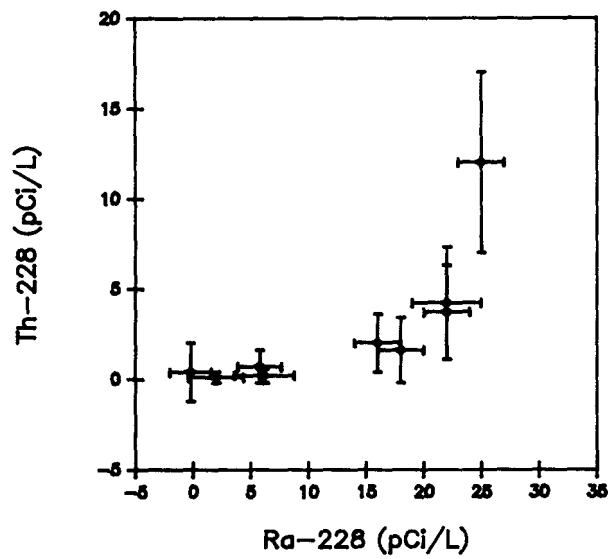
The Th-228 source may be from Ra-228 in solution. The increase in Th-228 with increasing Ra-228 (Fig. 16) supports the argument for a Ra-228 source in solution, though the non-linear relationship suggests other controlling factors on Th-228 abundance as well. It is surprising that the decay of dissolved Ra-228 does not result in the immediate adsorption of thorium onto the aquifer solids, or immediate precipitation as a thorium hydroxide. High salinity may again provide an explanation, as thorium has a strong tendency to form complex ions with chloride and sulfate (Durrance, 1986). Thorium may be kept mobile in saline



(a)



(b)



(c)

Figure 16(a) Th-228 versus Cl.
 Figure 16(b) Th-228 versus SO_4 .
 Figure 16(c) Th-228 versus Ra-228.

parts of the Culebra as thorium chloride and thorium sulfate complexes. The correlation between Th-228 and chloride and sulfate is positive, though weak ($r = 0.48$ and $r = 0.34$ respectively) (Fig. 16). Ra-228 content correlates well with Ra-226 content (Fig. 17), suggesting two possible relations. One is that where the Ra-226 parent (Th-230) is abundant, the Ra-228 parent (Th-232) may also be abundant. The second possibility is that both thorium isotopes are evenly distributed throughout the Culebra, and that the correlation between Ra-226 and Ra-228 reflects the equal geochemical influence upon the mobility of the radium isotopes. In other words, in areas where Ra-226 is particularly mobile, Ra-228 will be too.

The influence of the geochemical environment is probably the major factor controlling radium occurrence in the Culebra. There is no reason to postulate a steady decrease in the thorium content of the Culebra from east to west across the site, nor the near absence of thorium in the dolomite south of N.M. 128. Even if thorium content does vary, a systematic correlation between primordial Th-232 and Th-230 (produced as part of the uranium decay chain) seems unlikely. The correlation with chloride is good for both radium isotopes and appears to be the major factor controlling their abundance (Fig. 14 and 17).

Other Radionuclides

A number of other radionuclides were included in the analytical program, but not detected in significant amounts. Tritium analyses were performed, but the level of detection was not suitable for groundwater dating applications. Analyses were performed for Am-241, Pu-239+240, and Pu-238 in order to establish pre-operational levels in the WIPP area. No values above the minimum detectable level were obtained for any of these radionuclides.

Surprisingly, analyses for Cesium-137 revealed activities from 3.3 ± 1.3 to 5.1 ± 2.1 pCi/L in three Culebra water samples. The short half-life of Cesium-137 (about 30 years), its man-made origin, and strong tendency to be sorbed by clays make it an uncommon constituent in groundwater. Its presence in wells H-5, DOE-1, and H-11 might lead to speculation about a very rapid connection with surface recharge and a surface source of fallout Cs-137. However, it is far more likely that the Cs-137 reported is merely an artifact of the analysis of water with a

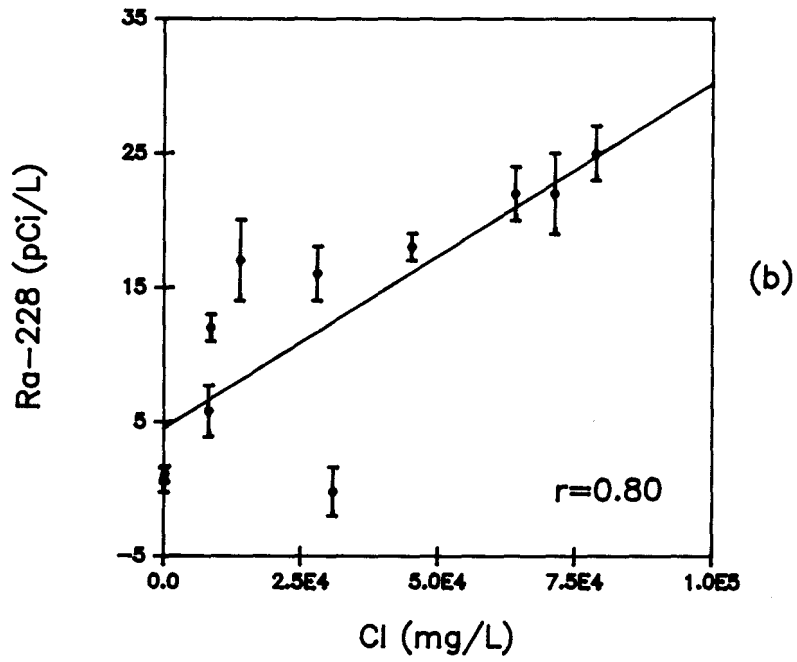
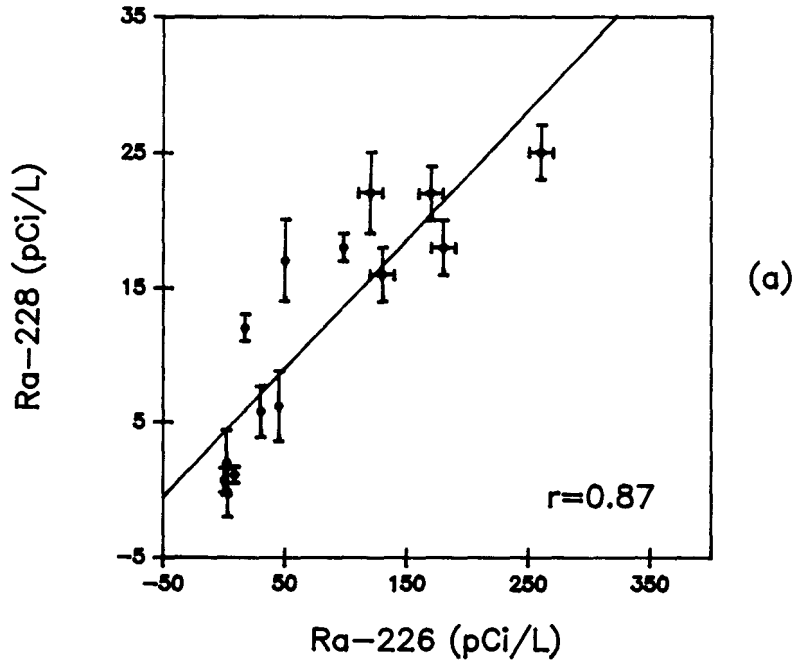
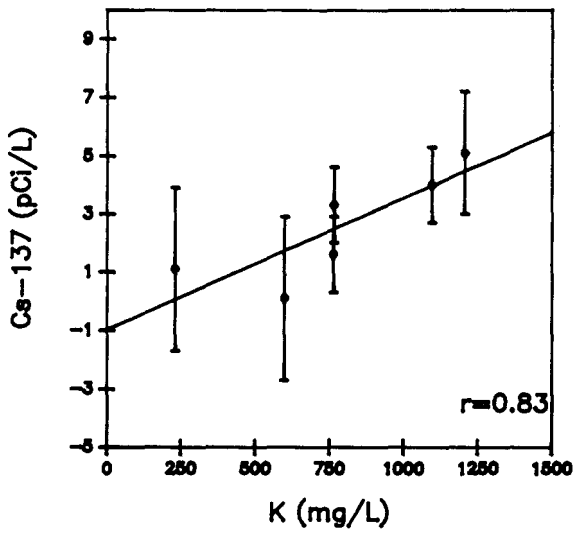


Figure 17(a) Ra-228 versus Ra-226.
 Figure 17(b) Ra-228 versus Cl.

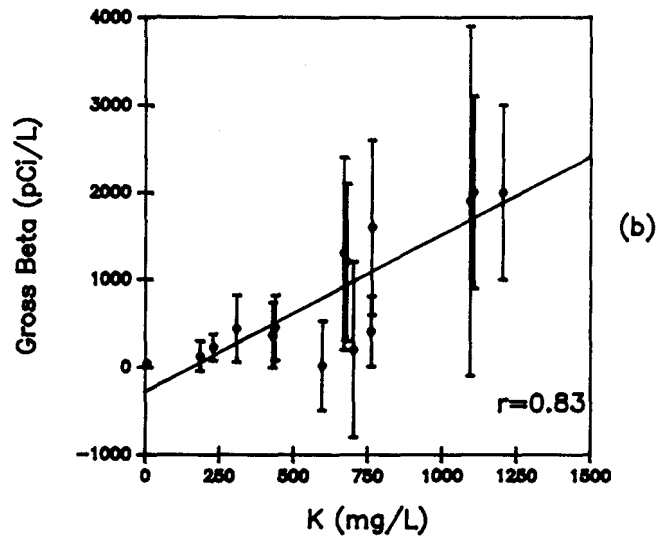
high potassium content. The AccuLabs Research analysis for Cs-137 is performed by chemical separation and beta counting and there is the possibility for some interference from other beta-gamma emitters in the Group 1A elements separated by chloro-platinate precipitation, if present in large quantities. The three samples where Cs-137 was reported also have high potassium contents (700-1200mg/L). The proportion of K-40 in total potassium is virtually a constant in all geologic media, so increasing potassium content implies increasing K-40. The strong correlation between Cs-137 and K, and between K and Gross Beta suggests that K-40 interference may account for the Cs-137 measured (Fig. 18).

A lake located in Nash Draw, Laguna Grande de la Sal, was also reported as having Cs-137 in two analyses performed in 1986 (9.8 ± 1.7 pCi/L in 4-86 and 28 ± 10 pCi/L in 10-86). This saline lake has a very high potassium content of around 13,000 mg/L. A water sample collected in 1987 was submitted to the State of New Mexico Scientific Lab Division for gamma spectroscopy analysis for Cs-137. This analysis resulted in no detection of Cs-137 at a lower limit of detection of 5 pCi/L. This gamma-spec analysis adds strong evidence that the analytical technique used by AccuLabs for Cs-137 analysis is not reliable for waters with high potassium contents.

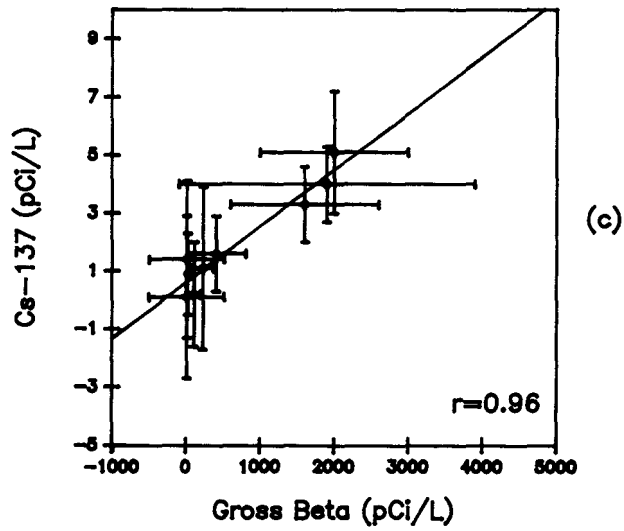
The reporting of Cs-137 in H-5B groundwater coexists with a Carbon-14 age of $16,500 \pm 5600$ years (Lambert, 1987 and F. Phillips, written communication, 1987). However, another well on the H-5 hydropad, H-5C, yielded a C-14 age of 2000 ± 3800 years, possibly due to contamination. Groundwater levels at H-5 also indicate a potentiometric high in the area around the hydropad, though Mercer (1983) stated that this could be due to the conversion to freshwater head. These coincidences warrant closer scrutiny of the hydrologic and geochemical characteristics of the area. In particular, repeated water analyses could investigate the carbon-14 dates of water from wells at the H-5 hydropad, and laboratory analysis of potassium-rich prepared solutions would indicate the impact of K-40 on the Cs-137 analysis.



(a)



(b)



(c)

Figure 18(a) Cs-137 versus K.
 Figure 18(b) Gross Beta versus K.
 Figure 18(c) Cs-137 versus Gross Beta.

IMPLICATIONS FOR GROUNDWATER FLOW PATTERNS

Major Ion Chemistry and Hydrochemical Facies

Groundwater flow directions, though uncertain due to fracture flow conditions and variable water densities, are believed to be predominantly toward the south and southwest (Fig. 13) (Haug et al. 1987). As noted by Neill et al. (1983) and Ramey (1985), there is an apparent inconsistency between the Culebra water chemistry and reported flow paths. In particular, as water moves from north to south, the TDS must decrease by an order of magnitude and the major hydrochemical facies must change from Na-Cl to Ca-SO₄ (Fig. 19). In this geologic setting, the only plausible mechanism for decreasing Cl, Na and K is the influx of a large quantity of low TDS water. As no fresh-water aquifers are located in the WIPP area, the source of the fresh water must be surface water recharge. The fresh-water hydraulic head of groundwater in the Magenta Member of the Rustler Formation is higher than that in the Culebra and therefore leakage could occur from the Magenta, through the predominantly gypsiferous Tamarisk Member, to the Culebra. However, though the Magenta contains less saline water than the Culebra over much of the site, south of the site (and including well H-4), the Magenta has a higher TDS than the Culebra (Table 2).

TABLE 2

| <u>WELL PAD</u> | <u>TDS IN CULEBRA GROUNDWATER/mg/L</u> | <u>TDS IN MAGENTA GROUNDWATER/mg/L</u> |
|-----------------|--|--|
| H-1 | 97,300* | 22,000* |
| H-2 | 12,500* | 10,300* |
| H-3 | 53,500 | 30,000* |
| H-4 | 19,800 | 22,300* |
| H-5 | 139,500 | 6,000* |
| H-6 | 55,650 | 5,700* |
| H-8 | 2,710 | 9,000* |
| H-9 | 3,040 | 5,100* |
| H-10 | 66,000* | 261,000* |
| W-25 | 17,000* | 12,000* |
| W-27 | 126,000* | 147,000* |
| W-30 | 109,000* | 18,500* |

*Data from Mercer (1983) as reported in Ramey (1985), all other values from the present study.

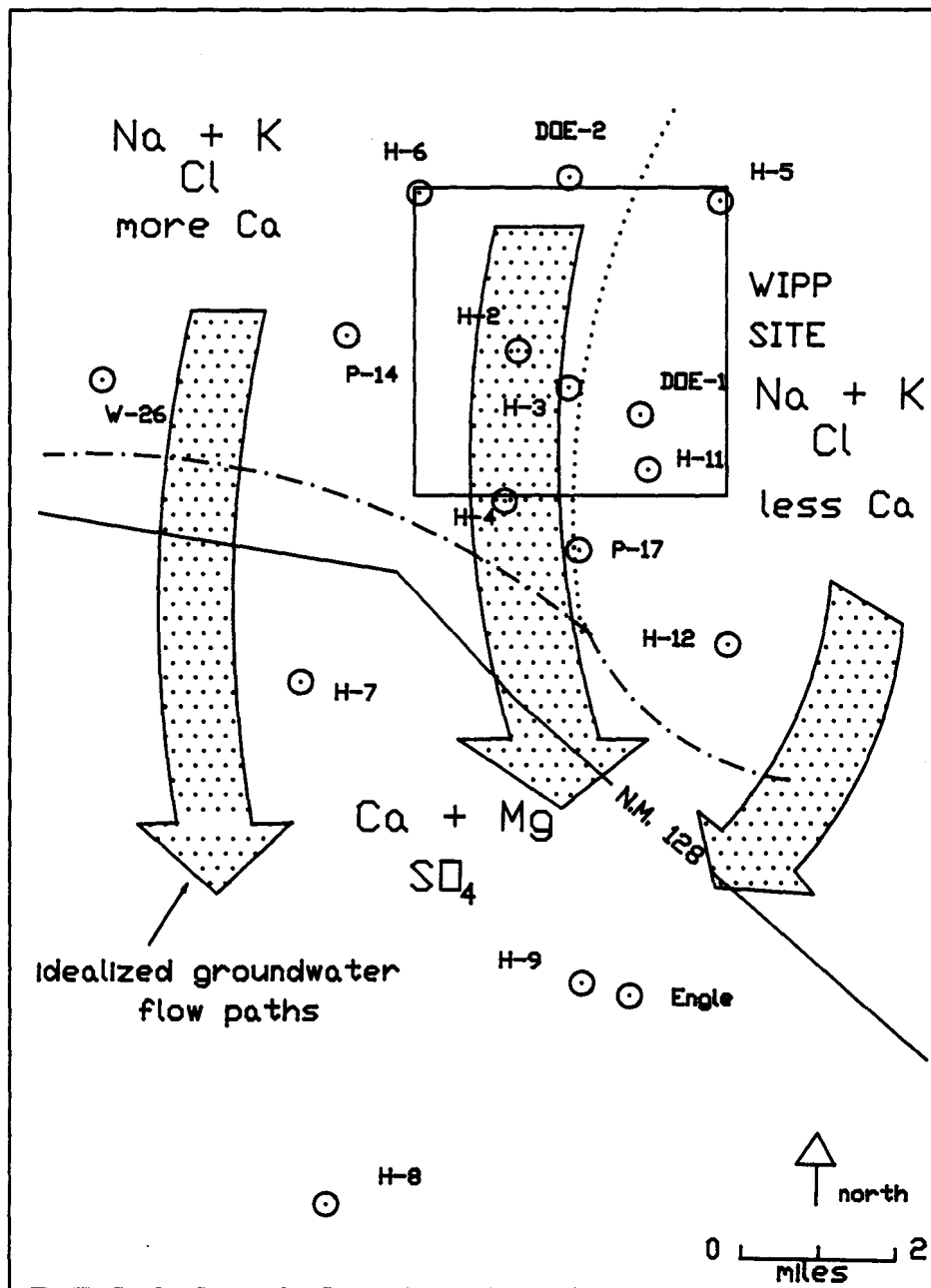


Figure 19. Hydrochemical facies map with superimposed, idealized, groundwater flow paths. (Please see Fig. 13 for the potentiometric head map upon which the flow paths are based.)

Water levels indicate that the Culebra is confined, even in the southern area, though connection with overlying units improves to the south. For instance, the fresh-water heads in the Magenta and Culebra in the wells at H-8 are similar, and the Magenta is unsaturated at well H-7A with its water presumably drained into the Culebra through fractures (Mercer, 1983). Dissolution such as that associated with the solution and fill processes active in Nash Draw also occurs east of the Nash Draw depression (Chaturvedi and Channell, 1985). This activity has created gypsum caves in the Forty-Niner member of the Rustler in the vicinity of the Gnome site (Fig. 1), within the southern, low-salinity water area. Such features could behave as conduits supplying fresher water to deeper Rustler units. Active gypsum dissolution, and the absence of halite (removed by earlier dissolution), are consistent with the Ca-SO_4 type water found in the southern area. In addition, the overlying Dewey Lake Redbeds contain zones of saturation, particularly in the James Ranch area along the boundary of the chemical facies. Mercer (1983) attributed these perched saturated zones to areas of localized recharge related to an extensive, thick active area of sand dunes.

Exclusive of the low-salinity southern area, the hydrochemical facies support the north to south movement of groundwater in the Culebra across with WIPP site. Wells that are located on generally the same north-south flow paths have similar ion ratios, though TDS values do vary. For instance, water from H-5, DOE-1, H-11, and H-12 all plot in a very tight group on the Piper diagram (Fig. 7). The same is true for wells H-4, H-6, and DOE-2. Groundwater from H-3 and P-17 is chemically and geographically located between the two groups, in an apparent mixing zone.

Water at wells P-14 and W-26 plot between the ion-ratio compositions of the Na-Cl type water and the Ca-SO_4 type water (Fig. 7). These wells are not located such that they appear to be in any mixing zone between the two water types. Rather than representing actual mixing, the intermediate composition of the groundwater at P-14 and W-26 may be the result of similar processes acting on the Culebra groundwater west of the site as are responsible for the major chemical changes observed south of the site. The increased dominance of Ca and SO_4 ions both to the south and west suggest that sulfate mineral equilibria is more important in controlling water chemistry in these areas than to the east. This is supported by the presence of gypsum karst in the Nash Draw and Gnome Site areas. The major

ion chemistry in Culebra groundwater at the WIPP site itself, and especially in the low-Ca eastern area, is dominated by halite dissolution.

The connection between chemistry and hydrology across the WIPP site may require reinterpretation when new data are available. Specifically, no major ion analyses were performed by EEG for wells H-1 and H-2. Mercer (1983) reported highly variable Culebra water chemistry in the approximately square mile area around wells H-1, H-2, and H-3. The recent analysis of H-2 reported by Uhland and Randall (1986) confirms a TDS value at H-2 of less than half that found at H-3. Though recharge of low TDS water could explain the salinity variation in the Culebra at the site, evidence of possible surface connections such as found in the area south of NM 128 is absent within the 4 x 4 mile area. Instead, the variation could be due to leakage of more saline water into the Culebra from underlying units. Abnormally high pressures have been found in the Salado and Castile evaporites (Mercer, 1987) and could provide a driving force for fluid movement upward. Given the low permeabilities (less than a microdarcy) in the Salado, such leakage is probably small in volume, but could have a major impact on water chemistry if restricted to certain areas. An apparent mixing line formed by the oxygen and hydrogen isotopic compositions of water in the Rustler, Salado, and Castile supports the vertical movement of brine through the evaporite section (Chapman, 1986).

Uranium Chemistry and Culebra Groundwater Flow

Geographically, the uranium content does not correspond well to the different hydrochemical facies. For instance, though the major ion chemistry of wells H-5, DOE-1, and H-11 is similar, U-238 varies from below significant detection at H-5, to 1.8 ± 1.0 pCi/L at DOE-1 and 2.9 ± 2.5 pCi/L at H-11 (compare Figs. 9 and 11). However, this is consistent with a trend of increasing uranium content along groundwater flow paths. Barker and Scott (1958) also noted a downgradient increase in uranium content in water in the Ogallala Formation and attributed this to longer residence times in the downgradient portions. This explanation could account for the U increase along the H-5, DOE-1, H-11 flowpath, but is not obviously appropriate for the western part of the area. In particular, the highest U-238 content is found at well H-7, but the stable element chemistry suggests the input of fresh (presumably younger) water in this area.

Uranium content and activity ratios can be loosely related to proposed groundwater flow paths (Figs. 11 & 20). Both total U-238 and the U-234/U-238 ratios are very similar for wells DOE-1 and H-11. However, H-5 has much less U-238 and a very high A.R. DOE-2 and H-3 have identical U-238 contents, but the A.R. in H-3 water is closer to equilibrium (1) than DOE-2, and is more similar to that at H-7. The sparsity of data make any conclusions tenuous, but it appears that along proposed groundwater flow paths, the U-238 content increases due to dissolution of uranium and thus the U-234/238 A.R. decreases (most unweathered rocks have 234/238 activity ratios of 1).

Lambert and Carter (1987) concluded from uranium values and U-234/U-238 activity ratios that groundwater flow had previously been from west to east in the Culebra, radically different from the proposed north to south flow direction. They based their conclusions on an eastward decrease in uranium content and increase in 234/238 activity ratios. Outside of Nash Draw, Lambert and Carter (1987) only had 4 wells with uranium data: W-30, H-4, H-5, and H-6. Now that uranium isotope data are available for more wells, the general west to east trend observed by Lambert and Carter is weakened. Rather, low uranium and high 234/238 activity ratios are found at wells H-2, H-4, and H-5, all of which are characterized by transmissivities less than $1 \text{ ft}^2/\text{day}$. For the more transmissive wells, there is a decrease in 234/238 ratios and an increase in uranium content as water moves down the potentiometric gradient, consistent with uranium dissolution along the flow path. The very high U-234/U-238 activity ratios at H-2, H-4, and H-5 suggest that these parts of the Culebra may contain relatively isolated flow systems.

Another conclusion of Lambert and Carter's (1987) uranium study was that the high U-234/U-238 activity ratios required a very long groundwater residence time (on the order of 10,000 to 30,000 years). Though a long uranium residence time is indicated by the high 234/238 ratios found at H-2, H-4, and H-5 (in order for U-234 to build up in solution by the recoil leach mechanism), the water in the aquifer could be moving much faster. An estimate of uranium retardation in the Culebra is required to derive any age for the groundwater. However, many workers (Hussain and Krishnaswami, 1980; Simpson et al., 1985; and Davis and Murphy, 1987) have expressed serious reservations about the reliability of applying

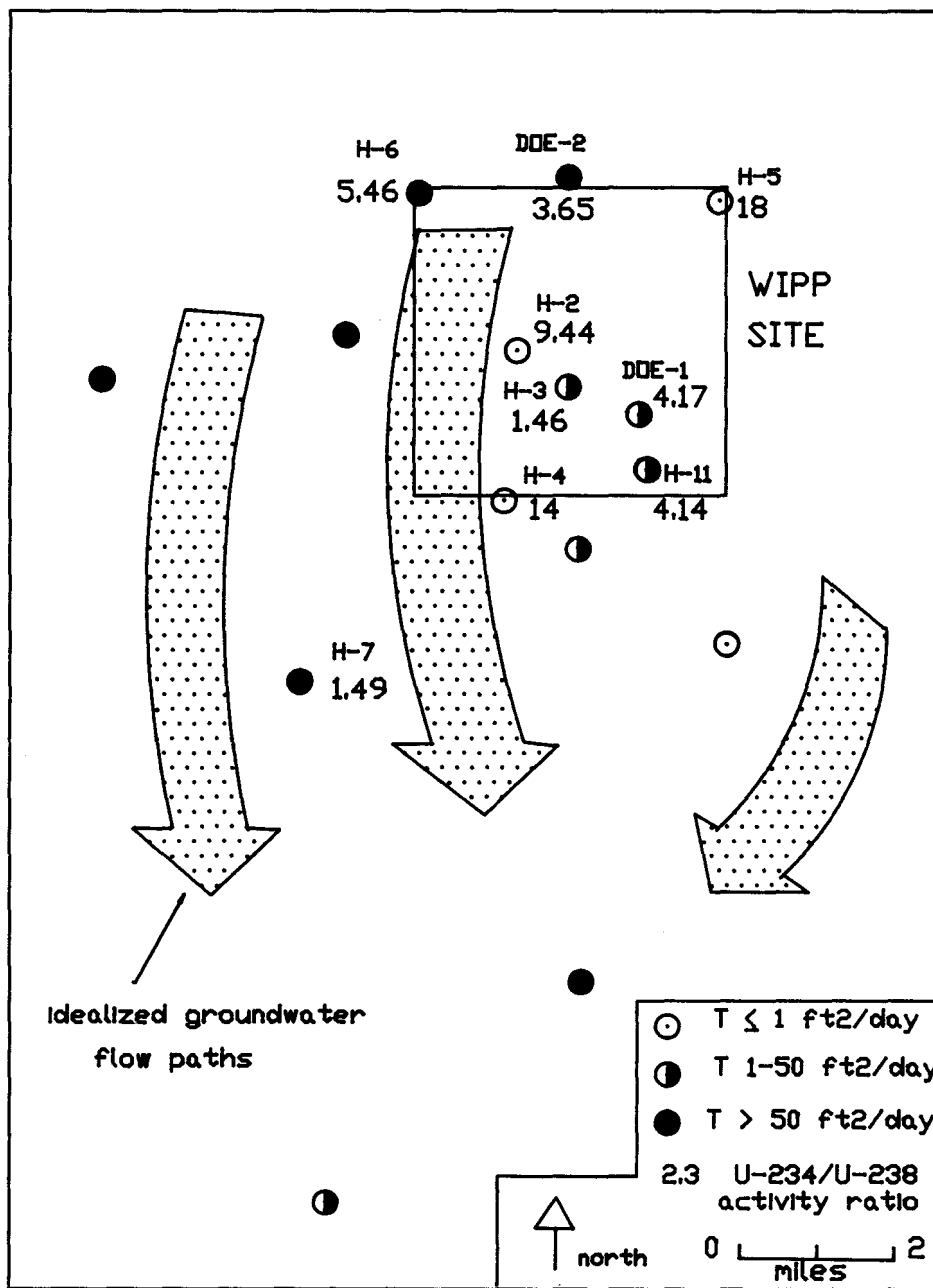


Figure 20. U-234/U-238 activity ratios with aquifer transmissivity and flow paths. (Please see Fig. 11 for a similar map of U-238 activities.)

uranium activity ratios to date groundwater because of the many assumptions involved.

Mineralogic Controls on Culebra Groundwater Chemistry

In the area north of N.M. 128, there is a loosely defined chemical division of the flow system running north-south through the middle of the site. The eastern half is characterized by higher TDS values, a Na+K-Cl type water, and high radium content. The western area has TDS values less than 75,000 mg/L, shows an increase in the amount of calcium relative to total cations, and has Ra-226 activities less than 100 pCi/L. The contact between the two zones appears gradational, with a steady decrease in chloride content from east to west.

The pattern of salinity and hydrochemical facies in the Culebra corresponds to regional changes in the overall mineralogy of the Rustler Formation. From east to west across the WIPP area, there is a progressive dissolution of halite and hydration of anhydrite to gypsum (Snyder, 1985) (Fig. 21). The southern area of low TDS values and Ca-SO₄ water corresponds to an area of complete removal of halite from the Rustler and widespread gypsification of anhydrite. The northeastern area of TDS values greater than 100,000 mg/L and almost pure Na+K-Cl brine coincides with the area where halite is present in the formation. The northwestern water, characterized by intermediate salinities and an increasing component of calcium in a predominantly Na-Cl brine, is found in the area of complete removal of halite and just within the area where halite occurs in the lower Unnamed Member of the Rustler Formation.

The chemistry of water in the Culebra Dolomite north of N.M. 128 is controlled primarily by the dissolution of halite. This is reflected in high salinity values and a predominance of Na and Cl ions in solution. Culebra groundwater chemistry south of N.M. 128 is primarily influenced by sulfate mineral equilibria, with little influence of halite. The higher calcium groundwater found in the northwestern area represents a transition, as halite is still the primary mineral influencing water chemistry, but sulfate mineral dissolution plays a more important role than found in the waters to the east.

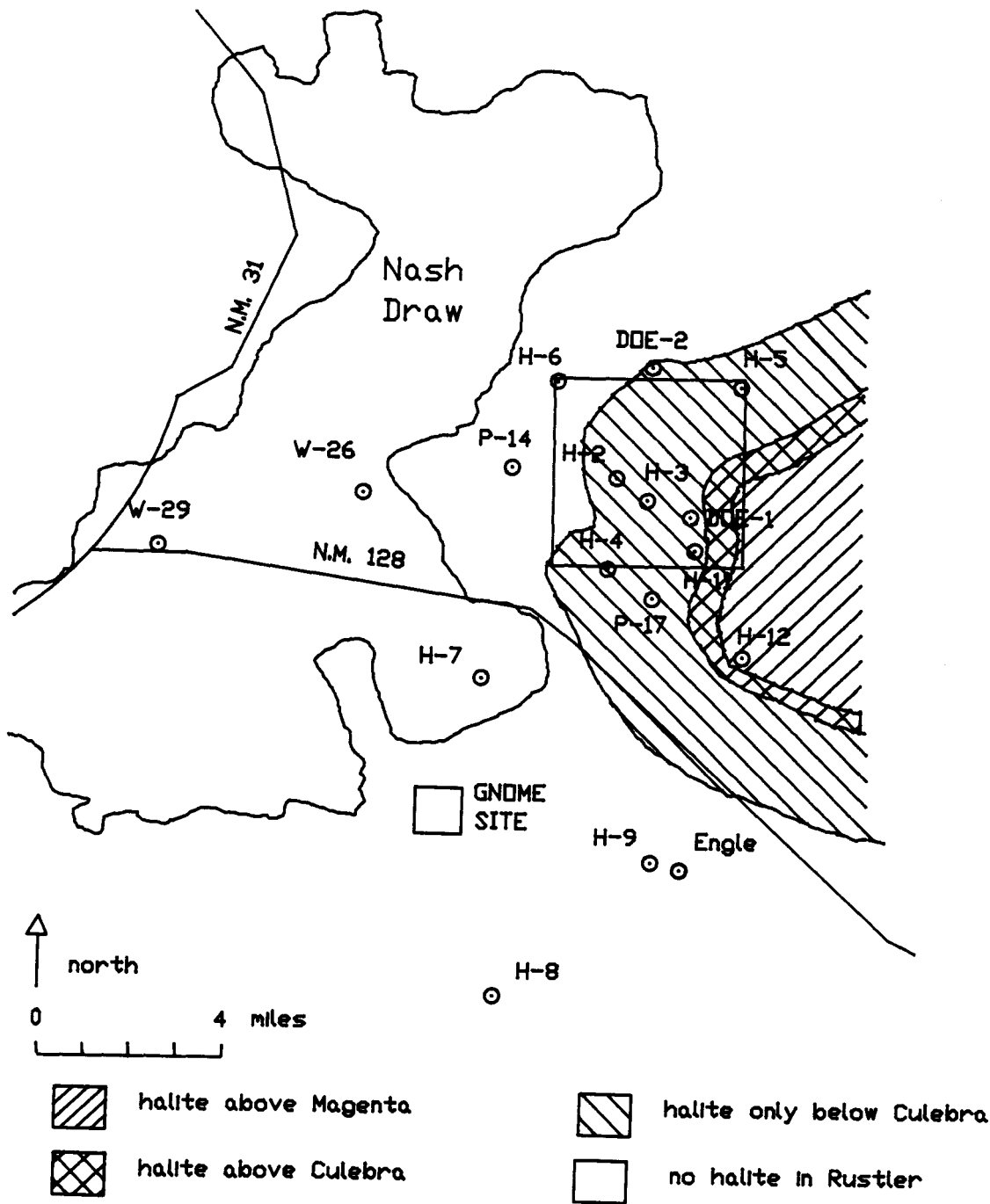


Figure 21. Pattern of absence of halite in the Rustler Formation across the WIPP site (modified from Snyder, 1985 and Chaturvedi and Channell, 1985).

The high potassium and magnesium content of groundwater from the Culebra in the eastern WIPP area does not require that the water have a very long residence time and that the aquifer have a low transmissivity, as suggested by Mercer (1983). The potassium and magnesium contents correlate well with chloride content, indicating that the high ion concentrations are all the result of evaporite mineral dissolution, which is a rapid reaction.

There is some indication from the groundwater chemistry that parts of the Culebra may contain relatively isolated flow systems. The salinity distribution, though consistent with mineralogy, requires rather specific flow paths without substantial mixing between areas of differing chloride content. The high 234/238 A.R. values observed in water from low-transmissivity wells suggests that these waters are relatively isolated from the rest of the flow system. The concept of discrete flow paths interspersed with areas of slower water movement is consistent with the fracture and possibly karst-related flow system that dominates the Culebra in the WIPP area. In turn, the incidence of fracturing is tied to dissolution of halite from the Rustler and underlying Salado. The introduction of fresher water recharge is also an important process responsible for the observed variations in chemical characteristics and, based on the water chemistry, occurs primarily in areas of extensive evaporite dissolution and development of gypsum karst.

IMPLICATIONS FOR RADIONUCLIDE TRANSPORT

Simpson et al. (1985) studied radionuclides in high chloride environments in the Delaware Basin, including several samples from the Culebra in WIPP wells. They concluded that though there may be some enhancement of uranium solubility in high chloride brines due to chloro-complexes, carbonate complexing is the dominant process influencing uranium activity. The present study supports their findings in that no strong relationship was detected between Cl content and uranium activity.

High radium contents were also noted in the Simpson et al. (1985) study. Simpson et al. (1985) concluded that radium solubility was indirectly tied to redox conditions because of redox controls on the solubility of manganese oxides, which in turn are efficient radium scavengers. The dissolution of Mn-oxyhydroxides in

oxygen deficient water allows for higher dissolved radium contents. Their samples ranged from surface water to strongly reducing oil-field brines and thus included a much wider range of redox conditions than the present investigation. Redox conditions in the Culebra do not appear to be strongly reducing, based both on field Eh values and the abundance of sulfate. The samples have field Eh values ranging from +32 to +444mv (Uhland et al. 1987; Uhland and Randall, 1986) and some relation between Eh and uranium concentration is evident. Though iron and manganese hydroxides are more soluble at Eh values between -100 and 200 mv (Hem, 1982), Ra-226 concentrations are still above 100 pCi/L in some of the samples with Eh values greater than 200 mv.

The high Ra-226 and Ra-228 contents observed in the present study, as well as reasonable correspondence of Ra-226 with the hydrochemical facies (Fig. 14), indicate that radium is relatively mobile in Culebra groundwater. Radium is not generally considered a mobile constituent in groundwater. In a 1982 study of radium and radon in groundwater of South Carolina, King et al. (1982) found that each well completed in similar zones and within a small area had distinct radium activities, suggesting that the radium source was probably located close to the borehole. This observation and the apparent greater migration of Rn-222 led to the conclusion that the transport of radium by groundwater may be "extremely limited due to continual exchange with the aquifer solids" (King et al., 1982, p. 1180). Hess et al. (1985) conclude that radium stays very close to the area where it is produced and does not accumulate with groundwater transport in aquifers.

Krishnaswami et al. (1982) studied the retardation of naturally occurring radionuclides in different hydrogeologic settings in Connecticut. They concluded that adsorption of radium and thorium from the aqueous phase onto adjoining surfaces is very rapid and that the residence time of these nuclides in water is only on the order of minutes or less. However, all of the samples examined by Krishnaswami et al. (1982) had TDS contents less than 2500 ppm. They noted that the lowest retardation factors occurred in the most saline samples, suggesting that water chemistry may be as important as aquifer lithology and hydrology in determining retardation factors.

There is no indication that the mobility of radium is limited in the Culebra near the WIPP site. Adsorption may become a more dominant process as the water moves south into the less saline area and radium content decreases dramatically.

The relatively high concentrations of both uranium and radium suggest that the Culebra in the vicinity of the WIPP site could be a favorable environment for transport of uranium and radium radionuclides. The high chloride contents coupled with relatively oxidizing conditions appear to be important to the build up of high concentrations of radium and uranium. The mobility of other nuclides in the Culebra geochemical environment needs to be investigated. The factors which contribute to radium and uranium solubility may also affect the solubility of other members of the waste inventory. The geochemical changes in the Culebra as the water moves south will affect the radionuclide transport characteristics. The processes of coprecipitation or cation exchange that may be responsible for the large decrease in radium content south of NM 128 could also affect the mobility of other elements, especially other alkaline earths like Sr-90. Likewise, the relatively large amounts of dissolved uranium indicate that it occurs in the Culebra groundwater in its more mobile, oxidized form, suggesting that the behavior of other radionuclides with oxidation-state dependent mobility (like the plutonium isotopes) should be evaluated carefully in the Culebra environment.

CONCLUSIONS AND RECOMMENDATIONS

The high salinities observed in Culebra groundwater are related to the dissolution of evaporite minerals, principally halite, along the flow path. Potassium and magnesium contents correlate well with chloride content, indicating that their source is also highly soluble evaporite minerals. There is no indication that high potassium and magnesium contents are related to long groundwater residence times and/or low transmissivities.

The distribution of salinities and hydrochemical facies in Culebra groundwater relates closely to the amount of evaporite dissolution in the formation. Groundwater in the eastern area, with TDS values greater than 100,000 mg/L and almost pure Na-Cl type brine, co-exists with the area where halite is found in the Rustler Formation. All of the halite in the Rustler in the area south of

N.M. 128 has already been removed and extensive gypsification and sulfate dissolution has occurred. Regional dissolution in the southern area is now primarily acting on sulfate minerals. This corresponds with the low salinities and Ca-Mg-SO₄ water found in the Culebra in the southern area. The western part of the WIPP Site and extending toward Nash Draw is geologically and chemically between the previous two extremes. Though all halite has been removed from the Rustler Formation in this area, dissolution of other evaporites and gypsification of anhydrite have not progressed as far as they have in the area south of N.M. 128. The water in the Culebra in this western area is still classified as a Na-Cl brine, but the salinities are lower than found in the eastern area and more calcium is found in solution.

The salinity differences and uranium isotopic data suggest that either the Culebra contains discrete, rapid flow paths interspersed with areas of slower groundwater movement and/or that young fresh water leaks into the aquifer. In areas connected by fractures, there is a very good homogenization of water-chemistry characteristics (such as between wells H-11 and DOE-1). The large decrease in water salinity south of NM 128 suggests a large input of fresher water recharge. Extreme salinity variations across the 4x4 mile site may be due to leakage of concentrated brines into the Rustler from underlying evaporite units.

Radiochemical data from Culebra groundwater indicate that both radium and uranium are relatively abundant in Culebra groundwater as compared to other groundwaters reported in the literature. Chloride content appears to be a major control on radium mobility, presumably due to competition for adsorption sites by accompanying cations. Uranium content relates to redox conditions and bicarbonate content. Differences between apparent controlling factors of radionuclide concentration in this study and previous work highlight the need for continued investigation of the processes controlling the distribution of naturally occurring radionuclides in the Culebra.

The high concentrations of radium isotopes in Culebra groundwater, as well as moderate amounts of uranium, provide important pre-operational information about Culebra water quality. The documented high concentration of radium cannot be confused with a release of radionuclides from WIPP. Additionally, the lack of

positive analytical results for other waste elements establishes their absence in the groundwater. A prior detection limits for the waste nuclides to be used for deciding if WIPP radionuclides are present in the groundwater will be given in the EEG environmental monitoring report (Kenney et al. in prep.). Observed variation in radium concentration in water from wells sampled a year apart emphasizes the importance of repeat sampling whenever possible to provide a better statistical data base.

Radionuclide analyses are proving to be of benefit for both evaluating radionuclide transport in the Culebra as well as establishing a radionuclide baseline. Future work should continue the analysis of radionuclides in WIPP area wells for as long as sampling continues (many wells are planned to be phased out of the DOE Water Quality Sampling Program after they are sampled three times, Colton and Morse, 1985). The ultimate plugging of WIPP wells as part of the plugging and sealing program heightens the value of the samples. The analytical suite may need to be expanded if naturally occurring analogs for waste nuclides can be identified. The groundwater data can then be evaluated in light of DOE's planned laboratory studies of the processes controlling sorption in the Culebra, and used as input for modeling compliance with the EPA Standards (40CFR191).

Major ion analyses should be performed for additional water samples from both the area south of N.M. 128 and the transition zone between WIPP and the southern area. The goal of this sampling will be to confirm the apparent groundwater flow from the northern zone to the south, and to quantify and locate the fresh water recharge that causes the dramatic change in salinity and chemical facies. This information is important in not only understanding the flow system in the Rustler, but also in providing information on radionuclide transport characteristics, as the southern area has a much different distribution of natural radionuclides than found to the north.

Another area requiring additional investigation is around the wells at H-5. Conflicting geochemical information leaves open the possibility for both very young and very old water in the Culebra at this well pad. The questionable detection of Cs-137 should be investigated by both repeat sampling and analysis and laboratory checks of the influence of K-40. The carbon-14 analysis should also be repeated.

The need for continued major ion analyses of WIPP wells which have already been sampled two or more times will depend on the results of a recent study by Robinson (1988). If Robinson (1988) finds good agreement between analyses performed at different times and by different labs, the need for continued analyses will be minimal. Large discrepancies between samples can and should be resolved by continued analyses. Radiochemical analyses have emphasized the importance of the water chemistry of the Culebra to radionuclide transport. Accurate knowledge of the chemical environment is thus vital to not only understanding groundwater flow paths, but also to evaluating potential radionuclide migration.

Appendix

CHEMICAL AND RADIOCHEMICAL DATA FOR CULEBRA GROUNDWATER

- Notes:
1. "*" by pH and Eh denote that these are the field values as reported in Uhland and Randall (1986) and Uhland et al. (1987).
 2. "Count Error" is the counting error representing the variability of the radioactive disintegration process at the 95% confidence level, 1.96σ .
 3. "MDL" stands for Minimum Detectable Level. Please see the report section entitled "Sample Collection and Analysis" for a discussion of the MDL calculation.

| WELL | H3B3 | Engle | DOE-2 |
|------------------------|--------|-------|--------|
| DATE | 2-85 | 3-85 | 3-85 |
| DENSITY | 1.022 | 1.015 | 1.06 |
| pH* | 7.3 | 7.4 | 7.0 |
| EH* (mv) | | | +444 |
| TDS (mg/L) | 55,300 | 3,000 | 57,800 |
| Na (mg/L) | 18,300 | 187 | 17,600 |
| K (mg/L) | 439 | 5.4 | 309 |
| Ca (mg/L) | 1,410 | 570 | 2,740 |
| Mg (mg/L) | 719 | 132 | 962 |
| Cl (mg/L) | 29,500 | 170 | 32,600 |
| SO ₄ (mg/L) | 4,900 | 1,880 | 3,470 |
| Li (mg/L) | 0.3 | | |
| F (mg/L) | | 2.9 | 2.2 |
| U (mg/L) | 0.035 | 0.020 | 0.053 |

50

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|-----|-----------------------|-----------------|-----|-----------------------|-----------------|-----|
| Gross Alpha | 150 | 670 | 814 | 19 | 33 | 39 | 850 | 820 | 962 |
| Gross Beta | 450 | 370 | 447 | 45 | 19 | 24 | 440 | 380 | 666 |
| Am-241 | | | | | | | | | |
| Pu-238 | | | | | | | | | |
| Pu-239+240 | | | | | | | | | |
| H-3 | -10 | 210 | 257 | -80 | 200 | 249 | 20 | 210 | 257 |
| Cs-137 | | | | | | | | | |
| Sr-90 | | | | | | | | | |
| Ra-226 | 130 | 10 | 10 | 5.6 | 1.0 | 1.0 | 170 | 10 | 10 |
| Ra-228 | | | | | | | | | |
| U-233+234 | | | | | | | | | |
| U-235 | | | | | | | | | |
| U-238 | | | | | | | | | |
| Th-228 | 2.0 | 2.2 | 2.4 | -0.7 | 1.5 | 1.6 | 4.0 | 2.4 | 2.4 |
| Th-230 | -0.8 | 1.4 | 1.4 | -0.1 | 0.4 | 0.4 | -0.9 | 1.3 | 1.4 |
| Th-232 | -0.1 | 0.5 | 0.6 | 0.4 | 0.8 | 0.8 | 0.1 | 0.7 | 0.8 |

| WELL | DOE-1 | H11B3 | H4B |
|------------------------|---------|---------|---------|
| DATE | 4-85 | 6-85 | 7-85 |
| DENSITY | 1.11 | 1.10 | 1.034 |
| pH* | 7.1 | 7.2 | 7.5-8.1 |
| EH* (mv) | +224 | +200 | +189 |
| TDS (mg/L) | 111,000 | 110,000 | 18,700 |
| Na (mg/L) | 40,500 | 37,800 | 5,190 |
| K (mg/L) | 703 | 680 | 185 |
| Ca (mg/L) | 1,460 | 1,580 | 690 |
| Mg (mg/L) | 1,370 | 1,360 | 409 |
| Cl (mg/L) | 61,400 | 62,000 | 6,670 |
| SO ₄ (mg/L) | 5,800 | 6,040 | 5,530 |
| Li (mg/L) | | 0.38 | 0.4 |
| F (mg/L) | 1.7 | 1.6 | 2.7 |
| U (mg/L) | 0.059 | 0.060 | 0.053 |

51

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|-----|-----------------------|-----------------|-------|-----------------------|-----------------|-------|
| Gross Alpha | -10 | 780 | --- | 490 | 570 | 641 | 220 | 160 | 857 |
| Gross Beta | 200 | 1,000 | --- | 1,200 | 900 | 1,074 | 130 | 170 | 1,190 |
| Am-241 | | | | | | | | | |
| Pu-238 | | | | | | | | | |
| Pu-239+240 | | | | | | | | | |
| H-3 | 40 | 200 | --- | -30 | 200 | 245 | 50 | 210 | 257 |
| Cs-137 | | | | | | | | | |
| Sr-90 | | | | | | | | | |
| Ra-226 | 160 | 10 | --- | 150 | 10 | 10 | 62 | 8 | 8.2 |
| Ra-228 | | | | | | | | | |
| U-233+234 | | | | | | | | | |
| U-235 | | | | | | | | | |
| U-238 | | | | | | | | | |
| Th-228 | -0.2 | 1.3 | --- | -0.2 | 0.8 | 0.8 | -1.3 | 1.3 | 1.4 |
| Th-230 | 0.1 | 0.6 | --- | -0.2 | 0.5 | 0.6 | -0.1 | 1.6 | 1.6 |
| Th-232 | 0.0 | 0.2 | --- | 0.0 | 0.1 | 0.1 | -0.1 | 0.4 | 0.4 |

| WELL | H12 | H5B | H6B |
|------------------------|---------|---------|--------|
| DATE | 8-85 | 8-85 | 9-85 |
| DENSITY | 1.120 | 1.120 | 1.060 |
| pH* | 7.3 | 7.4 | 7.0 |
| EH* (mv) | +229 | +91 | +290 |
| TDS (mg/L) | 123,000 | 144,000 | 56,900 |
| Na (mg/L) | 40,400 | 51,300 | 17,700 |
| K (mg/L) | 670 | 1,110 | 430 |
| Ca (mg/L) | 1,510 | 1,460 | 1,970 |
| Mg (mg/L) | 1,650 | 1,910 | 1,130 |
| Cl (mg/L) | 71,700 | 81,000 | 32,300 |
| SO ₄ (mg/L) | 6,520 | 6,730 | 3,390 |
| Li (mg/L) | 0.61 | <0.5 | <0.5 |
| F (mg/L) | 2.3 | 1.2 | 1.5 |
| U (mg/L) | 0.039 | 0.053 | 0.056 |

52

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|-------|-----------------------|-----------------|-------|-----------------------|-----------------|-----|
| Gross Alpha | 190 | 660 | 760 | 180 | 750 | 860 | 60 | 470 | 568 |
| Gross Beta | 1,300 | 1,100 | 1,335 | 2,000 | 1,100 | 1,311 | 370 | 370 | 447 |
| Am-241 | | | | | | | | | |
| Pu-238 | | | | | | | | | |
| Pu-239+240 | | | | | | | | | |
| H-3 | 80 | 210 | 257 | 140 | 210 | 257 | 30 | 200 | 245 |
| Cs-137 | | | | | | | | | |
| Sr-90 | | | | | | | | | |
| Ra-226 | 280 | 20 | 19.6 | 340 | 10 | 10 | 2.6 | 0.8 | 0.8 |
| Ra-228 | | | | | | | | | |
| U-233+234 | | | | | | | | | |
| U-235 | | | | | | | | | |
| U-238 | | | | | | | | | |
| Th-228 | 0.7 | 1.3 | 1.4 | 1.0 | 2.0 | 2.0 | -0.9 | 1.4 | 1.4 |
| Th-230 | -0.6 | 0.7 | 0.8 | 0.2 | 0.8 | 0.8 | 1.0 | 0.9 | 1.0 |
| Th-232 | -0.2 | 0.3 | 0.3 | 0.0 | 0.1 | 0.2 | 0.0 | 0.1 | 0.2 |

| WELL | H9B | W-26 | W-29 |
|------------------------|-------|--------|---------|
| DATE | 11-85 | 11-85 | 12-85 |
| DENSITY | 1.019 | 1.033 | 1.220 |
| pH* | 7.4 | 7.1 | 5.9 |
| EH* (mv) | +280 | +364 | +348 |
| TDS (mg/L) | 3,040 | 16,800 | 266,000 |
| Na (mg/L) | 150 | 3,820 | 75,400 |
| K (mg/L) | 7.4 | 360 | 20,800 |
| Ca (mg/L) | 560 | 1,290 | 675 |
| Mg (mg/L) | 150 | 425 | 4,750 |
| Ci (mg/L) | 195 | 8,490 | 147,000 |
| SO ₄ (mg/L) | 1,900 | 2,370 | 17,000 |
| Li (mg/L) | <0.5 | <0.5 | <0.5 |
| F (mg/L) | 2.8 | 1.5 | 4.5 |
| U (mg/L) | | | |

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|------|-----------------------|-----------------|------|-----------------------|-----------------|-----|
| Gross Alpha | | | | | | | | | |
| Gross Beta | | | | | | | | | |
| Am-241 | | | | | | | | | |
| Pu-238 | -0.02 | 0.06 | 0.06 | 0.06 | 0.10 | 0.1 | 0.20 | 0.29 | 0.3 |
| Pu-239+240 | -0.02 | 0.04 | 0.04 | 0.04 | 0.08 | 0.09 | -0.07 | 0.21 | 0.3 |
| H-3 | 110 | 190 | 233 | -20 | 190 | 233 | 130 | 200 | 243 |
| Cs-137 | | | | | | | | | |
| Sr-90 | | | | | | | | | |
| Ra-226 | 8.8 | 0.9 | 1.9 | 17 | 1 | 1.0 | 12 | 1 | 1.0 |
| Ra-228 | 1.1 | 0.6 | 0.8 | 12 | 1 | 1.1 | | | |
| U-233+234 | | | | | | | | | |
| U-235 | | | | | | | | | |
| U-238 | | | | | | | | | |
| Th-228 | | | | | | | | | |
| Th-230 | | | | | | | | | |
| Th-232 | | | | | | | | | |

| WELL | H8B | P14 | P17 |
|------------------------|---------|--------|---------|
| DATE | 1-86 | 2-86 | 3-86 |
| DENSITY | | 1.040 | 1.080 |
| pH* | 7.3-7.6 | 6.8 | 7.5-7.8 |
| EH* (mv) | +338 | +174 | +70 |
| TDS (mg/L) | 2,710 | 24,200 | 81,200 |
| Na (mg/L) | 55 | 4,200 | 26,200 |
| K (mg/L) | 4.6 | 60 | 875 |
| Ca (mg/L) | 520 | 3,640 | 1,560 |
| Mg (mg/L) | 160 | 740 | 1,450 |
| Cl (mg/L) | 30 | 13,900 | 45,200 |
| SO ₄ (mg/L) | 1,900 | 1,650 | 5,960 |
| Li (mg/L) | <0.5 | <0.5 | <0.5 |
| F (mg/L) | 2.1 | 1.5 | 1.93 |
| U (mg/L) | | | |

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|--|-----------------------|-----------------|-----|-----------------------|-----------------|-----|-----------------------|-----------------|-----|
|--|-----------------------|-----------------|-----|-----------------------|-----------------|-----|-----------------------|-----------------|-----|

| | | | | | | | | | |
|-------------|-------|------|-----|------|------|------|------|------|-----|
| Gross Alpha | | | | | | | | | |
| Gross Beta | | | | | | | | | |
| Am-241 | | | | | | | | | |
| Pu-238 | 0.01 | 0.19 | 0.2 | 0.00 | 0.10 | 0.1 | 0.30 | 0.51 | 0.5 |
| Pu-239+240 | -0.03 | 0.13 | 0.1 | 0.02 | 0.06 | 0.06 | 0.31 | 0.34 | 0.4 |
| H-3 | | | | 29 | 91 | 110 | 80 | 200 | 245 |
| Cs-137 | | | | | | | | | |
| Sr-90 | | | | | | | | | |
| Ra-226 | 0.0 | 0.3 | 0.3 | 50 | 2 | 2.0 | 98 | 3 | 2.9 |
| Ra-228 | 0.7 | 0.9 | 1.1 | 17 | 3 | 3.3 | 18 | 1 | 1.2 |
| U-233+234 | | | | | | | | | |
| U-235 | | | | | | | | | |
| U-238 | | | | | | | | | |
| Th-228 | | | | | | | | | |
| Th-230 | | | | | | | | | |
| Th-232 | | | | | | | | | |

| WELL | H7B | H2A | H3B3 |
|------------------------|------|------|--------|
| DATE | 3-86 | 4-86 | 5-86 |
| DENSITY | | | 1.055 |
| pH* | 7.25 | 8.7 | 7.4 |
| EH* (mv) | +261 | +32 | +150 |
| TDS (mg/L) | | | 51,700 |
| Na (mg/L) | | | 16,200 |
| K (mg/L) | | | 763 |
| Ca (mg/L) | | | 1,310 |
| Mg (mg/L) | | | 843 |
| Ci (mg/L) | | | 27,900 |
| SO ₄ (mg/L) | | | 4,650 |
| Li (mg/L) | | | 0.3 |
| F (mg/L) | | | 4.5 |
| U (mg/L) | | | |

55

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|-----|-----------------------|-----------------|-----|-----------------------|-----------------|-----|
| Gross Alpha | 48 | 38 | 11 | 290 | 190 | 214 | -310 | 480 | 625 |
| Gross Beta | 23 | 19 | 24 | 110 | 90 | 108 | 410 | 400 | 482 |
| Am-241 | 0.0 | 0.3 | 0.4 | -0.1 | 0.2 | 0.2 | 0.9 | 1.0 | 1.0 |
| Pu-238 | -0.4 | 0.7 | 0.8 | -0.2 | 0.7 | 0.8 | -2.2 | 3.5 | 3.5 |
| Pu-239+240 | 0.2 | 0.3 | 0.4 | 0.0 | 0.3 | 0.4 | -0.1 | 1.8 | 1.8 |
| H-3 | -120 | 230 | 280 | 10 | 220 | 269 | 30 | 220 | 269 |
| Cs-137 | 0.9 | 1.4 | 1.8 | 0.2 | 1.8 | 2.2 | 1.6 | 1.3 | 1.6 |
| Sr-90 | -0.6 | 0.6 | 0.8 | -0.5 | 1.1 | 1.4 | -1.3 | 1.5 | 1.8 |
| Ra-226 | 1.9 | 0.5 | 0.6 | 45 | 2 | 2 | 130 | 10 | 10 |
| Ra-228 | 2.0 | 2.4 | 2.7 | 6.2 | 2.6 | 3.1 | 16 | 2 | 2.4 |
| U-233+234 | 11 | 4 | 3.9 | 17 | 2 | 2 | 7.6 | 4.5 | 4.7 |
| U-235 | -0.1 | 0.3 | 0.4 | 0.2 | 0.2 | 0.2 | 0.6 | 1.3 | 1.4 |
| U-238 | 7.4 | 3.4 | 3.5 | 1.8 | 0.8 | 1.0 | 5.2 | 3.9 | 3.9 |
| Th-228 | 0.1 | 0.3 | 0.4 | 0.2 | 0.4 | 0.4 | 2.0 | 1.6 | 1.6 |
| Th-230 | -0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | -0.1 | 0.1 | 0.2 |
| Th-232 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 | 0.2 |

| WELL | H5B | H11B3 | DOE-1 |
|------------------------|---------|---------|---------|
| DATE | 5-86 | 6-86 | 7-86 |
| DENSITY | 1.123 | 1.097 | 1.113 |
| pH* | 7.6 | 7.3 | 7.1 |
| EH* (mv) | +53 | +124 | +132 |
| TDS (mg/L) | 135,000 | 111,000 | 125,000 |
| Na (mg/L) | 45,300 | 38,200 | 41,700 |
| K (mg/L) | 1,100 | 765 | 1,210 |
| Ca (mg/L) | 1,380 | 1,370 | 2,270 |
| Mg (mg/L) | 2,280 | 1,530 | 1,590 |
| Ci (mg/L) | 78,800 | 64,100 | 71,300 |
| SO ₄ (mg/L) | 6,550 | 6,260 | 6,500 |
| Li (mg/L) | 0.33 | 0.27 | 0.28 |
| F (mg/L) | 3.8 | 4.0 | 3.82 |
| U (mg/L) | | | |

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|-------|-----------------------|-----------------|-------|-----------------------|-----------------|-------|
| Gross Alpha | 300 | 1,800 | 2,174 | -300 | 1,300 | 1,621 | 700 | 1,700 | 2,021 |
| Gross Beta | 1,900 | 1,000 | 1,205 | 1,600 | 1,000 | 1,182 | 2,000 | 1,000 | 1,205 |
| Am-241 | 0.2 | 1.8 | 1.8 | 0.4 | 1.8 | 1.8 | 0.2 | 1.7 | 1.8 |
| Pu-238 | -0.4 | 7.7 | 7.6 | -6 | 11 | 11.2 | -4 | 11 | 11 |
| Pu-239+240 | -1.4 | 4.0 | 4.5 | -1.7 | 5.0 | 5.1 | -1.0 | 5.2 | 5.3 |
| H-3 | -60 | 230 | 278 | 10 | 220 | 269 | 240 | 220 | 271 |
| Cs-137 | 4.0 | 1.3 | 1.6 | 3.3 | 1.3 | 1.6 | 5.1 | 2.1 | 2.6 |
| Sr-90 | 0.0 | 0.9 | 1.2 | -0.7 | 0.9 | 1.0 | 0.0 | 1.3 | 1.6 |
| Ra-226 | 260 | 10 | 9.8 | 170 | 10 | 9.8 | 120 | 10 | 10.0 |
| Ra-228 | 25 | 2 | 2.4 | 22 | 2 | 2.2 | 22 | 3 | 3.3 |
| U-233+234 | 1.8 | 1.2 | 1.2 | 12 | 3 | 3.1 | 7.5 | 2.0 | 2.0 |
| U-235 | 0.0 | 0.1 | 0.1 | 0.0 | 0.1 | 0.2 | -0.1 | 0.1 | 0.2 |
| U-238 | 0.1 | 0.3 | 0.4 | 2.9 | 2.5 | 2.6 | 1.8 | 1.0 | 1.0 |
| Th-228 | 12 | 5 | 5.1 | 3.7 | 2.6 | 2.6 | 4.2 | 3.1 | 3.3 |
| Th-230 | -0.1 | 2.9 | 2.9 | -1.2 | 2.5 | 2.6 | 0.3 | 3.0 | 2.9 |
| Th-232 | 0.0 | 0.1 | 0.6 | 0.0 | 0.1 | 0.4 | 0.5 | 1.3 | 1.4 |

| WELL | H6B | DOE-2 | H4B |
|------------------------|--------|-------|--------|
| DATE | 7-86 | 8-86 | 11-86 |
| DENSITY | 1.056 | | 1.031 |
| pH* | 7.0 | 6.3 | 7.6 |
| EH* (mv) | +194 | +336 | +126 |
| TDS (mg/L) | 54,400 | | 20,900 |
| Na (mg/L) | 16,400 | | 5,920 |
| K (mg/L) | 597 | | 230 |
| Ca (mg/L) | 1,830 | | 665 |
| Mg (mg/L) | 1,200 | | 330 |
| Cl (mg/L) | 30,800 | | 8,150 |
| SO ₄ (mg/L) | 3,510 | | 5,600 |
| Li (mg/L) | 0.3 | | 0.41 |
| F (mg/L) | 4.15 | | 4.5 |
| U (mg/L) | | | |

| | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL | Activity ± (pCi/L) | Count. Error | MDL |
|-------------|-----------------------|-----------------|-----|-----------------------|-----------------|-----|-----------------------|-----------------|-----|
| Gross Alpha | 540 | 490 | 553 | 480 | 480 | 545 | 90 | 250 | 300 |
| Gross Beta | 10 | 510 | 623 | 10 | 510 | 623 | 230 | 150 | 178 |
| Am-241 | 1.0 | 2.1 | 2.2 | 0.0 | 0.4 | 0.4 | 0.2 | 1.2 | 1.2 |
| Pu-238 | 1.3 | 1.6 | 2.0 | -1.8 | 2.6 | 2.6 | 0.8 | 1.2 | 1.2 |
| Pu-239+240 | 2.7 | 3.1 | 3.1 | -0.3 | 1.3 | 1.4 | 0.2 | 0.6 | 0.6 |
| H-3 | -100 | 220 | 272 | -90 | 220 | 272 | -30 | 210 | 259 |
| Cs-137 | 0.1 | 2.8 | 3.5 | 1.4 | 2.7 | 3.3 | 1.1 | 2.8 | 3.5 |
| Sr-90 | 0.7 | 1.7 | 2.2 | -0.1 | 1.7 | 2.2 | 0.4 | 2.0 | 2.4 |
| Ra-226 | 2.8 | 0.4 | 0.4 | 180 | 10 | 10 | 30 | 1 | 1.0 |
| Ra-228 | -0.2 | 1.8 | 2.2 | 18 | 2 | 2.2 | 5.8 | 1.9 | 2.6 |
| U-233+234 | 7.1 | 1.7 | 1.8 | 19 | 2 | 2.0 | 14 | 3 | 3.1 |
| U-235 | 0.0 | 0.4 | 0.4 | 0.0 | 0.1 | 0.1 | -0.3 | 0.6 | 0.6 |
| U-238 | 1.3 | 1.2 | 1.2 | 5.2 | 1.2 | 1.2 | 1.0 | 2.2 | 2.2 |
| Th-228 | 0.4 | 1.6 | 1.8 | 1.6 | 1.8 | 2.0 | 0.7 | 0.9 | 1.0 |
| Th-230 | -0.5 | 1.8 | 1.8 | 0.8 | 1.0 | 1.0 | 0.0 | 0.4 | 0.4 |
| Th-232 | -0.2 | 0.8 | 0.8 | 0.1 | 0.7 | 0.8 | 0.0 | 0.1 | 0.1 |

| | |
|------------------------|--------|
| WELL | P17 |
| DATE | 12-86 |
| DENSITY | 1.080 |
| pH* | 7.5 |
| EH* (mv) | +75 |
| TDS (mg/L) | 88,800 |
| Na (mg/L) | 29,000 |
| K (mg/L) | 1,000 |
| Ca (mg/L) | 1,630 |
| Mg (mg/L) | 1,570 |
| Cl (mg/L) | 49,600 |
| SO ₄ (mg/L) | 6,040 |
| Li (mg/L) | 0.44 |
| F (mg/L) | 3.93 |
| U (mg/L) | |

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