U. S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

# Environmental geochemistry and processes controlling water chemistry, Cornudas Mountains, New Mexico

by

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Front cover: Cornudas Mountain, northern Chihuahuan desert. Soap tree yucca (*Yucca elata*) in foreground.

San Antonio Mountain along New Mexico - Texas boundary

Wind Mountain Tertiary alkaline intrusive complex

# INTRODUCTION

In the Spring of 1996, field work was carried out in support of a mineral resoruce and environmental assessment of the Caballo Resource Area in south central New Mexico in Otero and Sierra Counties, on lands administrated by the U. S. Bureau of Land Management, Las Cruces, New Mexico. This report covers the Cornudas Mountains area of critical environmental concern (ACEC). The purpose of this study is to access any environmental geochemical problems that may exist in this ACEC and to determine the major processes controlling the mobility and attenuation of elements in surface and ground water within the study area.

The climate of the area is semi-arid. No perennial surface water is present, therefore ground water quality is an important issue. Ground water is pumped from wells and used mostly to water livestock. Because of the importance of ground water quality, the determination of the ground water chemistry and the processes responsible for the controls on the mobility and attenuation of elements in the ground water is the focus of this study. In addition, potential environmental geochemical impacts that may result in future development, particularly mining, is discussed.

## Study Area

The study area is part of the BLM Resource Area and is located north of the New Mexico-Texas border in southern Otero County, approximately 60 miles east of El Paso, Texas (fig. 1). The study area lies within the Mexican Highland section of the Basin and Range physiographic province (Fenneman, 1931). The area is characterized by Tertiary-age alkaline igneous intrusive complexes that intrude Permian-age sediments. The igneous rocks form distinct topographic features on the low relief plateau with peaks raising from approximately 4900 feet to 7280 feet at the top of Wind Mountain (fig. 2).

The study area lies within the northern Chihuahuan desert. The climate is semi-arid with hot dry summers and mild winters. Average annual precipitation (fig. 2) varies from 12-14 inches (30-35 cm), with most precipitation occurring during thunderstorms in July and August (Mayer, 1995). Vegetation is mostly mixed desert scrub and desert grassland.

No perennial surface waters are present in the study area. A dendritic pattern of ephemeral streams is present and after storms these streams may flow for short periods of time. The study area and the surrounding area is internally drained with no outlet. Regional ground water flow, based on potentiometric surface elevations (fig. 3), is south and east toward the Salt Basin (Mayer, 1995).

## Geology

The study area lies along the northeastern portion of the Diablo Plateau, an up-faulted block surrounded by the Sacramento Mountains to the north and grabens on the east, west, and south. The bedrocks that make up the low-relief plain consist of Permian age limestones, dolomitic limestones, shales, and sandstones. Gypsum is present as seams, particularly in the Yeso Formation which contains as much as 19% gypsum (Pray, 1961). Tertiary age hypabyssal

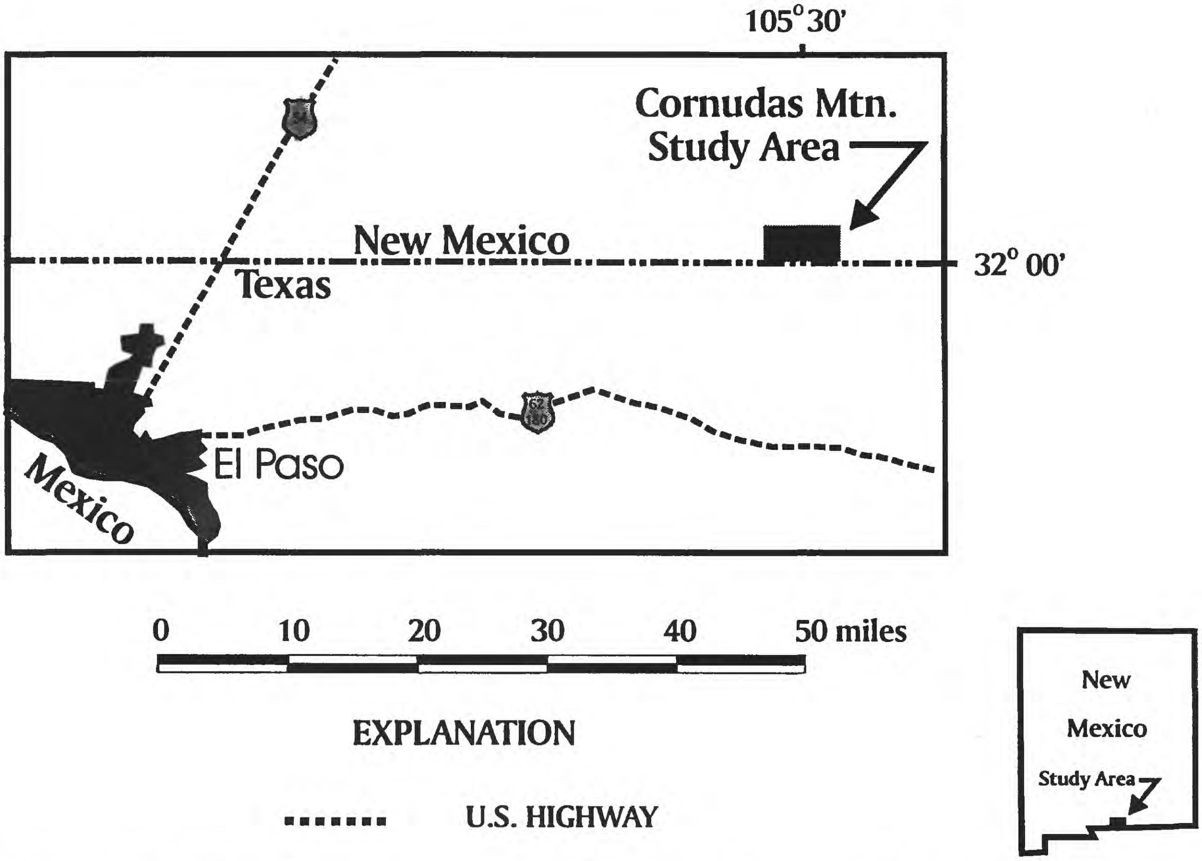

Figure 1.--Location map of the Cornudas Mountains study area, south-central New Mexico

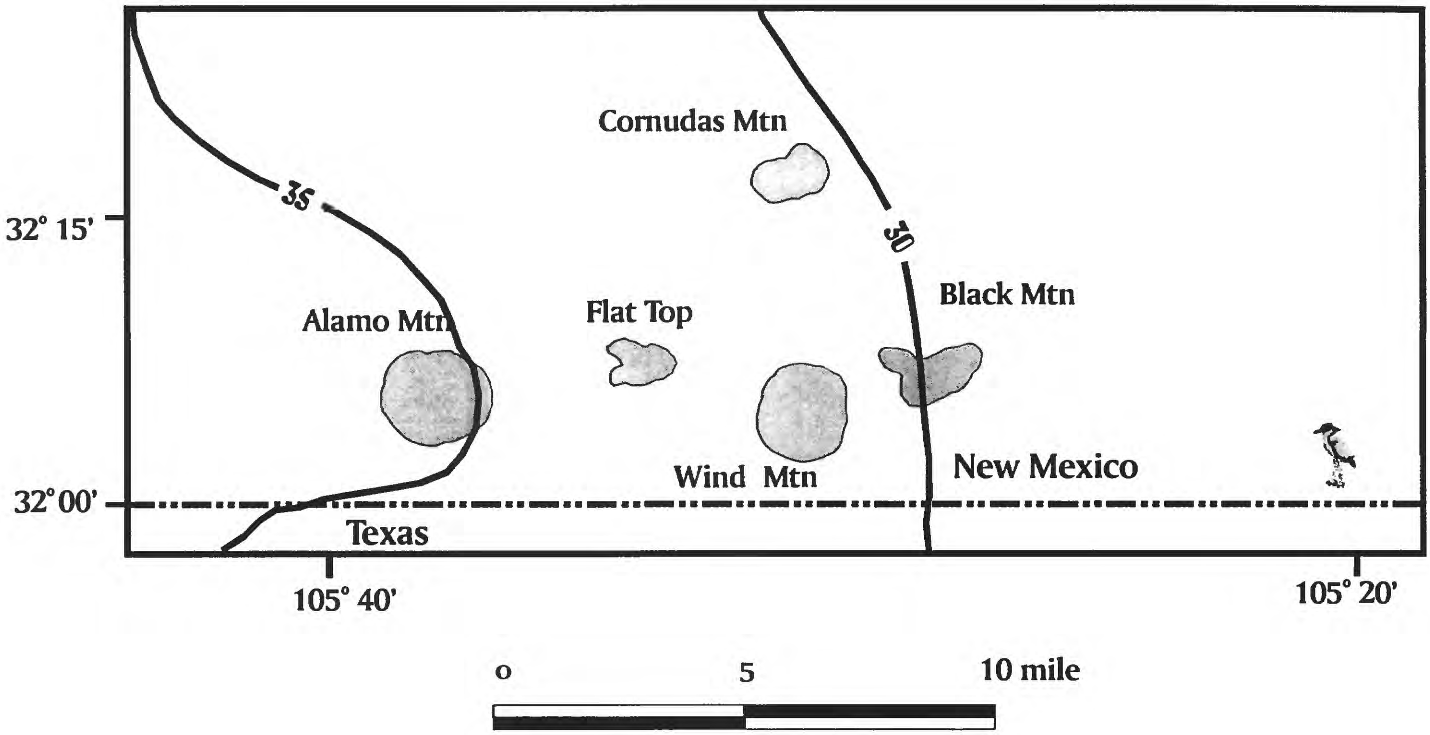

Figure 2.--Map showing annual precipitation in centimenters (after Mayer, 1995) for the Cornudas Mountains study area, south-central New Mexico

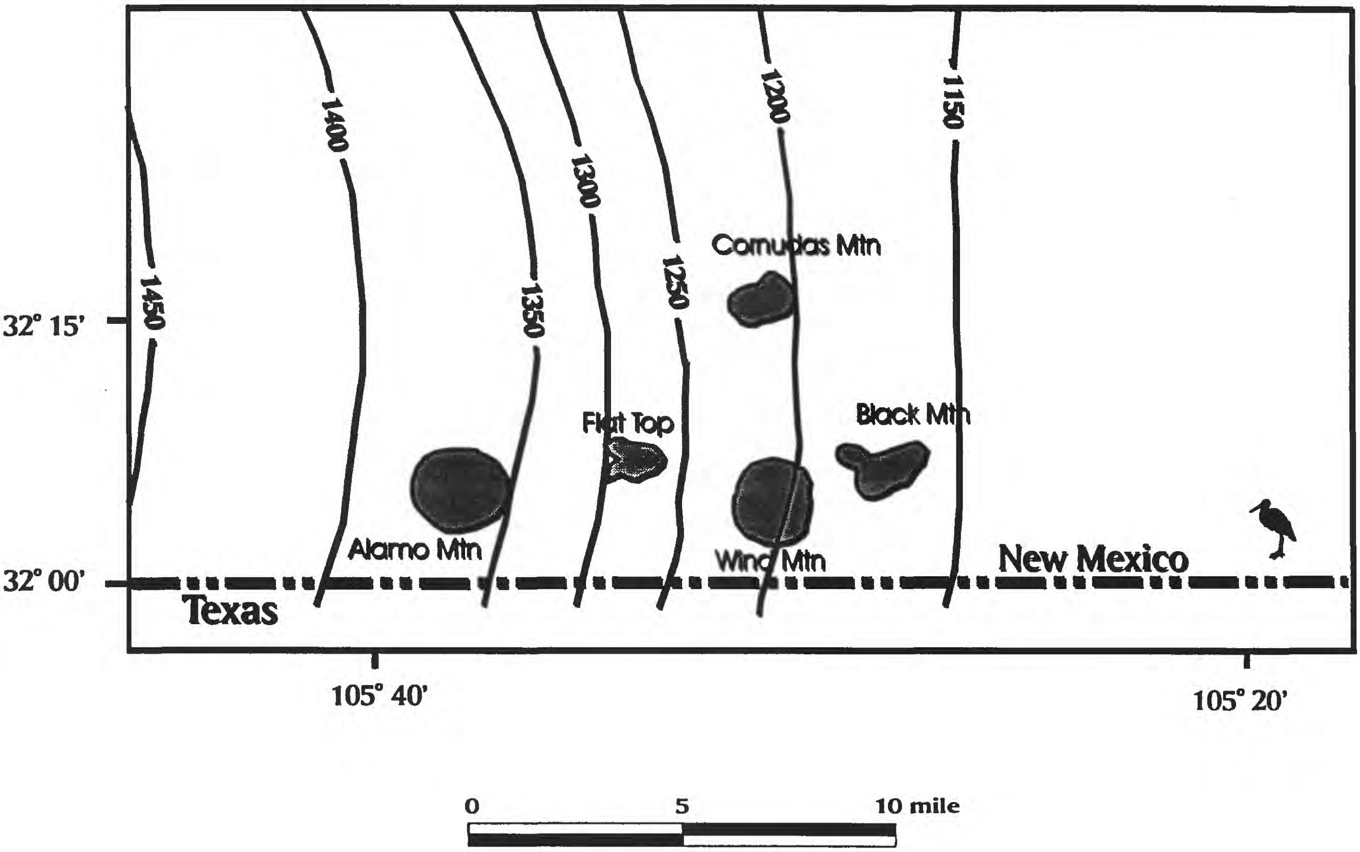

Figure 3.-- Potentiomentic surface elevations in meters above sea-level in the Cornudas Mountains study area, south-central, New Mexico (after Mayer, 1995)

alkalic igneous rocks intrude and dome the flat-lying Permian sediments. The igneous rocks consist of trachyte, nepheline bearing-augite syenite, nepheline syenite and phonolite (Schreiner,1994). A thin veneer of unconsolidated Quaternary deposits of clay, silt, sand, and gypsum partially cover portions of the Permian sediments. Much of this material is eolian in origin.

Previous geologic and mineral resource studies of this ACEC include Schreiner (1994), McLemore and Guilinger (1993), Barker and others (1977), Clabaugh (1941), and Zapp (1941). An investigation of the geology and mineral resources of the Caballo Resource Area is currently being undertaken by the USGS and the New Mexico Bureau of Mines and Mineral Resources.

## Mining History

The Cornudas Mountains ACEC has been prospected for a variety of metals, but to date, no production has occurred Schreiner (1994) and McLemore and Guilinger (1993). Deposits of gold and silver are associated with alkaline igneous rocks in New Mexico (McLemore and others, 1988 and North and McLemore, 1988), but have not been found in economic concentrations in the study area. Radioactive dikes associated with igneous complexes were prospected for uranium and thorium (Collins, 1958). Exploration for beryllium, rare earth elements, niobium, gold and silver also occurred in the past. Rare earth elements, niobium, titanium, zirconium, and fluorine were introduced by hydrothermal activity related to emplacement of the alkaline rocks, but not in economic concentrations McLemore and Guilinger (1993) and Warner (1956). In 1992, the U.S. Bureau of Mines conducted a mineral investigation of Wind Mountain and the Chess Draw area within the study area. Only minor concentrations of rare earth elements and niobium were identified, but no economic resources were determined. Schreiner, 1994, determined that nepheline syenite was suitable raw material for high-iron product uses such as amberglass and dark body ceramics. Presently, the mining of nepheline syenite for use in the glass and ceramics industries is under consideration.

Because no mining, milling, or smelting has taken place within the study area, no solid materials associated with mining are present within the study area. Therefore no samples of solid material were collected as part of the environmental geochemical investigation.

## Methods

Samples of waters were collected from 10 wells within the study area during April 25-26, 1996 (fig. 4). Generally, wells were pumping prior to arrival at the site. If the wells were not pumping, they were allowed to pump for 15 minutes before collecting the sample. Temperature, pH, and conductivity were measured at the site. Samples were collected into high-density polyethylene acid-washed bottles. For the dissolved cation analyses, a 60-ml sample was filtered through a 0.45 µm-membrane filter and acidified with reagent-grade concentrated nitric acid to pH<2. A second 60-ml sample was collected and acidified without filtering to determine total cations in solution. A 125-ml sample was filtered but not acidified for anion analyses. The samples were stored in an ice chest and kept cool until analyzed.

Upon returning to the laboratory, alkalinity as $HCO_3^-$, was determined by titration with

$H_2SO_4$ using a Grans plot technique (Orion Research, Inc.,1978). Ca, Mg, Na, K, and $SiO_2$ were determined by flame atomic absorption spectrophotometry (Perkin-Elmer Corp.,1976 ). Sulfate, chloride, nitrite + nitrate, and fluorine were determined by Water Resource Division (W. D'Angleo-analyst) using ion chromatography (Fishman and Pyen, 1979). The remaining elements were analyzed by ICP-MS by ACTLABS, Wheatridge, Colorado.

## RESULTS

The chemical analyses for the 10 well water samples (fig. 4) are shown in Table 1 . The ground waters are high in dissolved solids. Conductivity ranges from 866 to 3600 uS/cm. The pH values range from 6.6 to 8.28. The well waters are fresh to slightly saline and classified according to the dominant cation and anion. Eight of the ten wells are $Ca^{2+}$- $SO_4^{2+}$ dominant waters, U47 is a $Na^{+}$- $SO_4^{2+}$ dominant water and U43 is a $Ca^{2+}$, $Mg^{2+}$- $HCO_3^{-}$ dominant water. Well site U43 contains the most potable water. The U.S. Public Health Service (1962) recommends that a drinking water supply should contain less than 250 ppm sulfate or chloride, where better water is not available. Using this classification, the well waters are of poor quality for domestic use, but better water is not available. The most objectionable element in the well waters is sulfate followed by chloride. The waters are used mostly for watering livestock. Well site U43, has the freshest water, but contains the highest $NO_2$ - $NO_3$ concentration of 7.6 ppm.

The concentrations of the heavy metals in the well waters vary considerably. The highest concentrations of iron occurs at sites U38, U39, and U41 with values of 6200, 6580, and 4130 ppb respectively. The source of some of the Fe are the pump, pipes and rods, but the dissolution of Fe-bearing minerals in the subsurface must also be taking place. Much lower in concentrations and less variable are Mn and Al. Of the base metals, only Zn, Cu, and Mo occur in anomalous concentrations above normal background abundances, with values of Zn up to 450 ppb, Cu up to 20 ppb, and Mo up to 90 ppb (Table 1 ). When water is pumped from the wells, the water comes into contact with metal pumps, pipes, and rods, which is probably the source for the anomalous values of Zn, Cu, and Mo in the well water. Other trace elements are generally at background-type concentrations of less than 1 ppb.

At each well site, a filtered and unfiltered sample were collected in order to determine both the dissolved and the total concentrations of elements in the water. Any additional amounts of elements in the total fractions (unfiltered sample) is probably due to colloidal material in this fraction. The results are shown in Table 2. The concentrations of Li and Mo differed only minimally while the remaining elements differed from minimally to significantly between dissolved and total metals in the water. Therefore depending on the element, significant concentrations of metals are present in the water other than in dissolved form, but no discernable pattern was recognized.

In addition to this study, wells within the study area were sampled for chemical analyses at two other time periods. Eleven wells within the study area (fig. 5) were sampled in 1976 during the U.S. Department of Energy's National Uranium Resource Evaluation (NURE) program. Geochemical data for well waters collected during the NURE program were obtained from Hoffman and Buttleman (1994) and are shown in Table 3. In addition, in 1992, Mayer (1995) sampled 15 wells within the study area (fig. 6 and Table 4).

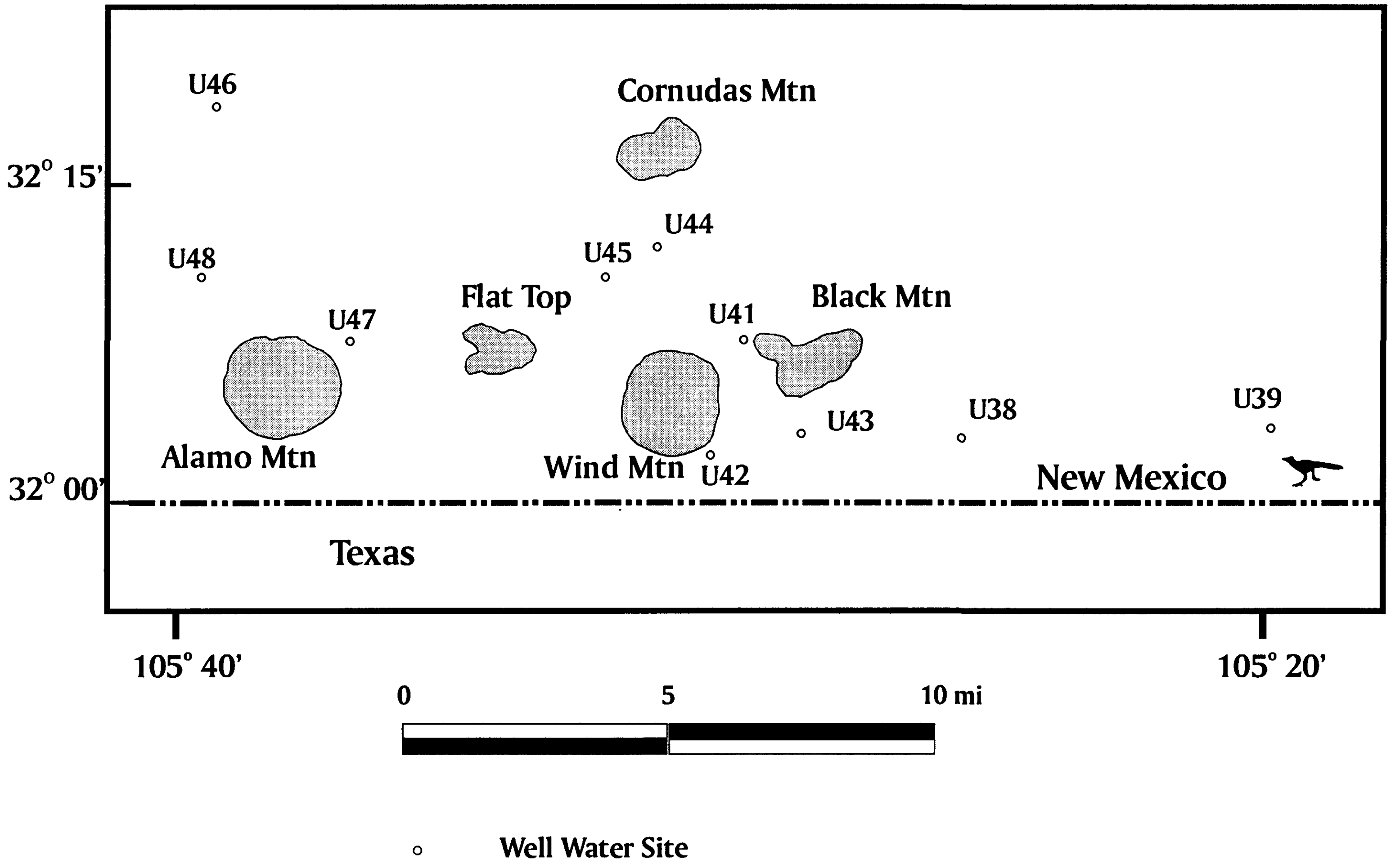

Figure 4.-- Map showing locations of wells sampled in the Cornudas Mountains study area, south-central New Mexico

Table 1. Chemical analyses of well waters collected in the Cornudas Mountains, New Mexico

| Site No. | Comments | pH | Conductivity uS/cm | Temperature Centigrade | Ca ppm | Mg ppm | Na ppm | K ppm |
|---|---|---|---|---|---|---|---|---|
| U38 | well | 7.21 | 2360 | 20.3 | 370 | 123 | 78 | 4.1 |
| U39 | Martin Lewis well | 7.25 | 2390 | 20.8 | 420 | 131 | 40 | 2.8 |
| U41 | well | 6.79 | 2710 | 22 | 530 | 122 | 74 | 4.9 |
| U42 | well | 6.95 | 1287 | 21.5 | 150 | 56 | 70 | 3.1 |
| U43 | well | 7.03 | 866 | 24.3 | 74 | 69 | 18 | 0.4 |
| U44 | well | 6.6 | 2290 | 23.4 | 310 | 111 | 120 | 4.7 |
| U45 | Chess well | 6.54 | 1785 | 20.1 | 250 | 88 | 64 | 3.5 |
| U46 | Pate well | 7.15 | 1241 | 17.4 | 145 | 54 | 62 | 3.4 |
| U47 | Alamo well | 8.01 | 3600 | 19 | 280 | 116 | 500 | 10 |
| U48 | Partnership well | 8.28 | 2740 | 21 | 130 | 88 | 430 | 9.1 |

Table 1 (cont.)

| SiO2 ppm | Alkalinity ppm | Sulfate ppm | Cl ppm | F ppm | NO2+NO3 ppm | Cu ppb | Zn ppb | Li ppb | Al ppb | Cr ppb | Mn ppb |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 305 | 1400 | 50 | 1.9 | <0.02 | 0.2 | 220 | 57 | 17 | 3 | 230 |
| 13 | 244 | 1500 | 32 | 1.4 | <0.02 | 3 | 450 | 43 | 22 | 1 | 360 |
| 23 | 268 | 1700 | 46 | 2.2 | <0.02 | 0.1 | 210 | 63 | 5 | 2 | 46 |
| 41 | 183 | 500 | 34 | 2.2 | 1.9 | 3 | 190 | 30 | 2 | 3 | 14 |
| 40 | 427 | 18 | 12 | 0.8 | 7.6 | 20 | 390 | 8 | 4 | 2 | 48 |
| 21 | 378 | 1000 | 110 | 2.3 | 2.6 | 4 | 29 | 58 | 11 | 5 | 7 |
| 24 | 380 | 780 | 48 | 2.2 | 2.1 | 5 | 120 | 50 | 16 | 2 | 8 |
| 24 | 285 | 470 | 36 | 2.3 | nd | 4 | 310 | 46 | 7 | 1 | 21 |
| 17 | 293 | 1900 | 170 | 3.3 | nd | 2 | 88 | 131 | 11 | 4 | 9 |
| 16 | 345 | 1100 | 170 | 4.6 | nd | 2 | 30 | 69 | 19 | 3 | 16 |

Table 1 (cont.)

| Fe<br>ppb | Co<br>ppb | Ni<br>ppb | As<br>ppb | Se<br>ppb | Br<br>ppb | Mo<br>ppb | U<br>ppb | Pb<br>ppb |
|---|---|---|---|---|---|---|---|---|
| 6200 | 1.6 | 14 | 0.3 | 1.5 | 410 | 20 | 9 | 0.5 |
| 6580 | 1.2 | 7 | <.2 | 1.9 | 210 | 8 | 4 | 0.6 |
| 4130 | 1.2 | 3 | 1.3 | 1 | 350 | 36 | <.02 | 0.6 |
| 179 | 0.3 | 2 | 1.6 | 11 | 300 | 28 | 16 | 0.6 |
| 133 | 0.7 | 9 | 0.4 | 2.4 | 150 | 5 | 14 | 0.6 |
| 87 | 0.5 | 5 | 0.5 | 14 | 920 | 26 | 19 | 0.5 |
| 178 | 0.5 | 4 | <.2 | 15 | 410 | 21 | 15 | 0.6 |
| 103 | 0.8 | 5 | 0.4 | 21 | 400 | 21 | <.02 | 0.5 |
| 90 | 0.5 | <.02 | 0.6 | 5.7 | 1540 | 32 | 12 | 0.6 |
| 46 | 0.3 | <.02 | 0.3 | 3 | 1580 | 90 | 8 | 0.6 |

Table 2. Comparisons of filtered and unfiltered well waters,
Cornudas Mountains, New Mexico

| SITE | TYPE | FE PPB | AL PPB | MN PPB | LI PPB | CU PPB | ZN PPB | MO PPB |
|---|---|---|---|---|---|---|---|---|
| U38 | Filtered | 6200 | 17 | 234 | 57 | 0.2 | 220 | 20 |
| | Unfiltered | 8650 | 14 | 245 | 56 | 21 | 406 | 19 |
| U39 | Filtered | 6580 | 22 | 358 | 43 | 3 | 450 | 8 |
| | Unfiltered | 10500 | 10 | 372 | 40 | 91 | 713 | 7 |
| U41 | Filtered | 4130 | 5 | 46 | 63 | 0.1 | 210 | 36 |
| | Unfiltered | 2540 | 7 | 47 | 61 | 1.3 | 261 | 33 |
| U42 | Filtered | 179 | 2 | 14 | 30 | 3 | 190 | 28 |
| | Unfiltered | 980 | 155 | 17 | 27 | 27 | 225 | 24 |
| U43 | Filtered | 133 | 4 | 48 | 8 | 20 | 390 | 5 |
| | Unfiltered | 7230 | 108 | 80 | 8 | 399 | 753 | 1.6 |
| U44 | Filtered | 87 | 11 | 7 | 58 | 4 | 29 | 26 |
| | Unfiltered | 607 | 15 | 7 | 54 | 5 | 27 | 23 |
| U45 | Filtered | 178 | 16 | 8 | 50 | 5 | 120 | 21 |
| | Unfiltered | 392 | 9 | 8 | 49 | 15 | 118 | 20 |
| U46 | Filtered | 103 | 7 | 21 | 46 | 4 | 310 | 21 |
| | Unfiltered | 43 | 5 | 19 | 44 | 4.3 | 282 | 17 |
| U47 | Filtered | 90 | 11 | 9 | 131 | 2 | 88 | 32 |
| | Unfiltered | 39 | 6 | 0.3 | 132 | 1.9 | 77 | 28 |
| U48 | Filtered | 46 | 19 | 16 | 69 | 2 | 30 | 90 |
| | Unfiltered | 29 | 8 | 0.5 | 68 | 3.8 | 7.3 | 77 |

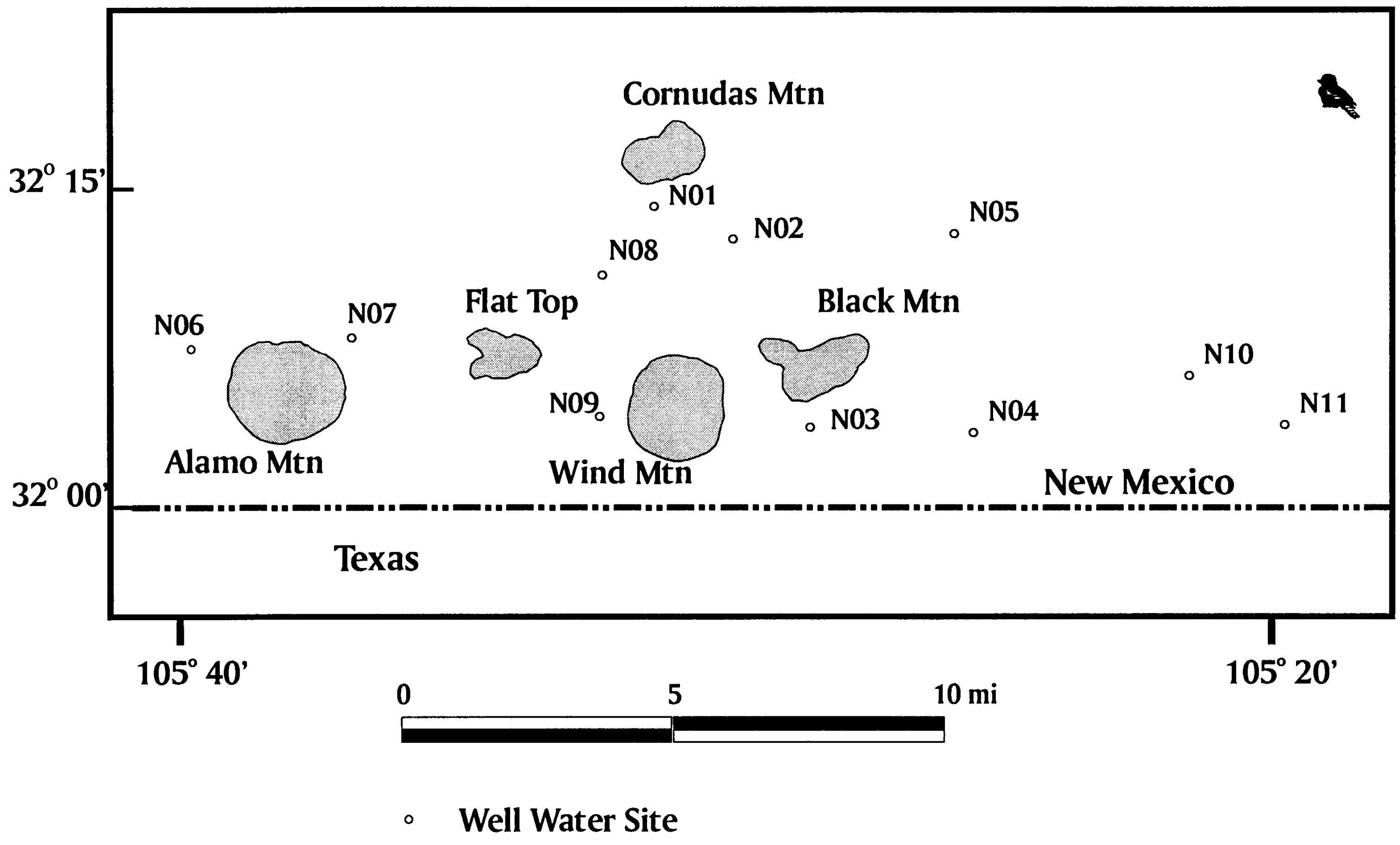

Figure 5.-- Map showing locations of wells sampled during the NURE program in the Cornudas Mountains study area, south-central New Mexico

Table 3. Chemical analyses of well waters collected during the NURE program in mid 1970's, from Hoffman and Buttleman (1993)

| SITE | TEMP deg C | PH | COND µS/cm | AL PPB | B PPB | BA PPB | CA PPM | CR PPB | CU PPB | FE PPB | K PPM | LI PPB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N01 | 26 | 6.90 | 1600 | 101 | 635 | 7 | 309 | <4 | 15 | 43 | 5.9 | 115 |
| N02 | 25 | 7.10 | 155 | 282 | 23 | 62 | 37 | 12 | 5 | 332 | 4.8 | 4 |
| N03 | 21 | 6.90 | 780 | 95 | 154 | 98 | 73 | <4 | 5 | 84 | 0.3 | 9 |
| N04 | 20 | 6.90 | 1650 | 112 | 516 | 13 | 415 | <4 | 10 | 624 | 4.6 | 139 |
| N05 | 26 | 7.10 | 1825 | 67 | 510 | 23 | 650 | <4 | 5 | 77 | 7.1 | 116 |
| N06 | 25 | 6.30 | 2100 | 38 | 1405 | 11 | 121 | <4 | 9 | 34 | 6.3 | 82 |
| N07 | 26 | 8.00 | 1750 | 338 | 1732 | 16 | 84 | 18 | 10 | 162 | 9.4 | 178 |
| N08 | 24 | 6.50 | 1300 | 16 | 439 | 14 | 247 | <4 | 3 | 48 | 3.1 | 76 |
| N09 | 19 | 7.10 | 550 | 19 | 124 | 42 | 62 | <4 | 12 | 23 | 4.7 | 10 |
| N10 | 25 | 7.60 | 1300 | 150 | 749 | 28 | 913 | <4 | 15 | 110 | 7.5 | 136 |
| N11 | 20 | 7.40 | 2200 | 24 | 306 | 12 | 428 | <4 | 5 | 296 | 2.7 | 57 |

Table 3 (cont.)

| MG PPM | MN PPB | MO PPB | NA PPB | NB PPB | NI PPB | P PPB | SR PPM | ZN PPB |
|---|---|---|---|---|---|---|---|---|
| 131 | 6 | 16 | 101 | 14 | <4 | <40 | 10.6 | 108 |
| 2 | 131 | 15 | 2 | <4 | <4 | 146 | 0.1 | 31 |
| 66 | 18 | 4 | 25 | <4 | <4 | <40 | 1.2 | 229 |
| 138 | 54 | 25 | 87 | 10 | 23 | <40 | 12.0 | 11018 |
| 165 | 21 | 12 | 56 | <4 | <4 | <40 | 16.7 | 892 |
| 61 | 9 | 95 | 467 | <4 | 21 | <40 | 4.9 | 68 |
| 92 | 9 | 16 | 320 | 13 | 39 | <40 | 6.6 | 82 |
| 85 | 19 | 24 | 62 | <4 | <4 | <40 | 7.3 | 239 |
| 33 | 27 | 169 | 37 | 14 | <4 | <40 | 4.4 | 1229 |
| 279 | 25 | 9 | 96 | 35 | 6 | 56 | 23.6 | 239 |
| 124 | 21 | 15 | 44 | 19 | 14 | <40 | 10.1 | 164 |

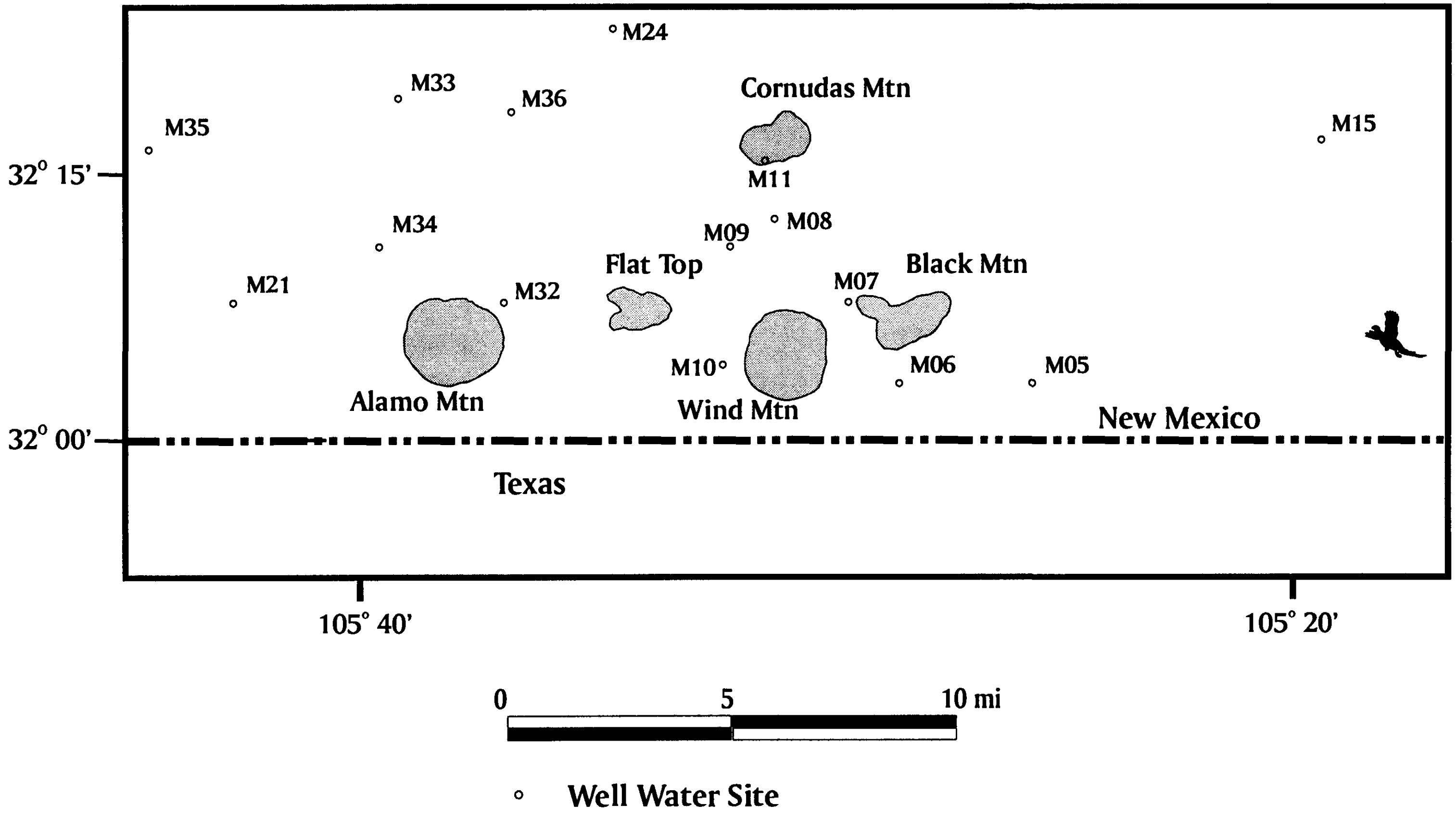

Figure 6.– Map showing locations of wells sampled by Mayer (1995) in the Cornudas Mountains study area, south-central New Mexico

Table 4. Chemical analyses of well waters from from the Cornudas Mountains area from Mayer (1995)

| SITE | TEMP deg C | pH | COND uS/cm | HCO3 ppm | Na ppm | K ppm | Mg ppm | Ca ppm | Cl ppm | NO3 ppm | SO4 ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|
| M05 | 20 | 7.1 | 2500 | 229 | 84 | 8.3 | 123 | 334 | 45 | 7.2 | 1120 |
| M06 | 18.6 | 7.15 | 700 | 564 | 15 | — | 70 | 71 | 11 | 29 | 15 |
| M07 | 19.8 | 6.98 | 2950 | 243 | 80 | 8.7 | 129 | 466 | 37 | 0.1 | 1490 |
| M08 | 19.3 | 6.95 | 2300 | 337 | 141 | 8 | 115 | 273 | 118 | 10 | 933 |
| M09 | 18.6 | 7.1 | 1600 | 359 | 58 | 8.1 | 84 | 220 | 40 | 9.8 | 655 |
| M10 | 20 | 7.66 | 700 | 293 | 35 | 9 | 32 | 58 | 18 | 4.4 | 81 |
| M11 | — | 7.4 | 200 | 52 | 5.5 | 1.3 | 3 | 27 | 1.8 | 17 | 19 |
| M15 | 23.9 | 6.98 | 2500 | 166 | 56 | 5.9 | 126 | 346 | 11 | 0.1 | 1410 |
| M21 | 20.7 | 6.91 | 3500 | 400 | 233 | 11 | 130 | 342 | 86 | 1.6 | 1360 |
| M24 | 15.2 | 7.37 | 1200 | 361 | 50 | 6.3 | 74 | 70 | 56 | 30 | 173 |
| M32 | 19.7 | 7.1 | 3450 | 340 | 421 | 9.6 | 92 | 257 | 118 | 0.1 | 1320 |
| M33 | 16.5 | 6.81 | 3000 | 289 | 61 | 8 | 52 | 136 | 28 | 24 | 396 |
| M34 | 18.6 | 7.26 | 3000 | 420 | 361 | 8.9 | 65 | 114 | 191 | 0.1 | 798 |
| M35 | 17.5 | 6.81 | 3300 | 467 | 84 | 12 | 139 | 441 | 47 | 5.7 | 1470 |
| M36 | 18.6 | 6.9 | 4350 | 426 | 375 | 34 | 167 | 340 | 238 | 0.7 | 1730 |

This present study and these other two studies represent three different ground water geochemistry baselines that can be compared to determine changes in the chemistry with time. Chemical analyses of ground waters from the two previous studies are shown in Tables 4 and 5 and a comparison of ground water chemistry of specific well sites collected during the three different time periods can be made (Table 5). The most significant trend between 1974 and 1996 is that conductivity increased (Table 6). The Alamo well had the greatest increase in conductivity (106%). For this site, the major elements, calcium and sodium had significant increases during this time period (233% and 56%). The remaining elements and pH did not vary significantly during this time period. At the other sites, none of the species or pH varied significantly during this time period.

High concentrations of nitrate (Table 4) was found by Mayer (1995). The comparisons of nitrate from Mayer (1995) and total $NO_2 + NO_3$ concentrations in well waters collected in this study are shown in Table 7. There is significant difference in the two sets of data that is difficult to explain. If Mayer (1995) values are correct, then the high values may be due to leaching of cattle waste. Cattle will congregate around wells. Leaching of nitrate from cattle waste during runoff after storms and leaking of nitrate into the ground water in the vicinity of the well may account for the high values. Addition investigation would be needed to document this.

## CHEMICAL MODELING OF THE WELL WATERS

To gain understanding of processes such as speciation of elements, redox conditions, and identification of minerals that may control the mobility, attenuation, and concentrations of elements in the waters, chemical modeling of the well waters was carried out using PHREEQC (Parkhurst, 1995). The modeling program assumes mineral-solution equilibrium. For some chemical reactions with slow kinetics, this may not be the case. The dominant cations in the well waters are simple cations of $Ca^{2+}$, $Na^+$, $Mg^{2+}$ and $K^+$ or sulfate complexes $CaSO_4^0$ and $MgSO_4^0$. The dominate anions are $SO_4^{2-}$, $HCO_3^-$, $Cl^-$, and $F^-$. Other dominant species include $Fe^{2+}$, $FeSO_4^0$, $Mn^{2+}$, $MnSO_4^0$, $Zn^{2+}$, $ZnSO_4^0$, $Cu^+$, and $Cu^{2+}$.

Saturation indexes were calculated for a suite of minerals to determine if concentrations of trace metals in water were controlled by mineral phases. The saturation index is a convenient means of expressing saturation states of minerals (Barnes and Clark, 1969 where:

$$SI=\log_{10} IAP/K_T.$$

In the expression, SI is the saturation index, IAP is the ion activity product, and $K_T$ is the equilibrium constant of the dissolution reaction at the temperature in question. We considered mineral phases supersaturated at $SI>0.35$, saturated at $SI= -0.35$ to $0.35$, and under saturated at $SI<0.35$.

The results (Table 8) indicate that for many of the well waters, gypsum, calcite, dolomite, and chalcedony are saturated or supersaturated with respect to the well waters, indicating that these phases play a major role in controlling the concentrations in the well waters. All the waters are saturated or super saturated with respect to calcite and chalcedony, four of the well waters are saturated with respect to gypsum, seven of the well waters are saturated or super saturated with

Table 5. Comparison of selected chemical analysis for a specific site collected in 1974, 1992, and 1996

| | TIME | SITE | pH | COND uS/cm | CA ppm | MG ppm | NA ppm | K ppm |
|---|---|---|---|---|---|---|---|---|
| Unnamed well #1 | 1974 | N04 | 6.9 | 1650 | 415 | 138 | 87 | 4.6 |
| | 1992 | M05 | 7.1 | 2500 | 334 | 123 | 84 | 8.3 |
| | 1996 | U38 | 7.21 | 2360 | 370 | 123 | 78 | 4.1 |
| Unnamed well #2 | 1974 | N03 | 6.9 | 780 | 73 | 66 | 25 | 0.3 |
| | 1992 | M06 | 7.15 | 700 | 71 | 70 | 15 | -- |
| | 1996 | U43 | 7.03 | 866 | 74 | 69 | 18 | 0.4 |
| Chess well | 1974 | N08 | 6.5 | 1300 | 247 | 85 | 62 | 3.1 |
| | 1992 | M09 | 7.1 | 1600 | 220 | 84 | 58 | 8.1 |
| | 1996 | U45 | 6.54 | 1785 | 250 | 88 | 64 | 3.5 |
| Alamo well | 1974 | N07 | 8 | 1750 | 84 | 92 | 320 | 9.4 |
| | 1992 | M32 | 7.1 | 3450 | 257 | 92 | 421 | 9.6 |
| | 1996 | U47 | 8.01 | 3600 | 280 | 116 | 500 | 10 |

Table 6. Comparisions of conductivity at four well sites for waters collected in 1974 and 1996

| SITE | COND uS/cm 1974 | COND uS/cm 1996 | DIFFERENCE PERCENT |
|---|---|---|---|
| well #1 | 1650 | 2360 | 43 |
| well #2 | 780 | 866 | 11 |
| Chess well | 1300 | 1785 | 37 |
| Alamo well | 1750 | 3600 | 106 |

Table 7. Comparisons of concentrations of nitrate (from Mayer, 1995) with nitrite + nitrate (this study)

| STUDY | SITE | CONCENTRATION |
|---|---|---|
| Mayer (1995) | M05 | 7.3 ppm nitrate |
| This study | U38 | <0.02 ppm nitrite + nitrate |
| Mayer (1995) | M06 | 29 ppm nitrate |
| This study | U43 | 7.6 ppm nitrite + nitrate |
| Mayer (1995) | M09 | 9.8 ppm nitrate |
| This study | U45 | 2.1 ppm nitrite + nitrate |
| Mayer (1995) | M08 | 10 ppm nitrate |
| This study | U44 | 2.6 ppm nitrite + nitrate |

Table 8. Satuation index values of four minerals for well waters, Cornudas Mountain New Mexico

| SITE | Eh (v) | GYPSUM | CALCITE | DOLOMITE | CHALCEDONY | FLUORITE |
|---|---|---|---|---|---|---|
| U38 | 0.051 | -0.26 | 0.37 | 0.54 | 0.04 | -0.14 |
| U39 | 0.042 | -0.2 | 0.36 | 0.5 | -0.06 | -0.37 |
| U41 | 0.134 | -0.09 | 0.04 | -0.26 | 0.18 | 0.07 |
| U42 | 0.179 | -0.85 | -0.32 | -0.77 | 0.43 | -0.2 |
| U43 | 0.169 | -2.45 | -0.01 | 0.29 | 0.38 | -1.31 |
| U44 | 0.264 | -0.44 | -0.14 | -0.4 | 0.12 | -0.05 |
| U45 | 0.259 | -0.56 | -0.29 | -0.75 | 0.22 | -0.08 |
| U46 | 0.165 | -0.88 | 0 | -0.19 | 0.25 | -0.12 |
| U47 | -0.034 | -0.33 | 0.92 | 1.73 | 0.08 | 0.16 |
| U48 | -0.007 | -0.76 | 1.04 | 2.2 | 0.02 | 0.2 |

respect to dolomite, and seven of the well waters are saturated with respect to fluoride.

The oxidation potential (Eh) of the well waters were calculated using PHREEQE, assuming equilibrium of the waters with respect to ferrihydrite. The Eh values ranged from the 0.264 to -0.034 volts (Table 8). The most oxidizing conditions are sites U44 and U45 which are both located along Cess Draw north of Wind Mountain. The most reducing conditions are sites U47 and U48, which are both located north of Alamo Mountain.

## PROCESSES CONTROLLING WATER CHEMISTRY

The source of water in the study area is precipitation which falls within the immediate area. The chemical composition of the water is derived from minerals with which the water comes into contact. Therefore the bedrock composition is a major factor in the type of natural waters generated within the study area. In addition, wind-bourn dust, picked up within the study area or from outside the study area, can be deposited within the study area as eolian material. Waters, coming into contact with this material, can pick up additional constituents. The most dominant processes controlling ground water chemistry within the study area are the dissolution of gypsum and the interaction of water with carbonate rocks.

Dissolution of gypsum: $CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$ [1]
Dissolution of calcite: $CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$ [2]
Dissolution of dolomite: $CaMg(CO_3)_2 + 2H_2O + 2CO_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$ [3]

Waters in contact with limestone and dolomitic limestone will have increased concentrations in $Ca^{+2}$, $Mg^{+2}$, and $HCO_3^-$ (reactions 2 and 3). The presence of the $HCO_3^-$ ion imparts an acid buffering capacity on the waters proportional to the concentration of $H^+$. The bicarbonate ion will consume $H^+$ ions and raise the pH (reaction 4).

Buffering of the $H^+$ by bicarbonate ion: $H^+ + HCO_3^- \rightarrow H_2CO_3$ [4]

The pH of water in equilibrium with calcite at 25°C and $PCO_2 = 10^{-3.21}$, which is the average $PCO_2$ of the ground waters using PHREEQEC, will be buffered by the calcite to a pH value of approximately 8.2 ( see Drever, 1982, p.46-49 for details on the calculations). If these waters come into contact with acid waters from processes such as oxidizing sulfides or acid rain, the waters have a natural buffering capacity for neutralizing the introduced acid.

The dissolution of gypsum is responsible for the high concentrations of $Ca^{2+}$ and $SO_4^{2-}$ of most of the well waters within the study area. Gypsum occurs within several formations within the Permian sedimentary rocks. Gypsum, which dissolves easily, has done so in the past and reprecipitated when runoff containing high concentrations of $Ca^{2+}$ and $SO_4^{2-}$ evaporated or formed temporary shallow lakes which dried up. This material then can be easily picked up by the wind and redistributed where it is again available for dissolution. So the gypsum is ubiquitous in both the surface and subsurface within the study area.

The presence and dissolution of gypsum is probably causing the process of dedolomitization in the subsurface. This process, described by Black and others (1983), begins with gypsum dissolution and the release of $Ca^{2+}$ ions to the water. With the increase in $Ca^{2+}$, calcium carbonate precipitates, decreasing the carbonate ions. The decrease in carbonate ions from the waters causes undersaturation and dissolution with respect to dolomite. The net effect of this process is the increase of $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$, a decrease in pH, and a slight decrease in bicarbonate concentration (reaction 1, 2, 5, and 6).

Dedolomitization

Dissolution of gypsum: [reaction 1]
Precipitation of calcite: $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$ [reaction 5]
Dissolution of dolomite: [reaction 3]

The $CO_{2\,(g)}$ will react with water: $CO_2 + H_2O \rightarrow HCO_3^- + H^+$ [reaction 6]

Other processes within the study area include: 1) dissolution of halite; 2) the precipitation of halite in the surface because of capillary action and evaporation; 3) oxidation of organic material and possibly petroleum in the aquifer causing a reduction in oxidation potential. The elevated chloride contents of the ground waters is probably due to dissolution of halite present in rocks such as the Mancos shale. Halite is often present during deposition of shales because of the high content $Cl^-$ in sea water. Because of the presence of gypsum and halite, ground waters in contact with the Permian shales will be high in $Ca^{2+}$, $Na^{2+}$, and $SO_4^{2-}$.

Chemistry of waters in contact with the igneous alkalic rocks will be much different from waters in contact with the Permian sedimentary rocks. These waters will evolve to $Ca^{2+}$ - $HCO_3^-$ waters of low ionic strength with pH values of neutral to slightly alkaline. They will not be as well buffered as the waters in contact with carbonate rocks. No well waters within the study area are derived solely from areas of igneous rocks. Precipitation which falls on the alkalic igneous rocks will evolve toward low-ionic strength waters, but then will mix with waters derived from the Permian sedimentary rocks.

As shown earlier, water at 25°C and $PCO_2 = 10^{-3.21}$ in contact with carbonate minerals, which are abundant in the bedrock of the study area, should be naturally buffered to a pH value of approximately 8.2. The pH values of the well waters are slightly acid to slightly alkaline, indicating that other processes are responsible for the lower pH. One process discussed earlier is dedolomitization which lowers pH. Sporadic petroleum and organic material is probably present within the sedimentary rocks. This material will oxidize and use up the oxygen in the ground water causing a decrease in the oxidation potential (reaction 7 and 8) and a reducing environments.

$$O_2 + CH_2O \rightarrow CO_{2(g)} + H_2O \qquad [7]$$
$$CO_{2(g)} + H_2O \rightarrow H^+ + HCO_3^- \qquad [8]$$

Another process which may be responsible for lowering pH is that some of the sulfate which is abundant in the ground waters may be reduced to $HS^-$ or $H_2S$ by the reducing environment. The process will generate $H^+$ which will lower the pH of the ground waters (reaction 9).

$$2CH_2O + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+ \qquad [9]$$

The reducing environment and acid pH values will also cause the release of iron and manganese to the ground waters. The net effect is well water with a pH of around 7 or slightly less instead of an alkaline value of 8.2. In addition, this slightly acidic and reducing solution will react with the casings, pump rods, and pipes, releasing elevated concentrations of iron, manganese, zinc, and copper to the ground waters and requiring the rods to be replaced sooner than normal.

## ENVIRONMENTAL GEOCHEMISTRY OF THE STUDY AREA

Natural and anthropogenic-related sources can contribute heavy metals and acid to the environment. The purpose of this section is to identify environmental problems that may presently exist or potentially exist if mining occurs within the study area in the future. The study area is sparsely populated, no industry is present, and no mining has taken place. There is no evidence, such as anomalous concentrations of metals in the ground water, that the large smelter in El Paso has any effect in the study area. Therefore, environmental concerns must be considered in the context of geology and in particular, the composition of the rocks. Any present geochemical environmental problems are the result of natural processes that occur when the rocks of the study area are subjected to chemical and mechanical weathering. Pyrite is the main mineral, that when oxidized, will release acid and heavy metals to the natural waters of an area. Pyrite is mostly absent from the study area. In addition, the type of rocks present in the area, namely limestones, sandstones, and alkalic igneous rocks, generally contain normal low concentrations of trace elements such as Zn, Cu, Pb, Cd, and Hg. Shales, particularly black shales, can have anomalous concentrations of metals, but this does not appear to be the case for shales in the study area. Based on the water samples from this study, other trace elements in the rocks, such as As, are also probably low. Consequently there are minimal heavy metals and acid released from the rocks to the waters during normal weathering.

Two lithologies present in the study area are effective for mitigating any acid drainage that may presently or in the future be generated: 1) limestones and dolomites and 2) caliche that is abundant and cements Quaternary alluvium. Tertiary lacustrine beds containing calcite may also occur. The carbonate minerals react with the waters, buffer the $H^+$, and raise the pH. Heavy metals such as Cu and Zn, if present, will hydrolyze and precipitate at the higher pH values.

The other major rock group in the study area are the akallic intrusions. These rocks have limited buffering capacity, mainly form minerals such as plagioclase. But the ubiquitous occurrence of calcite in the surficial material and sedimentary rocks surrounding these intrusions will provide buffering capacity to neutralize any acid generated in the surface.

Climate plays a significant role in geochemical processes. Water is necessary for chemical weathering to occur. The climate of the study area is semi-arid. Because of the low annual precipitation, chemical weathering at the surface probably takes place in pulses when surface water is present following runoff from storms. In contrast to the surface, within the zone of ground water, water is in continuous contact with the rocks and chemical processes are continuously taking place.

The geochemical environmental consequences of future mining depend on the type of mine that would be developed. Although unlikely, if a base metal-precious metal deposit containing pyrite was developed, acid and metal release would occur, but the large amounts of carbonate minerals in the surrounding rocks and surfical material would quickly buffer the acid and metals, and so the effect on the surface would be minimal. More likely would be the development of industrial minerals such as the nepheline syenite associated with Wind Mountain for brown glass (Schreiner,1994). This rock has limited buffering capacity, but there is none or minimal pyrite or other sulfide minerals present to generate acid and to degrade the water. Therefore there would be minimal impact on the water chemistry. Possible dewatering of the aquifer for mining use is not considered.

## CONCLUSIONS

Within the surface environment, runoff from precipitation will quickly acquire $Ca^{2+}$ and $SO_4^{2-}$ from the dissolution of abundant gypsum present in the Permian sedimentary rocks, wind blown dust, Quaternary alluvium and Tertiary lacustrine sediments (?). In addition, the abundant carbonate minerals will buffer the ephemeral surface waters to pH of approximately 8.2. Other processes affect the waters in the subsurface. Additional $Ca^{2+}$ and $SO_4^{2-}$ can be picked up by the ground water from the dissolution of gypsum within the sedimentary rocks as well as $Na^+$ and $Cl^-$ from halite. Dedolomitization in causes the increase of $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$, a decrease in pH, and a slight decrease in bicarbonate concentration. Although carbonate minerals are common in the subsurface, the presents of organic material and possibly petroleum in the aquifer can use up the oxygen causing a reducing environment. Some of the sulfate is reduced to $HS^-$ or $H_2S$, causing the pH to change from 8.2 to neutral to slightly acid. This water will dissolve metals such as iron, manganese, zinc, and copper from the well casing, rods, and pipes. These elevated concentrations of metals if released to the surface material, will quickly be reduced in metals and acid by buffering by carbonate minerals. Therefore they are of little consequences (except for more frequent replacement of well parts) in terms of the geochemical environmental problems.

The presence of cattle, particularly around the wells, may lead to an elevated concentrations of nitrate due to leaking of nitrate from cattle waste into the ground water in the vicinity of the well during storm runoff.

In summary, the main geochemical environmental concern presently in the study area is: (1) the presence of slightly saline water due to the abundant gypsum and sometimes halite; (2) the neutral to slightly acid ground waters due to dedolomitization or reduction of sulfate; and (3) the elevated concentrations of nitrate, possibly due to leaching of cattle wastes in the vicinity of well sites. These problems, except for the nitrate, are due to natural processes that have operated for at least 1000's of years. Possible future mining would probably have no significant impact on the chemistry of the surface or ground waters.

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