

DELINEATING CONTROLS ON THE COMPOSITION OF GROUND WATER IN THE  
VICINITY OF THE PANTEX PLANT, SOUTHERN HIGH PLAINS, TEXAS

Final Report

by

Alan E. Fryar and William F. Mullican III

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Noel Tyler, Director

The University of Texas at Austin

Austin, Texas 78713-8924

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## ABSTRACT

Chemical, isotopic, mineralogical, and bacteriological analyses indicate that the composition of ground water in the vicinity of the Pantex Plant reflects distinctive sources of recharge (both natural and anthropogenic) modified by initial evaporation, sediment-water interactions, and microbial processes. As observed regionally by others, the major-ion facies are predominantly Ca-Mg-HCO<sub>3</sub>, reflecting ion exchange; dissolution of feldspars, calcite, sepiolite, palygorskite, and CO<sub>2</sub> gas; precipitation of calcite, Na- and Ca-smectite, sepiolite, and palygorskite; exsolution of CO<sub>2</sub> gas; and oxidation of organic carbon. Above-background concentrations of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> indicate return flow of waste water, although NO<sub>3</sub><sup>-</sup> exceeds the drinking-water standard in only one well. NO<sub>3</sub><sup>-</sup> concentrations tend to be limited during recharge by microbially mediated denitrification in the vadose zone beneath playas.

Elevated levels of <sup>3</sup>H and <sup>14</sup>C indicate focused recharge beneath both playas and ditches. Focused recharge is also indicated by values of δD and δ<sup>18</sup>O that are enriched beneath playas. The coincidence of plots of δD versus δ<sup>18</sup>O with local seasonal meteoric water lines suggests minimal evaporation, which may reflect episodic recharge or recharge along preferential pathways. Depleted δD and δ<sup>18</sup>O of H<sub>2</sub>O and enriched δ<sup>13</sup>C of dissolved inorganic carbon indicate some diffuse infiltration to perched aquifers in interplaya areas, although the timing of such recharge is uncertain. Dissolved Si and <sup>14</sup>C provide evidence of percolation from the perched aquifers to the Ogallala aquifer beneath the Pantex Plant.

On the basis of <sup>3</sup>H concentrations >1 tritium unit (TU), travel times from land surface to perched aquifers beneath playas and ditches are <40 yr. <sup>3</sup>H values typically fall within the range observed regionally within the Ogallala aquifer and therefore are likely to reflect fallout from atmospheric testing outside of Texas. Increases in <sup>3</sup>H values in onsite perched aquifer wells between 1991 and 1994 might be ascribed to the arrival of the 1963 atmospheric-testing peak, smeared by hydrodynamic dispersion, at the water table. However, the presence of wastewater in

the Ogallala aquifer beneath Playa 5 indicates travel times  $\leq 26$  yr through the vadose zone. The maximum  $^3\text{H}$  concentration (44.4 TU) is still much less than the drinking-water standard of 6,300 TU. Additional sampling and analysis by enrichment and low-level counting are needed to monitor  $^3\text{H}$  concentrations. Beneath Playa 1, travel times between the perched and Ogallala aquifers, as calculated from  $^{14}\text{C}$  data by means of reaction-path modeling, may be  $\leq 19$  yr. However, these  $^{14}\text{C}$ -derived travel times should be viewed with caution because of various assumptions involved in reaction-path modeling.

Intrinsic processes that may limit ground-water contamination in the vicinity of the Pantex Plant include both vadose-zone denitrification and dilution due to mixing of Ogallala aquifer water with water percolating from the perched aquifers onsite. Variable geochemical conditions and heterogeneous hydraulic properties beneath playas may impair the efficiency of vadose-zone remedial strategies, such as soil-vapor extraction or amended biodegradation, that involve withdrawing contaminants or delivering nutrients. To minimize further leaching of contaminants to the perched aquifers, remediation of contamination in the vadose zone adjacent to ditches and playas should be given priority over remediation of vadose-zone contamination in interplaya areas, where recharge fluxes are relatively low to nonexistent.

## INTRODUCTION

### Purpose of Study

The Ogallala (High Plains) aquifer is the largest aquifer in the United States (Zwingle, 1993). Beneath the Southern High Plains of Texas, pumpage for irrigation and, to a lesser extent, for municipal, industrial, and domestic uses since the 1930's has caused water levels in the aquifer to decline locally more than 30 m (Knowles and others, 1984; Dugan and others, 1994). These declines have motivated numerous physically based studies of rates and sources of recharge to the Ogallala aquifer, as reviewed by Mullican and others (1995a). However, hydrochemical studies have been fewer. Hydrochemical studies can complement physically based studies by delineating

sources of recharge and rates of subsurface water movement, as well as by elucidating controls on water quality. In particular, studies of compositional evolution during recharge to and flow within the Ogallala aquifer, such as have been conducted for other regional aquifers in North America (Hendry and Schwartz, 1990; Plummer and others, 1990; Murphy and others, 1992), have been limited (Potratz, 1980; Wood and Petraitis, 1984).

Concern about the potential for contamination of the Ogallala aquifer in the vicinity of the U.S. Department of Energy (DOE) Pantex Plant in Carson County, Texas (fig. 1), has prompted hydrochemical studies as part of a comprehensive hydrogeologic characterization effort. In 1951, the U.S. Atomic Energy Commission (now DOE) established the Pantex Plant for the assembly of nuclear weapons (Battelle Pantex, 1994a). Those activities resulted in releases of high explosives, chromium, trichloroethylene (TCE), and other industrial compounds to ditches leading to playas, which have been assumed to function as evaporation pans and thus used as wastewater discharge ponds. Those constituents are now found in concentrations exceeding drinking-water standards within one or more perched aquifers that occur at depths of 64 to 94 m beneath the Pantex Plant. As a result, the Pantex Plant was named to the National Priorities List in 1994. Although no contamination of the Ogallala aquifer beneath the perched aquifers has been detected, the potential impact of such contamination is significant: the Plant's water-supply wells, numerous irrigation and domestic wells, and one of the three well fields of the City of Amarillo are located downgradient.

In this report, we examine analyses of solute concentrations in soil extracts and ground water; isotopic analyses of waters, soil gases, and sediments; and mineralogic and bacteriologic analyses of sediments in the vicinity of the Pantex Plant. In conjunction with potentiometric-surface mapping and ground-water modeling, we use these data to (1) identify sources of recharge, (2) constrain estimates of travel times through the unsaturated zones above and below the perched aquifers, and (3) identify plausible reactions by means of speciation calculations and reaction-path modeling. We review our findings in light of other regional studies and discuss the implications of our findings for contaminant transport and remediation at the Pantex Plant.

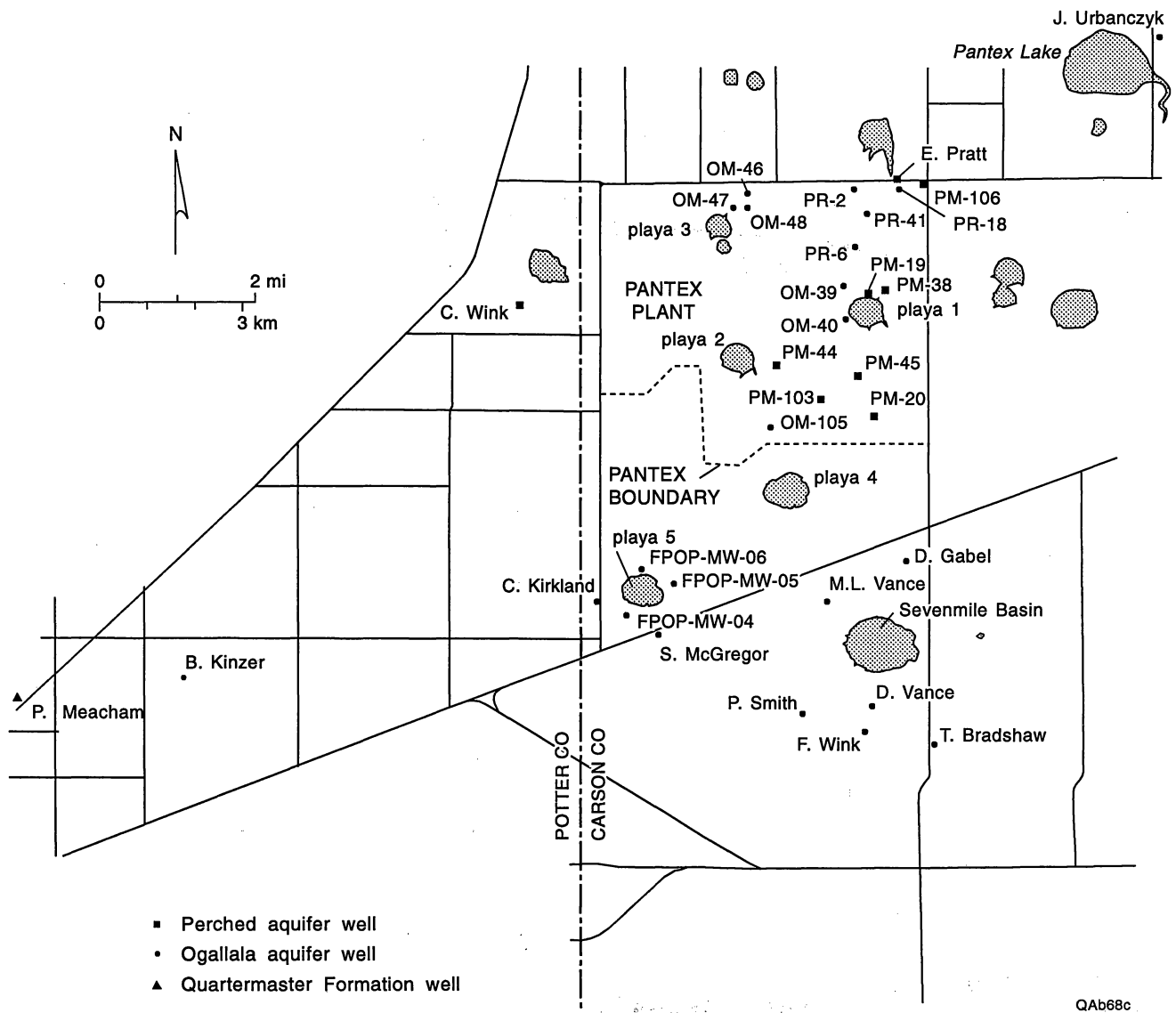


Figure 1. Location map of wells sampled by BEG in the area of the Pantex Plant. Landowners and/or tenants of private properties are indicated.



## Geology and Hydrogeology of the Study Area

Both the Ogallala aquifer and the perched aquifers discussed in this report occur within the Neogene Ogallala Formation, which lies unconformably on Permian to Triassic bedrock in the vicinity of the Pantex Plant. In the Southern High Plains, the basal portion of the Ogallala Formation is marked by three broad northwest-to-southeast-trending paleochannels separated by paleouplands (Gustavson and Winkler, 1988). The northernmost of these paleochannels, the Panhandle paleovalley, extends beneath the Pantex Plant. The paleochannels are filled with clayey to gravelly fluvial sediments and locally interbedded with clayey to sandy eolian sediments. Both paleochannel fills and paleouplands are overlain by eolian sediments of the upper Ogallala Formation and the overlying Blackwater Draw Formation, whose areal extent approximately coincides with that of the Southern High Plains (Gustavson and Winkler, 1988; Holliday, 1989). These eolian sediments contain numerous buried calcic soils, indicative of long periods of landscape stability in a subhumid to semiarid climate similar to the present (Gustavson and Holliday, 1991). The most notable calcic soil is the caprock caliche at the contact between the Ogallala and Blackwater Draw Formations. Besides calcite, the mineralogy of the Ogallala and Blackwater Draw Formations includes quartz, plagioclase, and K feldspar; the clay minerals kaolinite, illite, smectite, palygorskite, and sepiolite; secondary Fe and Mn oxides; and other minerals in trace amounts (A. J. Avakian, unpublished draft report, Bureau of Economic Geology, 1988).

The Southern High Plains are internally drained by ~25,000 playa lake basins—depressions that are circular to oval, typically less than 1.6 km in diameter, and less than 20 m deep (Gustavson and others, 1995; Sabin and Holliday, 1995). The centers of these depressions (playas), which temporarily pond runoff, are ephemeral wetlands underlain by Vertisols such as the Randall clay (U.S. Department of Agriculture, 1972). The origin of playas is a matter of long-standing debate and likely reflects a combination of geomorphic processes (Gustavson and others, 1995). However, playas appear to be coeval with the Blackwater Draw Formation and to have maintained

their positions, albeit with expansions and contractions forced by climatic fluctuations, over long periods in an aggrading landscape (Gustavson, 1995; Hovorka, 1995).

The Ogallala aquifer beneath the Southern High Plains is unconfined and is hydraulically isolated laterally by the Pecos River valley to the west, the Canadian River valley to the north, and the Caprock Escarpment to the east. For the purposes of this report, the Ogallala aquifer will be considered synonymous with the High Plains aquifer, following Mullican and others (1995a). Flow within the aquifer is regionally parallel to the slope of the land surface: southwest to northeast for the High Plains peninsula northeast of Amarillo, which includes the Pantex Plant, and northwest to southeast elsewhere. The Ogallala aquifer northeast of Amarillo is itself essentially isolated from the remainder of the aquifer to the southwest by a divide between the Canadian River valley and Palo Duro Canyon to the south (Mullican and others, 1995a). In the vicinity of the Pantex Plant, flow has been shifted northward by drawdown of the aquifer in the Panhandle paleovalley due to pumpage by the City of Amarillo (fig. 2). Currently, the depth to the Ogallala water table ranges from  $\leq 46$  m south and southwest of the Pantex Plant, where the saturated thickness of the aquifer is as little as 6 m (Knowles and others, 1982), to  $\geq 150$  m within the City of Amarillo Carson County well field, where the saturated thickness is  $\leq 117$  m (Coker and others, 1992). Prior to pumpage for irrigation and municipal use, which began in the vicinity of the Pantex Plant in the 1950's, discharge from the Ogallala aquifer occurred primarily through springs. Mullican and others (1995a) deemed fluxes between the Ogallala and underlying aquifers in the study area to be insignificant relative to recharge and internal fluxes within the Ogallala aquifer.

An increasing body of physical and chemical evidence indicates that, under current climatic conditions, natural recharge to the Ogallala aquifer beneath the Southern High Plains is focused through playas (Stone, 1984; Wood and Osterkamp, 1987; Scanlon and others, 1994). Recharge may occur along preferential pathways such as desiccation cracks, root tubules, and ped faces within the clayey playa soils and through coarser textured sediments in the annulus of the playa (Gustavson and others, 1993; Hovorka, 1995). Currently, natural recharge in interplaya uplands appears to be negligible owing to runoff and evapotranspiration (Aronovici and Schneider, 1972;

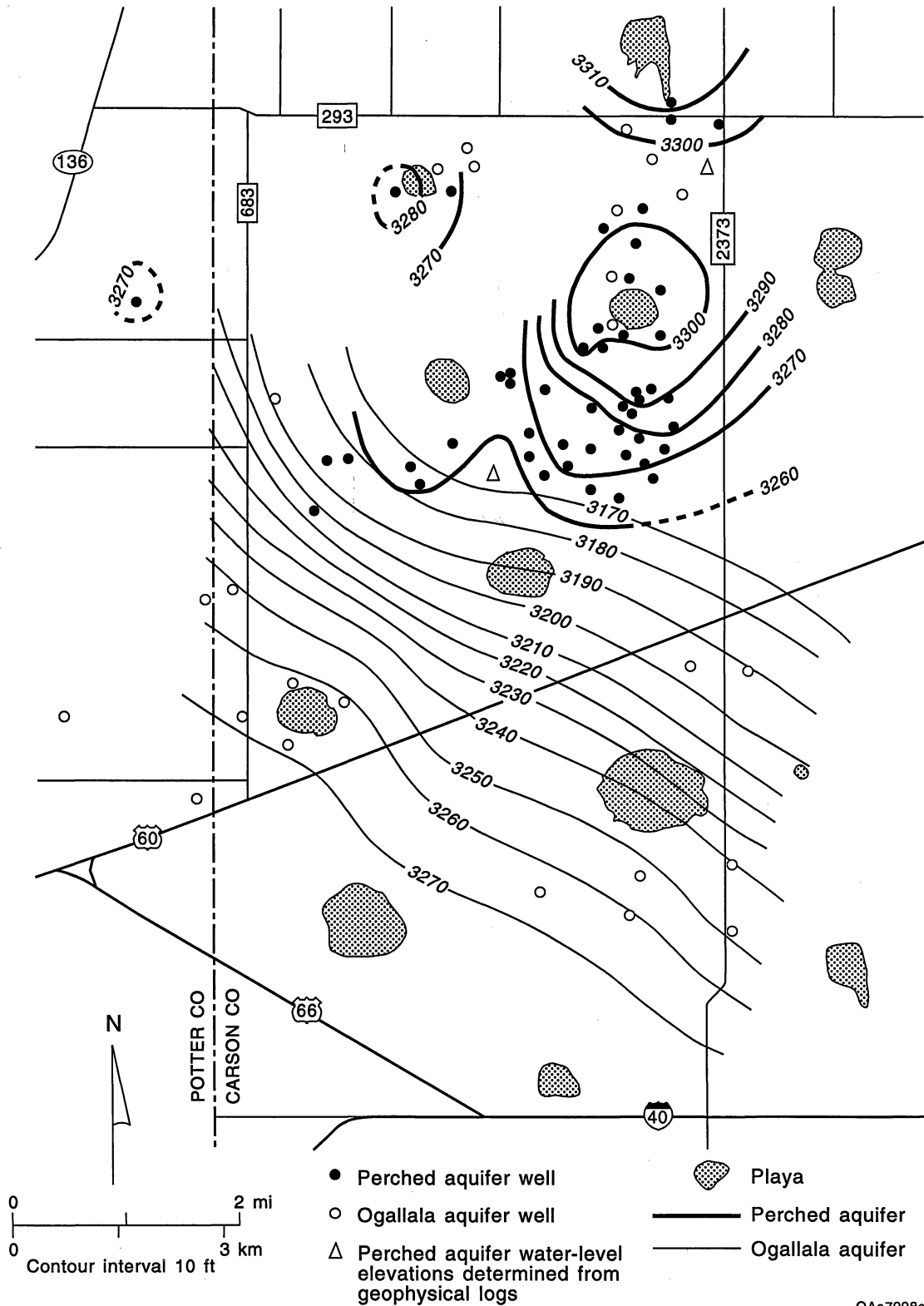


Figure 2. Revised potentiometric surface of the perched aquifers and a portion of the Ogallala aquifer in the vicinity of the Pantex Plant (contours dashed where inferred).

Stone, 1984; Scanlon and others, 1994). Recharge may be enhanced through playas by return flow from irrigation and from wastewater discharge, and it may also be induced in interplaya areas by ponding in artificial excavations (Aronovici and others, 1970). Estimates of natural, areawide (areal) recharge rates range as high as  $152 \text{ mm yr}^{-1}$  (Gould, 1906) but are typically  $<20 \text{ mm yr}^{-1}$  (Mullican and others, 1995a). However, effective (focused) rates of recharge are inversely proportional to the percentage of the land surface occupied by playas and are therefore likely to be higher than areal rates by a factor of  $\sim 30$  (Mullican and others, 1994).

Perched aquifers beneath the Southern High Plains of Texas, which may have first been recognized by Gould (1906), have also been reported outside of Carson County by Long (1961), E. P. Weeks (cited in Wood and Petraitis [1984]), Hoechst Celanese (1990), and the Texas Natural Resource Conservation Commission (C. Caldwell, personal communication, 1994). In the vicinity of the Pantex Plant, perched aquifers extend over a  $\geq 32 \text{ km}^2$  area and are marked by discrete, sometimes discontinuous mounds beneath playas (fig. 2). Two private wells drilled prior to 1940 (C. Wink and E. Pratt, fig. 1) indicate that perched aquifers in the vicinity of the Pantex Plant predate industrial activities and irrigation. However, wastewater discharges of  $\sim 1,500$  to  $3,800 \text{ m}^3 \text{ d}^{-1}$  between 1952 and 1988 have augmented by some undetermined amount the mound on the perched aquifer beneath Playa 1 at the Pantex Plant. In addition, infiltration of wastewater through ditches has resulted in TCE, 1,2-dichloroethylene, Cr, and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) plumes in interplaya areas beneath Zones 11 and 12, south of Playa 1 (Environmental Science and Engineering, 1993; Woodward-Clyde, 1993; Radian Corporation, 1994; Ramsey and others, 1995; Ramsey and Rainwater, 1995).

Perching of water in the vicinity of the Pantex Plant occurs on clayey strata, perhaps overbank deposits (Gustavson, 1995), in the middle Ogallala Formation. Values of vertical hydraulic conductivity ( $K_v$ ) of these perching strata, measured on cores under simulated overburden pressures, range from  $\sim 10^{-5}$  to  $10^{-8} \text{ mm s}^{-1}$  (Fryar and Mullican, 1995b). Development of perched aquifers requires that  $K_v$  be less than the recharge rate ( $q$ ) by at least a factor of 10 (Schneider and Luthin, 1978). The lateral extent of perched aquifers depends upon the difference

between  $K_v$  and  $q$  and upon the horizontal hydraulic conductivity ( $K_h$ ) of the perched aquifer. For a natural playa-focused  $q$  of  $206 \text{ mm yr}^{-1}$ ,  $K_v$  of the perching strata =  $1 \times 10^{-7} \text{ mm s}^{-1}$ , and  $K_h$  of the perched-aquifer sediments =  $7 \times 10^{-3} \text{ mm s}^{-1}$  (based on pump-test results), Mullican and others (1994) modeled a limiting radius of  $\leq 1,600 \text{ m}$  for a perched potentiometric mound. At that distance, all water moving through the perched aquifer would have percolated downward toward the Ogallala aquifer.

### Previous Studies of Regional Hydrochemistry

Studies of vadose-zone hydrochemistry in the Southern High Plains typically fall into one or more of three categories: ionic and isotopic studies of recharge, nutrient (N and C) cycling, and contamination of soils and perched ground water. Stone (1984, 1990), Scanlon and others (1994), and Wood and Sanford (1995) found that maximum  $\text{Cl}^-$  concentrations in soil water in interplaya settings exceed values beneath playas by as much as three orders of magnitude. The difference reflects concentration of  $\text{Cl}^-$  by evapotranspiration in interplaya settings and flushing or lack of accumulation of  $\text{Cl}^-$  beneath playas.  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations beneath playas receiving runoff from concentrated animal feeding operations (CAFOs), such as cattle feedlots, are higher than concentrations beneath non-CAFO playas (Lehman and others, 1970). Elevated  $\text{NO}_3^-$  concentrations tend to decrease to near-background levels at depths  $\leq 1.5 \text{ m}$  beneath the playa floor but may persist at greater depths beneath the margins of playas receiving CAFO runoff (Lehman and others, 1970; Clark, 1975; Stewart and others, 1994).

Perhaps the first systematic study of C cycling in the unsaturated zone beneath the Southern High Plains was that of Wood and Petraitis (1984), who monitored partial pressures of  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and Ar at various depths on the margins of two playas. Increases in  $P_{\text{CO}_2}$  and decreases in  $P_{\text{O}_2}$  with depth were attributed to aerobic microbial oxidation of dissolved and particulate organic carbon (OC) in recharging water below the soil zone, as supported by the correspondence between  $\delta^{13}\text{C}$  of  $\text{CO}_2$  and  $\delta^{13}\text{C}$  of soil humic acid. Wood and Petraitis (1984) concluded that dissolution of pedogenic  $\text{CaCO}_3$  and weathering of aluminosilicates by dissolved  $\text{CO}_2$  during recharge generate

more than half of the  $\text{HCO}_3^-$  in ground water at the sites studied. Beneath three playa basins on or near the Pantex Plant, Romanak and others (1993) and Bennett and others (1995) observed seasonal or spatial (lateral and vertical) variations in  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$  gas concentrations. Beneath the playa slope,  $\text{CO}_2$  concentrations varied slightly seasonally with root respiration but little with depth.  $\text{CO}_2$  concentrations beneath the annulus and floor were higher and increased with depth to ~5 m, owing to microbial oxidation of OC in recharging water, before decreasing at greater depths. Elevated  $\text{CO}_2$  concentrations and the presence of  $\text{CH}_4$  were attributed to impedance to gas exchange with the atmosphere under wet conditions. Like Wood and Petraitis (1984), Bennett and others (1995) concluded that dissolution of pedogenic  $\text{CaCO}_3$  beneath the annulus and floor represents a significant  $\text{CO}_2$  sink.

Concurrent with our study, Argonne National Laboratory (ANL) (1994) sampled 25 perched-aquifer monitoring wells for major and minor solutes, stable isotopes, and tritium ( $^3\text{H}$ ) to explain patterns of recharge in the vicinity of Zone 12 at the Pantex Plant. Differences in stable isotopic compositions of perched ground water were attributed to differences in recharge regimes. Depleted  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (deuterium, or  $^2\text{H}$ ) in interplaya areas supposedly reflect diffuse infiltration of summer and winter precipitation without significant evaporation, whereas enriched  $\delta^{18}\text{O}$  and  $\delta\text{D}$  adjacent to Playa 1 supposedly reflect recharge of partly evaporated summer precipitation. In contrast to  $\delta^{18}\text{O}$  and  $\delta\text{D}$ ,  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) was enriched in perched ground water in interplaya areas and depleted adjacent to playas. Depleted  $\delta^{13}\text{C}$  and elevated  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations were inferred to reflect greater biological activity and dissolution of  $\text{CaCO}_3$  beneath playas. On the basis of  $^3\text{H}$  concentrations  $\geq 0.8$  tritium units (TU) in 22 of 25 samples, a significant proportion of recharge was inferred to have occurred within the last 75 yr.

Regional studies of Ogallala-aquifer geochemistry have tended to focus upon regulated water-quality parameters (for example, total dissolved solids,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ , As, Se, and organic pesticides) (Reeves and Miller, 1978; Hopkins, 1993; Gutentag and others, 1984; Knowles and others, 1984). In the southern half of the Southern High Plains, where the Ogallala Formation thins above Cretaceous bedrock highs, the Ogallala aquifer is locally relatively saline

owing to evaporative concentration of ground water within 40 to 50 large lake basins (Wood and Jones, 1990; Wood and others, 1992). In the northern half of the Southern High Plains, ground water in the Ogallala aquifer is more dilute, and concentrations of regulated parameters are typically lower. Potratz (1980), who compiled hydrochemical data from State organizations and from the National Uranium Resource Evaluation program in Texas and New Mexico, calculated saturation indices with respect to various minerals and simulated the compositional evolution of rainwater to Ogallala-aquifer water along a generic reaction path in the northern half of the Southern High Plains. Potratz concluded that dissolution of soil CO<sub>2</sub>, calcite, plagioclase, dolomite, K feldspar, and biotite as well as precipitation of amorphous silica and calcite govern the major-ion composition of Ogallala-aquifer water in that region. In contrast, Wood and Nativ (1994) and Wood and Sanford (1995) contended that evaporation during recharge controls the concentrations of most major ions in that region of the Ogallala aquifer.

Nativ (1988) compiled hydraulic and hydrochemical data from State and Federal data bases and sampled 89 wells within 33 Texas counties for major and minor solutes, stable isotopes, and <sup>3</sup>H in order to delineate hydrochemical patterns within and rates and sources of recharge to the Ogallala aquifer. Nativ also collected 251 samples of precipitation during a 1-yr period at five stations on or adjacent to the Southern High Plains; selected samples were analyzed for δD, δ<sup>18</sup>O, <sup>3</sup>H, and Cl<sup>-</sup> (Nativ and Riggio, 1990). Nativ noted that ground water in paleovalley portions of the Ogallala aquifer exhibits a Ca-HCO<sub>3</sub> to mixed-cation-HCO<sub>3</sub> composition. Variable hydrochemical facies and isotopic compositions in paleoupland areas were attributed to low permeability of the Ogallala Formation and cross-formational flow from older units. Nativ (1988) concluded that the slight enrichment of δ<sup>18</sup>O and δD in ground water relative to precipitation and the prevalence of <sup>3</sup>H in ground water at depths ≤ ~60 m indicate focused recharge through playa basins having minimal evaporation.

## METHODS

### Sampling

From 1991 to 1994, we sampled 34 monitoring and water-supply wells in the vicinity of the Pantex Plant (fig. 1) for major and minor solutes, stable and radiogenic isotopes, and other water-quality indicators such as Eh (oxidation-reduction potential), pH, and temperature. These wells include 23 Ogallala-aquifer wells (12 upgradient from the Pantex Plant, 10 onsite, and 1 downgradient from the Pantex Plant), 10 perched-aquifer wells (2 offsite, 8 onsite), and 1 offsite well in the Permian-age Quartermaster Formation below the Ogallala aquifer (identified as Quartermaster Formation from Texas Water Development Board files). Among the wells we sampled, onsite perched-aquifer monitoring wells, Ogallala-aquifer monitoring wells, and Ogallala-aquifer production wells are prefixed PM-, OM- (or FPOP-), and PR-, respectively; offsite water-supply wells are named for the landowner. Eight Ogallala-aquifer wells and five perched-aquifer monitoring wells were sampled more than once.

Interest in  $\text{NO}_3^-$  as a possible product of high-explosive degradation and as a contaminant associated with wastewater discharge led us to analyze sediment samples from four playa basins (Pantex Lake, Playa 5, Texas Department of Criminal Justice [TDCJ], and Finley [not shown on fig. 1]). We also conducted isotopic and mineralogic analyses of interplaya core samples from wells OM-105 and PM-106 and isotopic analyses of gas samples collected beneath Playas 1 and 3 and the TDCJ playa by K. D. Romanak (Department of Geological Sciences, The University of Texas at Austin). Pantex Lake received treated sewage from 1942 to 1945 and from 1952 to 1968; Playa 1 has received process water from Pantex Plant industrial activities since at least 1952 and treated sewage since ~1968 (W. A. Laseter, Battelle Pantex, personal communication, 1993). Playa 5 received wastewater from a meat-packing plant from 1974 to 1977 and untreated sewage from ~1974 to 1992 (Texas Water Quality Board, 1977; D. Warren, City of Amarillo Utilities, personal communication, 1992; H. Wilson, Texas Tech Research Farm, personal communication,



1992). Pantex Lake and the TDCJ playa currently receive return flow from irrigation, whereas the Finley playa and Playa 3 have not received return flow.

Wells were pumped until three to five well-bore volumes had been purged, or until Eh, pH, and temperature readings had stabilized. Unless otherwise noted, ground-water samples were collected through 0.45- $\mu\text{m}$  inline filters in the field. Samples for analyses of metals and OC were preserved with 5 mL 6N acid (HCl or HNO<sub>3</sub>) per 500-mL bottle. DIC for  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  analyses was precipitated as SrCO<sub>3</sub> by adding a 30 percent NH<sub>4</sub>OH solution saturated with SrCl<sub>2</sub> (50 mL per 500-mL bottle for  $\delta^{13}\text{C}$ ; 500 mL per 50-L polypropylene carboy for  $\delta^{13}\text{C}$  and  $^{14}\text{C}$ ). Precipitate was decanted in the field and prepared for  $^{14}\text{C}$  analysis according to Dutton and others (1995). Samples for analyses of  $\delta^{13}\text{C}$  of dissolved OC (DOC),  $\delta^{15}\text{N}$ , and  $\delta^{18}\text{O}$  of NO<sub>3</sub><sup>-</sup> were frozen the day of collection and thawed in the laboratory prior to analyses. Sulfate for  $\delta^{34}\text{S}$  analysis was precipitated as ZnSO<sub>4</sub> or CdSO<sub>4</sub> by adding 5 mL of 5 percent Zn- or Cd-acetate to ~500 mL of water acidified with 5 mL 6N HCl.

### Analyses

Dissolved oxygen (DO) and HCO<sub>3</sub><sup>-</sup> alkalinity in ground-water samples were measured by digital titration in the field (Wood, 1981; Hach Company, 1992). Metals and metalloids were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) and by inductively coupled plasma-mass spectrometry (ICP-MS), anions by ion chromatography (IC) and potentiometric titration (for Cl<sup>-</sup>), and NH<sub>4</sub><sup>+</sup> by distillation at the Mineral Studies Laboratory (MSL) of the Bureau of Economic Geology (BEG). Although ICP-MS yields lower detection limits than ICP-OES, ICP-MS results have been deemed to be semiquantitative; therefore, concentrations of metals and metalloids represent ICP-OES analyses unless otherwise noted. DOC was measured by carbon analyzer using a persulfate oxidation technique at Controls for Environmental Pollution, Inc. (CEP) (Santa Fe, New Mexico). Synthetic organic compounds were measured by purge-and-trap gas chromatography, according to U.S. Environmental Protection Agency (EPA) method 624,

at CEP or at Accu-Labs Research, Inc. (Golden, Colorado). Both  $^3\text{H}$  and  $^{14}\text{C}$  were analyzed by gas proportional liquid-scintillation counting. Water samples were electrolytically enriched and analyzed for  $^3\text{H}$  with precision ( $1\sigma$ ) of 0.1 TU or  $\pm 3.5$  percent (whichever was greater) at the University of Miami (Florida) Tritium Laboratory.  $^{14}\text{C}$  was measured via benzene synthesis at Beta Analytic (Miami, Florida) and at the Laboratory of Isotope Geochemistry, University of Arizona (Tucson).

Except for  $\delta^{11}\text{B}$ , stable isotopes were analyzed by gas-source mass spectrometry (MS).  $\delta\text{D}$  and  $\delta^{18}\text{O}$  were analyzed at MSL, at Coastal Science Laboratories, Inc. (Austin, Texas), and at the Laboratory of Isotope Geochemistry.  $\delta\text{D}$  was measured on  $\text{H}_2$  gas generated by reacting water samples with hot Zn;  $\delta^{18}\text{O}$  was measured on water samples equilibrated with  $\text{CO}_2$  gas.  $\delta^{13}\text{C}$  of DIC was analyzed at MSL, at Beta Analytic, and at the Laboratory of Isotope Geochemistry. S. A. Macko (Department of Environmental Sciences, University of Virginia, Charlottesville) measured  $\delta^{13}\text{C}$  of DOC and of  $\text{CO}_2$  gas and  $\delta^{15}\text{N}$  of dissolved N and of  $\text{N}_2$  gas. L. I. Wassenaar (National Hydrology Research Institute, Environment Canada, Saskatoon, Saskatchewan) measured  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ .  $\delta^{34}\text{S}$  was analyzed at the Laboratory of Isotope Geochemistry. R. L. Bassett (Department of Hydrology and Water Resources, University of Arizona) measured  $\delta^{11}\text{B}$  by positive-ion thermal ionization MS. Values of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  are reported relative to standard mean ocean water,  $\delta^{11}\text{B}$  relative to NBSSRM-951,  $\delta^{13}\text{C}$  relative to Pee Dee belemnite,  $\delta^{15}\text{N}$  relative to atmospheric  $\text{N}_2$ , and  $\delta^{34}\text{S}$  relative to Cañon Diablo troilite. Precision ( $1\sigma$ ) was within  $\pm 5\text{‰}$  for  $\delta\text{D}$ ,  $\pm 0.3\text{‰}$  for  $\delta^{18}\text{O}$ ,  $\pm 0.6\text{‰}$  for  $\delta^{11}\text{B}$ ,  $\pm 0.073\text{‰}$  for  $\delta^{13}\text{C}$  (DIC) (analyzed at MSL), and  $\pm 0.20\text{‰}$  for  $\delta^{34}\text{S}$ .

Sediment core samples to be analyzed for  $\text{NO}_3^-$  were stored at temperatures  $\leq 0^\circ\text{C}$  (for Playa 5) or  $\sim 4^\circ\text{C}$  (for the TDCJ and Finley playas) and air dried prior to extraction with deionized water (at a sample:water weight ratio of 1:5). We did not acquire sediment samples for bacteriologic analyses using aseptic coring techniques but instead trimmed them using a sterilized knife to remove the skin of the core in the field; the knife was resterilized with methanol between samples. These samples were shipped in sterilized specimen cups at  $\sim 4^\circ\text{C}$  by overnight courier to Microbe Inotech Laboratories (St. Louis, Missouri), where they were analyzed according to

Britton and Greeson (1988) for most-probable numbers (MPNs) of denitrifying and  $\text{NO}_3^-$ -reducing bacteria. Clay mineralogy of core samples was determined by X-ray diffractometry (XRD) on 2- $\mu\text{m}$ , 1- to 2- $\mu\text{m}$ , and <1- $\mu\text{m}$  size fractions. Cation exchange capacity (CEC) was measured by saturating air-dried samples with sodium acetate solution, then extracting exchangeable  $\text{Na}^+$  with ammonium acetate solution and quantifying the extracted  $\text{Na}^+$  (Richards, 1954). Exchangeable cations were determined by saturating air-dried samples with ammonium acetate solution and quantifying the concentrations of cations in the supernatant (Thomas, 1982).

## RESULTS

### Major and Minor Solutes in Ground Water

As illustrated on the Piper diagram (fig. 3), which represents the relative concentrations of major cations and anions in percent  $\text{meq L}^{-1}$ , ground water in the study area is predominantly of a mixed cation- $\text{HCO}_3^-$  composition. This result is consistent with the findings of Nativ (1988) for the Ogallala aquifer in the northern half of the Southern High Plains. In comparison, figure 4 depicts major-ion compositions of ground water in nearby wells not sampled by BEG, including perched-aquifer wells at the Pantex Plant sampled by ANL (1994) and Ogallala-aquifer wells sampled by the City of Amarillo in its Carson County well field (City of Amarillo Utilities, unpublished data, 1990). (It should be noted that  $\text{HCO}_3^-$  concentrations were not measured by the City of Amarillo; we calculated them according to the relationship  $\text{HCO}_3^- = 1.967 \times [\text{total dissolved solids} - \text{ion sum}]$  [in  $\text{mg L}^{-1}$ ].) With few exceptions, Ogallala-aquifer waters are relatively narrowly clustered on both diagrams. Perched-aquifer waters are less homogeneous and (with the exceptional Ogallala-aquifer waters) tend toward higher proportions of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ . The sample from the Quartermaster Formation (P. Meacham, fig. 1) is marked by the highest proportion of  $\text{Na}^+$ .

Ground water in the study area is relatively dilute, with total dissolved solids concentrations of <600  $\text{mg L}^{-1}$  in 30 of 34 wells.  $\text{HCO}_3^-$  concentrations were highest (>330  $\text{mg L}^{-1}$ ; table 1) in

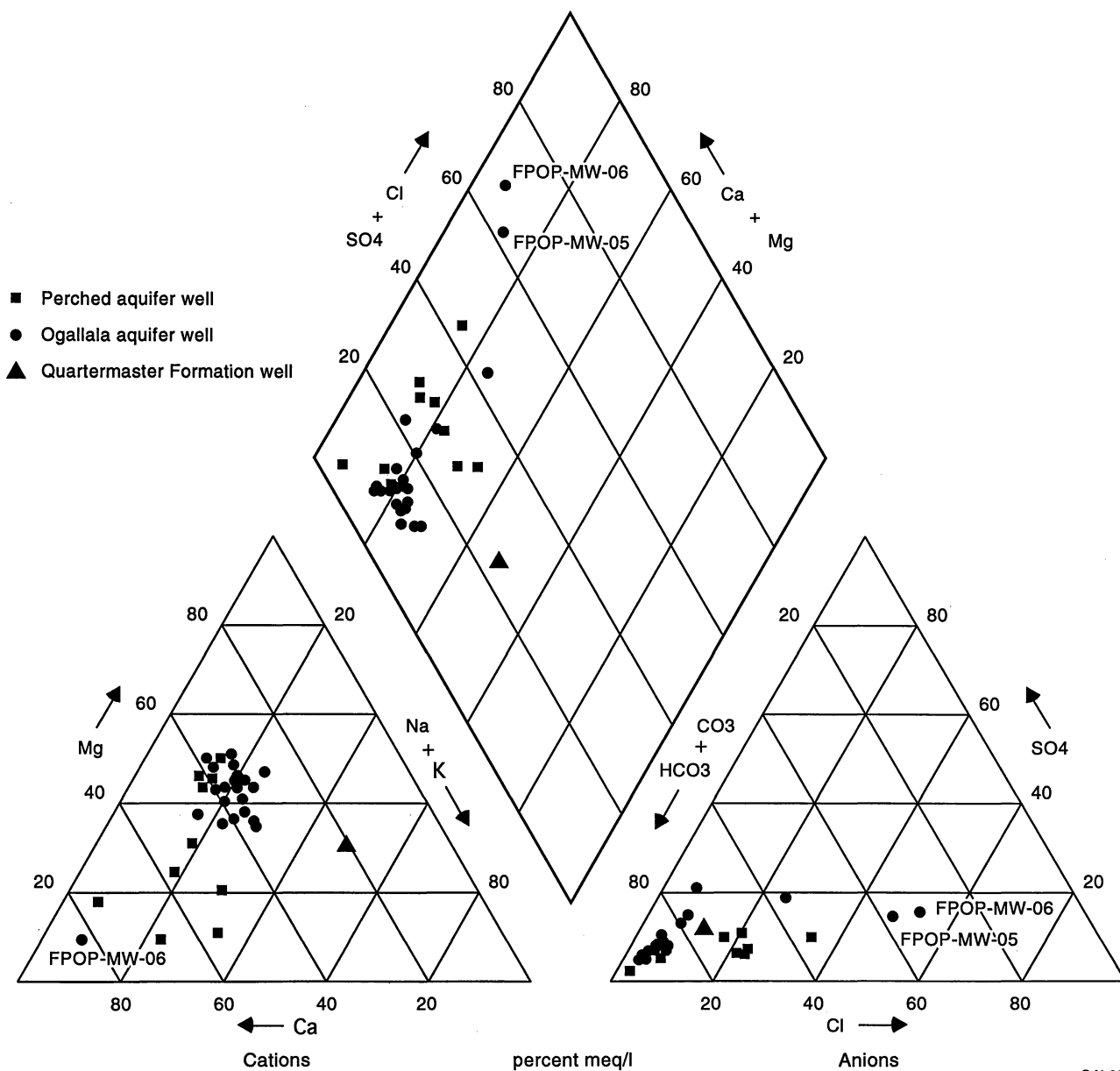


Figure 3. Piper diagram representing relative concentrations (in meq L<sup>-1</sup>) of major ions in wells sampled by BEG. The most recent data are plotted for wells sampled on more than one occasion.

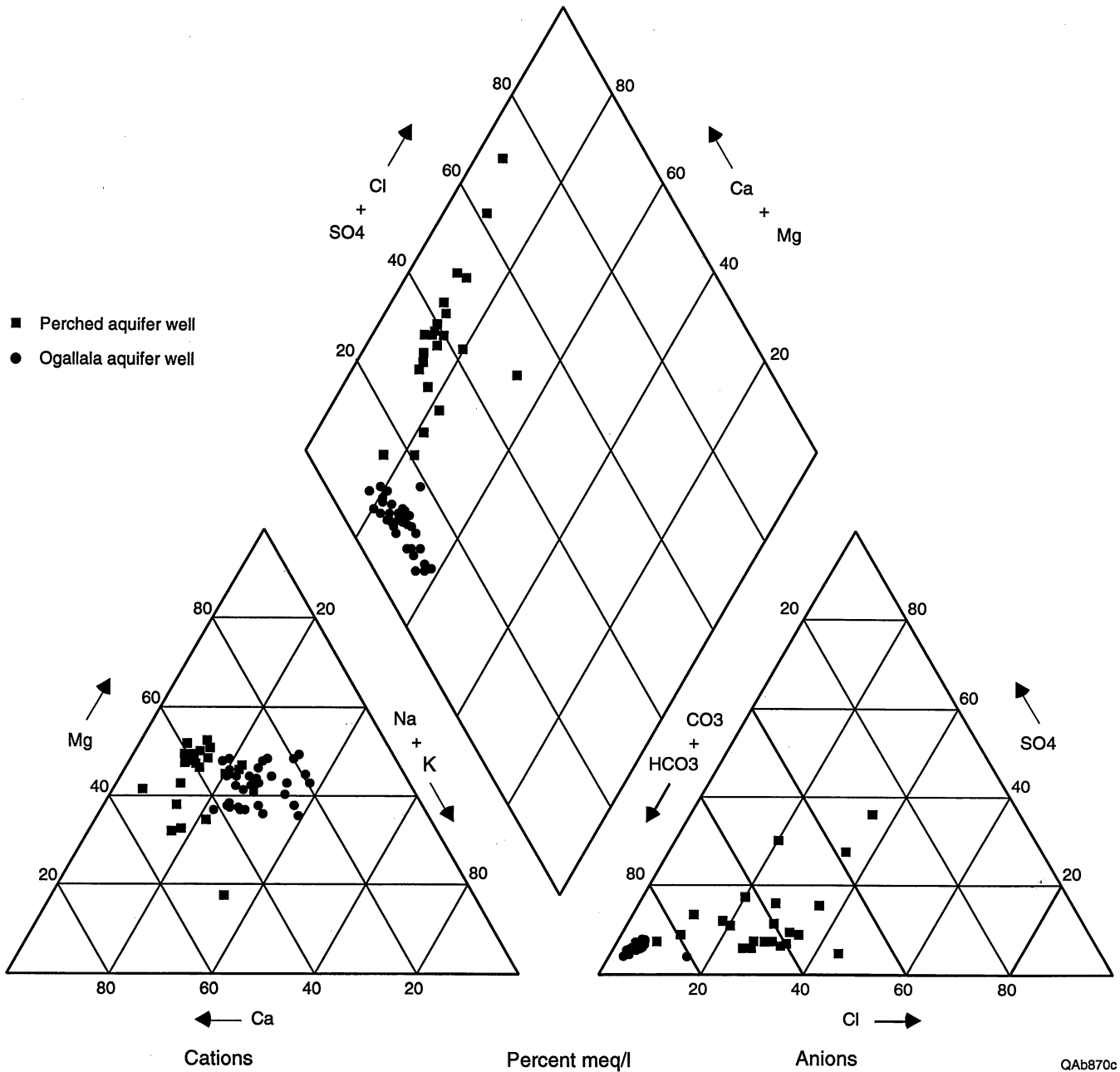


Figure 4. Piper diagram for major ions in perched-aquifer wells sampled by ANL in 1994 and in Ogallala-aquifer wells (Carson County well field) sampled by City of Amarillo Utilities in 1990.

Table 1(a). Solute and other water-quality data for wells sampled by BEG in 1991.

Well no.	Date	Na	K	Mg	Ca	Al	Fe	Co	Cr	Cu	Mn	Ni	Zn	Cd	Pb	Li	Sr	Ba
OM-39	10/7/91	20.4	5.60	26.9	41.5	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	0.22	<0.01	<0.11	*0.05	1.00	0.11
OM-40	10/14/91	23.9	6.07	26.9	38.4	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	0.10	<0.01	<0.11	*0.05	1.02	0.14
OM-46	12/10/91	25.1	6.81	27.8	33.8	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	<0.04	1.07	0.15
OM-47	12/11/91	12.1	6.67	19.7	39.6	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	<0.04	0.81	0.31
OM-48	12/11/91	18.3	6.96	27.6	39.2	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	<0.04	1.09	0.17
PM-19	10/10/91	30.4	3.22	10.1	106.0	<0.24	0.31	<0.03	<0.03	<0.03	<0.01	<0.07	*0.01	<0.01	<0.11	<0.04	0.32	0.20
PM-20	10/10/91	13.4	6.10	33.6	38.9	<0.24	<0.02	<0.03	*0.05	<0.03	<0.01	<0.07	*0.03	<0.01	<0.11	<0.04	1.16	0.15
PM-38	10/9/91	60.2	5.63	14.8	110.0	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	*0.02	<0.01	<0.11	<0.04	0.40	0.11
PM-44	10/8/91	13.0	4.85	15.7	40.3	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	0.10	<0.01	<0.11	<0.04	0.54	0.14
PM-45	10/9/91	14.4	6.70	39.8	58.6	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	0.10	<0.01	<0.11	<0.04	1.26	0.21
PR-2	10/11/91	30.1	5.64	23.4	38.7	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	0.04	<0.01	<0.11	<0.04	0.88	0.13
PR-6	10/15/91	21.1	5.61	24.9	42.7	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	0.11	<0.01	<0.11	*0.05	0.99	0.12
PR-18	10/8/91	25.9	5.58	24.0	42.5	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	<0.01	<0.01	<0.11	<0.04	0.96	0.14
PR-41	10/15/91	23.8	5.68	26.1	42.9	<0.24	<0.02	<0.03	<0.03	<0.03	<0.01	<0.07	*0.01	0.46	<0.11	*0.04	1.01	0.12

Table 1(a). (cont.)

Th	B	Si	F	Cl	Br	NO3	SO4	HCO3 (lab)	HCO3 (field)	T (°C)	Eh (mV)	pH (lab)	pH (field)
<0.38	0.15	15.5	1.72	11.4	<0.10	4.20	21.6		260	19.6	470		7.69
<0.38	0.16	17.4	1.50	8.81	<0.10	5.01	16.9		278	18.2	280		7.56
<0.42	0.17	15.3	1.70	9.15	<0.10	5.38	15.8	257	256	18.4	410	8.10	7.71
<0.42	0.09	14.0	0.71	4.76	<0.10	3.19	9.49	225	225	16.8	390	8.16	7.65
<0.42	0.13	13.8	0.98	6.88	<0.10	6.44	17.0	262	267	16.9	380	8.13	7.63
<0.38	1.07	8.69	0.35	34.1	<0.10	5.40	25.8	280	379	16.9	360	8.19	6.96
<0.38	0.35	12.2	1.30	22.6	<0.10	9.83	20.2		260	17.1	430		7.66
<0.38	0.50	8.02	0.21	67.2	<0.10	8.19	73.2		349	16.8	370		7.12
<0.38	0.08	9.01	0.92	14.4	<0.10	2.79	11.9		196	19.1	460		7.62
<0.38	0.09	11.1	1.19	47.3	<0.10	5.62	18.5		297	17.3	360		7.34
<0.38	0.15	14.0	1.31	8.88	<0.10	4.74	18.7		277	19.9	530		7.79
<0.38	0.15	15.6	1.71	11.0	<0.10	4.60	20.1		258	18.6	460		7.60
<0.38	0.15	14.5	1.39	8.61	<0.10	4.22	19.9		258	20.2	450		7.44
<0.38	0.14	14.2	1.43	10.7	<0.10	5.05	20.8		274	20.3	440		7.53

1. Concentrations in mg/L.

2. \* = near detection limit.

3. Detection limits for analytes that were never detected are given in Table 1(e).

Table 1(b). Solute and other water-quality data for wells sampled by BEG in 1992.

Well no.	Date	Na	K	Mg	Ca	Al	Fe	Co	Cr	Cu	Mn	Ni	Zn	Cd	Pb	Li	Sr	Ba
OM-39	10/13/92	20.7	6.02	26.1	41.5	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	0.53	<0.01	<0.12	*0.06	1.04	0.14
OM-40	10/7/92	23.0	5.94	26.7	39.0	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.03	<0.01	<0.12	*0.07	1.10	0.15
OM-105	10/14/92	25.9	6.77	23.9	37.9	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.03	<0.01	<0.12	*0.06	1.02	0.14
PM-19	10/8/92	31.6	3.66	10.3	117	<0.27	0.73	<0.03	<0.03	<0.03	*0.02	<0.08	*0.01	<0.01	<0.12	<0.04	0.37	0.21
PM-20	10/7/92	13.1	6.52	35.8	41.6	<0.27	<0.02	<0.03	0.2	<0.03	<0.01	<0.08	0.07	<0.01	*0.13	*0.05	1.28	0.17
PM-38	10/6/92	56.8	5.38	14.2	110	<0.27	<0.02	<0.03	<0.03	<0.03	*0.01	*0.10	*0.01	<0.01	<0.12	<0.04	0.41	0.13
PM-44	10/13/92	13.1	4.74	15.0	40.1	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.02	<0.01	<0.12	<0.04	0.56	0.15
PM-45	10/6/92	15.7	7.28	42.5	62.8	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.01	<0.01	<0.12	<0.04	1.43	0.23
PM-106	10/8/92	18.3	5.73	8.4	33.4	<0.27	<0.02	<0.03	<0.03	<0.03	*0.01	<0.08	*0.01	<0.01	<0.12	<0.04	0.56	0.11
PR-2	10/14/92	27.2	5.76	22.7	40.1	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	0.06	<0.01	<0.12	*0.05	0.95	0.15
PR-41	10/9/92	32.0	5.95	24.3	40.3	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.01	<0.01	<0.12	*0.05	1.01	0.12
E. Pratt	10/13/92	19.3	5.91	17.6	66.0	<0.27	*0.02	<0.03	<0.03	<0.03	*0.01	<0.08	0.14	<0.01	<0.12	<0.04	0.68	0.24
P. Smith	10/7/92	18.2	7.10	45.9	54.2	<0.27	*0.07	<0.03	<0.03	<0.03	<0.01	<0.08	0.10	<0.01	<0.12	*0.08	1.71	0.18
C. Wink	10/5/92	5.9	3.36	13.6	90.3	<0.27	0.44	<0.03	<0.03	<0.03	*0.02	<0.08	0.49	<0.01	<0.12	<0.04	0.62	0.35
F. Wink	10/9/92	20.4	6.52	40.7	42.6	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	0.08	<0.01	<0.12	*0.09	1.49	0.13



Table 1(b). (cont.)

Th	B	Si	F	Cl	Br	NO3	SO4	HCO3 (lab)	HCO3 (field)	DO	T (°C)	Eh (mV)	pH (lab)	pH (field)
<0.42	*0.15	17.3	1.53	9.80	<0.50	4.76	19.2	259	279	8.30	21.8		7.75	7.2†
<0.42	*0.12	19.5	1.56	6.91	<0.50	4.47	16.0	282		8.32	15.6		7.61	7.0†
<0.42	*0.12	19.4	1.78	6.17	*0.11	3.82	15.1	268	279	9.40	20.4	390	7.63	7.55
<0.42	1.05	10.6	0.26	42.0	<0.50	3.63	27.8	361	366	4.98	14.9		7.50	6.6†
<0.42	0.32	13.8	1.39	31.6	<0.50	17.2	20.9	234		11.3	16.6		7.85	7.0†
<0.42	0.39	9.8	0.28	48.5	<0.50	6.84	66.8	365		5.50	15.0		7.44	6.9†
<0.42	*0.04	11.2	1.01	9.44	<0.50	3.35	10.7	194	227	8.22	17.4		7.49	7.2†
<0.42	*0.05	13.3	1.01	56.9	<0.50	6.43	21.8	309		8.66	17.4		7.67	6.9†
<0.42	<0.04	15.8	0.49	17.8	*0.19	13.1	15.8	133	138	13.3	21.2	370	8.13	9.88
<0.42	*0.12	16.0	1.33	8.44	<0.50	5.23	18.6	262	332	7.70	18.4		7.60	7.1†
<0.42	*0.12	15.8	1.42	8.78	<0.50	5.92	19.8	276	293	9.54	19.4	470	7.54	7.58
<0.42	*0.04	10.5	0.32	45.8	0.65	13.7	20.9	211	248	9.40	19.4	340	7.55	7.51
<0.42	*0.09	20.3	1.12	13.0	*0.17	19.9	39.8	349	347	7.94	16.0	410	7.68	7.42
<0.42	<0.04	10.5	0.29	3.23	*0.13	4.97	8.47	332	369	3.24	24.0	500	7.68	7.15
<0.42	*0.12	22.5	1.46	6.99	*0.14	6.07	18.6	330	352	7.98	19.5	470	7.59	7.71

1. Concentrations in mg/L.

2. \* = near detection limit.

3. Detection limits for analytes that were never detected are given in Table 1(e).

4. † = pH measured by Battelle technicians.

Table 1(c). Solute and other water-quality data for wells sampled by BEG in 1993.

Well no.	Date	Na	K	Mg	Ca	Al	Fe	Co	Cr	Cu	Mn	Ni	Zn	Cd	Pb	Li	Sr
T. Bradshaw	5/12/93	23.5	6.11	29.3	38.7	<0.27	*0.03	<0.03	<0.03	<0.03	<0.01	<0.08	0.08	<0.01	<0.12	0.13	1.17
D. Gabel	5/13/93	20.3	6.49	27.4	33.1	<0.27	<0.02	<0.03	<0.03	<0.03	*0.02	<0.08	0.33	<0.01	<0.12	0.08	1.10
B. Kinzer	2/3/93	44.8	7.95	50.1	48.9	<0.27	<0.02	<0.03	<0.03	<0.03	0.31	<0.08	0.45	<0.01	<0.12	0.10	1.88
C. Kirkland	8/11/93	24.2	6.06	30.5	37.4	<0.27	*0.04	<0.03	<0.03	<0.03	<0.01	<0.08	*0.06	<0.01	<0.12	0.12	1.08
S. McGregor	5/12/93	19.5	6.36	29.7	36.5	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.01	<0.01	<0.12	0.09	1.24
P. Meacham	2/4/93	68.4	6.63	24.8	27.0	<0.27	<0.02	<0.03	<0.03	<0.03	0.31	<0.08	0.13	<0.01	<0.12	0.10	1.05
OM-40	11/22/93	25.5	6.35	27.3	39.2	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.03	<0.01	<0.12	*0.07	1.08
PM-19	11/17/93	37.5	3.15	10.6	120	<0.27	0.45	<0.03	<0.03	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	<0.04	0.37
PM-20	10/13/93	15.1	7.14	41.1	46.9	<0.27	*0.02	<0.03	0.57	<0.03	*0.01	<0.08	*0.01	<0.01	<0.12	*0.08	1.36
PM-38	11/1/93	62.5	5.72	13.2	101	<0.27	*0.03	<0.03	<0.03	<0.03	*0.01	0.13	*0.01	<0.01	<0.12	<0.04	0.36
PM-103	6/23/93	10.6	6.74	25.3	40.0	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.01	<0.01	<0.12	*0.05	0.95
PR-2	10/13/93	29.7	6.46	23.2	38.7	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.03	<0.01	<0.12	*0.07	0.88
PR-6	2/19/93	22.2	5.86	21.8	42.8	<0.27	*0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.01	<0.01	<0.12	*0.07	1.00
P. Smith	11/22/93	19.6	7.17	44.2	53.2	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.04	<0.01	<0.12	*0.07	1.62
D. Vance	5/11/93	26.6	6.7	36.7	46.3	0.33	*0.04	*0.04	<0.03	*0.03	<0.01	<0.08	*0.05	<0.01	<0.12	0.10	1.50
M. L. Vance	5/11/93	16.4	5.95	28.5	32.2	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.03	<0.01	<0.12	0.10	1.20

Table 1(c). (cont.)

Ba	Th	B	Si	F	Cl	Br	NO3	SO4	HCO3 (lab)	HCO3 (field)	DOC	TOC	DO	T (°C)	Eh (mV)	pH (lab)	pH (field)
0.07	<0.42	0.17	21.6	1.59	12.5	0.12	7.55	53.3	229	235			6.34	17.5	220	7.84	7.58
0.11	<0.42	0.17	18.6	1.65	12.5	0.13	6.44	16.6	246	252			4.28	17.9	160	7.96	7.69
0.12	<0.42	0.16	14.1	1.66	68.9	0.40	32.4	73.6	272	272			6.34	18.2	190	8.12	7.54
0.10	<0.42	0.18	27.5	2.79	7.82	*0.15	3.95	19.2	312				7.68	18.8	350	7.87	8.10
0.12	<0.42	0.19	25.0	1.81	8.44	<0.10	4.63	20.9	266	286			7.34	19.4	210	7.85	7.59
0.07	<0.42	0.45	22.8	2.17	27.5	0.14	7.48	37.4	281	297			7.12	17.2	210	8.11	7.97
0.14	<0.42	0.17	20.7	1.61	8.21	<0.1	4.95	17.0	281	287	0.5	0.6	7.98	15.1		7.97	7.50
0.18	<0.42	1.24	11.5	0.39	52.3	<0.1	5.74	26.8	364	352	1.7	0.9	4.08	15.5	290	7.94	7.03
0.17	*0.66	0.48	14.3	1.24	59.1	0.22	15.7	21.7	232	214			7.78	16.0	330	7.86	7.40
0.10	*0.84	0.57	10.3	0.36	54.3	<0.1	8.07	49.4	359	357			4.44	15.6	120	7.75	7.37
0.17	<0.42	0.12	12.4	1.50	29.1	0.17	6.57	13.7	198	181			8.46	19.9	250	7.82	8.10
0.13	*1.00	0.18	16.6	1.54	9.46	<0.1	4.92	21.5	261	251			7.08	24.8	160	8.09	7.26
0.12	<0.42	0.17	17.3	1.58	10.4	0.28	5.51	21.2	251	258			7.88	15.2		8.09	7.56
0.15	<0.42	0.13	21.3	1.22	14.0	*0.14	19.2	42.8	332	324	2.0	1.1	10.24	20.8	120	8.08	
0.11	<0.42	0.23	20.1	1.66	15.7	0.14	20.8	36.4	297	286			5.74	16.6	240	7.87	7.46
0.14	<0.42	0.23	24.9	1.99	13.0	0.12	5.53	19.0	238	262			6.64	17.2	230	7.83	7.63

1. Concentrations in mg/L.

2. \* = near detection limit.

3. Detection limits for analytes that were never detected are given in Table 1(e).

4. Except for C. Kirkland, lab pH values after May 1993 were measured on samples collected without headspace.

5. For 1993–1994 monitoring of PM-19, PM-20, PM-38, and OM-40, flow cells were not used for measuring T, Eh, or pH.

Table 1(d). Solute and other water-quality data for wells sampled by BEG in 1994.

Well no.	Date	Na	K	Mg	Ca	Al	Fe	Co	Cr	Cu	Mn	Ni	Zn	Cd	Pb	Li	Sr
FPOP-MW-04	11/4/94	22.29	5.48	30.89	37.43	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	*0.10	0.98
FPOP-MW-05	6/29/94	30.10	9.14	71.36	98.59	<0.27	0.24	<0.03	<0.03	<0.03	0.05	0.17	<0.02	<0.01	<0.12	*0.09	2.74
FPOP-MW-05	11/3/94	29.21	8.13	76.21	94.77	<0.27	*0.08	<0.03	<0.03	<0.03	0.04	0.23	<0.01	<0.01	<0.12	*0.10	2.39
FPOP-MW-06	6/29/94	26.50	15.94	23.84	299.9	1.42	1.08	<0.03	<0.03	<0.03	0.07	<0.08	0.05	<0.01	<0.12	<0.04	1.21
FPOP-MW-06	11/3/94	25.00	14.2	23.28	326.0	<0.27	<0.02	<0.03	<0.03	<0.03	*0.02	<0.08	<0.01	<0.01	<0.12	<0.05	1.04
OM-40	1/12/94	26.1	7.08	27.8	40.1	<0.27	*0.02	<0.03	<0.03	<0.03	<0.01	<0.08	*0.02	<0.01	<0.12	*0.06	1.00
OM-40	4/11/94	23.60	6.80	26.45	40.97	<0.27	*0.05	<0.03	<0.03	<0.03	<0.01	<0.08	*0.03	<0.01	<0.12	*0.07	1.03
OM-40	7/25/94	25.20	6.51	27.11	38.77	<0.27	0.15	<0.03	<0.03	<0.03	<0.01	<0.08	0.04	<0.01	<0.12	0.07	0.96
PM-101	11/1/94	10.00	5.24	22.35	31.71	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	0.28	<0.01	<0.12	<0.05	0.76
PM-101	11/1-2/94	10.28	5.58	22.92	31.98	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	0.23	<0.01	<0.12	<0.05	0.76
PM-101	11/2/94	10.68	5.22	23.76	33.38	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	0.06	<0.01	<0.12	<0.05	0.77
PM-19	2/1/94	38.5	4.10	10.7	118	<0.27	0.68	<0.03	<0.03	<0.03	*0.01	<0.08	*0.01	<0.01	<0.12	<0.04	0.35
PM-19	4/11/94	37.76	3.93	10.39	118.6	<0.27	1.15	<0.03	<0.03	<0.03	*0.01	<0.08	<0.02	<0.01	<0.12	<0.04	0.36
PM-19	7/27/94	38.91	4.00	10.01	110.5	<0.27	0.94	<0.03	<0.03	<0.03	*0.01	<0.08	<0.02	<0.01	<0.12	<0.04	0.32
PM-20	1/11/94	14.9	6.74	42.2	49.9	<0.27	<0.02	<0.03	0.55	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	*0.05	1.45
PM-20	4/12/94	15.88	7.59	42.17	54.49	<0.27	0.17	<0.03	0.58	<0.03	<0.01	<0.08	<0.02	<0.01	<0.12	*0.05	1.53
PM-20	7/27/94	17.72	7.65	43.17	50.38	<0.27	0.23	<0.03	1.45	<0.03	<0.01	<0.08	<0.02	<0.01	<0.12	0.06	1.4
PM-38	1/11/94	62.8	5.40	12.9	101	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	*0.16	<0.01	<0.01	<0.12	<0.04	0.33
PM-38	4/13/94	61.31	5.15	12.69	103.1	<0.27	0.36	<0.03	0.14	<0.03	<0.01	0.22	<0.02	<0.01	<0.12	<0.04	0.35
PM-38	7/25/94	62.98	5.24	12.61	98.63	<0.27	1.20	<0.03	0.35	<0.03	0.02	0.24	<0.02	<0.01	<0.12	<0.04	0.32
PR-2	1/12/94	31.0	6.23	32.1	40.2	<0.27	<0.02	<0.03	<0.03	<0.03	<0.01	<0.08	<0.01	<0.01	<0.12	<0.04	0.86
PR-2	7/27/94	31.34	6.17	22.60	37.94	<0.27	<0.03	<0.03	<0.03	<0.03	<0.01	<0.08	<0.02	<0.01	<0.12	0.05	0.82
P. Smith	1/13/94	19.6	6.48	45.7	53.8	<0.27	*0.03	<0.03	<0.03	<0.03	<0.01	<0.08	0.12	<0.01	<0.12	*0.08	1.62
P. Smith	4/12/94	19.60	7.87	43.03	54.10	<0.27	0.46	<0.03	<0.03	*0.05	*0.02	<0.08	0.14	<0.01	<0.12	*0.08	1.61
P. Smith	6/28/94	20.05	7.19	43.67	55.81	<0.27	<0.03	<0.03	<0.03	<0.03	<0.01	<0.08	0.11	<0.01	<0.12	*0.07	1.61
J. Urbanczyk	7/28/94	16.25	6.57	26.71	40.27	<0.27	0.08	<0.03	<0.03	<0.03	<0.01	<0.08	<0.02	<0.01	<0.12	0.04	0.97

Table 1(d). (cont.)

Ba	Th	B	Si	F	Cl	Br	NO3	SO4	HCO3 (lab)	HCO3 (field)	DOC	TOC	DO	T (°C)	Eh (mV)	pH (lab)	pH (field)
0.11	<0.42	*0.16	25.69	3.47	8.78	<0.1	4.23	26.7			3.1	1.2	7.70	13.9	410	7.86	7.55
0.07	<0.42	*0.12	20.5	*0.3	211.0	<0.1	13.2	85.5	269	272	1.6	1.1	6.12	19.5		7.35	7.17
0.07	<0.42	<0.10	19.4	1.54	196	<0.1	11.5	82.2		266	1.2	0.8	6.28	17.8	300	7.57	7.42
0.19	<0.42	<0.10	19.8	3.3	320.0	<0.1	56.7	107.0	337	354	1.6	1.7	5.52	16.9		6.9	6.91
0.08	<0.42	<0.10	14.04	1.73	324	<0.1	56.8	129.1		338	7.9	1.8	5.36	16.3	330	7.06	6.91
0.13	<0.42	0.17	19.3	1.46	7.33	<0.1	4.94	17.4	279	302	0.8	1.1	7.34	14.3	300	8.13	7.3†
0.14	<0.42	0.19	19.5	1.6	7.5	*0.12	5.3	16.8	280		1.6	0.8	7.86	18.4	350	7.6	7.34
0.14	<0.42	*0.2	18.9	1.5	7.7	<0.1	4.6	16.7	280		1.7	1.9	6.84	18.6		7.69	7.52
0.14	<0.42	<0.10	11.48	1.88	8.64	<0.1	4.64	11.8		216	2.3	2.6	7.46	18.0	410	7.88	7.84
0.13	<0.42	<0.10	11.95	1.9	9.3	<0.1	5.15	12.1		213	2.1	1.8	7.62	17.6	430	7.89	7.96
0.13	<0.42	<0.10	12.02	1.77	8.88	<0.1	4.55	11.2		260	1.9	8.5	7.14	17.6		7.84	7.82
0.18	<0.42	1.29	10.8	0.45	59.4	<0.1	4.07	24.8	359	364	1.3	0.9	4.42	14.6	330	7.59	6.82
0.18	<0.42	1.41	10.6	0.3	67.1	*0.18	4.1	24.7	349	346	1.9	1.1	4.26	17.6	220	7.08	7.18
0.17	<0.42	1.3	10.3	0.4	62.3	<0.1	4.0	27.3	341	357	1.3	1.4	4.12	16.4		7.21	7.05
0.17	<0.42	0.49	14.1	1.34	68.7	*0.30	17.6	24.5	224		1.7	1.6		14.7	290	8.07	7.4†
0.18	<0.42	0.5	14.0	1.5	89.3	<0.1	22.4	21.0	226	224	2.0	1.7	8.82	16.2	390	7.71	7.09
0.17	<0.42	0.4	13.7	1.8	73.9	<0.1	18.0	31.7	224	216	1.8	2.1	7.80	17.6		7.74	7.80
0.10	<0.42	0.56	10.0	0.54	52.8	<0.1	8.37	49.3	361	342	1.5	0.8		13.2	300	7.97	6.8†
0.1	<0.42	0.63	10.0	0.4	57.5	*0.19	10.4	46.9	358	355			4.62	15.2	380	7.21	6.88
0.11	<0.42	0.5	10.1	0.5	56.9	<0.1	9.7	46.7	353	370			4.36	17.0		7.41	6.98
0.13	<0.42	0.16	16.2	1.21	8.7	<0.1	5.21	20.6	261		1.8	1.8	7.02	19.1	270	8.07	7.19
0.13	<0.42	*0.2	15.8	1.6	9.3	<0.1	5.5	21	260	287			6.92	19.8		7.71	7.69
0.16	<0.42	0.14	20.3	1.15	15.2	<0.1	17.6	47.8	341	343	1.1	1.5	7.96	7.3	310	7.88	7.05
0.16	<0.42	*0.14	19.3	1.2	17.9	<0.1	19.1	40.4	343	351			7.32	21.3	350	7.6	7.50
0.15	<0.42	*0.14	19.4	1.0	18.2	<0.1	17.8	48.7	336	321			6.43	28.5			7.30
0.19	<0.42	*0.1	15.7	1.2	7.9	<0.1	4.5	11.9	262	282	1.2	1.2	7.26	18.8		8.02	7.64

1. Concentrations in mg/L.

2. \* = near detection limit.

3. Detection limits for analytes that were never detected are given in Table 1(e).

4. † = pH measured by Battelle technicians.

5. Except for C. Kirkland, lab pH values after May 1993 were measured on samples collected without headspace.

6. For 1993–1994 monitoring of PM-19, PM-20, PM-38, and OM-40, flow cells were not used for measuring T, Eh, or pH.

7. Where ZoBell solution was unavailable, the theoretical Eh of the ZoBell solution was used to calculate ground-water Eh.

Table 1(e). Detection limits (in mg/L) for solutes not detected in ground water.

Species	1991 samples	1992 samples	1993 samples	1994 samples
V	0.04	0.04	0.04	0.04
Ti	0.08/0.09	0.09	0.09	0.5
Mo	0.05/0.06	0.06	0.06	0.06
As	0.30/0.33	0.33	0.33	0.33
Sb	0.80/0.89	0.89	0.89	0.89
Se	0.69/0.77	0.77	0.77	0.77
Sn	0.09/0.10	0.10	0.10	0.10
Be	0.01	0.01	0.01	0.01
Zr	0.07/0.08	0.08	0.08	0.08
U	6.1/6.8	6.8	6.8	6.8
P	0.62/0.69	0.69	0.69	0.69
Ce	0.55/0.61	0.61	0.61	0.61
La	0.05/0.06	0.06	0.06	0.06
Rb	7.11/7.90	7.9	7.9	7.9
NH3	0.2	0.2	0.2	0.2

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Owing to instrument malfunction, Ti not analyzed on samples collected between Oct. 1993 and July 1994.

perched-aquifer wells within 1,000 m of Playa 1 and within 1,000 m of the C. Wink playa. Concentrations of  $\text{Cl}^-$ , which acts as a conservative tracer in dilute waters, were  $>20 \text{ mg L}^{-1}$  in 8 of 10 perched-aquifer wells but in only 3 of 23 Ogallala-aquifer wells (fig. 5). The highest  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  concentrations ( $326 \text{ mg L}^{-1}$ ,  $324 \text{ mg L}^{-1}$ , and  $56.8 \text{ mg L}^{-1}$ , respectively) occurred in well FPOP-MW-06. These elevated concentrations indicate that wastewater discharged to Playa 5 has percolated to the Ogallala-aquifer water table and is moving downgradient.  $\text{NO}_3^-$  concentrations were less than the Safe Drinking Water Act (SDWA) standard ( $44 \text{ mg L}^{-1}$  [ $10 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ ]) in all other wells, and the regional average  $\text{NO}_3^-$  concentration of  $14 \text{ mg L}^{-1}$  determined for water-supply wells by Anderson and Bernstein (1983) was exceeded in only five wells.

Among other solutes, only Si,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{F}^-$ , DO, and DOC were consistently detected, and only Si exhibited clear spatial trends. Concentrations of Si were lowest in the perched aquifers ( $10.1$  to  $15.8 \text{ mg L}^{-1}$ ), highest in the Ogallala aquifer upgradient from (that is, south and southwest of) the Pantex Plant ( $18.6$  to  $27.5 \text{ mg L}^{-1}$ ), and at intermediate values beneath the Pantex Plant ( $13.8$  to  $19.4 \text{ mg L}^{-1}$ ) (fig. 6). Si occurs predominantly as the neutral species  $\text{H}_4\text{SiO}_4^\circ$  within the pH range (7 to 8) typical of ground water in the study area. It should be noted that data from well PM-106 are suspect because the measured pH (9.88) was unusually high, perhaps because of contamination by cement during well construction (Lin-Hua and Atkinson, 1991). Traces of Fe, Zn, Mn, and Ni, which were detected in a minority of onsite and offsite wells, may be artifacts of well-casing corrosion. Cr concentrations as high as  $1.45 \text{ mg L}^{-1}$  (compared with the SDWA standard of  $0.05 \text{ mg L}^{-1}$ ) in well PM-20 are consistent with evidence of perched-aquifer contamination in adjoining monitoring wells (Environmental Science and Engineering, 1993; Woodward-Clyde, 1993; Radian Corporation, 1994). Synthetic organic compounds were not detected in either of the perched-aquifer wells sampled for them (PM-101 [Mullican and others, 1995b] and PM-106).

In both the perched and Ogallala aquifers, ground water was oxygenated and DOC concentrations were relatively invariant. DO concentrations for 28 wells ranged from 3.24 to

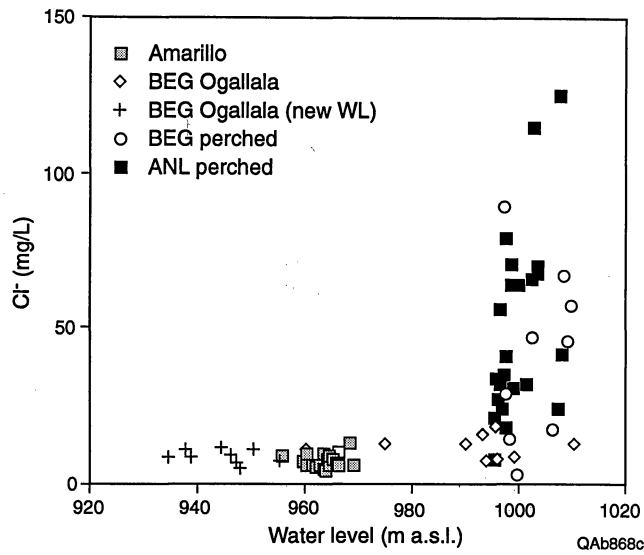


Figure 5.  $\text{Cl}^-$  concentrations (most recent values) for perched-aquifer wells sampled by BEG and by ANL (1994) and for Ogallala-aquifer wells sampled by BEG and by City of Amarillo Utilities between October 1991 and July 1994. Note that values for FPOP-series wells have not been plotted (in order to avoid using a logarithmic scale on the y-axis).

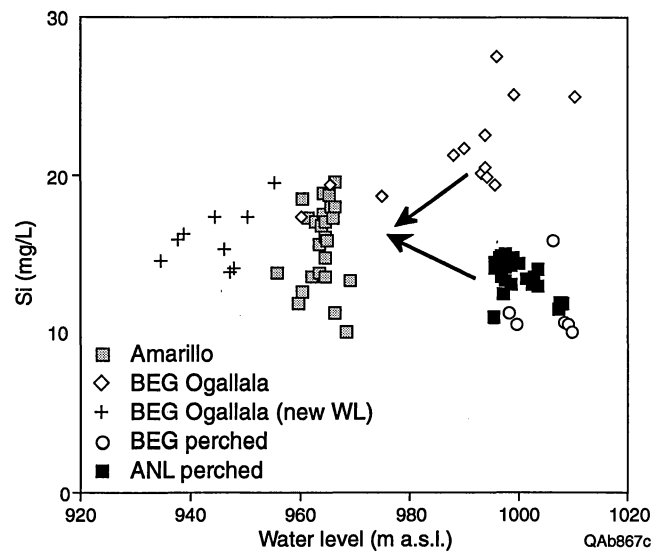


Figure 6. Si concentrations (most recent values) for perched-aquifer wells sampled by BEG and by ANL (1994) and for Ogallala-aquifer wells sampled by BEG and by City of Amarillo Utilities between October 1991 and July 1994. Note that values for FPOP-series wells have not been plotted.



13.3 mg L<sup>-1</sup> (median 7.34 mg L<sup>-1</sup>). Because H<sub>2</sub>O<sub>2</sub> was not measured, DO values could not be used to calculate Eh values (on the basis of the dissolved O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> redox couple) (Barcelona and others, 1989). However, measured values of Eh, which ranged from 190 to 530 mV, were typically less than Eh values calculated assuming equilibrium between atmospheric O<sub>2</sub> and H<sub>2</sub>O and greater than values calculated assuming equilibrium between atmospheric O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, thus also indicating oxic conditions. Although the range of DOC concentrations was 0.5 to 7.9 mg L<sup>-1</sup> in 11 wells (4 perched-aquifer and 7 Ogallala-aquifer wells), values for all but one well were ≤3.1 mg L<sup>-1</sup>, and the highest value seems spurious because total OC measured on an unfiltered split was only 1.8 mg L<sup>-1</sup>.

#### Isotopic Composition of Ground Water

As a result of isotopic fractionation during condensation, the abundances of D and <sup>18</sup>O in rain and snow vary linearly along local and global meteoric water lines (MWLs) (Craig, 1961). Our results indicate that both perched and Ogallala ground waters fall between the local winter and summer MWLs, which were calculated by least-squares linear regression on Amarillo data in Appendix 4 of Nativ (1988) (taking October 1984–March 1985 for winter and April–September 1985 for summer) (fig. 7). In the 10 perched-aquifer wells sampled, the most depleted values of δD and δ<sup>18</sup>O (−48‰ and −6.83‰, respectively) occurred in well PM-44, located between Playas 1 and 2 (table 2), and the most enriched values (−17‰ and −3.9‰) occurred adjacent to the C. Wink playa. In the Ogallala aquifer, values of δD and δ<sup>18</sup>O ranged from −41‰ and −6.8‰ beneath Sevenmile Basin, south of the Pantex Plant, to −17‰ and −2.7‰ adjacent to Playa 5. The well completed in the Quartermaster Formation exhibited the most depleted values of δD and δ<sup>18</sup>O (−53‰ and −8.0‰). δD and δ<sup>18</sup>O values obtained by different laboratories on the same samples agree within 8‰ and 0.9‰, respectively. The maximum values of δ<sup>18</sup>O in the perched and Ogallala aquifers are slightly (≤1.6‰) more enriched than the maximum values reported by ANL (1994) and Nativ (1988), respectively.

Table 2(a). Stable and radiogenic isotope data for water samples from wells sampled by BEG in 1991.

Well no.	Date	$\delta D$	$\delta^{18}O$	$\delta^{11}B$	$\delta^{13}C$ DIC (50-L)	$\delta^{13}C$ DIC (1-L)	$\delta^{34}S$	3H (TU)	14C (pmc)	e14C (pmc)
OM-39	7/22/91							-0.01		
OM-39	10/7/91	-41	-6.62		-6.7	-6.76	2.9	-0.06	38.5	0.4
OM-40	6/26/91							0.11		
OM-40	10/14/91	-42	-5.95		-7.7	-8.05	3.2	-0.06	31.3	0.6
OM-46	12/10/91	-41	-6.57	13.29	-7.8		3.3	0.13	23.9	0.4
OM-47	12/11/91	-42	-6.33	-2.14	-8.7		6.2	-0.10	32.8	0.6
OM-48	12/11/91	-41	-5.51	9.20	-8.9		4.1	0.16	28.5	0.4
PM-19	6/26/91							7.55		
PM-19	10/10/91	-38	-4.96		-12.9	-13.25	-1.0	8.71	109.4	1.1
PM-20	6/21/91							1.44		
PM-20	10/10/91	-41	-6.63		-3.1		5.2		62.6	0.6
PM-38	6/24/91							4.89		
PM-38	10/9/91	-46	-6.25		-11.5	-12.75	-2.3	5.11	90.5	1.0
PM-44	7/24/91							0.46		
PM-44	10/8/91	-48	-6.83		0.8	-4.49	3.0	0.42	63.5	0.8
PM-45	6/24/91							8.41		
PM-45	10/9/91	-35	-4.35		-9.5	-10.80	5.1	9.08	77.1	0.7
PR-2	10/11/91	-46	-6.49		-1.8	-8.09	4.1	-0.02	44.5	1.1
PR-6	8/6/91							-0.02		
PR-6	10/15/91	-43	-6.68		-7.0	-6.90	1.1	-0.02	31.2	0.4
PR-18	8/2/91							0.00		
PR-18	10/8/91	-42	-6.24		-7.2	-7.57	3.6	0.01	30.9	0.6
PR-41	8/2/91							0.11		
PR-41	10/15/91	-42	-6.04		-4.3	-8.07	3.4	0.07	35.7	0.4

1. Stable isotope abundances in ‰; precision and reference materials noted in Methods section.
2.  $\delta D$  and  $\delta^{18}O$  measured by MSL.
3. 3H concentrations measured as <0 TU are effectively 0 TU.
4. Precision of 3H analyses 0.1 TU or  $\pm 3.5$  percent (whichever is greater).
5.  $\delta^{13}C$  (DIC, 50-L) and 14C measured by Beta Analytic except for Dec. 1991 samples (Univ. of Arizona).
6. e14C = measurement error in percent modern carbon.

Table 2(b). Stable and radiogenic isotope data for water samples from wells sampled by BEG in 1992.

Well no.	Date	$\delta D$	$\delta^{18}O$	$\delta^{11}B$	$\delta^{13}C$ DIC (50-L)	$\delta^{13}C$ DOC	$\delta^{15}N$	3H (TU)	14C (pmc)	e14C (pmc)
OM-39	10/13/92			14.1		-16.7	16.5			
OM-40	10/7/92	-35	-5.7	13.3		-16.9	13.2			
OM-105	10/14/92	-33	-5.5	20.0	-7.9	-14.9	15.4	0.49	28.3	0.3
PM-19	10/8/92	-27	-4.7	17.9		-16.1	16.8	9.20		
PM-20	10/7/92			24.8		-12.6	8.0	2.32		
PM-38	10/6/92	-27	-5.0	43.4		-17.1	17.8	15.1		
PM-44	10/13/92			5.8		-13.8	19.1			
PM-45	10/6/92			-2.1		-17.7	16.0	12.8		
PM-106	10/8/92	-25	-4.3	14.7	-5.26	-18.2	13.6	0.75		
PR-2	10/14/92			19.8		-16.7	16.4			
PR-41	10/9/92			14.7		-16.7	16.5			
E. Pratt	10/13/92	-26	-4.8	7.4	-9.7	-16.1	16.1	1.45	66.9	0.8
P. Smith	10/7/92	-25	-4.6	12.8	-8.2	-16.8	19.5	44.3	84.8	0.9
C. Wink	10/5/92	-16	-3.7	18.0	-14.1	-16.8	16.4	1.84	85.0	1.0
F. Wink	10/9/92	-18	-3.7	7.5	-10.5	-16.4	14.8	5.86	69.6	0.8

1. Stable isotope abundances in ‰; precision and reference materials noted in Methods section.
2.  $\delta D$  and  $\delta^{18}O$  measured by MSL.
3. Precision of 3H analyses 0.1 TU or  $\pm 3.5$  percent (whichever is greater).
4. 3H concentrations measured as <0 TU are effectively 0 TU.
5.  $\delta^{13}C$  (DIC, 50-L) and 14C measured by Beta Analytic.
6. e14C = measurement error in percent modern carbon.

Table 2(c). Stable and radiogenic isotope data for water samples from wells sampled by BEG in 1993.

Well no.	Date	$\delta D$	$\delta^{18}O$	$\delta^{11}B$	$\delta^{13}C$ DIC (50-L)	$\delta^{13}C$ DIC (1-L)	$\delta^{13}C$ DOC	$\delta^{15}N$	$\delta^{34}S$	3H (TU)	14C (pmc)	$\epsilon^{14}C$ (pmc)
T. Bradshaw	5/12/93 (CSL)	-34 -41	-6.3 -6.8	11.70	-6.6		-12.5	16.9	-2.6	0.35	54.4	0.5
D. Gabel	5/13/93 (CSL) (UA)	-33 -40 -40	-5.9 -6.7 -6.0	9.50	-4.8		-12.1	18.8	2.5	0.03	61.9	0.6
B. Kinzer	2/3/93	-35	-5.9	12.42	-6.2		-19.9	12.6		15.6	84.6	0.7
C. Kirkland	8/11/93	-27	-5.2	11.80	-7.5				2.1	0.15	53.1	
S. McGregor	5/12/93 (CSL) (UA)	-32 -37 -38	-5.8 -6.3 -5.8	12.00	-6.4		-16.0	15.2	1.7	0.24	40.5	0.3
P. Meacham	2/4/93	-53	-8.0	20.80	-6.9				5.8		20.6	0.2
OM-40	11/22/93	-28	-6.1			-8.28						
PM-19	11/17/93	-25	-5.3			-13.95						
PM-20	10/13/93					-3.25						
PM-38	11/1/93	-19	-4.3									
PM-103	6/23/93			-0.32			-12.93	16.0		-0.03		
PR-2	10/13/93					-7.35						
PR-6	2/19/93			13.94			-17.3	16.9				
P. Smith	3/11/93									29.8		
P. Smith	11/22/93									40.2		
D. Vance	5/11/93 (CSL)	-30 -35	-5.6 -6.5	12.54	-6.0		-12.5	7.1	3.5	8.81	65.7	0.5
M. L. Vance	5/11/93 (CSL)	-32 -40	-6.0 -6.8	8.49	-5.6		-13.0	19.3	1.2	-0.12	47.0	0.4

1. Stable isotope abundances in ‰; precision and reference materials noted in Methods section.
2.  $\delta D$  and  $\delta^{18}O$  measured on May 1993 samples by MSL and (as noted) Coastal Science Labs (CSL) and Univ. of Arizona (UA).
3. 3H concentrations measured as <0 TU are effectively 0 TU.
4. Precision of 3H analyses 0.1 TU or  $\pm 3.5$  percent (whichever is greater).
5.  $\delta^{13}C$  (DIC, 50-L) and 14C measured by Beta Analytic.
6.  $\epsilon^{14}C$  = measurement error in percent modern carbon.

Table 2(d). Stable and radiogenic isotope data for water samples from wells sampled by BEG in 1994.

Well no.	Date	$\delta D$	$\delta^{18}O$	$\delta^{11}B$	$\delta^{13}C$ DIC (1-L)	$\delta^{15}N$	$\delta^{18}O$ NO3	3H (TU)
FPOP-MW-04	11/4/94	-42	-6.4					
FPOP-MW-05	6/29/94	-32	-4.7	17.92		12.9		6.69
FPOP-MW-06	6/29/94	-17	-2.7	22.20		29.0		8.37
OM-40	1/12/94				-8.23			
OM-40	7/25/94	-40	-6.5					0.02
PM-101	11/1/94							0.07
PM-101	11/1-2/94							0.26
PM-101	11/2/94							0.01
PM-19	4/11/94					19.1		
PM-19	7/27/94	-37	-6.0					
PM-20	1/11/94				-3.18		11.9	
PM-20	4/12/94					11.6		
PM-38	1/11/94						6.4	
PM-38	4/13/94					13.5		
PM-38	7/25/94	-25	-4.9					44.4
PR-2	1/12/94				-7.26			
P. Smith	1/13/94						8.2	40.4
P. Smith	4/12/94					16.6		
P. Smith	6/28/94					15.2		36.2

1. Stable isotope abundances in ‰; precision and reference materials noted in Methods section.
2.  $\delta D$  and  $\delta^{18}O$  measured by Coastal Science Labs.
3. Precision of 3H analyses 0.1 TU or  $\pm 3.5$  percent (whichever is greater).

In contrast to  $\delta D$  and  $\delta^{18}O$ , values of  $\delta^{13}C$  (DIC) in the perched aquifers were most depleted ( $\leq -12.75\text{‰}$ ) adjacent to Playa 1 and the C. Wink playa and most enriched ( $\geq -4.49\text{‰}$ ) in wells PM-44 and PM-20 (south of Playa 1). The occurrence of relatively enriched  $\delta D$  and  $\delta^{18}O$  and relatively depleted  $\delta^{13}C$  in the perched aquifers adjacent to playas, and relatively depleted  $\delta D$  and  $\delta^{18}O$  and relatively enriched  $\delta^{13}C$  in interplaya areas, is consistent with the findings of ANL (1994). No systematic spatial trends are evident for  $\delta^{13}C$  (DIC) in the Ogallala aquifer (range  $-10.5\text{‰}$  to  $-4.8\text{‰}$ ).  $\delta^{13}C$  (DOC) values in the perched and Ogallala aquifers are generally more depleted but fall in a narrower range ( $-19.94\text{‰}$  to  $-12.10\text{‰}$ ); the most enriched values occurred in interplaya perched-aquifer wells (PM-20 and -44) and in the Ogallala aquifer beneath Sevenmile Basin.

In contrast to Fryar and Mullican (1993), we report  $\delta^{13}C$  (DIC) values measured by MSL on  $SrCO_3$  from 500-mL water samples as well as  $\delta^{13}C$  (DIC) measured by Beta Analytic and the Laboratory of Isotope Geochemistry on  $SrCO_3$  precipitated in carboys for  $^{14}C$  analyses (table 2). For 7 of 10 wells where both 500-mL and carboy samples were analyzed, the two sets of  $\delta^{13}C$  (DIC) values agree within  $1.4\text{‰}$ ; differences  $>1.4\text{‰}$  may have resulted from incomplete fractionation of  $\delta^{13}C$  during  $SrCO_3$  precipitation in carboys. Unlike Fryar and Mullican (1993), we do not report values of  $\delta^{13}C$  of total dissolved C, which were measured on samples collected for  $\delta^{13}C$  (DOC) and  $\delta^{15}N$ , because we think freezing caused exsolution of  $CO_2$  and biased the results.

Values of other stable isotopes ( $\delta^{11}B$ ,  $\delta^{15}N$ ,  $\delta^{18}O$  of  $NO_3^-$ , and  $\delta^{34}S$ ) do not seem to show systematic spatial variations in either the perched aquifers or the Ogallala aquifer (table 2).  $\delta^{11}B$  values ranged from  $-2.14\text{‰}$  to  $43.4\text{‰}$  and did not appear to vary with B or  $Cl^-$  concentrations, which suggests that wastewater-derived B is negligible in ground water in the study area. Despite the variety of land-use settings and prospective sources of N, values of  $\delta^{15}N$  were fairly narrowly clustered (22 of 25 samples between  $12.5\text{‰}$  and  $19.5\text{‰}$ ).  $\delta^{15}N$  appears to vary inversely with  $NO_3^-$  concentration (fig. 8), although the most enriched value of  $\delta^{15}N$  and the highest  $NO_3^-$  concentration both occurred in well FPOP-MW-06 (adjacent to Playa 5).  $\delta^{18}O$  of  $NO_3^-$  values were determined for only three wells (PM-38, PM-20, and P. Smith) and were  $3.2\text{‰}$ ,  $11.9\text{‰}$ , and

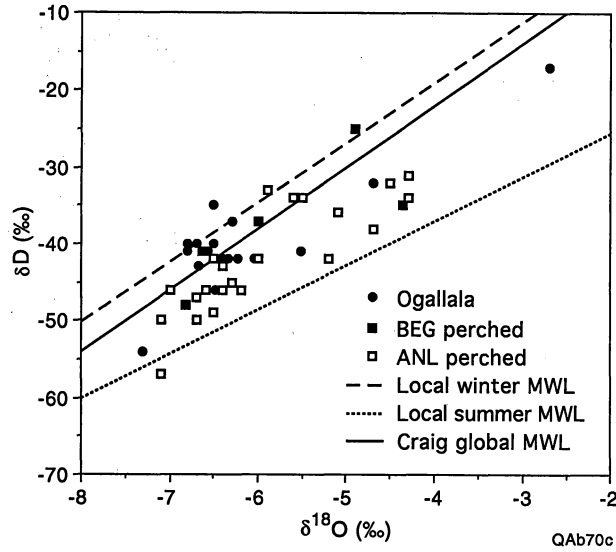


Figure 7. Relative abundances of deuterium ( $\delta D$ ) in ground water plotted versus relative abundances of oxygen-18 ( $\delta^{18}O$ ) (‰ standard mean ocean water [SMOW]). Note that 1992 BEG data, for which  $\delta D$  values may be in error, are not plotted. Local meteoric water lines (MWLs) calculated using data from Appendix 4 of Nativ (1988) (October 1984–March 1985 for winter, April 1985–September 1985 for summer). Global MWL of Craig (1961) and perched-aquifer data of ANL (1994) plotted for reference.

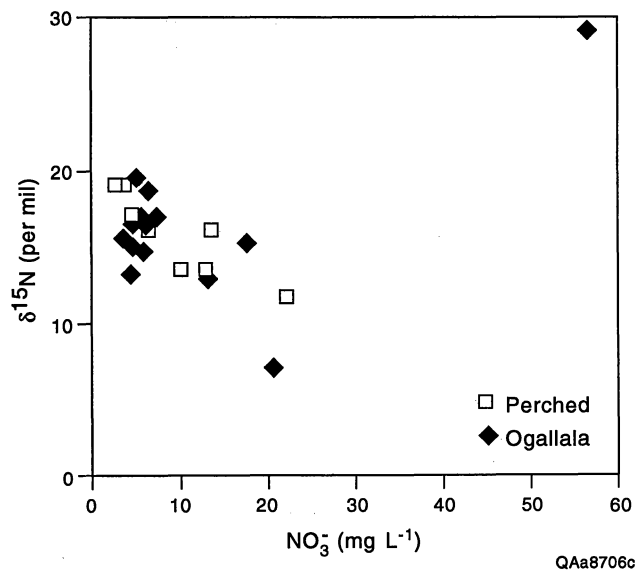


Figure 8. Nitrogen-15 abundances ( $\delta^{15}N$ ) as a function of  $NO_3^-$  concentrations in the perched and Ogallala aquifers.

8.2‰, respectively. The  $\delta^{34}\text{S}$  value for the well in the Quartermaster Formation falls in the range of values for the perched and Ogallala aquifers (-2.6‰ to +6.2‰), which in turn fall within the range observed regionally in the Ogallala aquifer by Nativ (1988) (-12.7‰ to +9.5‰).

Because of the likelihood of mixing of waters of different ages in unconfined aquifers (Dutton, 1995),  $^3\text{H}$  and  $^{14}\text{C}$  provide bounds upon, rather than absolute, ground-water ages. Those radioisotopes decay at different time scales, with half-lives of 12.43 yr for  $^3\text{H}$  (Mann and others, 1982) and 5,730 yr for  $^{14}\text{C}$  (Plummer and others, 1994). Prior to 1952,  $^3\text{H}$  concentrations in precipitation were probably 3 to 10 TU (Hem, 1985; Robertson and Cherry, 1989). From 1952 to 1963, atmospheric nuclear testing by the U.S. and the U.S.S.R. resulted in much greater  $^3\text{H}$  concentrations in precipitation, with a peak of 10,000 TU in the U.S. in 1963 (International Atomic Energy Agency, 1969). Since 1963,  $^3\text{H}$  concentrations have been declining gradually with rainout and decay toward pre-1952 levels. In this study, ground waters with  $^3\text{H}$  concentrations  $\geq \sim 1$  TU contain a measurable component of post-1952 recharge that can be used as a tracer of water movement during the operation of the Pantex Plant.

$^3\text{H}$  concentrations in perched aquifers are highest adjacent to and south of Playa 1 ( $\geq 8.71$  TU, maximum 44.4 TU for PM-38) (fig. 9; table 2). In the Ogallala aquifer, levels  $\geq 5.86$  TU have been detected in six wells south and southwest of the Pantex Plant, including the two downgradient monitoring wells (FPOP-MW-05 and -06) closest to Playa 5. In this area, perched aquifers have not been identified, and the shallowness of the Ogallala water table is comparable to that of the perched water tables to the north. Trends in  $^{14}\text{C}$  (fig. 10) are similar to those of  $^3\text{H}$ ; the highest  $^{14}\text{C}$  abundances (85.0 to 109.4 percent modern C [pmc]) and the youngest waters in the perched aquifers occurred adjacent to Playa 1 and the C. Wink playa. In the Ogallala aquifer,  $^{14}\text{C}$  abundances declined from  $\geq 53.1$  pmc south of Sevenmile Basin and southwest of Playa 5 to 23.9 to 44.5 pmc beneath the Pantex Plant.  $^{14}\text{C}$  was 20.6 pmc in the ground-water sample from the Quartermaster Formation.



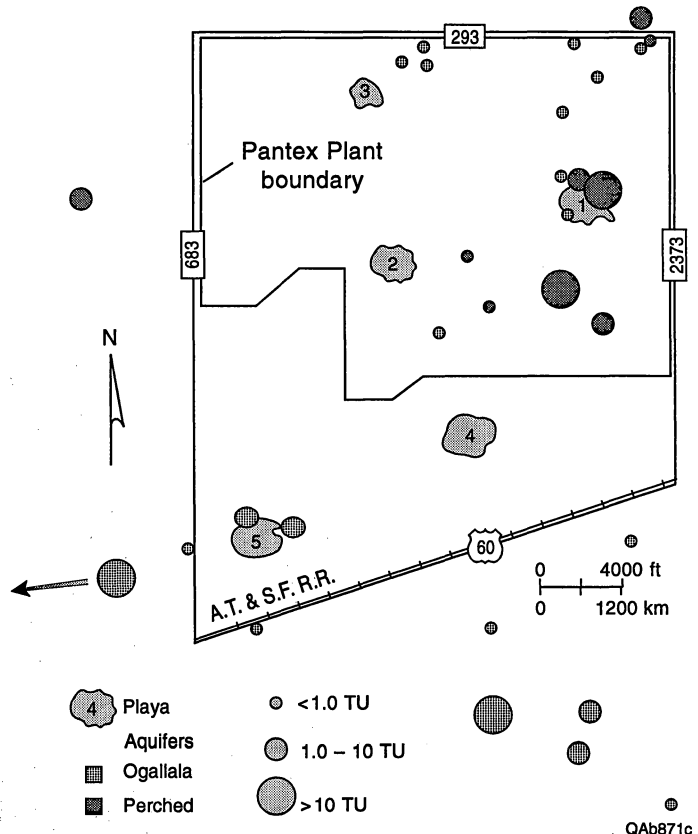


Figure 9. Tritium ( $^3\text{H}$ ) concentrations in the perched and Ogallala aquifers.

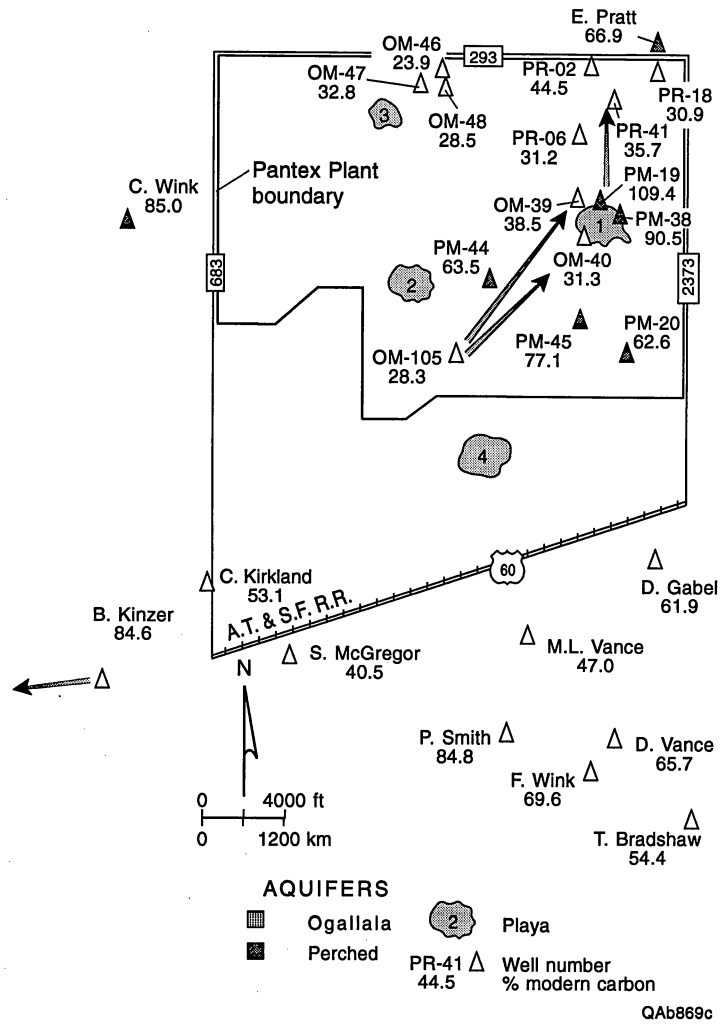


Figure 10. Carbon-14 ( $^{14}\text{C}$ ) abundances in the perched and Ogallala aquifers. Arrows show Ogallala-aquifer flow paths for which plausible-reaction path models were obtained.

## Temporal Variations in Water Chemistry

Repeated sampling (five to six times) between 1991 and 1994 indicated pronounced variations in solute concentrations in three perched-aquifer wells but not in three Ogallala-aquifer wells. In PM-19 and PM-20,  $\text{Cl}^-$  concentrations measured by BEG increased twofold to threefold; Cr concentrations in PM-20 increased by more than an order of magnitude (figs. 11 and 12). These trends are borne out by results of monthly to bimonthly sampling by Battelle Pantex (1992, 1993, 1994b, 1995) from 1991 to 1994. In particular, least-squares linear regression fits to plots of  $\text{Cl}^-$  concentration versus time give  $r^2$  values of 0.91 for PM-19 and 0.81 for PM-20;  $r^2$  for Cr concentration versus time for PM-20 is 0.70. Other parameters and other wells do not exhibit such clear trends, but the ranges in  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations in PM-38 (fig. 13) were greater than in OM-40, PR-2, and the P. Smith well (figs. 14 through 16). It should be noted that samples collected by Battelle Pantex were unfiltered, whereas BEG data represent filtered samples. However, except for  $\text{SO}_4^{2-}$ , concentrations were not consistently different between the two data sets; for reasons that are unclear,  $\text{SO}_4^{2-}$  concentrations for the filtered samples from PM-19, PM-20, PM-38, and OM-40 tended to be lower than those of Battelle Pantex.

Repeated isotopic analyses, although fewer, also indicated pronounced variations in perched-aquifer wells but not in Ogallala-aquifer wells. As mentioned previously, some differences in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  probably result from interlaboratory variability. However, increases of 21‰ in  $\delta\text{D}$  and 1.4‰ in  $\delta^{18}\text{O}$  in PM-38 between October 1991 and July 1994 indicate substantial temporal variability, contrary to the assertions of ANL (1994, p. 4–9). This variability, which is consistent with major-ion data and with water-level fluctuations during the same period in PM-19, PM-20, and PM-38 (Mullican, 1995), indicates movement of water through the perched aquifer adjacent to Playa 1. With the exception of PM-44, repeated sampling of perched-aquifer wells indicated systematic increases in  $^3\text{H}$  over periods of 3 mo to 3 yr (fig. 17). In PM-38,  $^3\text{H}$  concentrations increased from 4.71 TU in June 1991 to 44.4 TU in July 1994. In contrast,  $^3\text{H}$  concentrations for

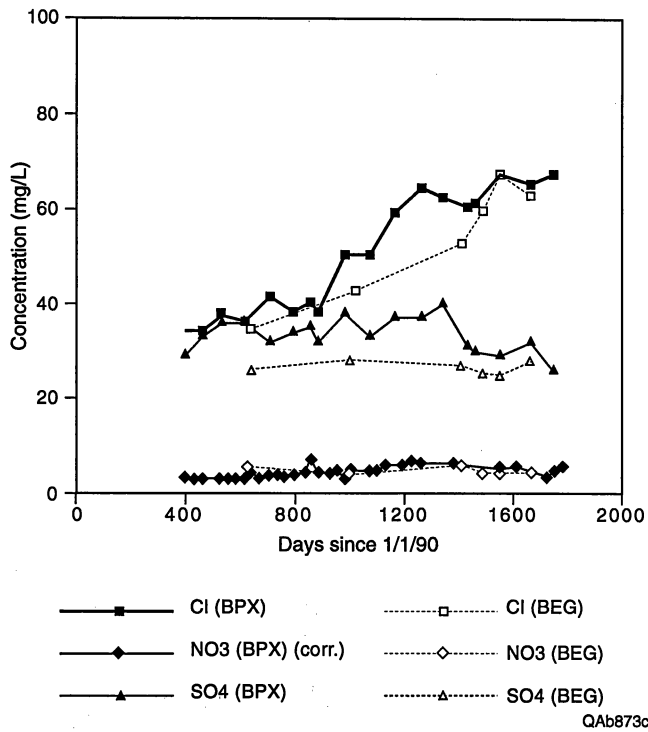


Figure 11. Chloride, nitrate, and sulfate concentrations obtained between 1991 and 1994 by Battelle Pantex (BPX) and by BEG in well PM-19. Note that some BPX nitrate concentrations, which were apparently reported as nitrate-nitrogen, have been corrected prior to plotting.

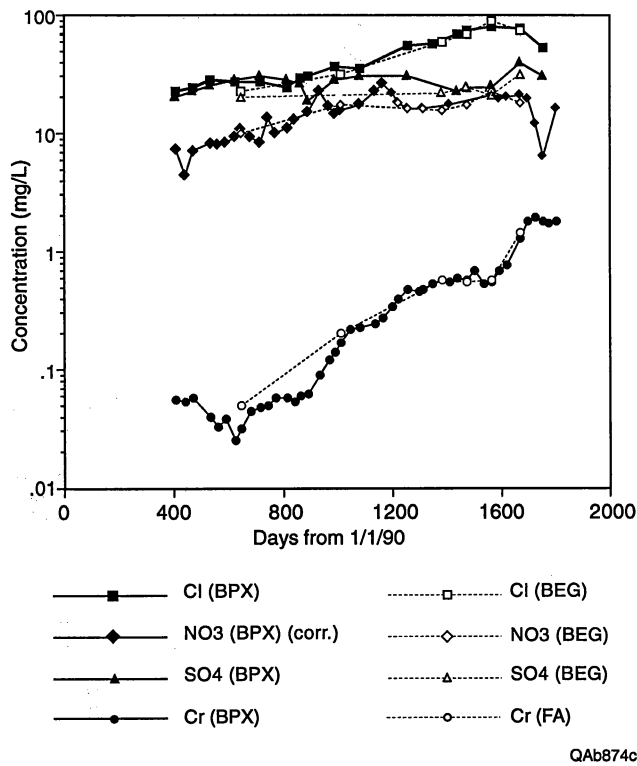
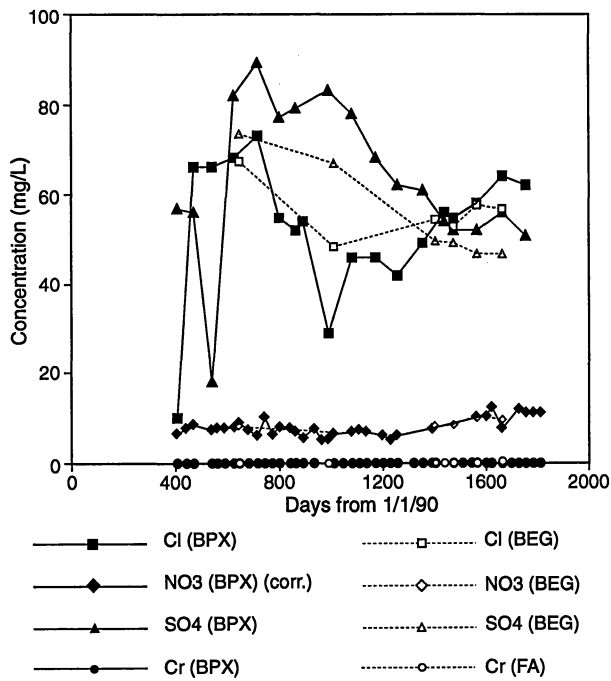
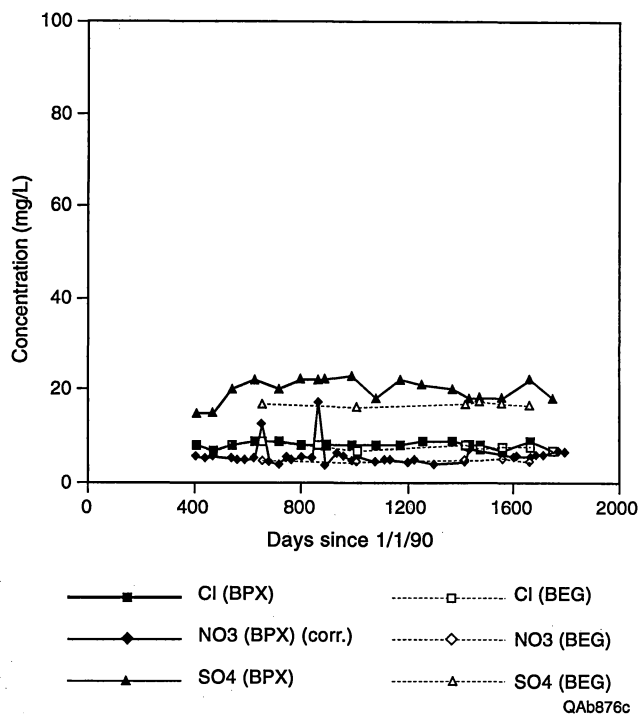


Figure 12. Chloride, nitrate, sulfate, and chromium concentrations (log scale) obtained between 1991 and 1994 by Battelle Pantex (BPX) and by BEG in well PM-20. Note that some BPX nitrate concentrations, which were apparently reported as nitrate-nitrogen, have been corrected prior to plotting.



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Figure 13. Chloride, nitrate, sulfate, and chromium concentrations obtained between 1991 and 1994 by Battelle Pantex (BPX) and by BEG in well PM-38. Note that some BPX nitrate concentrations, which were apparently reported as nitrate-nitrogen, have been corrected prior to plotting.



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Figure 14. Chloride, nitrate, and sulfate concentrations obtained between 1991 and 1994 by Battelle Pantex (BPX) and by BEG in well OM-40. Note that some BPX nitrate concentrations, which were apparently reported as nitrate-nitrogen, have been corrected prior to plotting.

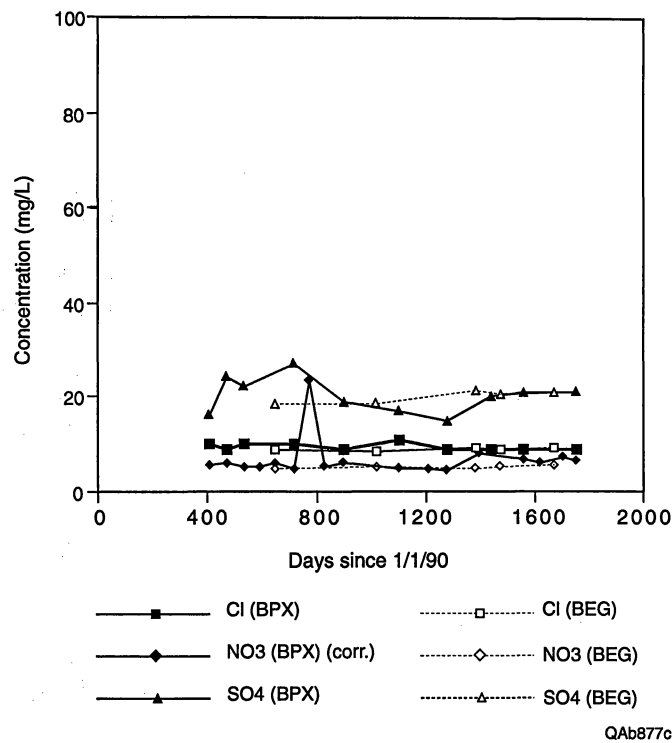


Figure 15. Chloride, nitrate, and sulfate concentrations obtained between 1991 and 1994 by Battelle Pantex (BPX) and by BEG in well PR-2. Note that some BPX nitrate concentrations, which were apparently reported as nitrate-nitrogen, have been corrected prior to plotting.

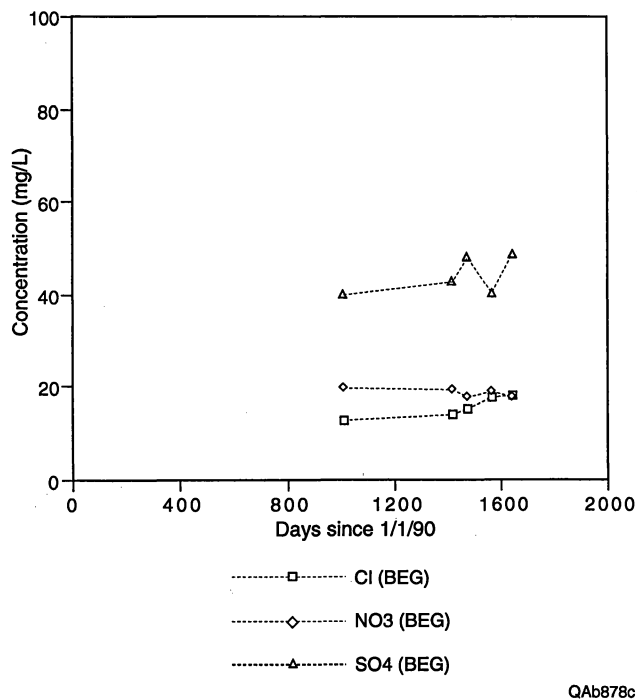
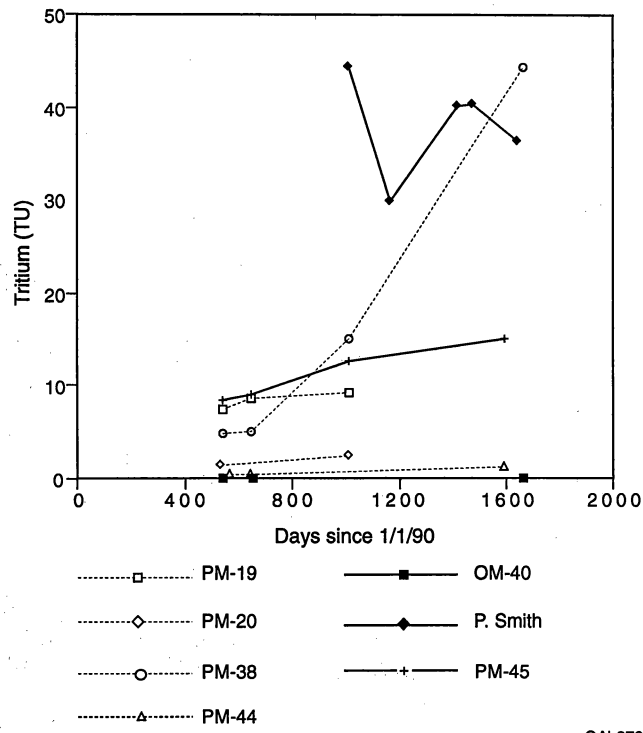


Figure 16. Chloride, nitrate, and sulfate concentrations obtained between 1992 and 1994 by BEG in the P. Smith well.



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Figure 17. <sup>3</sup>H concentration profiles in wells sampled over multiyear periods by BEG and ANL (1994 data for PM-44 and PM-45).

resampled wells in the Ogallala aquifer remained at or below their initial values; in summer 1994,  $^3\text{H}$  concentrations were 0.02 TU in OM-40 and 36.2 TU in the P. Smith well (table 2).

### Sediment and Soil-Gas Compositions

Various aspects of vadose-zone chemistry at the Pantex Plant are being addressed by other investigators (extractable  $\text{Cl}^-$  and  $^3\text{H}$  by Scanlon [1995]; extractable ions, sediment OC, soil-gas chemistry, and isotopic compositions of sediment and soil gas by Bennett and others [1995]). We will focus on extractable  $\text{NO}_3^-$ , counts of denitrifying and  $\text{NO}_3^-$ -reducing bacteria, clay mineralogy, CEC, exchangeable cations,  $\delta^{13}\text{C}$  of pedogenic carbonate, and  $\delta^{15}\text{N}$  of soil gas.

Extractable  $\text{NO}_3^-$  concentrations in playa basin sediments were typically greatest within 1 m of land surface, with secondary peaks at greater depths. The presence of multiple  $\text{NO}_3^-$  peaks with depth in sediment cores can be explained by stratigraphic heterogeneity, in which multiple flowpaths (such as individual macropores) are intersected by a borehole; by a history of discrete recharge pulses; or by changing  $\text{NO}_3^-$  concentrations in recharge. Within 3.4 m of land surface,  $\text{NO}_3^-$  concentrations in the annulus of Playa 5 exceeded those in the annulus of the TDCJ playa; within 1.4 m of land surface,  $\text{NO}_3^-$  concentrations in the floor of Playa 5 exceeded those in the floor of the Finley playa (fig. 18). Maximum  $\text{NO}_3^-$  concentrations in each playa ranged from  $7.45 \text{ mg kg}^{-1}$  at 0.1-m depth in borehole no. 3 at the Finley playa to  $719.7 \text{ mg kg}^{-1}$  at 0.6-m depth in borehole no. 8 at Playa 5, on the annulus adjacent to the old sewer outfall.  $\text{NO}_3^-$  concentrations decrease greatly with distance from the outfall; the maximum concentration in borehole no. 7 in the floor of Playa 5 was only  $24.5 \text{ mg kg}^{-1}$ .  $\text{NO}_3^-$  concentrations in Playa 5 "bottom sludge" in October 1992, two months before wastewater discharge ceased, were below detection limit ( $1.639$  to  $2.016 \text{ mg kg}^{-1}$ ) in two samples and were  $271.9 \text{ mg kg}^{-1}$  in a third sample (City of Amarillo Utilities, unpublished data, 1992).

At a given depth, MPNs of denitrifying bacteria in borehole no. 8 at Playa 5 were greater than MPNs of denitrifying bacteria in borehole no. 19 at Pantex Lake by factors of approximately 10 to  $>1,000$  (fig. 19). Maximum MPNs of denitrifiers occurred at depths  $\leq 2.5 \text{ m}$  and are  $>100,000$



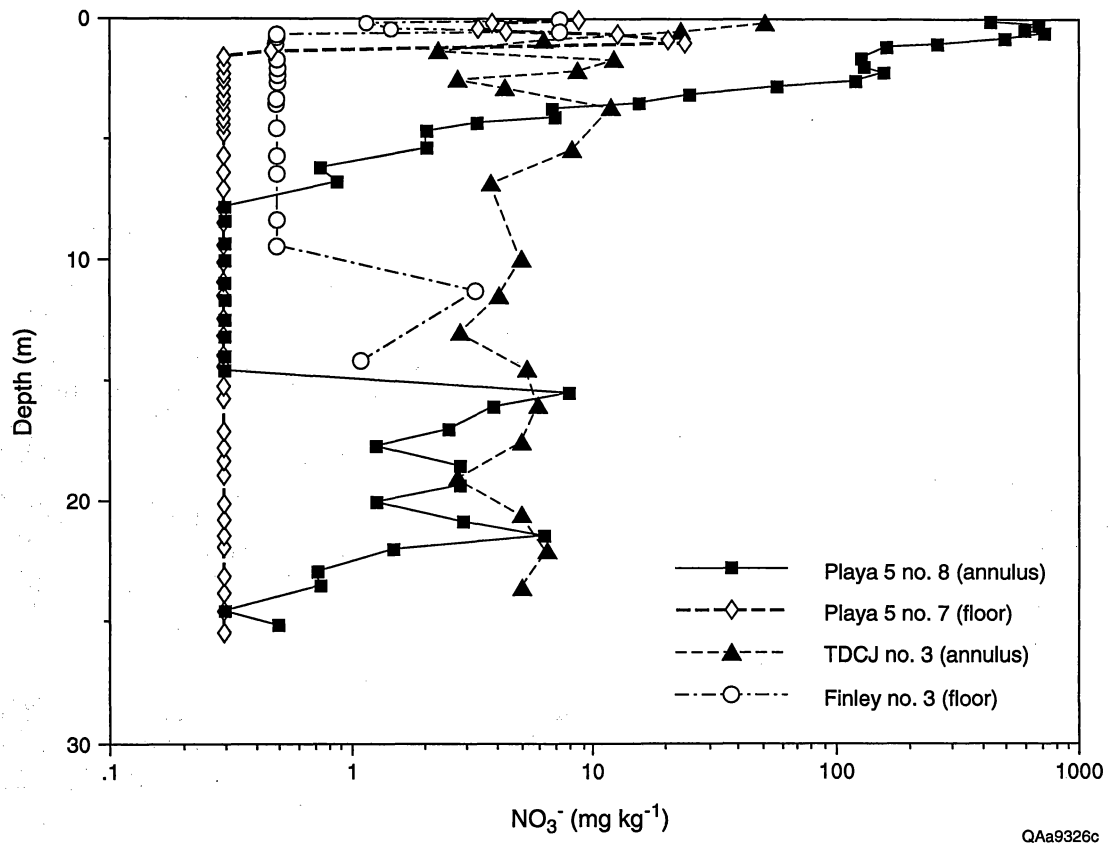
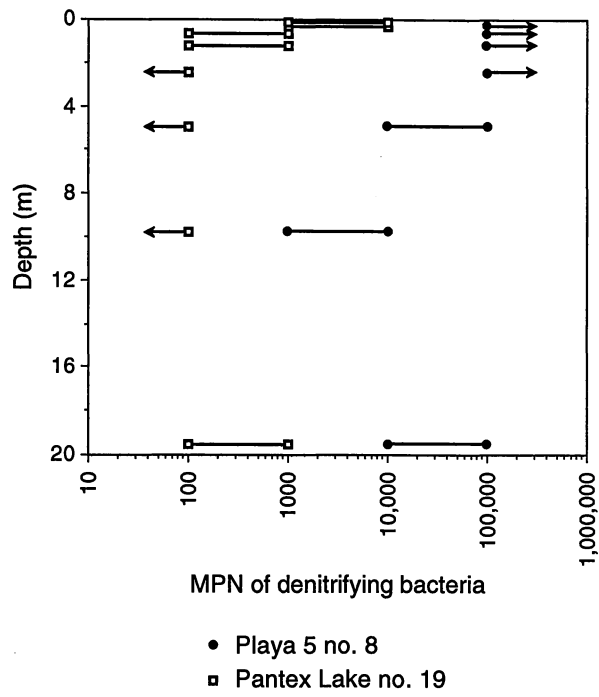


Figure 18. Extractable nitrate concentrations in playa sediment samples as a function of depth in selected boreholes. Geomorphic setting of each borehole is given in parentheses. Concentrations reported as below detection limit are plotted as equal to detection limit.

bacteria per gram of sediment in Playa 5 no. 8 and 1,000 to 10,000 bacteria per gram of sediment in Pantex Lake no. 19. In contrast, at depths <4.9 m, counts of NO<sub>3</sub><sup>-</sup>-reducing bacteria other than denitrifiers were greater in Pantex Lake no. 19 than in Playa 5 no. 8 (fig. 20). Maximum MPNs of NO<sub>3</sub><sup>-</sup> reducers (>100,000 per gram of sediment) occurred at depths ≤0.3 m in Pantex Lake no. 19 and ≥9.8 m in Playa 5 no. 8.

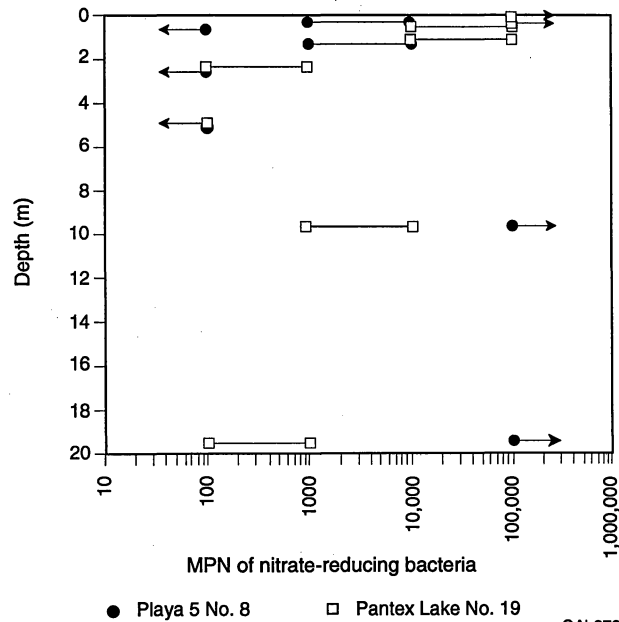
Determinations of clay mineralogy, CEC, exchangeable cations, and δ<sup>13</sup>C of pedogenic carbonate were made on core samples from wells OM-105 and PM-106. In OM-105, samples were collected at various depths within the Blackwater Draw Formation, within the caprock caliche, within the perching strata, and within the Ogallala aquifer; in PM-106, samples were taken across a 0.655-m transect across the caprock caliche. Only montmorillonite (smectite), illite, and kaolinite (listed in typical order from most to least abundant) were detected by XRD. The order of abundance was illite > montmorillonite > kaolinite in samples from the caprock caliche in OM-105; kaolinite predominated in the 1- to 2-μ fraction in the perching strata. Samples from the Blackwater Draw Formation in OM-105 yielded CEC values ranging from 11.67 to 30.42 meq 100 g<sup>-1</sup> and total concentrations of major exchangeable cations (TEC) ranging from 22.92 to 32.13 meq 100 g<sup>-1</sup> (table 3a). The discrepancy between CEC and TEC values may result from differences in extractions; exchangeable Ca<sup>2+</sup> may be overestimated in calcic soils (Thomas, 1982). Ca<sup>2+</sup> was the dominant cation measured in supernatant, followed by Mg<sup>2+</sup> and, to a lesser extent, K<sup>+</sup> and Na<sup>+</sup>. δ<sup>13</sup>C of pedogenic carbonate ranged from -0.31 to -5.70‰, with the lightest values (≤-4.96‰) occurring within the caprock caliche (table 3b).

Values of δ<sup>15</sup>N of soil-gas N<sub>2</sub> ranged from 0.0‰ (equivalent to δ<sup>15</sup>N of atmospheric N<sub>2</sub>) for one sample in the annulus of the TDCJ playa to -4.6‰ in the floor of the TDCJ playa (table 4). The range in δ<sup>15</sup>N of soil-gas N<sub>2</sub> was narrower in Playa 1 (-0.2 to -1.2‰) and in Playa 3 (-0.9 to -3.4‰), although the values from Playa 3 represent only two sampling points. The overall median value for all three playas was -0.8‰.



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Figure 19. Most probable number (MPN) of denitrifying bacteria (given as order-of-magnitude range) in sediment samples from borehole no. 8, Playa 5, and borehole no. 19, Pantex Lake. Arrows pointing left and right depict samples having <100 or >100,000 bacteria, respectively.



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Figure 20. Most probable number (MPN) of nitrate-reducing bacteria (given as order-of-magnitude range) in sediment samples from borehole no. 8, Playa 5, and borehole no. 19, Pantex Lake. Arrows pointing left and right depict samples having <100 or >100,000 bacteria, respectively.

Table 3(a). Concentrations of exchangeable cations and exchange capacity (in meq/100 g).

Sample no.	Na	K	Mg	Ca	TEC	CEC
PTX2:0.0/0.5	0.44	0.70	6.02	24.97	32.13	30.42
PTX2:8.0/0.5	0.86	0.59	3.87	25.05	30.37	23.01
PTX2:25/1.3	0.15	0.41	3.00	19.36	22.92	11.67
PTX2:48/2.0	0.08	1.01	10.63	19.93	31.65	24.99

Table 3(b).  $\delta^{13}\text{C}$  of pedogenic carbonate.

Sample no.	$\delta^{13}\text{C}$ (‰)
PTX2:8.0/0.5	-0.31
PTX2:25.0/1.3	-1.15
PTX2:80.0/0.25a	-5.68
PTX2:80.0/0.25b	-5.70
PTX2:80.0/0.25c	-5.65
PTX3:64/1.85	-3.67
PTX3:64/2.0a	-5.07
PTX3:64/2.0b	-5.04
PTX3:64/2.0c	-4.96
PTX3:64/4.0	-4.25

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The sample number represents the boring and the depth of the top of the sample (for example, PTX2:8.0/0.5 = core from OM-105 at 8.5-ft depth; PTX3:64/1.85 = core from PM-106 at 65.85-ft depth).

Table 4. Abundances of nitrogen-15 in soil-gas samples from Playa 1, Playa 3, and the TDCJ playa.

<b>Gas well no.</b>	<b>Sample depth (m)</b>	<b><math>\delta^{15}\text{N}</math> (‰)</b>
<b>P1-02</b>	-2.2	-0.5
<b>P1-04</b>	-2.1	-0.4
<b>P1-06</b>	-4.5	-0.8
<b>P1-07</b>	-1.2	-1.2
<b>P1-09</b>	-4	-0.2
<b>P1-10</b>	-0.9	-0.3
<b>P3-1-01</b>	-2.8	-3.2
<b>P3-1-02</b>	-3	-0.9
<b>T1-01</b>	-1.5	-0.4
<b>T1-01</b>	-3	0
<b>T1-04</b>	-7.3	-4.6
<b>T9-02</b>	-3.2	-1.2
<b>T9-03</b>	-2.3	-0.1
<b>T11-01</b>	-1.3	-1
<b>T11-01</b>	-3.1	-0.8

## DISCUSSION

### Sources and Timing of Recharge

Enriched  $\delta D$  and  $\delta^{18}O$  values in ground water beneath playas and mounding of the perched water table beneath Playa 1 and the next playa north (Fryar and Mullican, 1995b) provide evidence for focused recharge. Nativ (1988) and ANL (1994) attributed enrichment to partial evaporation during recharge, consistent with our observation that  $Cl^-$  concentrations in ground water are greater than in rainwater. However, the coincidence of our  $\delta D$  versus  $\delta^{18}O$  plots with the calculated local MWL suggests that evaporation during recharge is minimal. Surficial evaporation typically causes such plots to be subparallel to the MWL (Gat and Tzur, 1967), and evaporation during infiltration typically displaces such plots downward but parallel to the MWL (Allison and others, 1984), neither of which was observed here. The apparent discrepancy between  $Cl^-$  and  $\delta D$  and  $\delta^{18}O$  has been addressed by Wood and Sanford (1995), who hypothesized that D and  $^{18}O$  might be contributed primarily by recharge moving along preferential pathways, whereas the bulk of  $Cl^-$  might move slowly through the matrix.

Episodic recharge, another plausible mechanism, does not require solute fluxes to be distinct from water fluxes.  $Cl^-$  could be concentrated in near-surface sediments by evapotranspiration following short or low-intensity precipitation events, particularly if runoff from playa basin slopes is not generated. In our study area,  $Cl^-$  concentrations in interplaya and playa sediments unaffected by return flow (Scanlon and others, 1994) were commonly higher than in ground water unaffected by return flow ( $\leq 14.4 \text{ mg L}^{-1}$ ). Subsequently,  $Cl^-$  could be leached to ground water by flushing of accumulated salts from near-surface sediments during prolonged or high-intensity rainfall events. Although Wood and Sanford (1995) assumed that  $Cl^-$  concentrations in runoff equal those in rainfall, no data were presented to support that assumption. In our scenario, runoff and infiltration would have to be sufficiently rapid ( $\geq \sim 10 \text{ mm hr}^{-1}$  infiltration) to minimize evaporative fractionation of D and  $^{18}O$  (Gat and Tzur, 1967). Ramsey and Rainwater (1995) determined

Stage II infiltration rates (transitional to steady state) of 1.2 to 1450 mm hr<sup>-1</sup> during double-ring infiltrometer tests in Playas 2, 3, and 4 at the Pantex Plant.

Elevated levels of <sup>3</sup>H and <sup>14</sup>C indicate younger waters and focused recharge beneath ditches and playas. Although the source of <sup>3</sup>H cannot be proven, our results and those of ANL (1994) (with one exception: 60 TU for PTX08-1009) fall within the range of 0 to 45 TU (corrected for decay to 1994) observed regionally in the Ogallala aquifer by Nativ (1988). These results suggest that <sup>3</sup>H observed in most wells on or near the Pantex Plant likely originated from fallout from atmospheric testing outside of Texas. The statistical significance associated with increases in <sup>3</sup>H concentrations in perched-aquifer monitoring wells sampled by BEG and ANL has not been assessed. Increases in <sup>3</sup>H might also be ascribed to the arrival of the 1963 atmospheric-testing peak, smeared by hydrodynamic dispersion, at the water table, but the presence of post-1968 wastewater in the Ogallala aquifer beneath Playa 5 (at depths comparable to perched aquifers onsite) suggests the 1963 testing peak could have already arrived in the perched aquifer. It should be stressed that <sup>3</sup>H concentrations in the perched aquifer wells (up to 60 TU) are well below the drinking-water standard of 6,300 TU ( $2.0 \times 10^{-5}$  μCi mL<sup>-1</sup>). These <sup>3</sup>H analyses are primarily of interest in tracing water movement. Furthermore, additional sampling and analyses by enrichment and low-level counting are needed to monitor <sup>3</sup>H concentrations.

Artificially enhanced recharge is also evidenced by perched-aquifer Cl<sup>-</sup> concentrations that are typically greater than background concentrations in the Ogallala aquifer. For most wells in which contaminants or elevated levels of Cl<sup>-</sup> were detected, <sup>3</sup>H concentrations (including data of ANL [1994]) were >1 TU, indicating mixing of water pumped from the Ogallala aquifer (containing little or no <sup>3</sup>H) with modern, tritiated precipitation. Ramsey and Rainwater (1995) measured sustained infiltration rates of 6.7 mm hr<sup>-1</sup> for the Zone 12 West Ditch and ~10 mm hr<sup>-1</sup> for the Zone 12 East Ditch, to which most wastewater was discharged, leading to Playa 1 at the Pantex Plant. These results may be consistent with the apparent lack of evaporative fractionation of D and <sup>18</sup>O in

underlying perched ground water. Elevated levels of  $\text{Cl}^-$  may have resulted from artificial leaching of  $\text{Cl}^-$  accumulated in interplaya soils or from industrial processes at the Pantex Plant rather than from a second cycle of evaporation.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of perched ground water beneath ditches probably reflect water pumped from the Ogallala aquifer rather than the diffuse infiltration of summer and winter precipitation suggested by ANL (1994). In the absence of information to the contrary, we assume industrial processes did not fractionate D and  $^{18}\text{O}$ .  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values in the perched aquifer beneath Playa 1 are more depleted than those in the perched aquifer adjacent to the C. Wink playa, which has not been impacted by return flow; this suggests mixing of return flow and naturally recharged ground water beneath Playa 1.

Vadose-zone hydraulic and hydrochemical data from the vicinity of the Pantex Plant indicate that negligible natural recharge currently occurs in interplaya settings (Aronovici and Schneider, 1972; Scanlon and others, 1994). Wells PM-44, PM-101, PTX10-1007, and PTX10-1008 (the latter two sampled by ANL but not by BEG), which are located in the main perched aquifer between playas and away from ditches, are currently uncontaminated and have near-background  $\text{Cl}^-$  and  $^3\text{H}$  concentrations ( $\leq 21 \text{ mg L}^{-1}$  and  $\leq 1.2 \text{ TU}$ , respectively). Perched ground water in interplaya areas may have been naturally recharged by diffuse infiltration during cooler, wetter paleoclimatic conditions. Such conditions have been invoked by Scanlon and others (1994) as a possible explanation for decreased  $\text{Cl}^-$  concentrations below the evapotranspirative peak in interplaya boreholes. However,  $\delta\text{D}$  and  $\delta^{18}\text{O}$  provide only equivocal evidence of interplaya recharge under differing paleoclimatic conditions because the most depleted values in perched ground water include both uncontaminated and contaminated interplaya wells (ANL, 1994). Dating uncontaminated perched ground water in interplaya areas is problematic; although the lowest  $^{14}\text{C}$  value in the perched aquifers (63.5 pmc) was obtained for PM-44, that value is uncorrected for the effects of reactions involving OC,  $\text{CO}_2$ , or  $\text{CaCO}_3$ .  $^3\text{H}$  concentrations  $> 0.1 \text{ TU}$  in PM-44 and PTX10-1007 suggest a limited contribution from recharge within the past 60 to 80 yr, but whether that contribution results from diffuse infiltration or lateral mixing with artificially recharged ground water is uncertain.



Focused recharge to the Ogallala aquifer upgradient from the Pantex Plant is associated in part with wastewater or with older wells that may be susceptible to leakage. The five Ogallala-aquifer wells with the highest  $^3\text{H}$  concentrations ( $>6$  TU) also have the highest  $\text{Cl}^-$  and  $\text{NO}_3^-$  concentrations ( $>15$  and  $>11$   $\text{mg L}^{-1}$ , respectively). Two of these wells (FPOP-MW-05 and -06) are downgradient from Playa 5; a third (P. Smith) is downgradient from a man-made pond on rangeland. However, comparison of  $\text{Cl}^-$  profiles from playa and interplaya boreholes in Sevenmile Basin (B. R. Scanlon, Bureau of Economic Geology, unpublished data, 1993) indicates that playa-focused recharge also occurs naturally in this area. Downgradient, beneath the Pantex Plant, the leveling off of  $^{14}\text{C}$  abundances and the decline in Si concentrations suggest that the Ogallala aquifer is recharged via percolation downward from the perched aquifers, consistent with the results of ground-water flow modeling by Mullican and others (1994). In a subsequent section on reaction-path modeling, we discuss using  $^{14}\text{C}$  to constrain estimates of travel times through the unsaturated zone between the perched and Ogallala aquifers.

The similarity in ionic and isotopic compositions between Ogallala-aquifer wells unaffected by return flow and the P. Meacham well suggests a downward-directed component of flow from the Ogallala aquifer to the Quartermaster Formation in the study area. Compared with wells in Permian strata sampled by Nativ (1988), ground water in the P. Meacham well is chemically similar to that observed in Randall County and less saline than observed several kilometers to the northwest in the Canadian River valley. However, the elevation of the Ogallala-aquifer water table ( $\sim 1,030$  m above sea level in winter 1979–1980 [Knowles and others, 1982, p. 365]) was lower than the water-level elevation measured in the P. Meacham well (1,058 m above sea level in April 1971 [Texas Water Development Board, unpublished data]), which indicates upward flow. Because water-level declines due to pumpage were probably 3 to 15 m (Nativ, 1988, her fig. 14), reversal of gradient due to drawdown seems unlikely. Instead, it is possible that (1) the water level measurement in the P. Meacham well, which was taken on the day of drilling, had not fully recovered or (2) the well is located on the discharge limb of a local flow system. Elevated  $\text{SO}_4^{2-}$  ( $53.3$   $\text{mg L}^{-1}$ ) and depleted  $\delta^{34}\text{S}$  ( $-2.6\%$ ) in the T. Bradshaw well may reflect oxidation of pyrite within, and upward flow

from, the Lower Dockum Group (Triassic), which overlies the Quartermaster Formation south and southwest of the Pantex Plant (Dutton and Simpkins, 1986, p. 17; Nativ, 1988, her fig. 16).

### Saturation Index Calculations

Using the geochemical model NETPATH (Plummer and others, 1994) for individual wells, we determined the speciation of various elements in solution and calculated solute activities (concentrations corrected for electrostatic attraction with other solutes) to obtain saturation indices with respect to various minerals. The saturation index is defined as  $SI = \log (IAP K_T^{-1})$ , where IAP is the ion activity product for the ions comprising each mineral and  $K_T$  is the equilibrium solubility constant of the compound at the temperature of the solution. Supersaturation ( $SI > 0$ ) indicates that precipitation of a compound is thermodynamically favorable, whereas undersaturation ( $SI < 0$ ) indicates that dissolution is favored; saturation occurs at  $SI = 0$ . However, precipitation does not automatically accompany supersaturation; slow rates of reaction can inhibit precipitation.

Among major minerals, ground water ranges from nearly saturated to slightly supersaturated with respect to calcite (table 5). Even though quartz may be the predominant mineral on a volumetric basis within the Ogallala Formation,  $SiO_2$  appears to neither precipitate nor dissolve within the perched and Ogallala aquifers. Ground water in the study area is supersaturated with respect to quartz and undersaturated with respect to amorphous silica (table 5). At temperatures characteristic of ground water (approximately  $18^\circ C$ ), the rate of precipitation of quartz is sufficiently slow that direct precipitation of quartz is unlikely. Quartz would form via nucleation of amorphous silica if ground water were supersaturated with respect to amorphous silica (Steeffel and van Cappellen, 1990). Because we are not aware of petrographic evidence for the presence of amorphous silica in the Ogallala Formation, we consider dissolution of that phase to be unlikely.

As suggested by thin-section and scanning electron microscopy (SEM) observations, dissolution of feldspars and precipitation of clay minerals may control the cycling of  $SiO_2$  in the perched and Ogallala aquifers. Observations of vacuoles in feldspars provides plausible evidence

Table 5. Saturation indices (SIs) for solid phases of interest for wells sampled by BEG. SIs calculated using initial set of data for wells sampled on more than one occasion.

Well no.	SI calcite	SI am. silica	Si quartz	SI sepiolite
T. Bradshaw	-0.046	-0.34	0.979	-1.197
FPOP-MW-04	-0.087	-0.232	1.111	-1.125
FPOP-MW-05	-0.041	-0.378	0.927	-2.192
FPOP-MW-06	0.208	-0.369	0.954	-4.37
D. Gabel	0.052	-0.409	0.907	-0.965
B. Kinzer	0.045	-0.53	0.784	-1.49
C. Kirkland	0.591	-0.251	1.058	1.256
S. McGregor	0.062	-0.293	1.013	-0.884
P. Meacham	0.274	-0.316	1.004	0.262
OM-39	0.18	-0.502	0.802	-1.184
OM-40	0.029	-0.44	0.874	-1.588
OM-46	0.093	-0.499	0.814	-1.118
OM-47	0.043	-0.523	0.8	-1.786
OM-48	0.072	-0.53	0.793	-1.619
OM-105	0.05	-0.412	0.887	-1.525
PM-19	-0.051	-0.728	0.595	-5.828
PM-20	0.083	-0.585	0.736	-1.494
PM-38	0.061	-0.761	0.562	-5.008
PM-44	-0.002	-0.733	0.574	-2.604
PM-45	-0.018	-0.627	0.693	-2.772
PM-101	0.133	-0.62	0.695	-1.143
PM-103	0.427	-0.607	0.695	0.13
PM-106	1.529	-0.817	0.476	5.65
PR-2	0.283	-0.551	0.751	-1.034
PR-6	0.087	-0.491	0.821	-1.624
PR-18	-0.05	-0.536	0.764	-2.347
PR-41	0.067	-0.546	0.754	-1.946
E. Pratt	0.173	-0.669	0.637	-2.789
P. Smith	0.062	-0.353	0.976	-1.602
J. Urbanczyk	0.146	-0.49	0.82	-1.386
D. Vance	-0.025	-0.363	0.962	-1.609
M. L. Vance	-0.016	-0.276	1.045	-0.812
C. Wink	0.177	-0.706	0.569	-4.341
F. Wink	0.317	-0.34	0.965	-0.298

of weathering (S. D. Hovorka, Bureau of Economic Geology, personal communication, 1995). SEM photomicrographs illustrate crystals of an unidentified authigenic clay mineral, possibly smectite, occasionally filling pores in core samples from the Ogallala aquifer, although the timing of such precipitation is unknown. Calculating saturation indices of feldspars and clay minerals (except for sepiolite, which is nonaluminous) is problematic because Al concentrations were uniformly below the detection limit of 0.24 to 0.27 mg L<sup>-1</sup> by ICP-OES. Al concentrations were above the ICP-MS detection limit of 0.005 mg L<sup>-1</sup> in 5 of 14 wells (OM-40, PM-44, PM-45, PR-2, and PR-6). NETPATH calculations using ICP-MS data for Al in those wells indicated undersaturation with respect to albite and anorthite and supersaturation with respect to K-feldspar, illite, Ca-smectite, and kaolinite (table 6). In 30 of 34 wells, ground water is undersaturated with respect to sepiolite (table 5).

To examine dissolution and precipitation of common aluminosilicates, we have constructed phase diagrams. We follow common practice (e.g., Freeze and Cherry, 1979) in assuming that Al is conserved (maintained in the solid phase) in the weathering of aluminosilicates. Using NETPATH, we calculated the activity ratios of Na<sup>+</sup> to H<sup>+</sup> and of Ca<sup>2+</sup> to (H<sup>+</sup>)<sup>2</sup>. By plotting the logarithm of each of these ratios versus the logarithm of the activity of H<sub>4</sub>SiO<sub>4</sub><sup>o</sup>, we can determine whether water from a particular well lies in the stability field of (is prone to precipitate) a particular feldspar or clay mineral. Using the equilibrium thermodynamic relationships of Tardy (1971) for standard temperature and pressure (STP) (25°C and 1 atm), which reasonably approximate conditions in ground water, we observed that albite and anorthite are prone to dissolve and clay minerals are prone to precipitate (figs. 21 and 22). Tardy (1971) did not include sepiolite and palygorskite, which are globally uncommon but locally important in the Ogallala and Blackwater Draw Formations. (Palygorskite is also not included in the NETPATH thermodynamic data base.) Perched ground-water samples (except for PM-106, which is believed to be erroneous) plot close to the smectite-kaolinite boundary, suggesting equilibrium between those two phases, whereas Ogallala ground-water samples plot within the Na- and Ca-smectite stability fields. The absence of authigenic kaolinite, illite, and K-feldspar in SEM photomicrographs suggests that those phases are

Table 6. Saturation indices for aluminosilicate phases for wells in which Al concentrations measured by ICP-MS exceeded the detection limit of 5 µg/L (8.0 µg/L, OM-40; 8.8 µg/L, PM-44; 18.9 µg/L, PM-45; 32.5 µg/L, PR-2; 20.2 µg/L, PR-6).

	SI albite	SI anorthite	SI K-feldspar	SI illite	SI kaolinite	SI Ca-smectite
<b>OM-40</b>	-0.782	-2.85	1.05	2.68	4.05	3.28
<b>PM-44</b>	-1.91	-3.31	0.075	1.49	3.34	2.10
<b>PM-45</b>	-1.18	-2.34	0.927	3.27	4.92	3.99
<b>PR-2</b>	-0.47	-1.86	1.21	3.21	4.41	3.64
<b>PR-6</b>	-0.60	-2.11	1.24	3.31	4.63	3.91

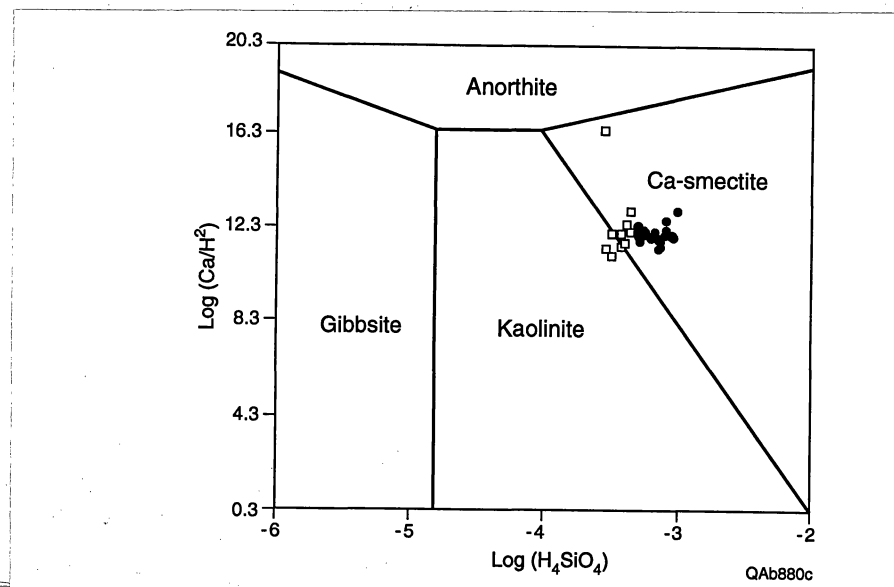


Figure 21. Activity-activity diagram depicting stability of Ca-smectite with respect to perched- (open-square) and Ogallala- (closed-circle) aquifer waters.

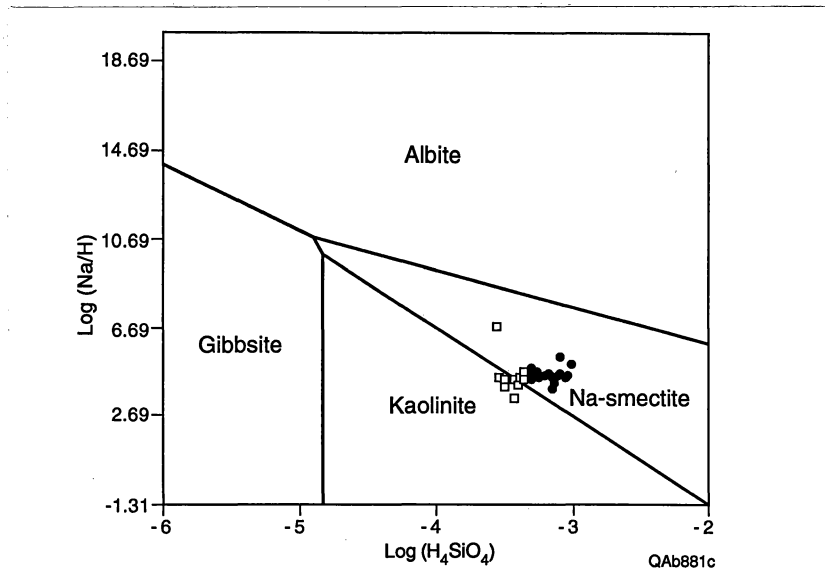


Figure 22. Activity-activity diagram depicting stability of Na-smectite with respect to perched- (open-square) and Ogallala- (closed-circle) aquifer waters.

not currently precipitating from ground water in the study area. Appelo and Postma (1993, p. 214–215) noted that replacement of smectite by kaolinite may be impeded by slow reaction kinetics.

Apart from the assumption of STP conditions, other limitations to the use of phase diagrams should be noted. The kaolinite-gibbsite equilibrium constant given by Tardy (1971) has since been revised slightly (Robie and others, 1978); equilibrium constants for other reactions (and thus phase boundaries) may also have changed. More fundamentally, the thermodynamic relationships do not account for variable compositions associated with solid-phase substitution. For example, the composition of smectite varies with substitution of Mg for Al in the octahedral sheets and with substitution of Al for Si in the tetrahedral sheets of the crystal lattice. Na<sup>+</sup> and Ca<sup>2+</sup> (and other monovalent and divalent cations) are electrostatically bound in the interlayers between tetrahedral sheets to satisfy charge deficiencies created by substitution.

## Reaction-Path Modeling

### Phases and Constraints

Reaction paths have been modeled (1) between land surface and the perched aquifers; (2) along a hypothetical transect in the perched aquifers; and (3) between wells in the Ogallala aquifer, including mixing with water from the perched aquifers, to elucidate controls on the composition of ground water. Accounting for changes in solute chemistry along flowpaths allows us to estimate travel times on the basis of <sup>14</sup>C data and the proportions of recharge mixing with through-flowing ground water. We entered hydrochemical data for wells of interest into NETPATH (Plummer and others, 1994) and identified the solutes likely to constrain reactions in ground water and the possible phases (minerals, gases, organic matter, and ion exchange) involved (table 7). As a first approximation, end-member compositions were assumed for feldspars, clay minerals, and calcite. The formulas for Na- and Ca-montmorillonite given by Tardy (1971) and provided in the NETPATH data base actually refer to beidellite, the smectite end member representing octahedral substitution. We modified the list of phases to include true

Table 7. Constraints and phases used for NETPATH models.

Constraints	Phases
C	albite ( $\text{NaAlSi}_3\text{O}_8$ )
Ca	anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ )
Al	calcite ( $\text{CaCO}_3$ )
Mg	Ca-smectite ( $\text{Ca}_{0.125}\text{Si}_4(\text{Al}_{1.75}\text{Mg}_{0.25})(\text{OH})_2\text{O}_{10}$ )
Na	Na-smectite ( $\text{Na}_{0.25}\text{Si}_4(\text{Al}_{1.75}\text{Mg}_{0.25})(\text{OH})_2\text{O}_{10}$ )
Si	palygorskite ( $\text{Mg}_2\text{Al}_2\text{Si}_8\text{O}_{20}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ )
redox state†	sepiolite ( $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ )
	$\text{CO}_2$ (g)
	$\text{O}_2$ (g)†
	$\text{CH}_2\text{O}$ †
	Ca/Mg exchange
	Ca+Mg/Na exchange

† = land-surface-perched-aquifer models only



montmorillonite, the smectite end member representing tetrahedral substitution, which is much more common than beidellite (Eslinger and Pevear, 1988; M. J. Dudas, Department of Soil Science, University of Alberta, unpublished course notes, 1988).

We allowed ion exchange between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and between  $\text{Na}^+$  and  $\text{Ca}^{2+} + \text{Mg}^{2+}$  (ternary exchange, in which the ratio of  $\text{Ca}^{2+}$  to  $\text{Mg}^{2+}$  equaled the ratio in ground water in the final well along a flowpath). Prior to reaction-path modeling, we calculated ranges in ion-activity products (IAPs) for Na-Ca, Na-Mg, and Ca-Mg exchange for various wells according to the equation

$$\text{IAP} = (N_B^{1/z_B}) \times (N_A^{1/z_A})^{-1} \times (a_A^{1/z_A}) \times (a_B^{1/z_B})^{-1} \times (K_N)^{-1}. \quad (1)$$

Here  $N$  is the equivalent adsorbed fraction (the ratio of the adsorbed cation concentration [in meq  $100 \text{ g}^{-1}$ ] to CEC or TEC),  $a$  is solute activity,  $z$  is the valence, A and B represent the two cations in the exchange reaction, and  $K_N$  is the selectivity coefficient (analogous to the equilibrium constant). Because measured CEC values were less than TEC values, we used TEC values to calculate IAPs. Ranges of IAP values, which were calculated because of variability in exchangeable cation concentrations, usually overlapped ranges of selectivity coefficients reported by Bruggenwert and Kamphorst (1982) and Appelo and Postma (1993, their table 5.5). Although approximating ternary exchange by two binary exchange reactions (Na-Ca and Na-Mg) is a simplification, the overlap between IAP values and selectivity coefficients suggests that exchange of major cations along flowpaths occurs reversibly.

The mass transfer module of NETPATH (NEWBAL) calculates the addition and loss of specified phases, accounting for mixing and evaporation where required, necessary to reproduce changes in solute chemistry between wells along a flowpath. The masses transferred for each combination of phases (defined as a reaction model) must honor the solute constraints specified by the user. However, the results are generally nonunique; multiple reaction models may be generated for a single flowpath. In addition, NEWBAL does not evaluate whether the reactions involved are

thermodynamically feasible. Instead, the user is obligated to review the output from the speciation module to determine whether a given phase is subject to dissolution or precipitation.

NEWBAL also conducts isotopic mass-balance calculations, wherein dissolution of phases containing isotopes of interest (in our case,  $^{13}\text{C}$  and  $^{14}\text{C}$ ) is nonfractionating and wherein precipitation or exsolution of such phases follows a Rayleigh-distillation process with specified fractionation factors. Where C isotope data are involved, the isotopic mass balance is based on total dissolved C. Therefore, the isotopic composition of DOC and of dissolving phases (for example, calcite and  $\text{CO}_2$  gas) must be specified. Wells lacking data on DOC concentrations or on  $\delta^{13}\text{C}$  of DOC were assigned values (some of which were averaged) from other wells in this study. For precipitation of calcite and exsolution of  $\text{CO}_2$  gas, we selected the fractionation factors of Mook (1980). For each flowpath, the user must determine whether the difference between calculated and observed  $\delta^{13}\text{C}$  values at the final well is acceptable (for example, within analytical uncertainty) and must recognize models in which  $^{14}\text{C}$ -derived travel times are nonsensical (for example,  $<0$  yr). We accepted reaction models for which (1) calculated  $\delta^{13}\text{C}$  values were within 1‰ of observed values and (2)  $^{14}\text{C}$ -derived travel times were within approximately an order of magnitude of independently derived values (based on  $^3\text{H}$  data or velocity calculations using Darcy's law).

#### Land Surface to Perched Aquifers

Modeling chemical evolution between rainwater and perched ground water under natural recharge was limited by the small number of perched-aquifer wells unaffected by return flow. Based on the availability of isotopic data, we chose the C. Wink well and PM-44 to represent such wells adjacent to a playa and in an interplaya setting, respectively. For rainwater, we assumed  $\delta^{13}\text{C} = -7\text{‰}$  (the average value for atmospheric  $\text{CO}_2$  given by Keeling [1958]) and  $^{14}\text{C}$  activity = 100 pmc. We used the precipitation-weighted average of major-ion concentrations (W. W. Wood, U.S. Geological Survey, and R. Nativ, Hebrew University of Jerusalem, unpublished data, 1993) and  $\delta\text{D}$  and  $\delta^{18}\text{O}$  abundances (Nativ, 1988) measured on samples collected at Amarillo International Airport between October 1984 and September 1985 (table 8). Because of evidence of

Table 8. Weighted average concentrations of major solutes,  $\delta D$ , and  $\delta^{18}O$  in rain samples collected at Amarillo International Airport between October 1984 and September 1985 (W. W. Wood, U.S. Geological Survey, and R. Nativ, Hebrew University of Jerusalem, unpublished data, 1993). Solute concentrations in mg/L,  $\delta D$ , and  $\delta^{18}O$  in ‰ SMOW.

<b>pH</b>	<b>Ca</b>	<b>Mg</b>	<b>Na</b>	<b>K</b>	<b>Sr</b>	<b>NH4</b>	<b>Si</b>	<b>HCO3</b>	<b>F</b>	<b>Cl</b>	<b>NO3</b>	<b>SO4</b>	<b><math>\delta D</math></b>	<b><math>\delta^{18}O</math></b>
6.24	1.26	0.14	0.73	0.38	0.005	1.45	1.06	5.10	0.024	0.58	1.68	3.04	-60	-8.3

OC oxidation beneath playas (Wood and Petraitis, 1984; Bennett and others, 1995), we initially included redox as a constraint and O<sub>2</sub> and CH<sub>2</sub>O (representing OC) as phases. Ranges of δ<sup>13</sup>C of playa-sediment OC (−15.4 to −27.3‰) and of vadose-zone CO<sub>2</sub> (−14 to −27‰) were taken from data provided by V. T. Holliday (Department of Geography, University of Wisconsin–Madison) and K. D. Romanak (Department of Geological Sciences, University of Texas at Austin), respectively. Following Keller (1991), we assumed that oxidation of OC does not fractionate <sup>13</sup>C, although Suchomel and others (1990) and Blair and others (1985) suggested that fractionation may be possible. We also assumed, as observed by Keller (1991), that <sup>14</sup>C of DOC = <sup>14</sup>C of DIC.

For simulations of playa-focused and interplaya recharge, we did not obtain plausible reaction models that included dissolution of O<sub>2</sub>. Upon deleting O<sub>2</sub> as a phase, we obtained multiple plausible models that specified evaporation during playa-focused recharge (table 9). These models variously involved oxidation of OC; dissolution of CO<sub>2</sub> gas, anorthite, calcite, palygorskite, and sepiolite; precipitation of Ca- and Na-smectite, palygorskite, and sepiolite; exsolution of CO<sub>2</sub> gas; and ion exchange. For interplaya recharge with evaporation, plausible models involved oxidation of OC; dissolution of albite, anorthite, and calcite; precipitation of calcite, Ca- and Na-smectite, palygorskite, and sepiolite; exsolution of CO<sub>2</sub> gas; and ion exchange. Model-derived evaporation factors ranged from 8.09 to 49.2 for C. Wink and 8.51 to 103 for PM-44. Evaporation factors calculated independently using Cl<sup>−</sup> (dividing concentrations in ground water by the weighted average concentration in precipitation) are 5.6 for C. Wink and ≤25 for PM-44. As noted above, Cl<sup>−</sup>-based evaporation factors may overestimate actual evaporation during episodic recharge. Therefore, we conducted additional simulations without allowing evaporation. Those simulations resulted in multiple plausible reaction models for rain water to C. Wink (table 9) but no plausible models for rainwater to PM-44, which suggests that diffusive, interplaya recharge (when it occurs) is accompanied by evaporation.

Accounting for intermediate mass transfers, such as those associated with surficial and vadose-zone C cycling, is problematic in inverse reaction-path modeling. Both rainwater and ground water are at or near equilibrium with atmospheric O<sub>2</sub> and contain little DOC, and only δ<sup>13</sup>C

Table 9. Phases involved in plausible reaction models.

Rainwater— C. Wink (evaporation, redox)	Rainwater— C. Wink (no evaporation, redox)	Rainwater— C. Wink (evaporation, no redox)	Rainwater— C. Wink (no evaporation, no redox)	Rainwater— PM-44 (evaporation, redox)	Rainwater— PM-44 (evaporation, no redox)
anorthite + calcite + sepiolite ± palygorskite ± Ca-smectite - Na-smectite - CH <sub>2</sub> O + CO <sub>2</sub> (g) ± Ca+Mg/Na exch. - Mg/Ca exch. ±	albite + anorthite + calcite + sepiolite ± palygorskite ± Ca-smectite - Na-smectite - CH <sub>2</sub> O + CO <sub>2</sub> (g) + Ca+Mg/Na exch. ± Mg/Ca exch. ±	anorthite + calcite + sepiolite ± palygorskite ± Ca-smectite - Na-smectite - CO <sub>2</sub> (g) + Ca+Mg/Na exch. - Mg/Ca exch. ±	albite + anorthite + calcite + sepiolite ± palygorskite ± Ca-smectite - Na-smectite - CO <sub>2</sub> (g) + Ca+Mg/Na exch. ± Mg/Ca exch. ±	albite + anorthite + calcite ± sepiolite - palygorskite - Ca-smectite - Na-smectite - CO <sub>2</sub> (g) - Ca+Mg/Na exch. ± Mg/Ca exch. -	calcite - CO <sub>2</sub> (g) - Ca+Mg/Na exch. + Mg/Ca exch. -
OM-105+C. Wink+ PM-44 — OM-40 anorthite + sepiolite + Na-smectite - Mg/Ca exch. -	OM-105+C. Wink+ PM-44 — OM-39 anorthite + sepiolite + palygorskite + Ca-smectite - Na-smectite - Mg/Ca exch. -	OM-40+C. Wink— PR-41 albite + anorthite + Ca-smectite - CO <sub>2</sub> (g) - Mg/Ca exch. -	OM-40+C. Wink+ PM-44 — PR-41 anorthite + sepiolite + palygorskite + Ca-smectite - Na-smectite - Ca+Mg/Na exch. +		

1. For each transect, not all phases were necessarily involved in each model.
2. For minerals, CH<sub>2</sub>O, and CO<sub>2</sub> (g), + = precipitation, - = dissolution, and ± = precipitation or dissolution.
3. For Ca+Mg/Na exchange, + = Ca+Mg adsorption and Na desorption; - = Na adsorption and Ca+Mg desorption.
4. For Mg/Ca exchange, + = Mg adsorption and Ca desorption; - = Ca adsorption and Mg desorption.

and elevated  $\text{HCO}_3^-$  concentrations tend to preserve in ground water the evidence of OC oxidation during recharge. Moreover, it is uncertain whether oxidizing OC is primarily particulate (with resultant dissolution of  $\text{CO}_2$  gas by recharging waters) (Wood and Petraitis, 1984) or dissolved. Forcing dissolution of  $\text{CO}_2$  gas without including redox as a constraint or  $\text{O}_2$  gas or  $\text{CH}_2\text{O}$  as phases resulted in multiple plausible reaction models for playa-focused recharge (with evaporation factors of 8.09 to 16.8) and one plausible model for interplaya recharge (with an evaporation factor of 8.51) (table 9). Discounting evaporation once again resulted in multiple plausible models for playa-focused recharge but no plausible models for interplaya recharge. Although this approach is clearly a simplification of processes beneath playas, it may be more realistic in interplaya areas, in which a larger proportion of  $\text{CO}_2$  is likely to be derived from root respiration (Bennett and others, 1995).

As noted previously,  $^3\text{H}$  concentrations indicate post-1952 recharge in the C. Wink well (1.84 TU) and possibly in PM-44 (1.2 TU in May 1994 [ANL, 1994]).  $^{14}\text{C}$  activities calculated by NETPATH for recharge to those wells depend upon the  $^{14}\text{C}$  values specified for OC,  $\text{CO}_2$  (g), and pedogenic soil carbonate (as  $\text{CaCO}_3$ ). Although data are lacking for  $^{14}\text{C}$  of  $\text{CaCO}_3$ , apparent ground-water ages  $\leq 40$  yr (taken as the difference between calculated and observed  $^{14}\text{C}$  activities) can be obtained using reasonable values for  $^{14}\text{C}$  of  $\text{CO}_2$  (g) (from table 1 of Thorstenson and others, 1983) and  $^{14}\text{C}$  of OC. However,  $^{14}\text{C}$  dating of recharge is problematic in part because of (1) the likelihood of mixing of ground waters of different ages (as noted previously) and (2) the likelihood that the  $^{14}\text{C}$  activity of soil water is buffered by soil gas under open-system conditions (Plummer and others, 1994). Ingassing occurs when  $^{14}\text{CO}_2$  concentrations in soil gas (which depend upon both the activity of  $^{14}\text{C}$  and the mole fraction of  $\text{CO}_2$ ) are greater than in soil water. Apparent  $^{14}\text{C}$  ages of soil water from southern Nevada, where recharge has been negligible for thousands of years, were much younger than those determined by  $\text{Cl}^-$  mass balance calculations, which suggests diffusion and ingassing of  $^{14}\text{CO}_2$  at depths of 30–146 m (Chapman and others, 1994; Tyler and others, 1995). In contrast, the rate of soil-water advection beneath playas is likely to be greater than that of gaseous diffusion, which raises the possibility of soil water dissolving

$^{14}\text{CO}_2$  in the shallow subsurface and outgassing  $^{14}\text{CO}_2$  deeper in the vadose zone. Without data on  $^{14}\text{C}$  in soil water beneath playas, we cannot evaluate this possibility at present.

Potentiometric-surface mapping and ground-water flow modeling indicate that radial flow occurs within the perched aquifers. We modeled chemical evolution along a hypothetical transect from C. Wink to PM-44, ignoring interplaya recharge. However, no modeled combination of reactions could reproduce observed  $\delta^{13}\text{C}$  (DIC) values in PM-44 within 4‰. Although the model parameters were not given, ANL (1994, p. 4–33) also reported that “no reasonable model of chemical reactions in the (perched) aquifer results in the isotopic and chemical evolution of the low carbon isotope compositions to high carbon isotope compositions observed at Pantex.” Ground-water compositions in PM-44, PM-101, PTX10-1007, and PTX10-1008 appear to reflect interplaya recharge of uncertain age. Lateral chemical evolution may occur naturally within the perched aquifers closer to playas, but it appears to be masked by return flow in monitoring wells and in the E. Pratt well.

#### Perched Aquifers to Ogallala Aquifer

Reaction models were identified for pairs of Ogallala-aquifer wells located approximately along predevelopment ground-water flowlines. Between each pair of Ogallala-aquifer wells, we simulated mixing with water from the perched aquifers (C. Wink and/or PM-44) with and without reactions. These simulations necessitated the assumption, which will be addressed in more detail subsequently, that compositional evolution in the vadose zone between the perched aquifers and the Ogallala aquifer is negligible and that reactions occur in the Ogallala aquifer after mixing (if at all). We chose the same phases and constraints involved in modeling evolution of rainwater to perched ground water, except that we (1) excluded  $\text{CH}_2\text{O}$  as a phase, (2) specified no dissolution of calcite or  $\text{CO}_2$  (g), and (3) used  $\text{Cl}^-$  and  $\delta^{18}\text{O}$  to constrain mixing without reactions.

Because the perched aquifers are laterally extensive, and presumably separate water in the underlying vadose zone from  $^{14}\text{CO}_2$  (g) in the overlying vadose zone, we assumed that  $^{14}\text{C}$  could

be used to calculate travel times between the perched and Ogallala aquifers ( $t_{pc.-Og.}$ ) according to the equation:

$$t_{pc.-Og.} = (t_{mixed} - (t_{Og.-Og.} \times x_{Og.})) \times (x_{pc.})^{-1}. \quad (2)$$

Here,  $t_{mixed}$  is the  $^{14}C$  “age” of the mixed water calculated by NETPATH,  $t_{Og.-Og.}$  is the travel time between wells in the Ogallala aquifer, and  $x_{pc.}$  and  $x_{Og.}$  are the fractions of perched and upgradient Ogallala-aquifer water in the mixture, respectively. We determined ranges of  $t_{Og.-Og.}$  from the predevelopment, steady-state potentiometric surface simulated by Mullican and others (1995a), assuming an effective porosity ( $n_e$ ) of 0.15 to 0.35 (Castany [1967], cited in de Marsily [1986, his fig. 2.17]). Using output files from the flow model MODFLOW (McDonald and Harbaugh, 1988) as input to MODPATH (Pollock, 1989), we generated forward and reverse particle tracks (at 10-yr time steps) from Ogallala-aquifer wells of interest. Forward tracks from upgradient wells along transects were usually not identical to reverse tracks from downgradient wells; therefore, we visually estimated travel time along each particle track to a point parallel with the well of interest. Resulting values of  $t_{Og.-Og.}$  ranged from 36 to 770 yr (table 10a).

Most models for which  $\delta^{13}C$  was within 1‰ of observed and  $t_{pc.-Og.}$  was  $>0$ , including all models allowing mixing without reactions, were still eliminated because  $t_{pc.-Og.}$  exceeded  $t_{Og.-Og.}$  by more than an order of magnitude. Travel times between playas and the perched aquifers (over distances greater than those separating the perched and Ogallala aquifers), as well as travel times across the perching strata calculated from Darcy’s law (Mullican, 1995), are comparable to  $t_{Og.-Og.}$ . Moreover, given the hydrochemical and lithologic similarities between the perched and Ogallala aquifers, it is unlikely that reactions would occur during relatively short residence times in the Ogallala aquifer without having occurred (prior to mixing) during relatively long residence times in the overlying vadose zone. Plausible reaction models occur along a set of transects beneath Playa 1, from OM-105 to OM-39 and -40 and from OM-40 to PR-41 (table 10b; fig. 10). These models support petrographic observations of clay-mineral precipitation within the Ogallala aquifer. Percentages of perched ground water mixing with Ogallala-aquifer water along each transect



Table 10(a). Approximate travel times, determined from particle tracks generated using MODPATH, between Ogallala-aquifer wells.

Upgrad. Og. well	Downgrad. Og. well	tOg.-Og. (yr) (n eff. = 0.15)	tOg.-Og. (yr) (n eff. = 0.25)	tOg.-Og. (yr) (n eff. = 0.35)
S. McGregor	OM-105	770	460	330
OM-105	OM-40	320	190	140
OM-105	OM-39	370	220	160
OM-105	OM-46	730	440	314
OM-105	OM-47	700	420	300
OM-105	OM-48	680	410	290
OM-40	PR-6	300	180	130
OM-40	PR-41	530	320	230
OM-39	PR-6	150	90	64
OM-39	PR-41	420	250	180
PR-6	PR-41	200	120	86
PR-41	PR-18	83	50	36

Table 10(b). Estimated ranges of travel times between the perched and Ogallala aquifers and fractions of water derived from the perched aquifer in downgradient Ogallala-aquifer wells, determined using NETPATH.

Upgrad. Og. well	Downgrad. Og. well	Perched well(s)	tpc.-Og. (yr) (n eff. = 0.15)	tpc.-Og. (yr) (n eff. = 0.25)	tpc.-Og. (yr) (n eff. = 0.35)	C. Wink wtr. (%)	PM-44 wtr. (%)	total pc. wtr. (%)	Screen elev., downgrad. Og. well (m above sea level)
OM-105	OM-40	C. Wink+PM-44	730	1800	2200	3.04	7.65	10.7	888.2-897.3
OM-105	OM-39	C. Wink+PM-44	19	290	400	2.89	64.7	67.6	921.1-927.8
OM-105	OM-39	C. Wink+PM-44	1300	1600	1600	4.88	59.8	64.7	921.1-927.8
OM-40	PR-41	C. Wink	(-1000)	1300	2400	8.30		8.30	849.5-914.7
OM-40	PR-41	C. Wink+PM-44	(-2000)	(-570)	33	4.43	8.65	13.1	849.5-914.7
OM-40	PR-41	C. Wink+PM-44	(-2000)	(-560)	49	4.44	8.67	13.1	849.5-914.7
OM-40	PR-41	C. Wink+PM-44	(-880)	380	930	4.94	9.43	14.4	849.5-914.7

Calculated values (in columns) that are less than zero are shown in parentheses.

ranged from 8.30% between OM-40 and PR-41 to 67.6% between OM-105 and OM-39. Plausible (positive) values of  $t_{pc.-Og.}$  ranged from 19 yr between OM-105 and OM-39 ( $n_e = 0.15$ ) to 2,400 yr between OM-40 and PR-41 ( $n_e = 0.35$ ). Reaction models that mixed waters from both C. Wink and PM-44 with Ogallala-aquifer water yielded values of  $t_{pc.-Og.}$  proportional to the amounts of water contributed from each of those wells. Not surprisingly, values of  $x_{pc.}$  and  $t_{pc.-Og.}$  appear to decrease and increase, respectively, with the depth of the screened interval in the Ogallala aquifer (compare OM-39 and OM-40 [table 10b]).

The selection of plausible reaction models should be viewed with caution because of various simplifications, some of which (for example, the selection of C. Wink and PM-44 to represent the compositions of perched ground water and the assumption of end-member aluminosilicate mineralogies) have already been noted. The assumption that chemical evolution in the lower vadose zone is negligible could be examined by forward reaction-path modeling using PHREEQE (Parkhurst and others, 1980), but the assumption that  $^{14}C$  in soil water is unbuffered by  $^{14}CO_2$  (g) can probably only be assessed by sampling in the lower vadose zone. We have assumed that despite extensive drawdown within the Ogallala aquifer, ground-water compositions are at steady state in wells unimpacted by return flow. In the absence of longer term monitoring, the lack of compositional trends in onsite Ogallala aquifer wells since 1991 supports this assumption. We have also assumed, as shown by Phillips and others (1989) for the Ojo Alamo and Nacimiento aquifers of the San Juan Basin, that hydrodynamic dispersion exerts a negligible influence on  $^{14}C$  distributions. Our study is typical of regional-aquifer studies (for example, Plummer and others, 1990) in relying upon water-supply wells, which are commonly screened over thicknesses of meters to tens of meters. Sampling from such wells results in depth-integrated data masking vertical geochemical gradients (Ronen and others, 1987).

#### Evidence of Denitrification

As noted above, inverse modeling of chemical evolution cannot necessarily reproduce intermediate mass transfers (such as cycling of C and N) that are not preserved in ground-water

chemistry.  $\text{NO}_3^-$  concentrations are typically  $<10 \text{ mg L}^{-1}$  in both rainwater and ground water in the study area, yet considerable loading of N can occur at land surface. We hypothesize that denitrification, the bacterially mediated reduction of  $\text{NO}_3^-$  to gaseous  $\text{N}_2$  via the intermediates  $\text{NO}_2^-$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$  (Payne, 1981), plays a significant role in buffering  $\text{NO}_3^-$  concentrations in ground water. Anaerobic conditions induced by the degradation of organic matter can promote denitrification. Denitrification can occur beneath the soil zone if electron donors (in this instance, dissolved or particulate OC) are present in sufficient quantity. Wastewater can carry sufficient DOC to promote denitrification at depths of 30 m in arid regions (Ronen and others, 1987).

Evidence for denitrification in the study area is provided not only by counts of denitrifying bacteria in playa sediments but also by values of  $\delta^{15}\text{N}$  of soil gas depleted relative to atmospheric  $\text{N}_2$  and by relatively enriched values of  $\delta^{15}\text{N}$  accompanying relatively low  $\text{NO}_3^-$  concentrations in ground water. Fractionation of  $^{15}\text{N}$  during denitrification can increase  $\delta^{15}\text{N}$  of the remaining dissolved  $\text{NO}_3^-$  by as much as 30‰ (Mariotti and others, 1981). The depletion of  $\text{O}_2$  and the presence of high  $\text{CO}_2$  and  $\text{CH}_4$  in soil gas (Bennett and others, 1995) suggest microbial processes beneath playas that would include denitrification. More numerous populations of denitrifying bacteria at Playa 5 relative to Pantex Lake may be a consequence of relatively recent wastewater discharge at Playa 5. However, it is unclear why populations of  $\text{NO}_3^-$ -reducing bacteria other than denitrifiers appear not to have been similarly stimulated.

Because ground waters (whether contaminated or not) in our study area are oxygenated, denitrification within the Ogallala aquifer would probably be restricted to narrow intervals near the water table into which anoxic wastewater is flowing. Because DOC concentrations in our ground-water samples were typically  $<2 \text{ mg L}^{-1}$  and “large quantities of reduced inorganic compounds or solid labile OC” (such as lignite; Korom, 1992) have not been reported from the Ogallala Formation,  $\text{NO}_3^-$  reduction is probably not occurring within anaerobic microsites in the Ogallala aquifer. Denitrification is unlikely to occur under the aerobic conditions observed in the Ogallala aquifer; we are unaware of evidence of aerobic denitrification in any ground water (Korom, 1992).

Our results indicate that the existence of anaerobic conditions beneath playas does not preclude the influx of atmospheric  $O_2$  to ground water. Oxygenated water can percolate through macropores while the clayey soil matrix remains anaerobic. Dissolved  $O_2$  and  $NO_3^-$  could diffuse from macropores into the soil matrix and there be reduced by microbial oxidation of OC. Blanchard and Kitchen (1993) have invoked this reaction sequence to explain low  $NO_3^-$  concentrations in fractured clayey till. Subsequently, residual (partly denitrified)  $NO_3^-$  might diffuse back out of the soil matrix if  $NO_3^-$  concentrations in macropores become lower than concentrations in the matrix. Alternatively, pulses of dissolved or particulate OC in infiltrating water, such as following seasonal dieback of vegetation (Keller, 1991) or occasional releases of wastewater, could lead to reduction of  $O_2$  and  $NO_3^-$  within macropores. These pulses might subsequently be displaced by oxygenated pulses of infiltrating rainwater or reoxidized by atmospheric  $O_2$  diffusing laterally inward from beneath the margins of playas (W. W. Wood, U.S. Geological Survey, personal communication, 1992). In each of these cases,  $N_2$  generated by denitrification is unlikely to be converted back to  $NO_3^-$  (Starr and Gillham, 1993).

If rates of denitrification are rapid relative to rates of infiltration and solute flux through the vadose zone,  $NO_3^-$  concentrations in recharge arriving at the water table should be minimized. However, the  $NO_3^-$  concentration of  $56.8 \text{ mg L}^{-1}$  in well FPOP-MW-06 (adjacent to Playa 5) indicates that denitrification of wastewater (inferred from the  $\delta^{15}N$  value of  $29.0\text{‰}$ ) is not always sufficient to bring recharge within drinking-water standards. The presence of wastewater in the Ogallala aquifer is corroborated by the high  $Cl^-$  concentrations in FPOP-MW-06 and the downgradient well FPOP-MW-05 ( $320$  and  $211 \text{ mg L}^{-1}$ , respectively).  $^3H$  levels of  $8.44$  and  $6.68 \text{ TU}$  in FPOP-MW-06 and FPOP-MW-05, respectively, indicate post-1952 recharge. In neighboring upgradient and downgradient wells,  $Cl^-$  and  $^3H$  concentrations are  $<10 \text{ mg L}^{-1}$  and  $<0.5 \text{ TU}$ , respectively, but DO and DOC concentrations are not appreciably different than in FPOP-MW-06 and FPOP-MW-05. The similarity in DO concentrations is additional evidence that denitrification is a vadose-zone process in the study area. The generally low DOC concentrations suggest that denitrification might be limited by the amount of labile OC available.

## CONCLUSIONS

Chemical, isotopic, mineralogical, and bacteriological analyses indicate that the composition of ground water in the vicinity of the Pantex Plant reflects distinctive sources of recharge (both natural and anthropogenic) modified by sediment-water interactions, microbial processes, and some evaporation. Reaction-path modeling supports this conclusion and helps to constrain both percentages of perched ground water mixing with water in the Ogallala aquifer and travel times between the perched and Ogallala aquifers. Delineating sources of recharge and reactions is facilitated by the proximity of the study area to a hydrologic divide in the Ogallala aquifer, the presence of numerous wells in both the perched and Ogallala aquifers, and the existence of data from previous and concurrent regional investigations.

Although we have not focused upon the fate and transport of contaminants, our work offers several implications for contaminant remediation. Intrinsic processes which may limit ground-water contamination include both vadose-zone denitrification and dilution due to mixing of Ogallala aquifer water with water percolating from the perched aquifers. Variable geochemical conditions and heterogeneous hydraulic properties beneath playas may impair the efficiency of vadose-zone remedial strategies, such as soil-vapor extraction or amended biodegradation, that involve withdrawing contaminants or delivering nutrients. To minimize further leaching of contaminants to the perched aquifers, remediation of contamination in the vadose zone adjacent to ditches and playas should be given priority over remediation of vadose-zone contamination in interplaya areas, where recharge fluxes are relatively low. As discussed in Fryar and Mullican (1995a), we recommend measuring contaminant adsorption onto perched-aquifer sediments, examining vertical variability in the compositions of ground water and water in the lower vadose zone, and delineating the extent of ground-water contamination emanating from Playa 5.

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