

# **Summary Hydrogeologic Assessment**

## **U.S. Department of Energy**

### **Pantex Plant, Carson County, Texas**

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## EXECUTIVE SUMMARY

In 1990, the Bureau of Economic Geology (BEG) and the Department of Geological Sciences (DOGS) at The University of Texas at Austin and the Water Resources Center (WRC) at Texas Tech University began a five-year program, funded by the Department of Energy (DOE) through the Governor's Office of the State of Texas, to characterize the geohydrology of Pantex Plant. The purpose of this work, which is summarized in this report, was to provide data and information that would assist in the remediation of contaminated sites at Pantex and support the State of Texas in its review of the Department of Energy's (DOE's) remediation program. The results of this investigation describe the physical setting and heterogeneities that control movement and distribution of contaminants and the processes that affect rates and fate of contaminants. The fate and distribution of contaminants, the selection and application of appropriate remediation approaches, the evaluation of the effectiveness of remediation technologies, and the proper monitoring of the affected environment all depend on knowledge of the controls and rates of active processes at Pantex Plant.

Significant results of this work include the following: (1) recharge to the Ogallala and perched aquifers is focused through playas and drainage ditches and ponds in interplaya areas; (2) recharge is such a rapid process that surface waters have reached the main perched aquifer in less than 40 yr; (3) waters of the perched aquifer are mounded beneath Playa 1 and flow approximately radially away from the crest of the mound; (4) the water-saturated fine-grained zone at the base of the perched aquifers is an aquitard that allows waters to flow into the underlying unsaturated zone; (5) strata that contain the Ogallala and perched aquifers, as well as strata that are recharge pathways beneath playas and ditches, are heterogeneous and locally compartmentalized; (6) playa, Blackwater Draw Formation and Ogallala Formation strata contain numerous preferential flowpaths such as root tubules and fractures; (7) denitrification is occurring in the vadose zone; (8) in the upland ditch environments, TNT and HMX are most likely to sorb, whereas RDX will be relatively mobile; in the playas where soil organic carbon *and* soil surface area are maximal, mobility of explosive constituents is minimal; (9) total infiltration through Playas 1–5 between 1952 and 1991 likely ranged from 52,000 to 835,000 acre-inches (534 to 8,587 ha m); (10) microbial activity beneath playas produces carbon dioxide under aerobic conditions and methane under anaerobic conditions; (11) wetlands such as playas function as sinks for nutrients added from the waste-water treatment facility and runoff water; (12) a waste generation history was developed for the operations conducted at the Pantex facility since it was reactivated in 1951 through the late

1980's. In addition, a multiwell pump test and networks of shallow high-resolution seismic cross sections and stratigraphic sections were completed.

The results of this work to date are described in 35 milestone reports, 27 published articles, 7 theses or dissertations, 16 quarterly reports, and 4 annual reports in addition to this summary report. Eleven final contract reports will be completed by August 31, 1995.

Although many important insights have been achieved, several aspects of the geohydrologic system, which are potentially important to achieving a successful conclusion to the remediation program at Pantex, remain open to investigation. In addition, there are many opportunities to apply the results of these studies to respond to new situations as they arise or to achieve cost savings through improved approaches to remediation.

Completion of remediation of ground waters at the Pantex Plant is likely to require additional remediation support efforts such as (1) documentation of flow rates and processes affecting movement of water and contaminants from the main perched aquifer to the Ogallala aquifer, (2) detailed simulations of applied technologies such as pump and treat for perched aquifers to predict effectiveness and cost efficiency, (3) application of the characterization results to sites of suspected contaminant transport (such as the Bureau's assessment of contaminant flow to well PX SB04), (4) continuing analysis of past and ongoing monitoring results of perched and Ogallala aquifers to evaluate evolving water quality, (5) application of noninvasive geophysical techniques for specific issues or as a monitoring technology that integrates data between monitoring points (wells), (6) additional multiwell pump tests to help determine the ranges of hydraulic characteristics of the main perched aquifer, (7) synthesis of existing and new stratigraphic data currently planned wells to determine hydrogeologic boundaries within the perched aquifer to optimize placement of remediation wells, and (8) assessment of the intrinsic remediation option because of the recognized low levels of contaminants in ground waters at the Pantex Plant and because of the recognized importance of natural denitrification and biological activity in the vadose zone.

The following sections summarize the work of each of the participating groups: the Bureau of Economic Geology, the Department of Geological Sciences, and the Water Resources Center.

#### BUREAU OF ECONOMIC GEOLOGY

#### THE UNIVERSITY OF TEXAS AT AUSTIN

Contaminant distribution, monitoring plans, and the application of remedial technologies depend on an understanding of site stratigraphy. Ogallala Formation, Blackwater Draw Formation, and playa sediments are heterogeneous assemblages that have varying hydraulic

properties. Preferential ground-water flow paths such as root tubules and fractures are common in these sediments. Therefore, remediation strategies applied to the perched aquifer must accommodate the heterogeneity of these sediments.

Refraction and reflection seismic data were collected across Sevenmile Basin, Pantex Lake, and at playa and interplaya areas at Pantex Plant to compare Ogallala stratigraphy beneath playas with Ogallala stratigraphy in nonplaya areas. Differences in seismic velocities indicate that there are significant textural differences between sediments beneath playa basins and those beneath uplands, which in turn suggests differing hydraulic properties between the two environments. Specifically, seismic data suggest that the Caprock calcrete is missing beneath parts of playa basins locally facilitating recharge.

Unsaturated zone studies provide basic information required to evaluate different remediation approaches. Hydraulic and hydrochemical data from playa and interplaya settings suggest that recharge to both the perched and Ogallala aquifers is focused beneath playas and is negligible in undisturbed interplaya settings. Analysis of playa sediments shows that recharge is mostly along preferential pathways. Applied tracer tests conducted in playa and interplaya settings indicate that preferential flow is important, particularly for transport of adsorbed contaminants in playa settings. Results of these studies also indicate that recharge to the Ogallala and perched aquifers is much faster than previously suspected. Remediation strategies applied at Pantex must therefore consider the rapid recharge rates that are likely to occur beneath playas and interplaya ponded areas.

Perched aquifers above the regional Ogallala (High Plains) aquifer underlie most of the Pantex Plant. Shallow seismic reflection data illustrate that the fine-grained zone at the base of the perched aquifers is present beneath most of the Pantex Plant. Vertical hydraulic conductivities within the fine-grained zone vary by three orders of magnitude. Multiwell pumping tests document significant local heterogeneity in the main perched aquifer. For example, differences in vertical hydraulic conductivity in the fine-grained zone at the base of the main perched aquifer are suggested by variations in spreading distances of the ground-water mound beneath the point of recharge (Playa 1). Water-level fluctuations in monitor wells also illustrate that a significant volume of water is moving through the perched aquifer annually. It is important to note that if water levels continue to decline, the volume of remaining accessible perched ground water may be significantly reduced naturally. These observations indicate that remediation options must consider heterogeneous hydrologic conditions in the perched aquifer as well as the relatively rapid rate of flow of contaminated perched ground water through the perching layer to the unsaturated Ogallala section below.

Three different conceptual and numerical models were used to evaluate ground-water flow in the Ogallala and perched aquifers. Modeling results illustrate that (1) focused recharge

through playas is supported by numerical simulations, (2) flow of perched ground water is radial away from mounds beneath playas and away from noses on the potentiometric surface under ditches, (3) the fine-grained zones are not impermeable, and (4) potentially contaminated ground water has been flowing from the main perched aquifer to the Ogallala aquifer. As stated above, hydrologic conditions, aquifer heterogeneity, and flow through the perching layer are important considerations in planning remediation alternatives at Pantex Plant.

Results of hydrochemical modeling indicate that contaminant migration to the perched aquifers in undisturbed interplaya regions away from playas and ditches is likely to be slow and may be negligible. Conversely, contaminant migration at points of focused recharge, such as playas and ditches, may be relatively rapid if it is not limited by reactions such as sorption and biodegradation. These results indicate that scheduling remediation activities is important. Contaminated sites that underlie areas of surface-water ponding such as playas, ditches, or excavated landfills will continue to contribute to the contaminant load of the perched aquifer because of recharge through the contaminated site. These sites should be considered as high-priority areas for remediation. Areas of contamination where recharge is not a factor should be given a lower priority for remediation.

Tritium concentrations  $>1$  TU in the perched aquifer indicate the occurrence of post-1952 recharge. Even more rapid recharge is indicated by the detection of waste water, which was discharged to Playa 5 between 1968 and 1975, in the Ogallala aquifer. Evidence of leakage downward from the perched aquifers to the Ogallala aquifer indicates that continued monitoring of water quality in Ogallala-aquifer wells is appropriate, even though contamination of the Ogallala aquifer beneath the Pantex Plant has not been detected.

In ground water, enriched  $d^{15}N$  values, low nitrate concentrations, and dissolved oxygen concentrations  $>3.24$  mg  $L^{-1}$  indicate the existence of anaerobic conditions conducive to denitrification in the vadose zone and to the biodegradation of contaminants. Oxygenated water may also percolate through macropores, whereas the clayey soil matrix remains anaerobic. Dissolved oxygen and contaminants such as chromium (VI) and chlorinated solvents could diffuse from macropores into the soil matrix and be reduced there by microbial oxidation of sediment. Both variable geochemical conditions and heterogeneous hydraulic properties may impair the efficiency of vadose-zone remedial strategies, such as soil vapor extraction or amended biodegradation, that involve withdrawing contaminants or delivering nutrients.



DEPARTMENT OF GEOLOGICAL SCIENCES  
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Examination of the geochemical controls on the fate and transport of organic contaminants in the vadose zone under the ditches and playas of the Pantex facility suggests that volatile organic contaminants (VOC) will strongly sorb to soils at very low moisture contents. Moisture content at depths greater than a few centimeters, however, is high enough and the fraction of organic carbon is low enough to keep VOC sorption relatively low and vapor-phase concentrations high. In this type of system, VOC compounds will be transported in the vapor phase by diffusion along concentration gradients, or be advected along pressure gradients, with little retardation. At very high moisture contents, vapor-phase transport is limited by the lack of air-filled porosity, and volatile organic contaminants will dissolve into the aqueous phase according to their individual Henry's Law constants. In this environment, transport will be by aqueous-phase advection and diffusion barely retarded by limited sorption and partitioning.

In the upland ditch environments, sorption capacity is at a minimum and mobility is highest, especially when high-volume low ionic strength runoff waters are in the ditch system. Here, TNT and HMX are most likely to sorb, whereas RDX will be relatively mobile. In the playas, however, where soil organic carbon *and* soil surface area are maximal, the mobility of explosives is minimal, and surface binding is favored.

This study found that soils from the Zone 12 ditch were contaminated by both sorbed and particulate HMX, but primarily sorbed RDX. Sorbed HMX and RDX readily desorb in water, with equilibrium concentrations approaching 75 percent of their aqueous solubilities. Because the solubility of RDX and TNT is much greater than HMX, these compounds are more readily transported in the aqueous phase, whereas HMX is more likely to be retained in the solid phase.

The elevated CO<sub>2</sub> concentrations at depth are attributed to microbial oxidation of organic matter in the playa subsurface. Under wet conditions, water and carbon recharge into the vadose zone immediately beneath the playa, supplying substrate, nutrients, and moisture to the native microorganisms but limiting vertical gas permeability. Microbial carbon oxidation produces carbon dioxide as it consumes oxygen, and with the limited vertical diffusion of oxygen, anaerobic conditions can be attained, producing methane from either fermentation or bicarbonate methanogenesis.

WATER RESOURCES CENTER

TEXAS TECH UNIVERSITY

Infiltration into the five playas on the Pantex Plant was estimated using the U.S. Army Corps of Engineers Storage-Overflow-Runoff-Model (STORM) and WaterBalance, a model developed for playas. Preliminary results of these analysis indicate that total infiltration between 1952 and 1991 for Playas 1-5 ranged from 52,000 to 835,000 acre-inches.

As a heavy metal cation, chromium is known to sorb to soils and may be retarded as it moves through the porous media. The nature of the sorption process in the subsurface soils directly affects the selection of possible remediation alternatives.

Wetlands such as playas may remove or store nutrients from runoff and waste water. Soil and plant parameters were evaluated in areas dominated by cattail (*Typha domingensis*) or pink smartweed (*Persicaria pennsylvanicum*). The nutrients measured were nitrogen, phosphorus, copper, iron, manganese, and zinc. Copper, iron, and manganese soil nutrient concentrations were significantly greater in soils beneath the cattail than the smartweed. On the basis of the nutrient accumulations, this wetland appears to function well as a sink for added nutrients from the waste-water treatment facility and runoff water.

## INTRODUCTION

In November of 1990, the Bureau of Economic Geology (BEG) and the Department of Geological Sciences (DGS), The University of Texas at Austin, and the Water Resources Center (WRC), Texas Tech University, initiated a research program to describe the geohydrology of the region surrounding the DOE's Pantex Plant in Carson County, Texas (see figure 1 in the following section describing regional stratigraphy for the location of the Pantex Plant). These efforts were undertaken to support the State of Texas in its ongoing review of the DOE's ground-water monitoring and remediation program. This work was supported by DOE through a grant (No. DE-FG04-90AL65847) to the Governor's Office.

The following report summarizes the major elements of study programs designed to examine the subsurface geological framework or stratigraphy of the Blackwater Draw and Ogallala Formations and playa-filling sediments (BEG); surface-water flow and collection in playas (WRC); water flow and transport processes in the unsaturated zone, the perched aquifers, and the Ogallala aquifer (BEG); geochemistry of waters of the saturated and unsaturated zones (BEG); geochemistry of playa waters and sediments (DGS); and the biology of playas (WRC).

# Regional Stratigraphy of the Tertiary Ogallala and Quaternary Blackwater Draw Formations

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## INTRODUCTION

The Tertiary Ogallala Formation and the Quaternary Blackwater Draw Formation were examined in order to provide a stratigraphic framework for hydrogeologic assessments of the Ogallala (High Plains) and perched aquifers and unsaturated zones that underlie the U.S. Department of Energy's Pantex Plant and surrounding areas (fig. 1). The distribution of contaminants, the rates of contaminant migration, the design of monitoring schemes, and the application and evaluation of remedial technologies all depend on an accurate understanding of the stratigraphy. In particular, a significant effort was made to describe stratigraphic heterogeneity of the Ogallala and Blackwater Draw Formations at both regional and local scales and playa sediments at local scales. Heterogeneities, such as variations in sediment size or structures such as fractures in sediments, are important factors in determining ground water flow rates, recharge rates, and ultimately the potential effectiveness of remediation strategies.

The late Tertiary Ogallala Formation, which is comprised mostly of fluvial and eolian sediments, lies unconformably on Permian Quartermaster Formation or Triassic Dockum Group strata in the vicinity of the Pantex Plant. Permian strata are primarily red sandstones and mudstones, halite, gypsum/anhydrite and dolomite. Triassic strata include fluvial sandstones and lacustrine mudstones. The Quaternary Blackwater Draw Formation, which is comprised of eolian sand and silt, is separated from the Ogallala Formation by the Ogallala Caprock.

These investigations, which were based primarily on core and geophysical log analyses, document the vertical and geographic distribution of differing lithologies within the Ogallala and Blackwater Draw Formations. Core descriptions are accompanied by geophysical logs and thus can be used for verification of log interpretations. In turn, these data were used to construct stratigraphic cross sections in the Pantex area based on correlation and interpretation of geophysical logs. This work was based on the detailed examination of more than 60 outcrops, description of core from more than 75 wells, and analyses of logs from more than 100 wells. Outcrops and core were examined for primary sedimentary structures, texture, pedogenic and biogenic structures,  $\text{CaCO}_3$  content, and color.

## Structural Setting

The area surrounding the Pantex Plant overlies the northeast margin of the Paleozoic Palo Duro Basin. Upwarping of the margins of the Palo Duro Basin during post-Permian time placed thick sequences of bedded Permian evaporites in the structural position where they were susceptible to dissolution by ground water (Gustavson and Finley, 1985). Dissolution of Permian halite (salt) and gypsum has strongly affected the northeastern margin of the basin where approximately 212 m of salt has been dissolved beneath the Pantex Plant (McGookey and others, 1988). As a result of dissolution, subsidence of the Tertiary Ogallala Formation and the Quaternary Blackwater Draw Formation occurred both during and subsequent to deposition of these formations. Dissolution of salt has allowed subsidence of overlying units, resulting in a structural basin with in excess of 120 m of relief beneath and to the northeast of the Pantex Plant. This subsidence basin is in part responsible for the Panhandle paleovalley, which contains the thickest known sequence of Ogallala sediments in the Texas Panhandle (Gustavson, 1986; Gustavson and Winkler, 1988) (fig. 1).

Subsidence resulting from dissolution of Permian bedded salt prior to and during deposition of the Ogallala and Blackwater Draw Formations has strongly influenced the distribution of these sediments. For example, fluvial systems, which carried sediments across the High Plains during early Ogallala time, were cut off from sediment and water sources by dissolution-induced subsidence along structural trends, which now are the Pecos and Canadian River Valleys. Subsidence changed the style of Ogallala sedimentation from mixed fluvial/eolian to entirely eolian, and this style of sedimentation has continued during deposition of the Blackwater Draw Formation during the Quaternary (Gustavson and Winkler, 1988). Subsidence has also influenced the development of many of the larger playa basins in the Pantex Plant area (see Paine, this report; Paine, 1994e).

## OGALLALA AND BLACKWATER DRAW LITHOFACIES

Seven lithofacies were described from regional examinations of the Ogallala Formation including fluvial gravel; sand and gravel; sand; fine sand, mud, and clay; eolian sand; and very fine sand and coarse silt (table 1). In the Pantex area fluvial sands and gravels occur in the Panhandle Paleovalley. Gravels predominate in the lower 60 to 90 m of the section, and coarse fluvial sands are more common in the middle 60 to 90 m. However, the upper 30 to 45 m of the Ogallala Formation and all of the Blackwater Draw Formation are mostly eolian fine sand to coarse silt. Four lithofacies have been described from the Blackwater Draw Formation, including

Table 1. Ogallala Formation lithofacies and interpreted depositional environments.

<b>Lithofacies</b>	<b>Sedimentary, diagenetic and pedogenic characteristics</b>	<b>Depositional environments</b>
I. Gravel	Mostly flat-bedded, clast supported, partly imbricated, locally CaCO <sub>3</sub> -cemented, matrix-supported, or upward-fining pebble-to boulder-sized gravel. Typical basal Ogallala deposits.	High-energy ephemeral stream
II. Sand and gravel	Mostly trough cross-stratified upward-fining coarse sand-to pebble-sized gravel; locally CaCO <sub>3</sub> cemented.	High-energy ephemeral stream
III. Sand (fluvial)	Flat-bedded to planar-, trough-, or ripple-cross-stratified medium sand; locally with clay silt drapes; locally CaCO <sub>3</sub> cemented or upward-fining.	Ephemeral stream
IV. Fine sand and mud	Locally channel-filling, in part upward-fining, laminated, fine sand and mud; common desiccation cracks; common CaCO <sub>3</sub> nodules.	Abandoned channel or floodplain
V. Clay	No preserved primary sedimentary structures, desiccation cracks partly filled with silt to very fine sand, CaCO <sub>3</sub> nodules, large wedge-shaped soil aggregates bounded by fractures with slickensides.	Ephemeral pond
VI. Sand (eolian)	Eolian trough cross-stratified, well-sorted, fine to medium sand, well rounded frosted grains, locally with preserved clay bands, rhizcretions, or CaCO <sub>3</sub> nodules, locally CaCO <sub>3</sub> cemented.	Eolian dunes associated with an ephemeral stream
VII. Very fine sand and coarse silt	Coarse silt to very fine sand, no preserved primary sedimentary structures, locally common open root tubules, rhizcretions, and CaCO <sub>3</sub> nodules; locally buried B (soil) horizons preserve high clay content or sand or silt filled desiccation cracks.	Loess accumulation on grassland savanna or prairie

eolian very fine to fine sand; very fine sand coarse silt; and rare intervals of lacustrine laminated sand, silt, and clay (table 2). Each lithofacies is characterized by a distinct set of sedimentary and pedogenic characteristics and typically is characteristic of a distinct depositional environment. Furthermore, it is important to recognize that texturally distinct lithofacies are characterized by different values of hydraulic conductivity.

## REGIONAL OGALLALA AND BLACKWATER DRAW STRATIGRAPHY

Plates I and II illustrate the regional stratigraphy of the Ogallala and Blackwater Draw Formations in the vicinity of the Pantex Plant. These cross sections are based on wireline logs, descriptions of core from the Bureau of Economic Geology (BEG) stratigraphic test well BEG/PTX No. 2 (OM-105), and cuttings descriptions from most of the other wells on the cross sections. The sections illustrate well the lateral extent of fine-grained clay-rich units. Descriptions of cuttings show the distribution of gravel and sand, but wireline logs do not distinguish sand from gravel, nor do they distinguish coarse fluvial sand from fine eolian sand. For these reasons, only the fine-grained floodplain overbank or lacustrine deposits have been correlated from well to well. Nevertheless, these cross sections illustrate the regional vertical and lateral heterogeneities of the Ogallala Formation.

The boundary between the Ogallala Formation and the overlying Blackwater Draw Formation is made obvious in outcrop by the presence of the Caprock calcrete (caliche) at the top of the Ogallala Formation and by a distinct increase in redness of sediments of the Blackwater Draw in comparison to the Ogallala. The Caprock calcrete cannot be recognized on wireline logs and is difficult at best to recognize in cuttings. Subtle changes in color are also typically not recognized in cuttings. For these reasons the contact between the Blackwater Draw and Ogallala Formations is not shown on regional stratigraphic cross sections.

Several fine-grained units are present beneath the Pantex Plant including the lower part of the main perched aquifer, which functions as a perching layer, or aquitard, at a depth of 76 to 98 m. This unit is present beneath all of the eastern half of the Pantex Plant, extends south beyond Sevenmile Basin, and north beyond the City of Amarillo well field. Figures 3 and 4, which are composites of core data and gamma-ray log traces from stratigraphic test wells drilled by the BEG, provide detailed descriptions of the Ogallala and Blackwater Draw Formations on the Pantex Plant. For example, the main perched aquifer in both wells consists of sequences of water-saturated laminated sand and silt that fine upward to clay. Two upward-fining sequences are present in BEG/PTX No. 2 (OM-105), and four upward-fining sequences are present in BEG/PTX No. 3 (OM-106). Core and geophysical logs from these two wells illustrate the heterogeneity of the lower part of the main perched aquifer beneath the Pantex

Table 2. Blackwater Draw Formation lithofacies and interpreted depositional environments. This table does not include sediments that partly fill draws or playa basins on the Southern or Central High Plains.

<b>Lithofacies</b>	<b>Sedimentary, diagenetic and pedogenic characteristics</b>	<b>Depositional environments</b>
1. Very fine to fine sand	Fine to very fine sand with no preserved primary sedimentary structures; rare to common $\text{CaCO}_3$ nodules or filaments; large $\text{CaCO}_3$ nodules may be pedodes; rare to common root tubules;	Sand sheet and atmospheric dust on grassland savanna or prairie
2. Very fine sand and coarse silt	Coarse silt to very fine sand, no preserved primary sedimentary structures, locally common open root tubules, rhizcretions, and $\text{CaCO}_3$ nodules; locally buried B (soil) horizons preserve high clay content or sand or silt filled desiccation cracks.	Sand sheet and atmospheric dust on grassland savanna or prairie
3. Laminated very fine sand, silt, and clay	Thinly laminated very fine sand, silt, and clay; upward fining centimeter-scale sequences; desiccation cracks;	Ephemeral pond
4. Clay	No preserved primary sedimentary structures, desiccation cracks partly filled with silt to very fine sand, $\text{CaCO}_3$ nodules, large wedge-shaped soil aggregates bounded by fractures with slickensides.	Ephemeral pond



Plant. Vertical hydraulic conductivity for clays versus fine sands from these sequences differ by as much as three orders of magnitude.

Figure 5 is a cross section designed to illustrate the variations in sediment texture within the upper coarse-grained part of the main perched aquifer (see Mullican and Fryar, this report, for a discussion of perched-aquifer hydrology). Lithologic descriptions from eight closely spaced wells are plotted to show the distribution of lithologies within the main perched aquifer, the potentiometric surface of the main perched aquifer, and the contact between the coarse-grained and fine-grained fractions of the main perched aquifer. The coarse-grained section ranges in texture from gravel to sand, and the fine-grained part of the main perched aquifer is interbedded clay, silt, and sand. Furthermore, even in these closely spaced wells, correlation of lithofacies can not be done with certainty.

#### PEDOGENIC AND BIOLOGIC STRUCTURAL HETEROGENEITIES

Pedogenic structures, which are commonly preserved in buried soils in Ogallala and Blackwater Draw sediments, include fractures that bound ped (soil aggregates) faces. Fractures are commonly lined with clay cutans,  $\text{CaCO}_3$  filaments, and Mn oxide/hydroxide films. Large curved fractures with slickensides bound wedge-shaped clay soil aggregates in buried vertisols and may nearly penetrate clay sequences.

Biologic structures such as root tubules are found throughout the Ogallala and Blackwater Draw Formations. Open tubules, which are typically ~1 mm in diameter, range up to 6 mm in diameter and are preserved as discontinuous open conduits at depths as great as 114 m in the Ogallala Formation. Root tubules are commonly lined with Mn oxide/hydroxide films or with  $\text{CaCO}_3$ . Tubules penetrate all sediment types, including pedogenic  $\text{CaCO}_3$  nodules and buried calcrete horizons. The deepest tubule occupied by a modern root was encountered at 14 m. The root hair, which was approximately 0.2 mm in diameter, occupied a root tubule that was approximately 3 mm in diameter. This root hair in a large root tubule illustrates that roots are opportunistic and will invade existing root holes to potentially enhance the connectivity of tubules. Burrows are less commonly preserved than tubules but are typically 1 to 2 cm in diameter, commonly circular in cross section, and loosely filled with sediment. Most of these features show evidence of ground-water flow indicating that they are or were preferred flow paths.

## SUMMARY

A hierarchy of stratigraphic heterogeneities characterizes both the Ogallala and Blackwater Draw Formations in the vicinity of the Pantex Plant and influences hydrologic variables such as conductivity and transport of contaminants. Heterogeneities include grain-size differences on both regional and local scales, such as fine-grained overbank or lacustrine deposits interbedded with coarse-grained fluvial units and sand to silt to clay upward-fining sequences within the overbank deposits. Structural heterogeneities include fractures and root tubules.

## APPLICATIONS OF STRATIGRAPHIC STUDIES TO GROUND-WATER REMEDIATION

Ogallala and Blackwater Draw sediments are heterogeneous on several scales. For example, on regional scale, Ogallala strata are made up of interbedded gravels, sands, and clays, which have different hydraulic properties. On a local scale, strata that make up the fine-grained unit at the base of the main perched aquifer are a series of upward-fining sequences of laminated sand, silt, and clay with vertical hydraulic conductivities that vary by three orders of magnitude (Mullican and Fryar, 1995). Furthermore, potential pathways for preferential ground water flow are common in these sediments. Therefore, it is likely that only those remediation options that are designed to accommodate the heterogeneity of the Ogallala and Blackwater Draw sediments will be effective.

## UNRESOLVED ISSUES

Stratigraphy of the Ogallala and Blackwater Draw Formations beneath the Pantex Plant remains incompletely understood. For example, few wells penetrate below the perched aquifer. As a consequence, there are neither core nor modern logs available to determine the stratigraphy of these strata. It is important to understand the nature of both the saturated and unsaturated zones beneath the main perched aquifer because contaminated waters of the main perched aquifer may be leaking through the fine-grained zone at the base of the main perched aquifer.

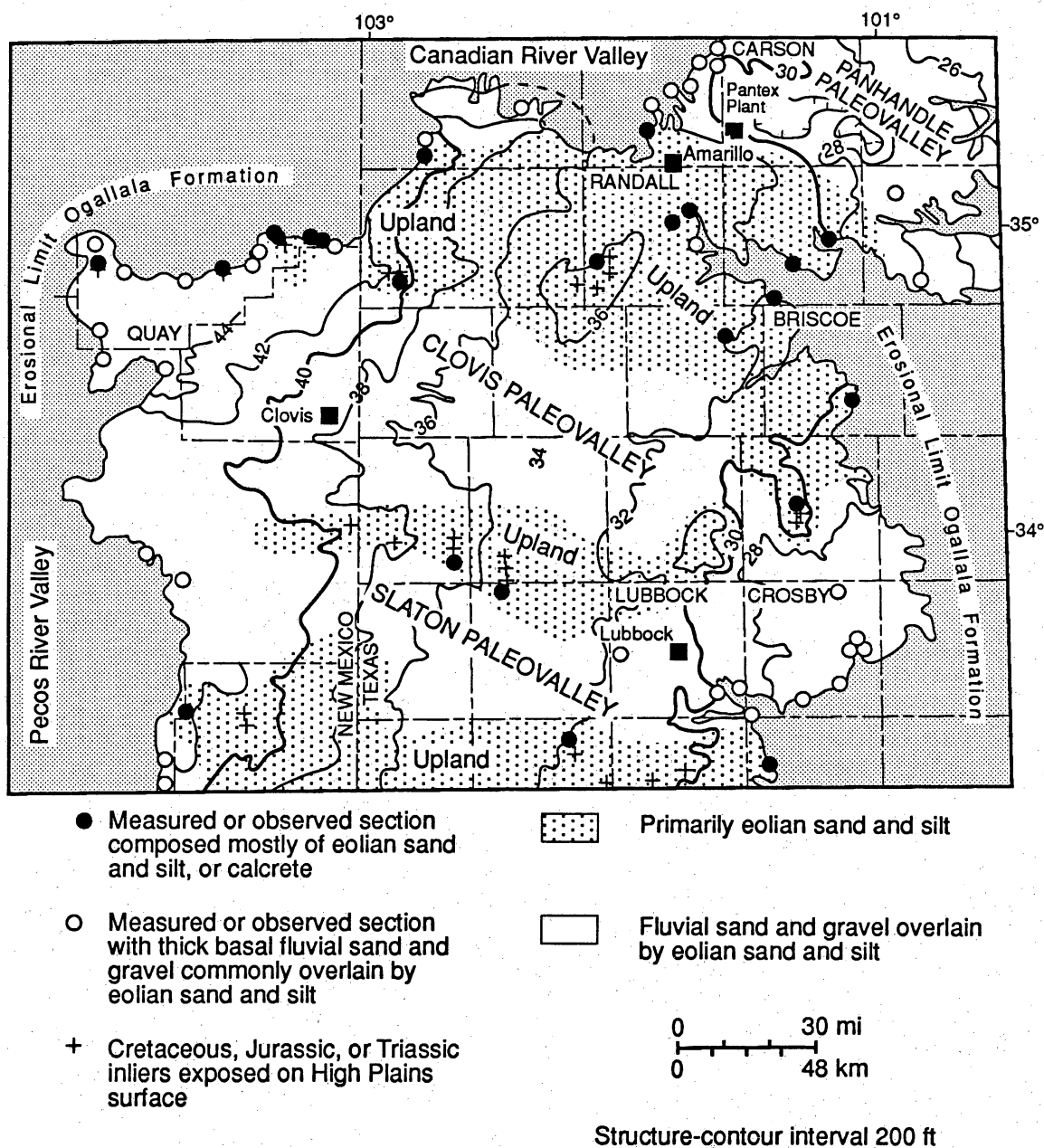


Figure 1. Regional structure-contour map on the pre-Ogallala erosional surface illustrates paleotopographic highs (stippled) and paleovalleys. Paleovalleys are partly filled with fluvial sediments that are in turn overlain by eolian deposits (open circles). Paleouplands are overlain by eolian deposits (filled circles). Circles identify locations where exposures were examined. Crosses identify inliers of pre-Ogallala strata.

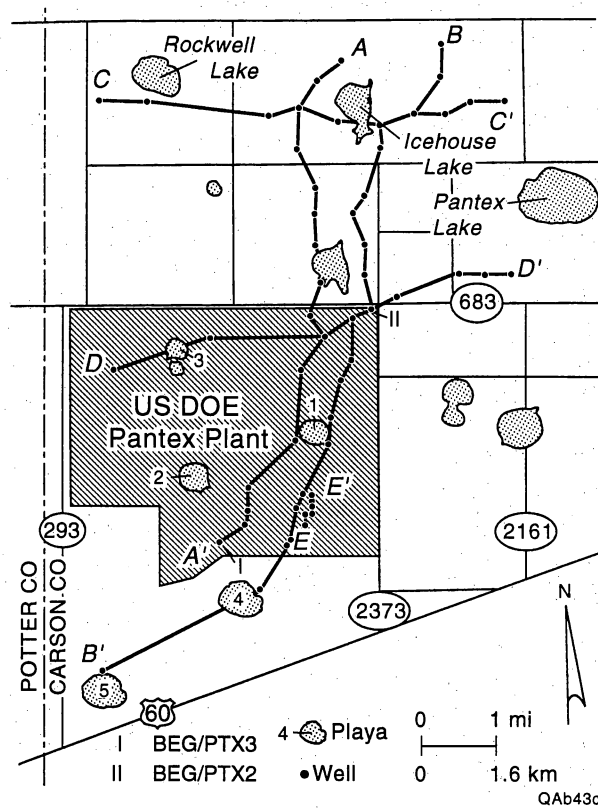


Figure 2. Location map for stratigraphic sections A-A', B-B', C-C', D-D', and E-E'.

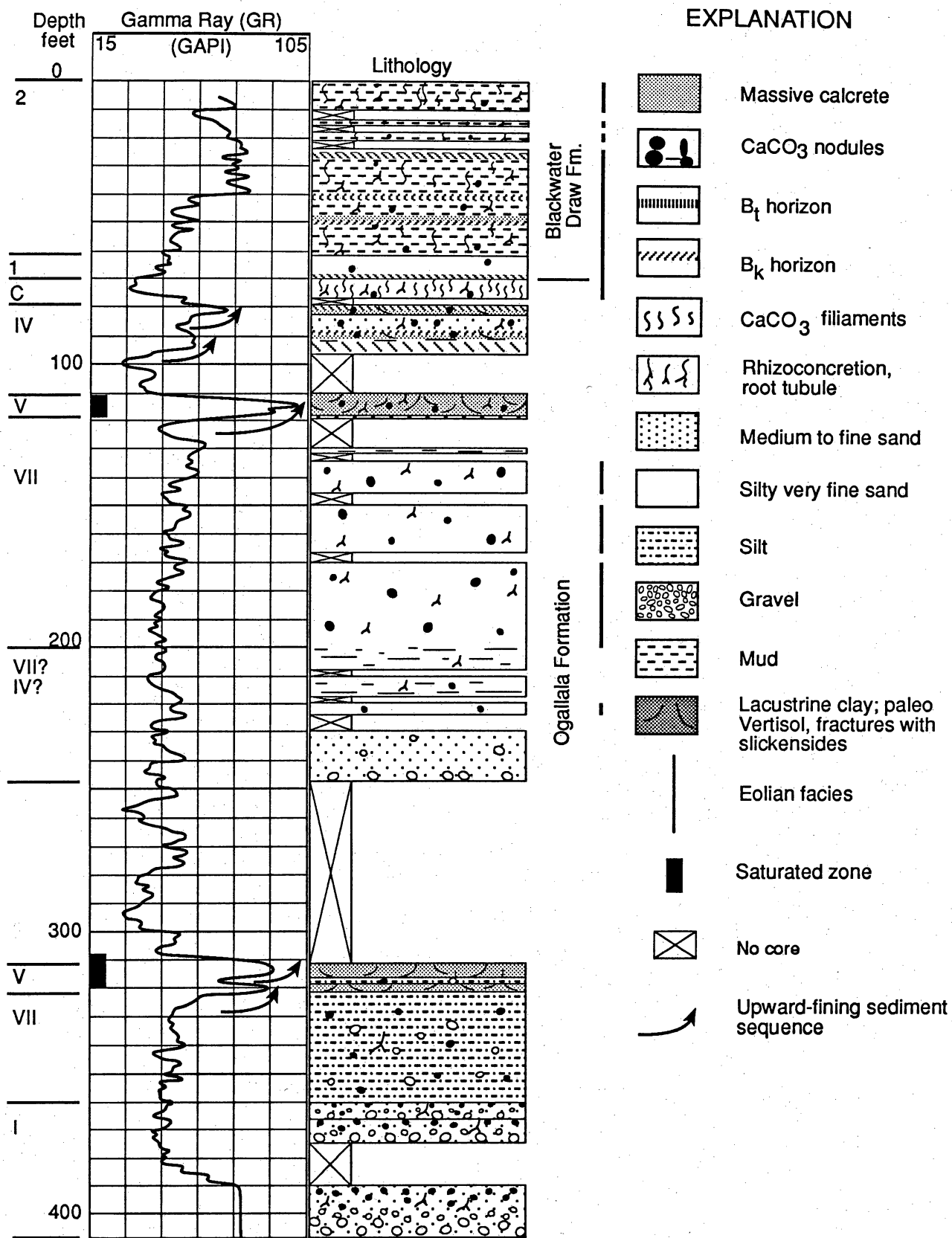


Figure 3. Stratigraphic section of Ogallala and Blackwater Draw Formations interpreted from core from BEG/PTX No. 2. Lithologies are plotted opposite a gamma-ray log trace. Zones saturated with ground water are shown as black bars.

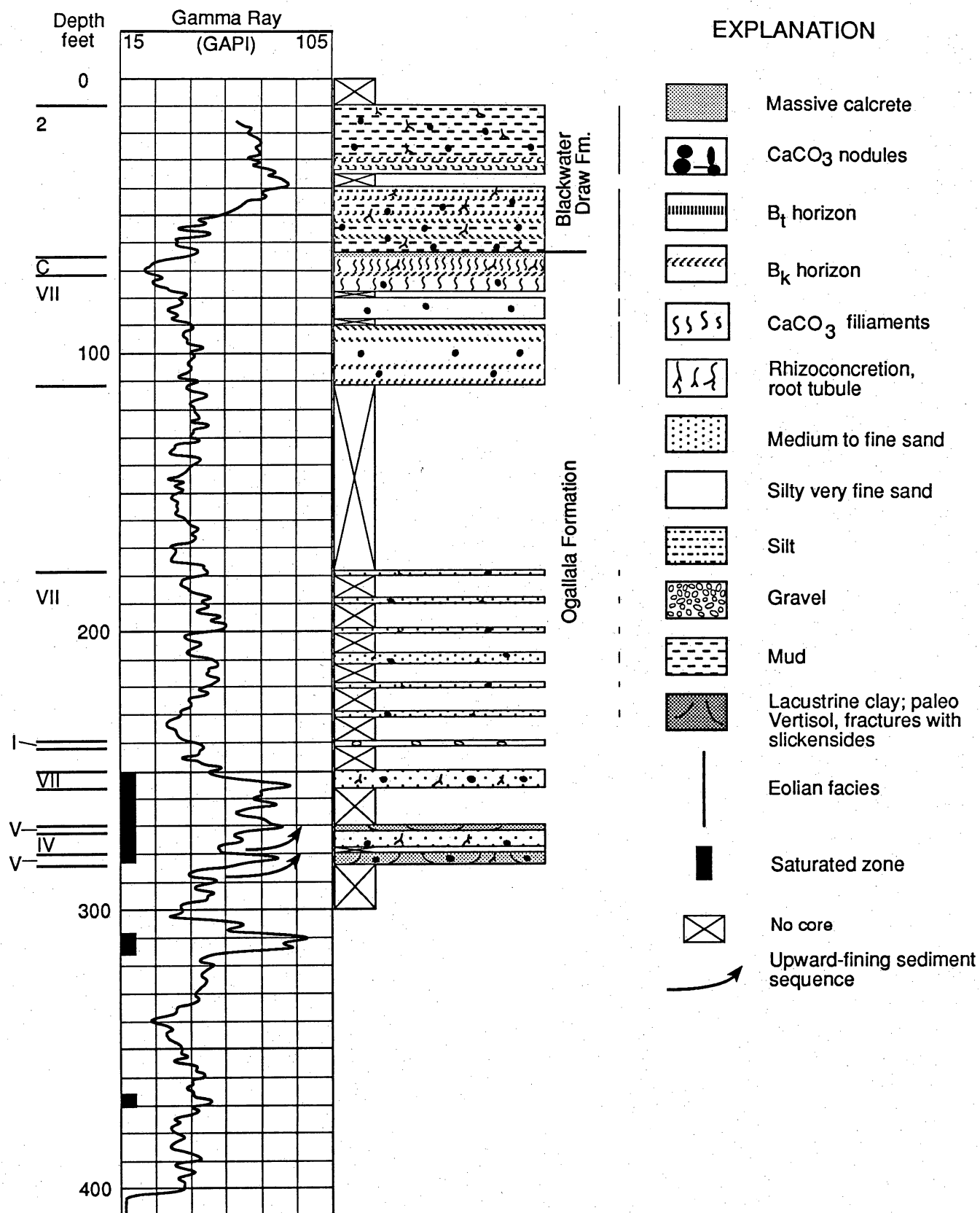


Figure 4. Stratigraphic section of Ogallala and Blackwater Draw Formations interpreted from core from BEG/PTX No. 3. Lithologies are plotted opposite a gamma-ray log trace. Zones saturated with ground water are shown as black bars.

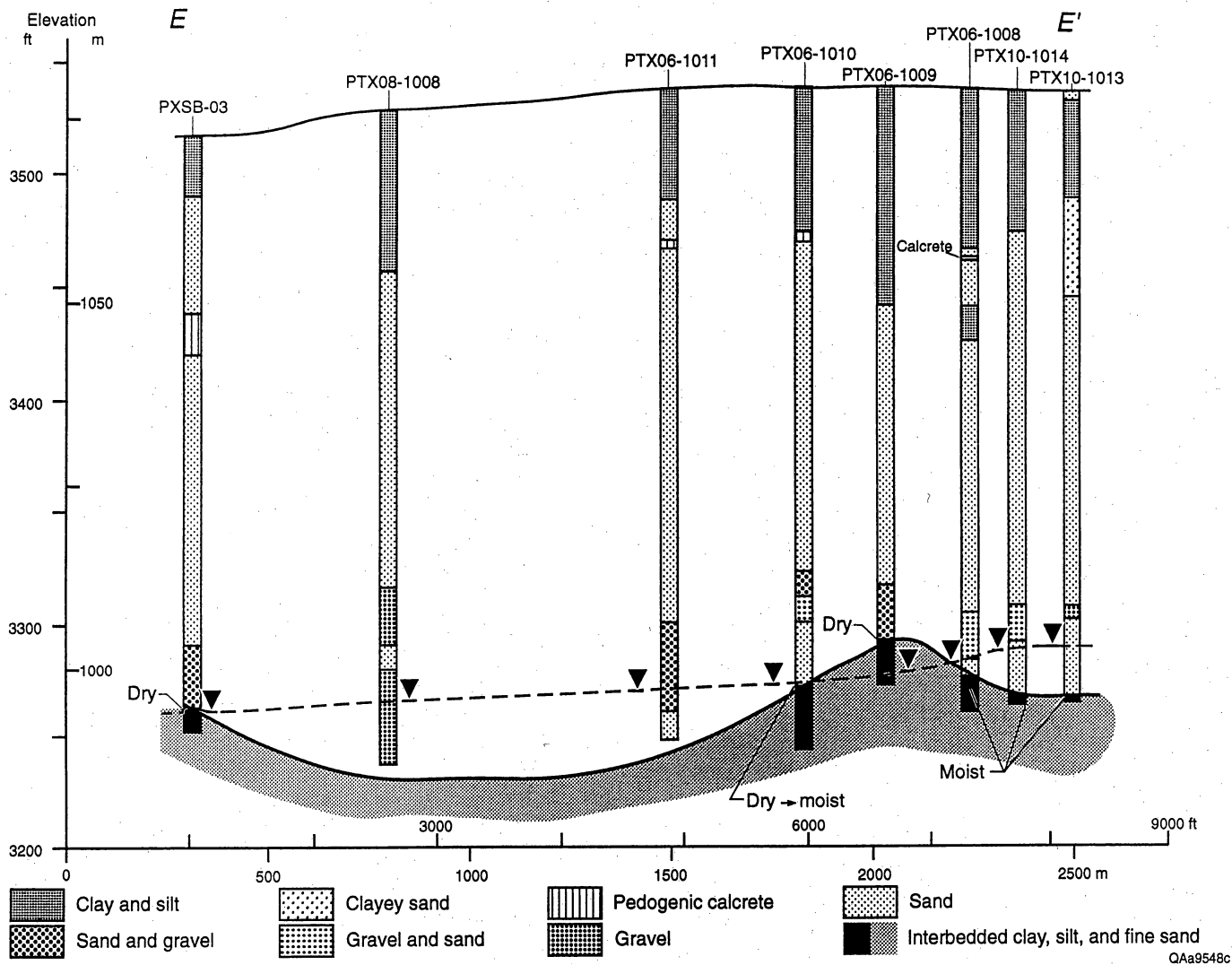


Figure 5. Cross section E-E' showing the lithologic variability of the sediments containing the perched aquifer. See figure 2 for location.

# Playa Basin Stratigraphy

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## INTRODUCTION

Playa lakes are abundant, small ephemeral lakes that occur in shallow depressions on the surface of the Southern High Plains. Playa lakes that lie within the boundaries of the Pantex Plant historically have collected precipitation runoff, storm- and waste-water discharge, and contaminants. Ephemeral playa lakes are floored by Randall clay soil, which serves to slow recharge and pond water. Areas of special interest include (1) the floor of the playa lake, where water is ponded for the longest time; (2) the annulus or shoreline zone, which is only submerged at high water levels; and (3) drainages, which centripetally drain the playa basin slopes and concentrate flow into the playa. Playa floor and annulus comprise the playa; basin slope and upland are described as interplaya. Study of sediments beneath playas was undertaken to better understand the role of playas in recharge of potentially contaminated water, to provide a geologic framework for unsaturated zone hydrologic and geochemical studies, and to provide data needed to evaluate remediation scenarios.

## Methods

Stratigraphic studies of playas documented (1) the types, thickness, and geometry of sediments beneath the floors of playa lakes and (2) the character and distribution of fractures, soil structures, and roots that might influence the distribution of permeability. Sediments in 12 playa lakes in the vicinity of the Pantex Plant were examined using 76 hollow-stem auger cores (totaling 1,614 m of core), ground-penetrating radar transects, trenching, and examination of exposures in large excavations. Description of a spectrum of playa basins of a variety of sizes and recharge behaviors defines the characteristics that are similar in playa basins and the features that are variable and also documents the long-term maintenance of the seasonally ephemeral lakes and their responses to past climatic changes. These observations can be used to constrain the assumptions made about subsurface stratigraphy and recharge from the playas on the Pantex Plant. Playas off the Pantex Plant were examined in preference to those on the plant because: (1) basic data are needed about the typical heterogeneity of playa sediments, and borehole and trench data could be collected and analyzed faster and at lower cost in offsite



areas where there was no history of contamination and (2) baseline data are needed in playas with minimal modification to the playa and to the recharge regime, which could better be collected in playas offsite. Cores from two playas historically used for ponding waste water, Playa 5 and Pantex Lake, were examined to determine the effect of artificially prolonged recharge on playa sediments.

## PLAYA STRATIGRAPHY

Playa lake basins in the Pantex area all contain thick sequences (5 to 18 m) of Quaternary lake sediments (Hovorka, 1995). A facies classification for playa lake and related sediments has been developed (fig. 6). Facies include: (1) upland and basin slope accretionary eolian facies (clayey silt with buried soil horizons typical of the type Blackwater Draw Formation), (2) gray and red lacustrine clays, (3) lacustrine/eolian sand beds, (4) clays with interbedded or admixed sand laminae, (5) poorly sorted lacustrine delta deposits, and (6) lower fine to medium sand. Lake sediments interfinger with calcic soils and red-brown loam of the Blackwater Draw Formation near the edges of the playas. The lower sand unit underlies both playas and uplands in the Pantex area at depths of 10 to 20 m.

The geometry of sediments beneath all playa basins in the Pantex area is highly heterogeneous (fig. 7). Vertical heterogeneities result from changes in sediment supply, lake expansion and contraction, delta progradation, and variation in the intensity of soil development (Hovorka, 1995). Lateral heterogeneities reflect the asymmetry of playa basins, localized sediment input, and variation in the amounts and types of sediment reworking. Cross sections document that in a playa setting, generalizing from a few test holes will produce an inaccurate image of the composition beneath the playa. In particular, playas are highly asymmetrical when comparing the complex stratigraphy of the southern and eastern sides with the moderately to highly erosional northern and northwestern side. The annulus of the playa is also extremely variable over short distances both along and perpendicular to the lake shore.

## PERMEABILITY DISTRIBUTION AND EVIDENCE OF PREFERENTIAL FLOW

One of the goals in examining playa sediments was to seek resolution of the discrepancy between the observed low permeability and ability to pond water, which is typical of Randall clay soils, and the hydrologic observation that playa lakes focus recharge to the underlying aquifers. Prior to this study, several concepts for facilitating recharge through playas have been suggested. These are: (1) flow through the annulus, (2) intermittent rapid flow through the dry

cracked playa floor, and (3) preferential flow through the clay.

The concept of annular flow suggests that most of the recharge would take place at high water levels in the playa lake, when water is ponded at or over the annulus. If the annulus lacks a clay layer at the surface, recharge could proceed rapidly through coarser grained soils. Annular recharge has been proposed by a number of workers (White and others, 1946; Cronin; 1964; Havens, 1966; Wood and Osterkamp, 1987) to account for rapid water level declines at high water levels (Reddell, 1994).

In this study of the subsurface character of playa sediments, additional details about the annulus are documented (fig. 7). No highly permeable strata are encountered at the surface in the annulus. Clayey sediments extend to the high water level in the playa lakes. The clayey surface sediments high in the annulus are slightly thinner, siltier, and dryer than their equivalents in the playa. Slight increases in carbonate content toward the upper annulus suggest that surface sediment is more frequently dry and not as well flushed in the annulus as in the playa floor.

Underlying the surface sediments in the annulus is a wedge of Blackwater Draw slope facies. This facies was observed all the way around the lake, generally at depths of 1 m or less. The Blackwater Draw slope facies contains minor amounts of carbonate, which is relict from upland soil-forming processes. This carbonate has not been flushed, but organic material has been translocated downward into the slope facies along cracks, documenting downward flux of fluids. The silty clay loam of the Blackwater Draw slope facies beneath the annulus may have somewhat higher hydraulic conductivities than the sediments of the playa floor, either because of its texture or its soil microstructure. However, wedges of Blackwater Draw facies generally show as much or more gleying and discoloration by organic material beneath the playa floor than beneath the annulus, suggesting that flow through the annulus is probably less than beneath the playa floor. In general, neither the surface soils nor the immediately underlying Blackwater Draw facies contain diagenetic evidence of higher rates of downward flow of water through the annulus than through the playa floor. More complete removal of carbonate from carbonate-bearing facies and more abundant evidence of downward translocated organic material beneath the floor of the playa suggest that more flow has occurred beneath the playa floor where ponding is prolonged.

One exception to this observation was documented on the north shore of Playa 5 near the site of the former sewage outfall. Here, because the north side of the playa appears to have been more erosional than it is in most lakes, lake sediments overlie well-sorted fine sand at depths of 3.3 m. Organic and limonitic coloration of pods and beds of sand to depths of about 6 m document a type of diagenesis that is uncommon in unmodified baseline playas. Carbonate is mostly not leached from this sand, possibly documenting relatively short duration of flushing

or nonpiston flow. The observed reactions are tentatively attributed to recharge of fluids derived from sewage. Artificially high water levels or direct discharge of water to the annulus may be important in augmenting flow through the annulus in this situation.

Another potential area where flow may be focused in the annulus is where drainages have eroded surface sediments, created complex subsurface stratigraphy, and increased the potential for ponding. Two boreholes drilled into the major drainage on the northern side of TDCJ playa suggest that this may be the case under natural conditions. The deltaic and interbedded sediments near the present lake shore were not particularly sandy; however, they were damp, and carbonate has been leached from Blackwater Draw facies for 15 m beneath the deltaic sediments to a total depth of 21 m. A borehole further up the drainage encountered sediment that was more moist than typical upland cores and has decreased carbonate in Blackwater Draw facies to a depth of 6 m. Decreased carbonate content from typical Blackwater Draw slope facies suggests long-term recharge and leaching may be driven by ponded water in the drainage channel. These natural drainages potentially serve as partial analogues to ditches on the Pantex Plant where water has been ponded on Blackwater Draw sediments.

Discontinuous sand units are commonly encountered in the annulus at depths of about 6 m on the southern shores of playas. These sands show abundant evidence of alteration by oxidizing as well as reducing fluids and translocation of clay; however, the timing of these diagenetic events is unconstrained. Further analysis is needed to document whether these sands play a role in modern recharge.

Intermittent flow through the dry playa floor occurs through the large desiccation cracks that act as conduits to enhance permeability. During initial flooding, these cracks transmit fluids rapidly. As the clays swell and the cracks shut, the rate of flow decreases. Initial high flow rates followed by decreased rates have been measured using infiltrometers on the playa floor (Zartman and others, 1994). Observations on cores and trenches during playa stratigraphic studies provided additional information about flow beneath playas.

Open cracks are abundant in the dry near surface clays. At depths greater than about 1 m, shrink-swell mechanisms produce abundant slickensided fractures. In all the playas examined in the Pantex area, beds of well-sorted fine sand were cored beneath the playa at depths of 1.3 to 5 m. Stacked sequences of older lake clays and sands produce the total thickness of lake sediments.

Flow through the lake clay soils occurs at higher rates than is typical for clay even after several days ponding (Zartman and others, 1994) as well as when the soil was moist and cracks were mostly shut prior to ponding (Xiang and others, 1993). Ponding tests were conducted in TDCJ playa with FD&C blue organic dye and bromide added to the ponded water. The ponds were then drained and trenches cut to expose the dyed areas. The distribution of dye showed

that soil structures and roots transmit fluids even when soils are moist (cracks are shut), so that water penetrates to more than a meter depth within a few hours. Planar soil structures were dyed blue but were not planes of weakness under tension, as demonstrated by attempts to peel the soils off to expose the blue surfaces. The planar surfaces were weak under shear, probably because of higher water content along the surfaces. When the trench dried out over the following months, typical wide, deep desiccation cracks opened along the blue-dyed surfaces. No sand filling or other macroscopic textural contrasts are apparent, and the microfabrics that control the cracking behavior have not yet been documented. Additional work is needed to understand the behavior of these abundant and potentially dynamic structures.

The role of slickensided fractures beneath the modern cracked soils on recharge is not documented. Apertures on slickensided fractures are small even where the sediment was stiff because of lower water content. The rates and processes by which slickensided fractures transmit fluids have not been observed, but inspection suggests that because the fractures are abundant and well connected, they could be very effective in transmitting fluid. Slickensided clays form a layer between the surface cracked zone and underlying sand beds in all of the playas studied.

Evidence of preferential flow is abundant in playa sediments. In the surface lake clays with Randall soils, the shrink-swell cracks and root tubules that have been observed to transmit water in short-term ponding tests are stained by dark organic material, showing that long-term translocation of organic material has occurred along these pathways under natural conditions. These features are observed throughout the playa and in every playa sequence examined. Originally oxidized calcareous soils beneath lake sediments are gleyed, clay illuviated, and pedogenic carbonate partly or totally leached, demonstrating long-term downward flow, especially along cracks and other soil structures.

Older, stiffer gray and red lake sediments contain numerous iron- and manganese-oxide or hydroxide stained fractures. Reduction within and adjacent to many sand beds suggests that the sands have served as conduits for reducing fluids. Vertical fractures served as conduits for both oxidizing and reducing fluids in permeable, well-sorted sands, as well as in low-permeability sediments. These features document that fractures dominate the entire playa section, not just the surface environment.

Effects of modern recharge have not yet been separated from the diagenetic alterations produced during preceding cycles of high lake level. Many textures seem to be most easily related to the environment that produced the overlying sedimentary facies, not the modern surface environments. For example, oxidation of lake sediments and precipitation of pedogenic calcite related to former upland progradation and more ephemeral lakes are preserved beneath lakes, as is gleying beneath older lake units beneath interplaya Blackwater Draw faces. The

modern episode of relatively large lakes with relatively prolonged ponding has not pervasively reduced older sediments nor has it removed all of the previously accumulated carbonate. Either modern surface waters are at chemical equilibrium with the host sediment at shallow depths and therefore fail to alter deeper sediments, or flow is occurring along discrete flow paths and bypasses the bulk of the older sediment. Additional hydrologic and geochemical testing is required to determine the extent to which features serve as preferential pathways for recharge of surface waters.

#### APPLICATIONS OF PLAYA STRATIGRAPHIC STUDIES TO REMEDICATION OF THE PANTEX PLANT

Playas sediments are strongly heterogeneous both laterally and vertically. This implies that a few test holes are not adequate to characterize the distribution of any contaminants that have moved into the sediments beneath a playa. Heterogeneities might be expected to locally enhance flow, moving high concentrations of contaminant during recharge/contamination events, or to retard flow, possibly producing remnant concentrations of contaminant after most has been flushed. The highest stratigraphic variability is observed beneath the annulus. Drainages and contrasts between northern and southern playa margins are other significant features to be tested for variable flow histories in contaminated areas.

Stratigraphic studies of playa sediments have documented evidence that recharge has occurred beneath playa lakes as well as beneath the annulus (shoreline). Textural and diagenetic evidence suggests that flow is dominated by preferential pathways, which has implications for the rates, volumes, and geochemical reactions during flow. Sedimentary heterogeneity indicates that flow probably occurs along different types of pathways at different depths beneath the playa surface. In the Randall clay soil, pathways include roots and root tubules and open soil shrink-swell cracks on the dry floor of the playa. The same cracks seem to function as preferential pathways even when the soil is wet and the cracks are shut. Beneath the surface soil, abundant slickensided fractures may serve as preferential pathways for flow. Sand beds beneath the playa may play a role in fluid transport. Evidence of flow though the most of the annulus is less well developed than the playa floor. Flow beneath the annulus appears to be focused at drainages and by artificially enhanced recharge.

## UNRESOLVED QUESTIONS

The stratigraphic complexity of playa stratigraphy leaves many questions unresolved about the relative rates, timing, and processes of flow in different parts of the playa. More hydrologic and geochemical data are needed in specific facies settings, preferably where natural, contaminant, or introduced tracers are available. The relative volumes of flow at (1) episodic high water levels, (2) normal water levels, or (3) the initial flood entering a dry playa may have important implications for the ultimate distribution of contaminants. The role of different types of fractures and sand beds in creating preferential flow and geochemical reactions under various water-level conditions has not been documented and is expected to be complex. The sedimentary character of the playa sediment documents highly variable long- and short-term climatic conditions in the playa, but the effect of these conditions on flow is not clear. Many of these same characteristics are also important to processes such as intrinsic bioremediation and predictions of the effectiveness of these processes to attenuate contaminant over time.

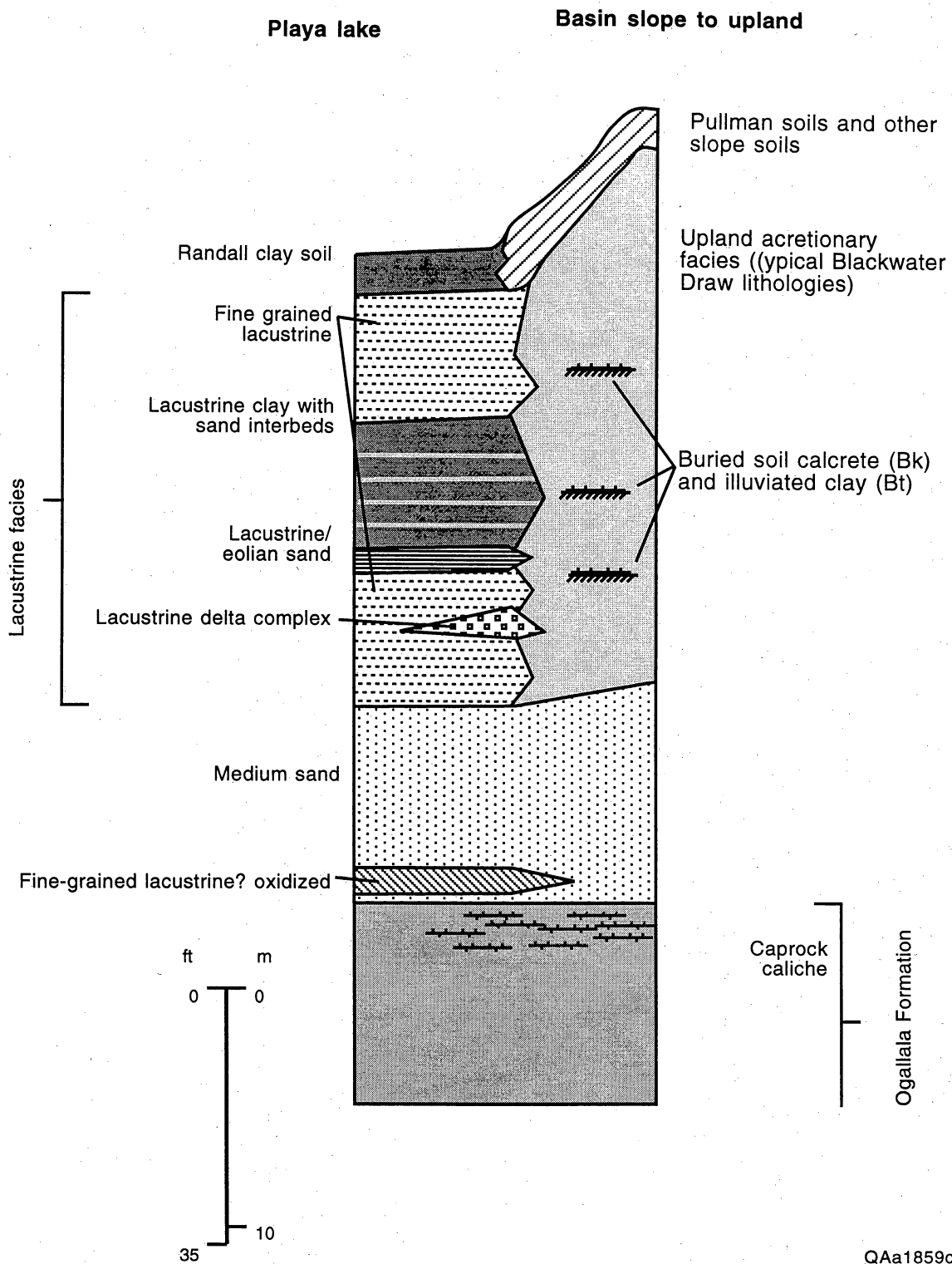


Figure 6. Generalized playa stratigraphic section, showing major facies.

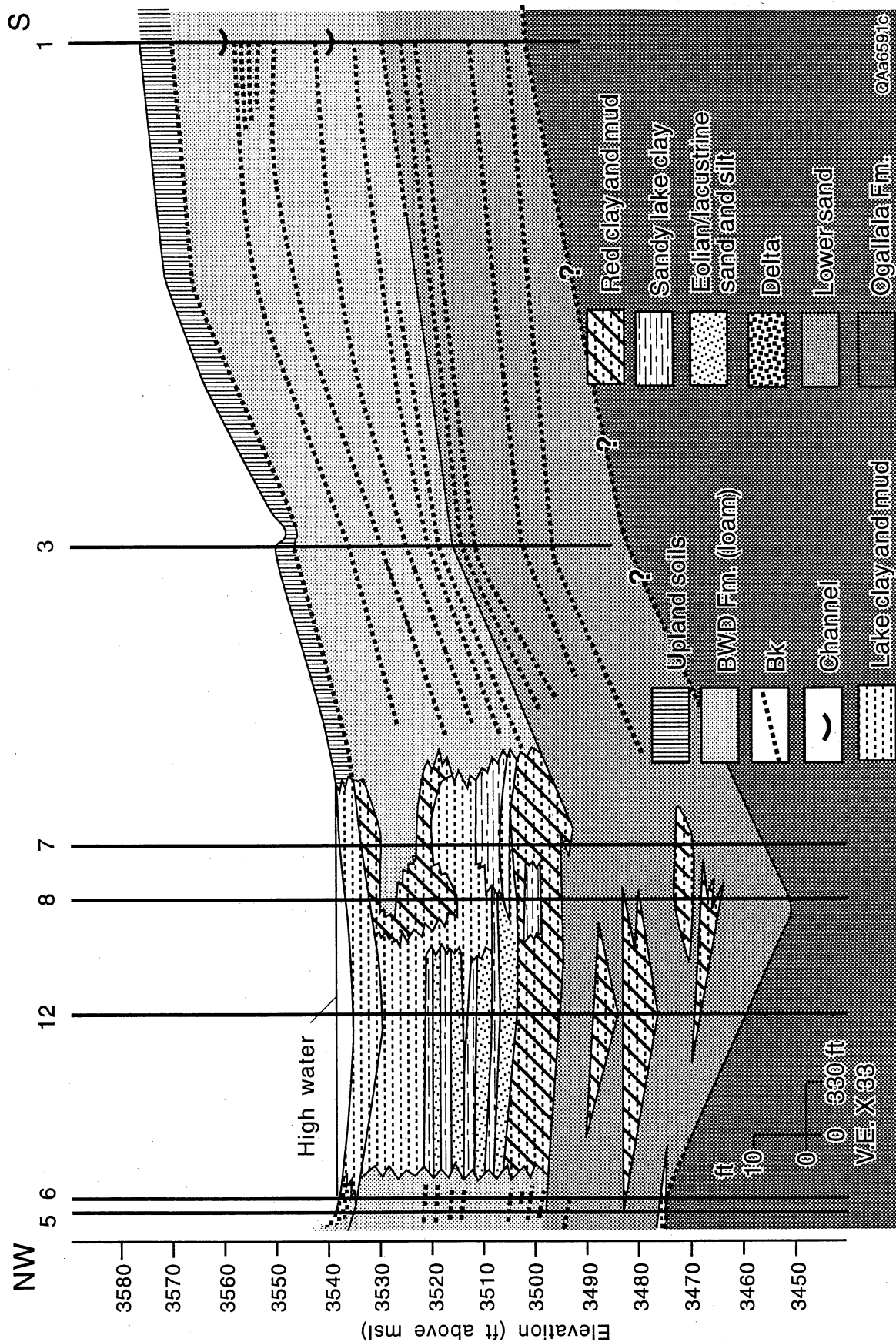


Figure 7. North-south cross section through Wink playa, showing typical complex facies relationships in the subsurface beneath playas.



## Summary of Pantex Area Seismic Studies

*by Jeffrey G. Paine*

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### INTRODUCTION

The primary objective of the Bureau of Economic Geology's (BEG) geophysical program at Pantex was to use noninvasive geophysical methods (principally shallow seismic reflection profiling) to help understand the hydrogeological framework of the Pantex Plant and surrounding areas. Subsurface targets of interest include the top of the Ogallala Formation (the "Caprock"), internal Ogallala stratigraphy (particularly units which may retard the flow of ground water from the surface to the main Ogallala aquifer), and the surface of the underlying Permian or Triassic bedrock. These studies have led to a better understanding of stratigraphic differences between playa basins, which serve as sites of focused recharge for the Ogallala and perched aquifers and between playa and interplaya areas, where little Ogallala recharge occurs. The data are also an important part of the Pantex data base, which can provide important information needed to respond to issues as they arise. The seismic data, for example, were used to evaluate possible flow paths to recently completed wells along the eastern boundary of the plant.

Shallow seismic refraction and reflection techniques provided new information on the stratigraphy, structure, and physical properties of the upper 200 to 300 m beneath the surface in the Pantex area. Geophysical and drillers' logs from nearby borings, monitoring wells, and water supply wells supported interpretations of features on the seismic reflection sections. Through 1994, BEG collected 50 km of shallow seismic reflection data in interplaya and playa basin settings in the Pantex area (fig. 8 and table 3) (Paine, 1992, 1993, 1994a, b, c, d).

Table 3. Line lengths for shallow seismic reflection data collected in the vicinity of the Pantex Plant in 1991, 1992, 1993, and 1994. Line locations shown on figure 8.

	Length (km)
Interplaya lines	
PRL1	6.5
PRL2	7.3
PRL3	11.3
PRL4	6.5
PRL5	3.2
Total interplaya lines	34.8
Playa basin lines	
PRL7 (Sevenmile Basin)	4.5
PRLA (Playa 3)	1.8
PRLB (Playa 3)	1.8
PRLC (Pantex Lake)	3.2
PRLD (Playa 5)	1.9
PRLE (Playa 5)	1.9
Total playa basin lines	15.1
Total interplaya and playa basin lines	49.9

## FIELD TESTS AND DATA ACQUISITION

Seismic investigations in the Pantex area began with extensive seismic tests, including a noise test, a walkaway source test, a refraction survey, and a common depth point reflection survey. These tests were conducted near the northeast corner of the Pantex Plant. The Bison EWG-III, a noninvasive, stackable 230 kg accelerated weight drop unit, was used during all refraction, reflection, and downhole seismic data acquisition. Data were recorded on a 48-channel seismograph.

A vertical seismic profile was acquired at stratigraphic test well BEG-PTX No. 2 (OM-105). This profile was performed on a well that reached pre-Ogallala deposits at a depth of 123 m. In addition to discovering which lithologic units are the best reflectors of seismic energy (one of the most prominent is a middle Ogallala fine-grained zone that perches ground water beneath much of the Pantex Plant), we determined the seismic velocity structure near the well. This was a critical step in assigning depth estimates to seismic reflectors, which are only represented in two-way traveltime on seismic sections.

## Interplaya Areas

Nearly 35 km of regional shallow seismic reflection data was collected in interplaya areas of the Pantex Plant and the adjacent Carson County Amarillo water well field in 1991 (fig. 8 and table 3). Cross sections along the interplaya lines were constructed using drillers' logs and available geophysical logs from wells near the seismic lines. These sections were used to guide stratigraphic interpretations of the processed seismic data.

The base of the Ogallala Formation, the top of the prominent fine-grained zone within the Ogallala Formation, and the top of the Ogallala Formation were interpreted from available drillers' and geophysical logs in the Pantex area. These interfaces are all targets of the seismic work. It is clear from both logs and seismic data that there is considerable relief on the pre-Ogallala surface and that the middle Ogallala fine-grained zone appears to be present in virtually every well in the two-quadrangle area (Sevenmile Basin and Pomeroy 7.5' quadrangles), which includes the Pantex Plant and the Amarillo well field.

Interplaya seismic reflection data (lines PRL1, 2, 3, 4, and 5; fig. 8) show prominent reflections that include, from shallowest to deepest, (a) Horizon 1, a surface that is suspected to be the main perching horizon for perched aquifers in the region; (b) Horizon 2, a thin, fine-grained unit in the lower Ogallala; and (c) Horizon 3, the top of pre-Ogallala bedrock. Reflectors have been correlated to available downhole geophysical data along reflection line PRL2 (fig. 9), which is an east-west line along the northern boundary of the Pantex Plant. On this line, all major surfaces have gentle apparent dips to the east; the reflector (Horizon 1) that correlates to the main perching horizon is present along most of the line but fades in some areas. The bedrock surface beneath line PRL2 (Horizon 3) is irregular and includes at least two lows that are 200 to 300 m across and may represent either collapse or erosional features.

Reflectors visible on lines PRL1 (eastern boundary of the Pantex Plant), PRL3 (a north-south line across the central part of the Pantex Plant), and PRL5 (western boundary of the Pantex Plant) have been converted from time to depth (figs. 10, 11, and 12) and correlated to reflectors and geophysical log patterns along line PRL2 at the northern boundary of the plant. These north-south lines show that the lower Ogallala and bedrock surfaces (Horizons 2 and 3) deepen to the north and that the perching horizon (Horizon 1) is found at a relatively consistent elevation across most of the Pantex Plant.

Generalized maps of the main perching horizon (Horizon 1), the lower Ogallala fine-grained zone (Horizon 2), and the top of bedrock (Horizon 3) at the Pantex Plant were constructed from calculated horizon elevations along reflection lines PRL1, 2, 3, and 5. The map of the main perching horizon (fig. 13) shows that this horizon is estimated to be at elevations of 980 to 1,015 m above sea level beneath most of the plant. Reflection lines across Playas 3

and 5 show that this horizon deepens beneath the basins enclosing these playas, perhaps related to dissolution-induced subsidence. Detailed studies of the southern part of line PRL1 appear to show that a broad channel, identified from Pantex Zone 12 boreholes by Argonne National Laboratory, extends southeastward near the top of the middle Ogallala perching horizon.

Horizon 2 is the next major reflector below the middle Ogallala perching horizon. Correlations with geophysical logs along line PRL2 (fig. 9) show that Horizon 2 is a relatively thin fine-grained zone within the dominantly coarse grained fluvial deposits of the lower Ogallala Formation. Unlike the main perching horizon, Horizon 2 deepens to the northeast (fig. 14); calculated elevations for this horizon are near 960 m at the southwest part of the Pantex Plant and deepen to 910 to 920 m at the northeast corner of the plant. Total relief on this surface is 40 to 50 m beneath the plant.

The deepest stratigraphic level of interest, the Permian or Triassic bedrock (Horizon 3, fig. 15), also deepens markedly to the northeast at the Pantex Plant. This major reflecting horizon has been correlated across the plant from stratigraphic picks made from drillers' and geophysical logs along seismic line PRL2 (fig. 9). Estimated elevation of this reflector is 940 to 950 m at the southern part of the plant, deepening to 870 to 880 m at the northeastern corner of the plant and about 890 m at the northwest corner of the plant. Excluding playa basins, relief on this surface is more than 70 m, greater than that for overlying major reflecting horizons.

Analysis of line PRL3 and nearby well log data suggests that the interbedded fine-grained zone (Horizon 1) that perches ground water beneath parts of the Pantex Plant extends northward across the well field. Potentially correlative fine-grained zones have been documented across a wide area that includes the Pantex Plant, Sevenmile Basin, Pantex Lake, and the Amarillo well field. Similarly, several fine-grained zones or clay-rich sequences within the middle part of the Ogallala Formation are illustrated on stratigraphic cross sections (Plates I and II) and described in the section on regional and playa stratigraphy. Other potentially correlative Ogallala deposits have been described north of the well field in exposures in the Canadian River valley. These fine-grained zones represent sediments deposited in low-energy depositional environments such as floodplains, numerous relatively small lakes, or fewer large lakes.

### Playa Basins

Refraction spreads and 15 km of reflection data were collected across Sevenmile Basin, Pantex Lake, and Pantex Playas 3 and 5 to examine Ogallala stratigraphy beneath playas for

comparison with Ogallala stratigraphy in nonplaya areas. Subsurface seismic images across these four Pantex-area playa basins show that, at each basin, all major reflecting horizons dip into these basins and that relief on these surfaces increases with age (fig. 16), indicating that subsidence has influenced the formation of these basins.

Seismic reflection data collected across Sevenmile Basin show prominent reflections from within the Ogallala Formation and the top of bedrock. Less prominent reflections are visible from within the Permian to Triassic bedrock. Conversions from two-way traveltime to actual depth of these reflectors indicate that there is considerable relief on older surfaces beneath Sevenmile Basin and that the modern surface mimics the underlying surfaces. Relief increases with depth and reflectors in pre-Ogallala strata dip toward the basin center, indicating that subsidence has played an important role in basin formation. Continuing subsidence during Ogallala and Blackwater Draw deposition has not been proven but is suggested by observations that (1) younger horizons show less relief than older ones and (2) there has been enough sedimentation to completely fill the basin, yet its topographic expression remains.

About 6.8 km of shallow seismic reflection data was collected in 1993 in playa basin settings at Playa 3 and Pantex Lake. Horizons that produce prominent reflections at Playa 3 include, from shallowest to deepest, (a) a horizon at 20- to 30-m depth that probably represents the Ogallala Caprock, (b) a horizon that is suspected to be the perching horizon for an Ogallala perched aquifer, (c) a fine-grained zone within the generally coarse grained lower Ogallala Formation, and (d) the top of pre-Ogallala bedrock. Interpretations from lines at Playa 3 are similar to those at Sevenmile Basin: relief on reflecting horizons increases with depth beneath the playa, and bedrock reflectors dip into the basin. As at Sevenmile Basin, these observations suggest that subsidence (probably caused by dissolution of underlying Permian evaporites) has played an important role in the formation of Playa 3. In addition, the Ogallala Caprock reflector is discontinuous or absent directly beneath Playa 3, suggesting that either (a) the Caprock never formed there because the site was a basin since Ogallala time and was persistently wet or (b) the Caprock did form and was subsequently removed by erosion or dissolution.

Pantex Lake seismic reflection line PRLC reveals the presence of five major reflecting horizons beneath the playa basin that can be correlated to recurring geophysical log patterns in nearby water wells. Horizon 0, the shallowest reflector, is interpreted to be from the Ogallala Caprock and is not visible directly beneath Pantex Lake. Horizon 1 is interpreted to be the top of a fine-grained zone at the upper end of a thicker, relatively fine grained section in the middle part of Ogallala Formation. This upper fine-grained zone is probably stratigraphically equivalent to a similar zone that forms a perched aquifer in places above the main Ogallala aquifer on the Pantex Plant. Horizon 2, the strongest reflector on the seismic section, marks the boundary between a lower Ogallala resistive and generally coarse grained (clayey sand to

gravelly sand) zone and the conductive, generally fine grained zone composing the middle Ogallala section. Horizon 3 is interpreted to be a thin, fine-grained unit within the lower Ogallala coarse-grained zone. Horizon 4, the deepest reflector recognized, is interpreted to be the top of Permian or Triassic bedrock. As at larger (Sevenmile Basin) and smaller (Pantex Playa 3) playa basins nearby, each horizon visible on the Pantex Lake reflection line mimics surface topography near the playa. Increasing relief with age indicates that subsidence has been important in the formation of the basin. Lower compressional wave velocities and the absence of an Ogallala Caprock reflector beneath Pantex Lake suggest that pedogenic carbonate is less abundant directly beneath Pantex Lake than it is beneath uplands adjacent to the lake. Pedogenic carbonate either formed beneath Pantex Lake and was subsequently removed by erosion or dissolution, or it never formed beneath a perennially wet basin that has probably existed at the site since Ogallala deposition.

Significant findings from playa basin studies were that (1) these playas range in size from relatively small (Playa 3) to relatively large (Sevenmile Basin); (2) at all these playas, deeper reflecting horizons have more relief than shallower ones, indicating that syndepositional subsidence has played a role in basin development; and (3) seismic velocities are lower beneath the playa floors than beneath the upland, indicating that pedogenic carbonate is less abundant beneath the playa floors. This suggests that these basins have existed at least since sometime during Ogallala deposition.

#### APPLICATION TO REMEDIATION

Seismic data collected and analyzed by BEG have several applications to remediation. One of the most significant subsurface stratigraphic horizons is the perching horizon, which also is the strongest seismic reflector above the base of the Ogallala Formation. This important horizon is relatively easy to detect seismically and to map across the Pantex Plant and adjacent areas. The base of the Ogallala is also a major reflecting horizon; the depth to this horizon, when compared with the depth of the Ogallala aquifer, can yield more accurate estimates of the saturated thickness of the Ogallala than would be obtained using generalized basal Ogallala maps based on widely spaced well logs. Seismic data also suggest that there are significant textural differences between sediments beneath playa basins and those beneath uplands, which in turn suggests differing hydraulic properties between the two environments. This is important because the bulk of regional Ogallala aquifer recharge occurs through playas, yet most hydraulic data have come from wells outside playa basins. Seismic data have also been used to locate zones of potential preferential flow within the perched aquifer beneath the Pantex Plant, such as the eastern extension of a broad channel identified in Zone 12 borings by Argonne National

Laboratory. Finally, seismic velocity variations between playa and nonplaya areas have demonstrated that pedogenic carbonate is more abundant beneath nonplaya areas, strengthening the argument for preferential Ogallala recharge through playas.

#### RECOMMENDED FUTURE WORK

Several issues have been identified in the course of our geophysical investigations in the Pantex area that could be resolved with further work. First, what is the nature of the perching layer above the main Ogallala aquifer? Seismic data show this layer clearly. Well log data from the Pantex area suggest that the perching layer lies at the top of a middle Ogallala stratigraphic zone that includes several vertically stacked fine-grained units. These units that underlie the main perching layer probably also serve to retard ground-water flow from the perched aquifer to the main Ogallala aquifer. Seismic definition of the distribution of these subsidiary units is important for resolving the flow paths of water and contaminants from the perched aquifer to the Ogallala. Second, seismic reflection data suggest that relief on key stratigraphic surfaces increases with depth beneath playa basins, which has been interpreted to mean that the basins are old and that subsidence has played a role in basin formation and may continue to the present. These interpretations, which suggest that Ogallala and Blackwater Draw stratigraphy differ in playa and interplaya areas (see section on playa stratigraphy), should be verified by wells drilled to bedrock beneath the floor of one or more playas. These wells would provide needed information on the hydraulic properties of sediments between the perching layer and the main Ogallala aquifer in areas where most recharge occurs. Third, electromagnetic profiling should be used to directly observe a recharge event across a playa basin or in an interplaya setting beneath a ditch. Changes in the degree of water saturation in the subsurface before and after significant rainfall will cause changes in electrical conductivity of the soil, which can be measured noninvasively using electromagnetic instruments. Monitoring over time would show how, where, and at what rate the recharge plume moves.

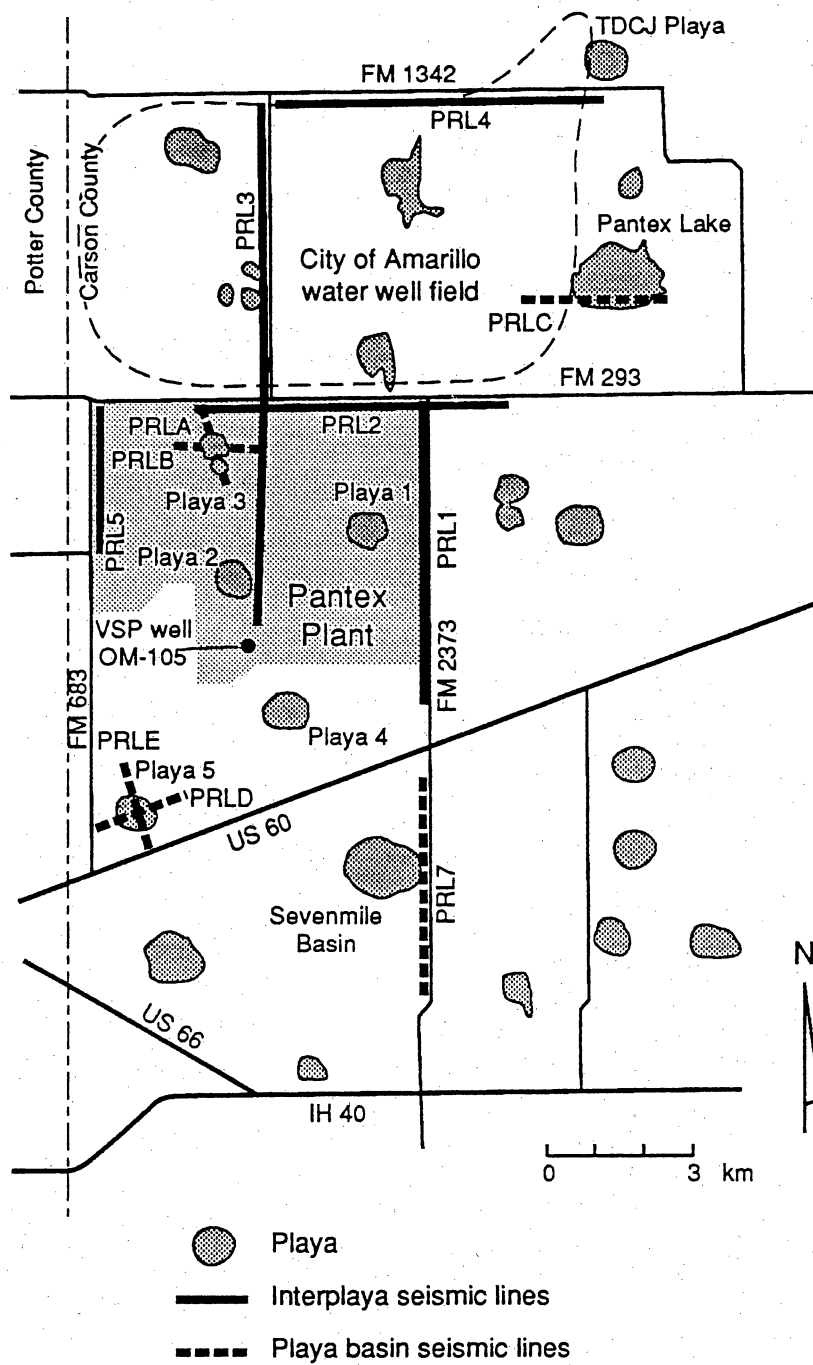


Figure 8. Location of playa and interplaya seismic lines in the vicinity of the Pantex Plant. Outlined area encloses the City of Amarillo water well field.



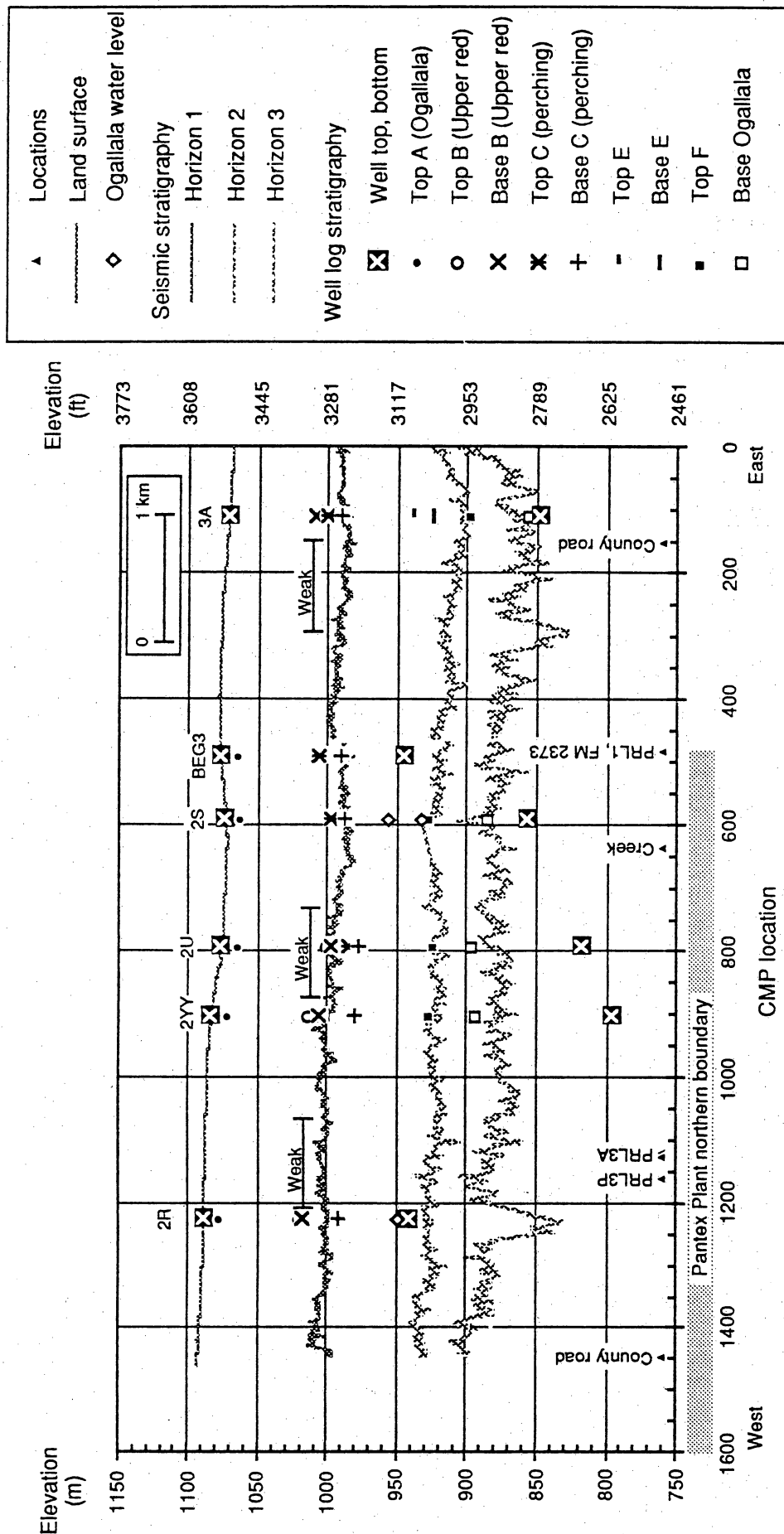


Figure 9. Interpreted major reflecting horizons along line PRL2 at the northern boundary of the Pantex Plant. Also shown are stratigraphic picks (R. Langford, pers. comm., 1994) from wells adjacent to PRL2 that were used to interpret the reflecting horizons. Horizon 1 is interpreted as the top of the middle Ogallala perching horizon, Horizon 2 is interpreted as a fine-grained zone within the generally coarser grained lower part of the Ogallala, and Horizon 3 is interpreted as the top of Permian or Triassic bedrock.

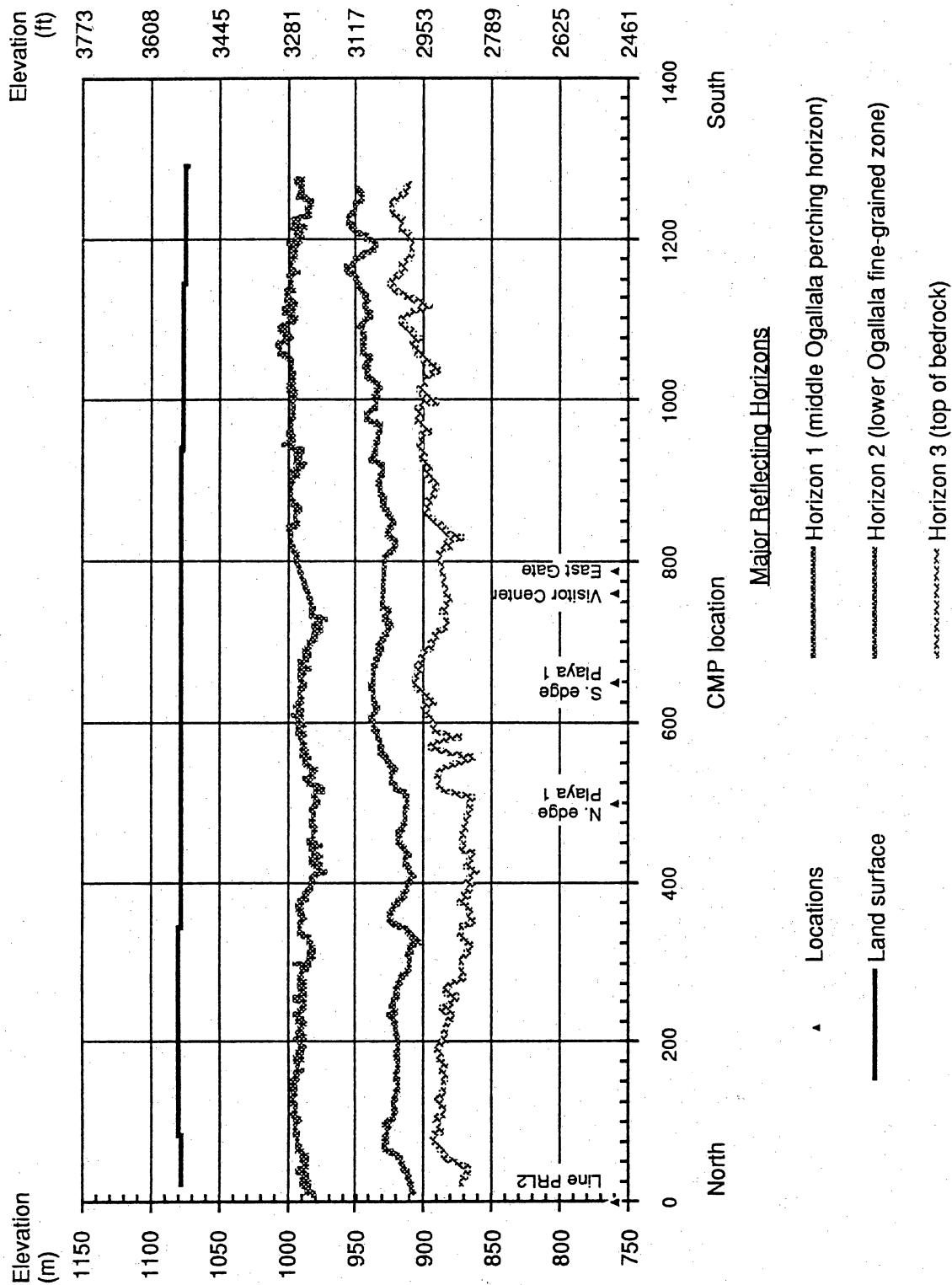


Figure 10. Interpreted major reflecting horizons along line PRL1 at the eastern boundary of the Pantex Plant. Horizon 1 is interpreted as the top of the middle Ogallala perching horizon, Horizon 2 is interpreted as a fine-grained zone within the generally coarser grained lower part of the Ogallala, and Horizon 3 is interpreted as the top of Permian or Triassic bedrock.

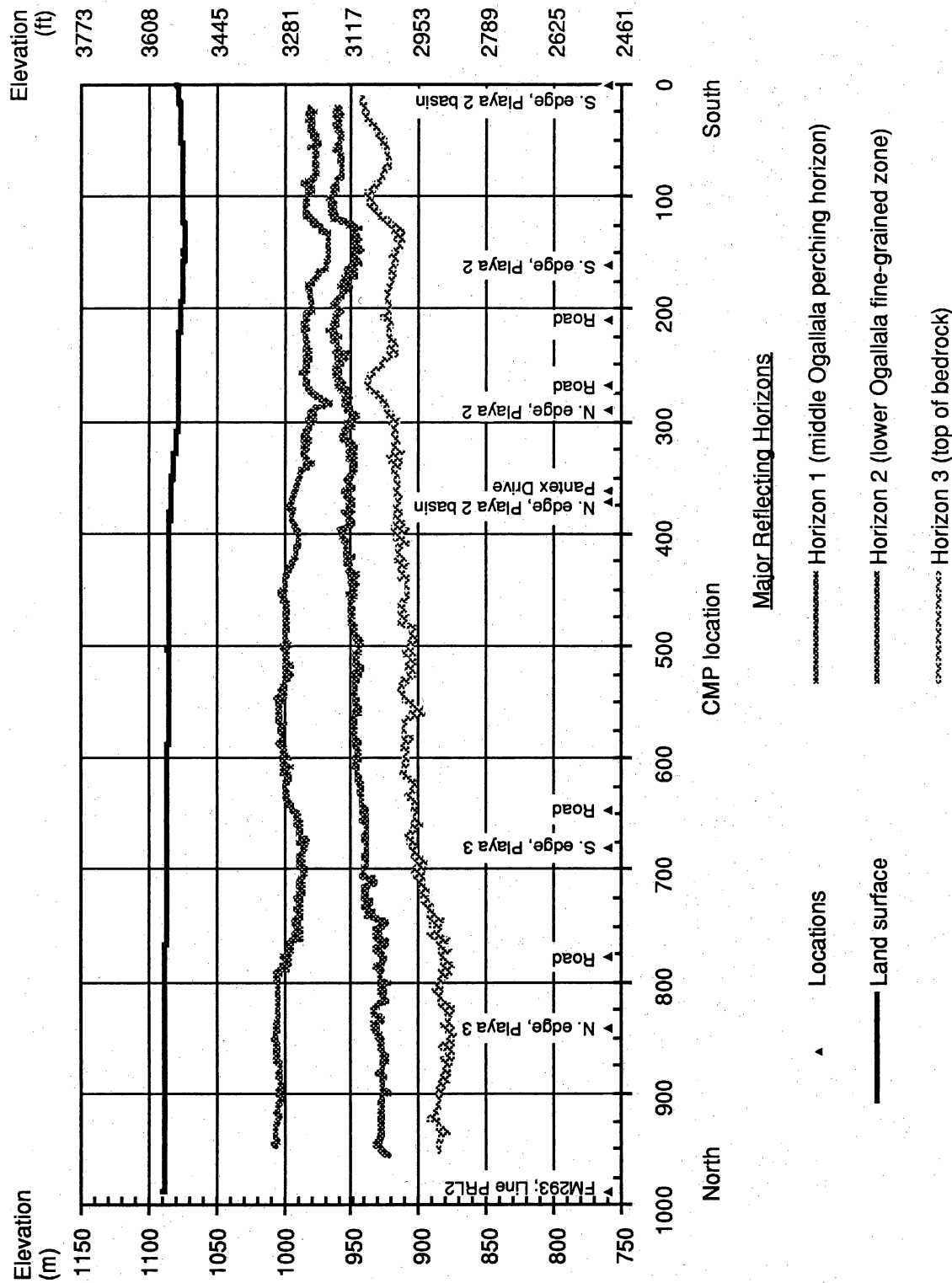


Figure 11. Interpreted major reflecting horizons along line PRL3P. Horizon 1 is interpreted as the top of the middle Ogallala perching horizon, Horizon 2 is interpreted as a fine-grained zone within the generally coarser grained lower part of the Ogallala, and Horizon 3 is interpreted as the top of Permian or Triassic bedrock.

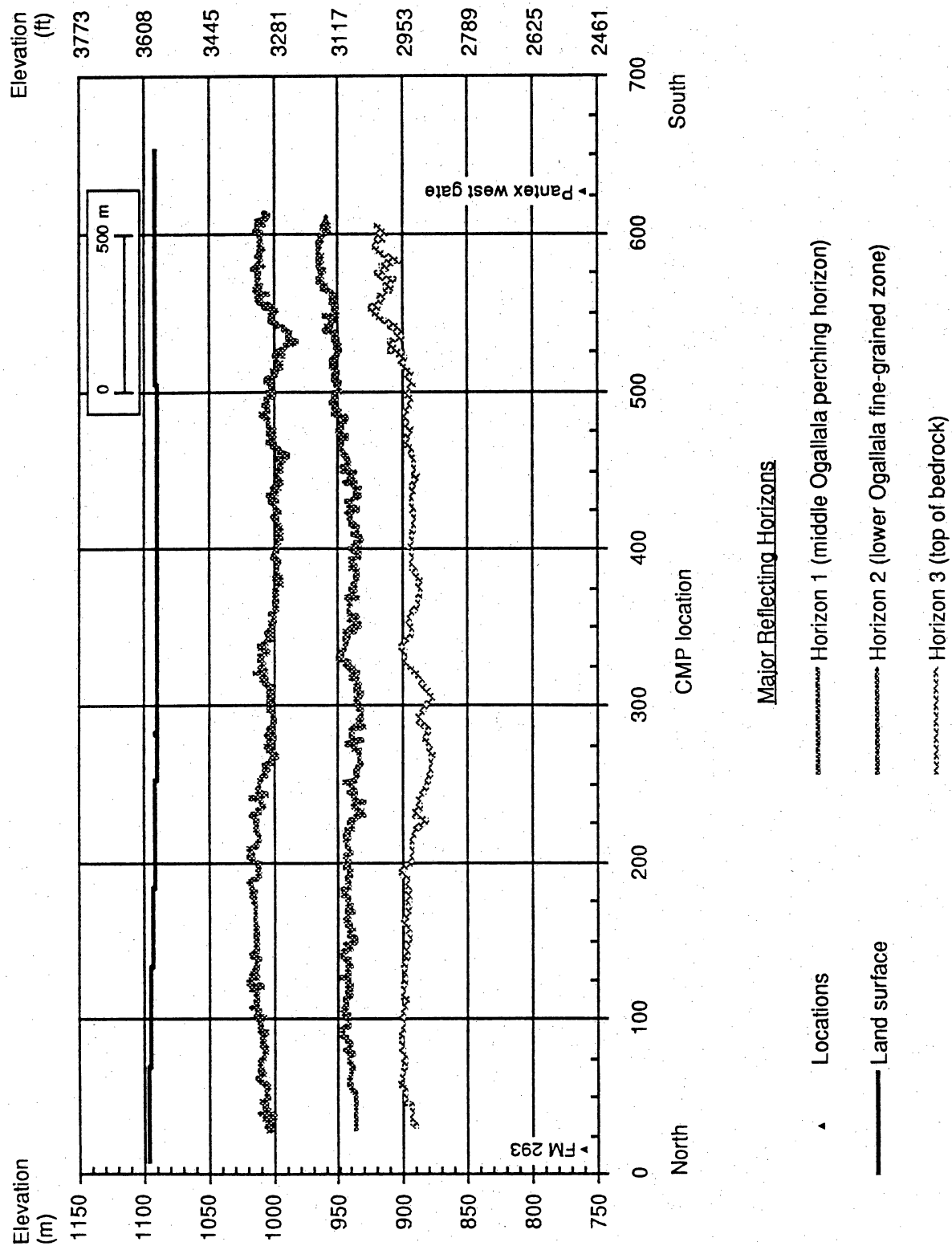


Figure 12. Interpreted major reflecting horizons along line PRL5 at the western boundary of the Pantex Plant. Horizon 1 is interpreted as the top of the middle Ogallala perching horizon, Horizon 2 is interpreted as a fine-grained zone within the generally coarser grained lower part of the Ogallala, and Horizon 3 is interpreted as the top of Permian or Triassic bedrock.

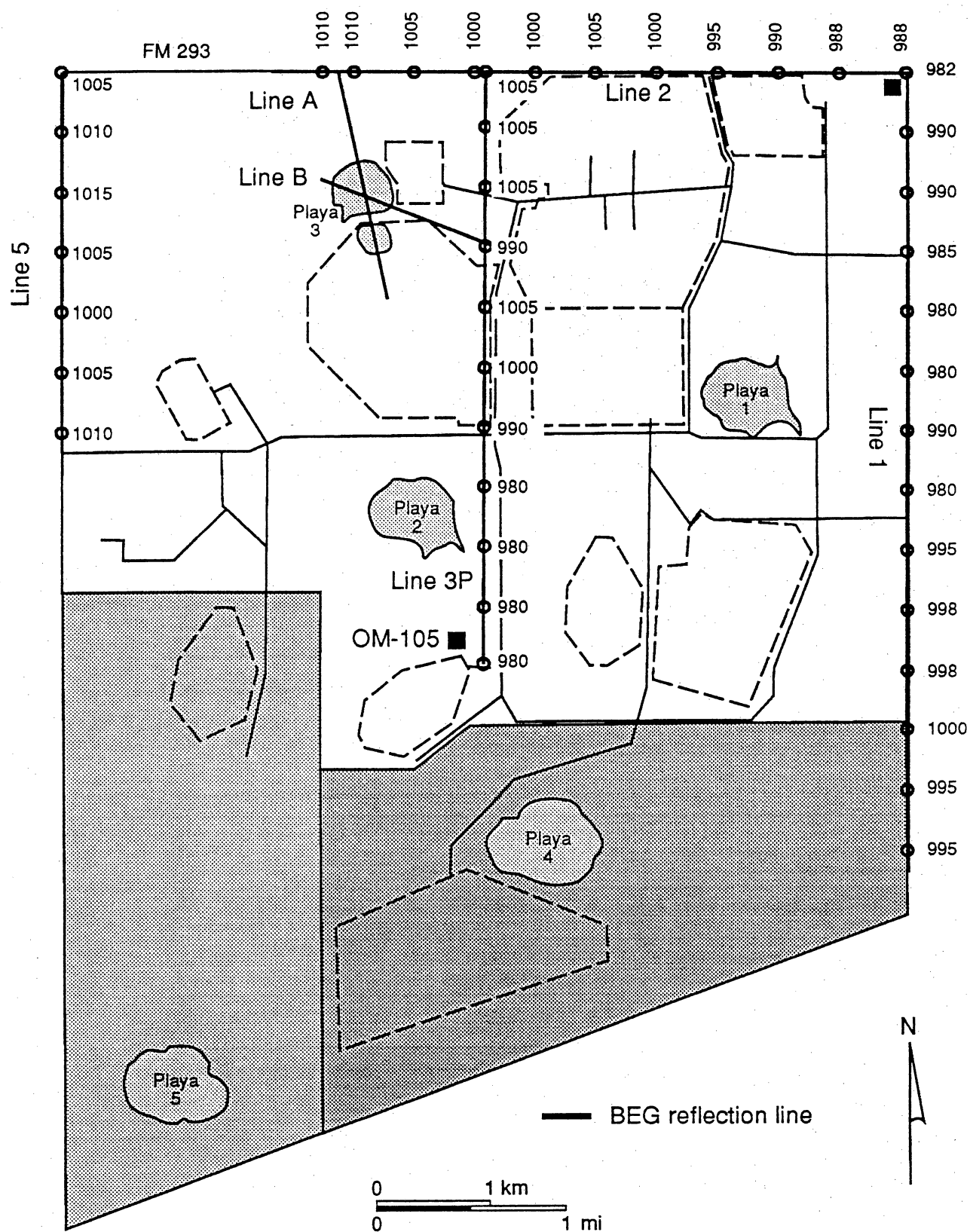


Figure 13. Calculated depths to seismic Horizon 1, interpreted as the middle Ogallala perching horizon.

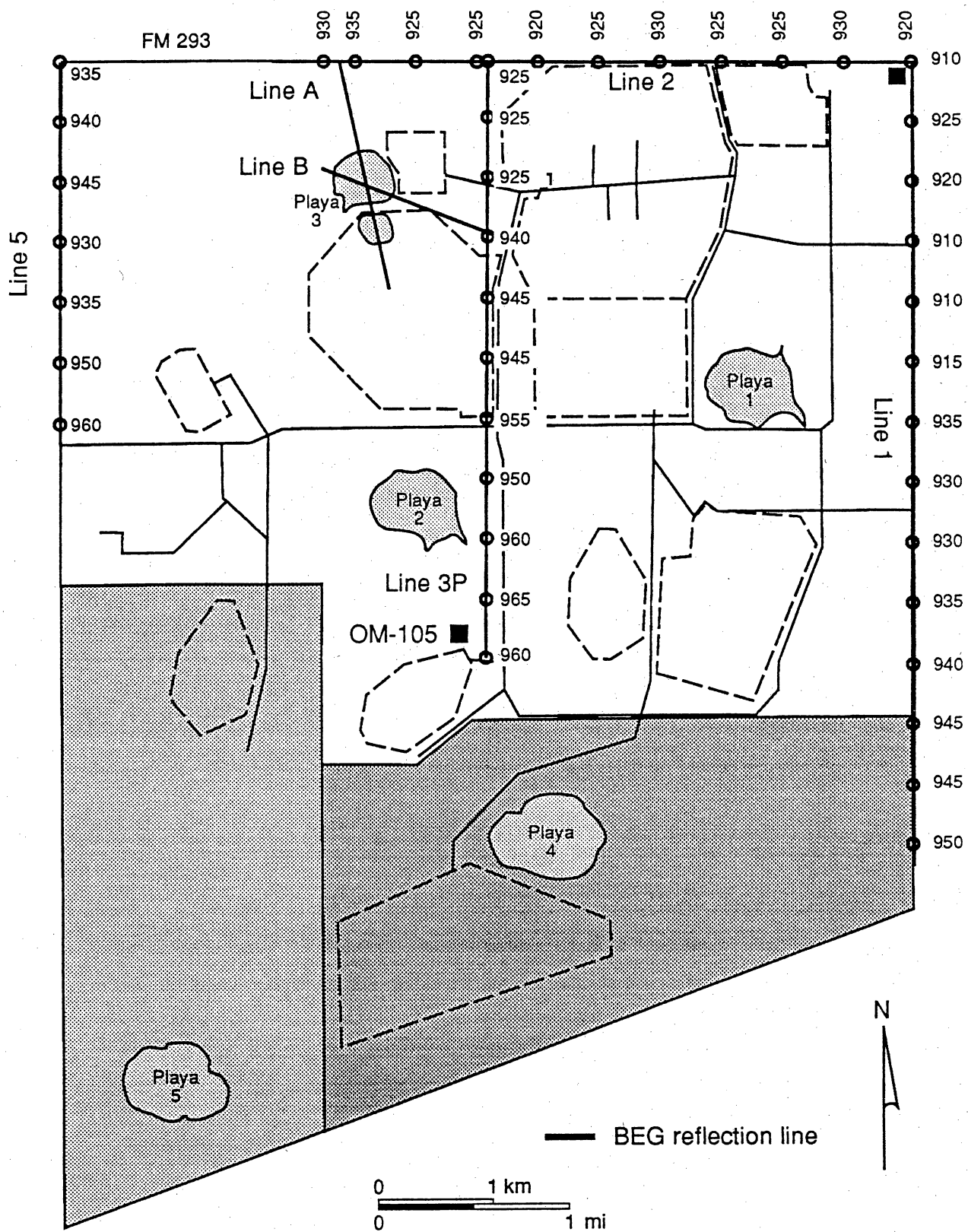


Figure 14. Calculated depths to seismic Horizon 2, interpreted as a lower Ogallala fine-grained zone.

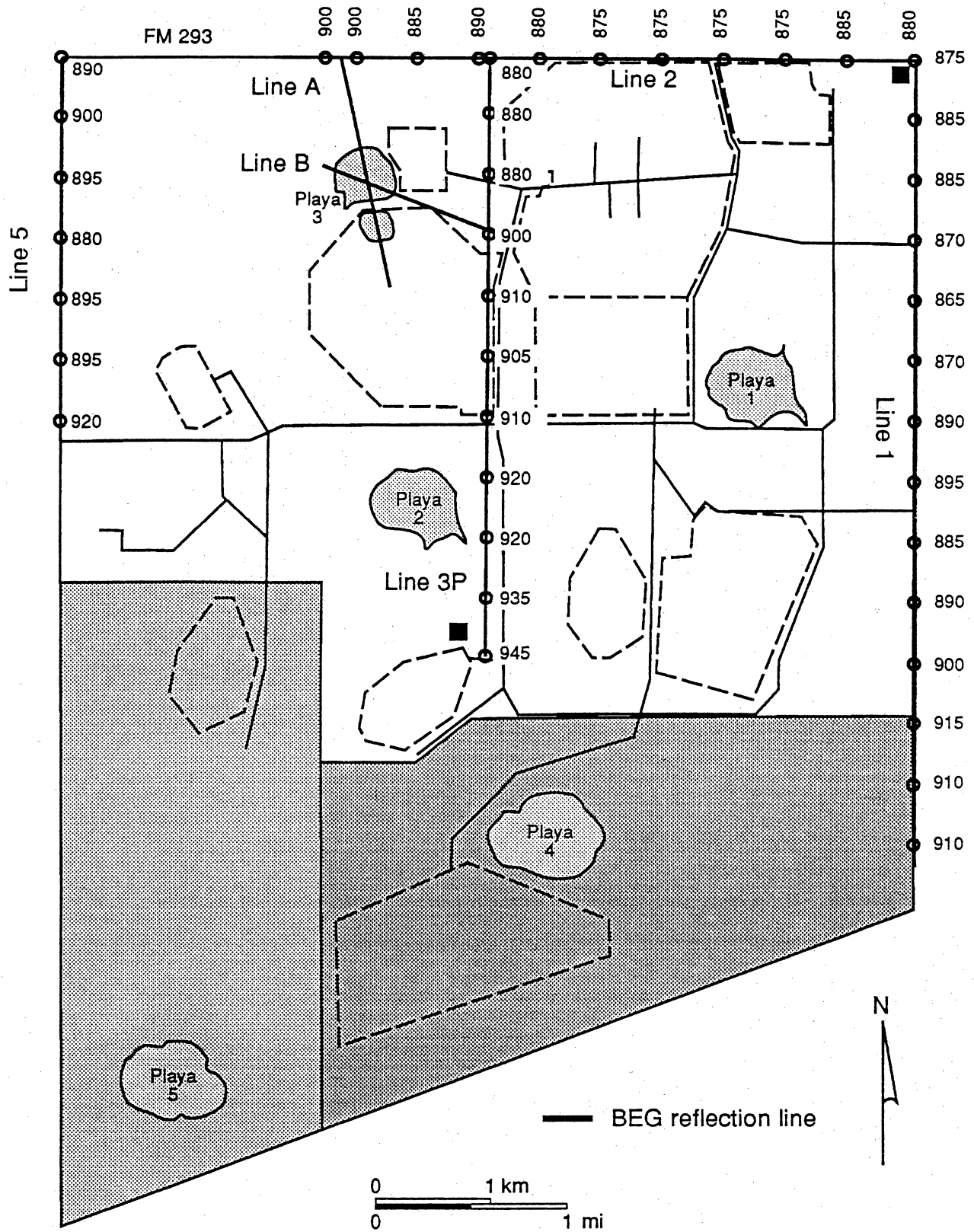


Figure 15. Calculated depths to seismic Horizon 3, interpreted as the top of Permian or Triassic bedrock.

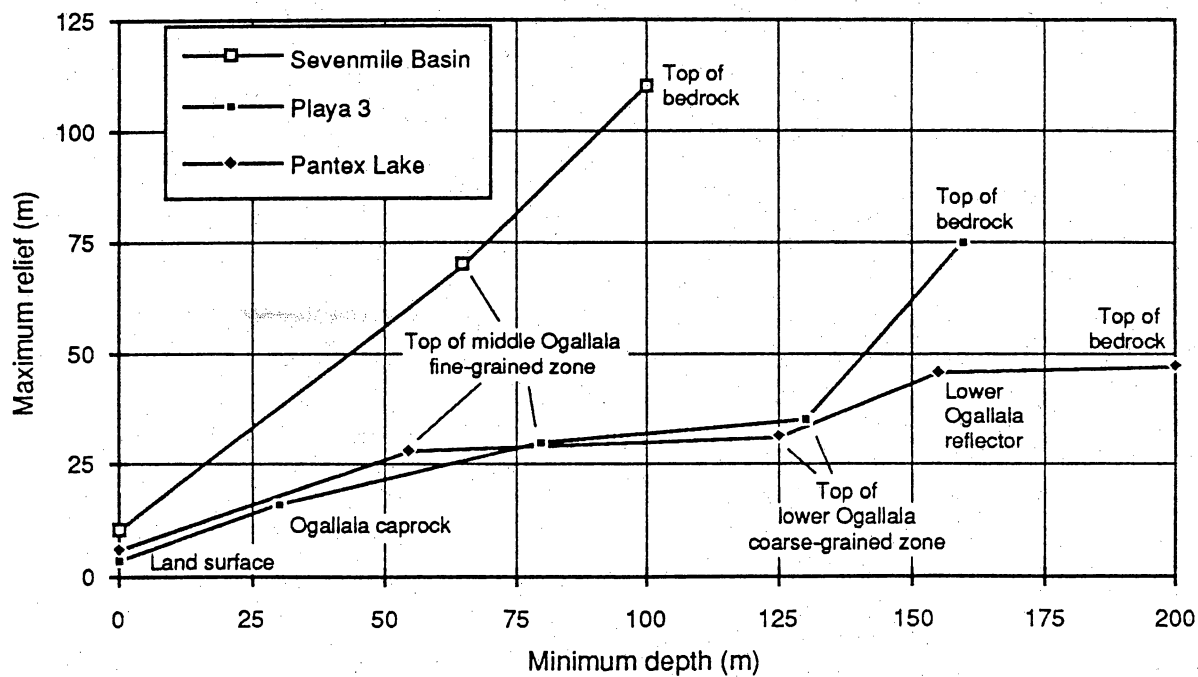


Figure 16. Relationship between maximum relief on major reflecting horizons and depths to horizons at Sevenmile Basin, Playa 3, and Pantex Lake.



# Hydrologic Characterization of the Unsaturated Zone

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## INTRODUCTION

The objectives of the unsaturated zone studies were (1) to determine spatial variability in subsurface water fluxes and (2) to evaluate controls on subsurface water movement. Both of these objectives are important to design and implementation of remediation technologies. Of critical importance are estimation of water flux in the unsaturated zone beneath playas and comparison with water flux in adjacent interplaya sediments within the study area. Data from hydraulic and chemical approaches complement each other and provide a comprehensive conceptual model of unsaturated flow processes in this system. In addition, focused recharge beneath playas allows contaminants to migrate rapidly to the ground water and to bypass the buffering capacity of much of the unsaturated zone (Gee and Hillel, 1988). Evaluation of subsurface flow is important in determining the distribution of contaminants in the unsaturated zone and is critical for development of an effective remediation strategy.

## Soil Physics Approach

Hydraulic methods included measurement of water content and water potential. Water content is discontinuous across different soil textures; therefore, variations in water content with depth cannot be used to determine the direction of water movement. Temporal variations in water content are used to detect the movement of water pulses through the system. Under steady flow conditions, water potential is continuous across different soil textures, and water potential data provide information to assess the direction of the driving forces for liquid water movement.

## Environmental and Applied Tracers

Quantitative estimates of water flux can be obtained by applying the chloride mass balance approach, when the source of chloride is assumed to be from precipitation and dry fallout. The water flux can be estimated by dividing the chloride deposition rate by the chloride concentration in soil water. The residence time represented by chloride at depth  $z$  can be

evaluated by dividing the cumulative total mass of chloride from the surface to that depth by the annual chloride deposition.

There are many assumptions associated with the chloride mass balance approach. These assumptions include one-dimensional vertical downward piston type flow, precipitation and dry fallout as the only source of chloride, annual chloride deposition constant with time, and steady state chloride flux equal to the chloride deposition rate. In the Pantex study area, runoff provides an additional source of chloride to the playas that was not quantified; therefore, chloride profiles in sediments beneath the playas were only used qualitatively for comparison with profiles in the interplaya settings.

The subsurface distribution of bomb pulse tracers such as tritium and chlorine-36 from atmospheric testing of nuclear weapons outside of Texas provides information on water movement during the past 30 to 40 yr. Tritium (half-life  $12.43 \pm 0.05$  yr) concentrations increased from 10 to  $\geq 2000$  TU during atmospheric nuclear testing (IAEA, 1983) that initiated in 1952 and peaked in 1963 to 1964. Tritiated water can exist in both liquid and vapor phases; therefore, tritium is a tracer for liquid and vapor water movement.

In addition to environmental tracers, applied tracers can be used to evaluate flow processes over a short time interval. Application of dyes such as FD&C blue organic dye and Rhodamine WT is used to delineate flow paths and to evaluate the importance of preferential flow. These organic dyes are used as analogs of tracers that sorb, whereas chemical tracers such as bromide are used to represent conservative tracer movement. Many of these applied tracer experiments have been conducted in humid regions to evaluate the importance of preferential flow along pathways such as cracks and root tubules.

Soil samples were collected for laboratory measurement of water potential from 30 boreholes and for particle size, gravimetric water content, and chloride concentration from 17 of these boreholes following procedures outlined in Scanlon (1994). These boreholes were drilled in seven playa and adjacent interplaya settings (fig. 17). Samples for tritium analyses were collected from one borehole beneath Wink Playa. Borehole depths ranged from 4 to 31 m.

Ponding experiments were conducted in June 1993 and in December 1994 in and adjacent to TDCJ playa to delineate flow pathways in near surface sediments. FD&C blue organic dye and bromide were added to the ponded water. Trenches were then dug to reveal the distribution of dye in the subsurface.

## RESULTS

### Soil Texture, Water Content, and Water Potential

Although soil samples were collected from seven playas and adjacent interplaya settings, only results from four of the playa–interplaya regions (Finley, TDCJ, and Wink, Playa 5; fig. 17) are presented in this section. Surficial sediments beneath playas (fig. 18e and 18m) are more clay rich than corresponding zones in the interplaya setting (fig. 18a, 18f, and 18j).

The percent carbonate in sediments beneath playas was much lower than that in interplaya sediments, generally  $\leq 10$  percent. Zones of high carbonate (up to  $\sim 45$  percent) were found in the shallow subsurface (upper 1 to 2 m) in interplaya settings and mark the location of calcic soils as shown in pits.

Water content is generally much higher in profiles beneath the playas than in profiles in interplaya settings (fig. 18b, 18g, and 18l). The water content variations cannot be explained solely by differences in texture, and they reflect higher subsurface water fluxes beneath playas than in interplaya settings. Time of sampling relative to ponding within playas cannot account for the differences in water content because the profiles beneath the playas could only be drilled during dry periods. Some profiles sampled after rainfall had highest water content in near surface sediments. This is most obvious in profiles in interplaya areas and showed that the wetting front penetrated to depths of 0.1 to 0.2 m where water contents decreased with depth from approximately  $0.25 \text{ g g}^{-1}$  to  $0.14 \text{ g g}^{-1}$  (fig. 18b and 18g).

Water potentials in samples collected beneath the playa were much higher than those in the interplaya sediments (fig. 18). The high water potentials are consistent with the high water contents in profiles beneath playas. The calculated hydraulic head gradient is close to unity beneath the playas and suggests that water is draining beneath the playa. Water potentials of soil samples collected in interplaya settings were lower than those measured in playa settings, particularly in the upper 5 to 10 m. In the interplaya setting, water potentials increased with depth except in the shallow subsurface after rainfall (fig. 18). Boreholes sampled after a long dry period had low water potentials in near-surface sediments (Wink 17,  $-30 \text{ MPa}$  at 0.05-m depth). These low water potentials in near-surface sediments indicate that the sediments are dry. The upward decrease in water potentials indicates that there is an upward driving force for liquid and isothermal vapor flow.

Water potentials were monitored adjacent to Playa 5 in April 1994 when the surficial sediments were wet (fig. 19). Psychrometers in the upper 0.8 m showed a rapid reduction during the first 2 to 3 mo when these sediments were drying out and remained very low after that time ( $\sim -6$  to  $-8 \text{ MPa}$ ), which indicates extremely dry conditions. Water potentials

monitored at greater depths remained fairly uniform over the 1-yr monitoring period. The vertical distribution of water potentials shows an upward decrease in water potentials, which indicates an upward-driving force for water movement (fig. 20). Water potentials plot close to or to the right of the equilibrium line at depths  $\geq 9$  m, which indicates drainage of water in this section of the profile. Field-monitored water potentials are similar to laboratory-measured water potential profiles based on soil samples collected in interplaya settings (fig. 20).

### Environmental Tracers

Chloride concentrations in profiles sampled beneath the playas were uniformly low, generally less than  $100 \text{ g m}^{-3}$  (fig. 18). This provides further evidence for high subsurface water fluxes and indicates that either chloride never accumulated or it has been flushed out. This is consistent with the low carbonate concentrations in sediments beneath playas. In contrast to the low chloride concentrations in the playa setting, maximum chloride concentrations in interplaya settings were high and ranged from  $1,706 \text{ g m}^{-3}$  at 2-m depth in Finley 1 (fig. 18c) to  $4,171 \text{ g m}^{-3}$  at 1-m depth in Wink 1 profile (fig. 18). Chloride profiles in interplaya settings are bulge shaped and decrease sharply below the peak (1- to 2-m depth) to low concentrations. High maximum chloride concentrations in interplaya settings are attributed to evapotranspiration that concentrates chloride.

Tritium levels in the soil water beneath Wink playa ranged from 4.4 to 77 TU (fig. 21). These values indicate post-1952 water flux to a depth of 29 m. The tritium profile has multiple peaks. The highest tritium concentration of 77 TU was found at 21-m depth. This zone of fairly high tritium concentrations (39 to 77 TU) from 18- to 21-m depth corresponds to a zone of low water contents ( $2.7$  to  $4.6 \text{ g g}^{-1}$ ) and sandy sediment. Tritium concentrations were low in the base of the profile (27 to 29 m):  $<13$  TU in an unenriched sample and  $4.4 \pm 0.4$  TU in an enriched combined sample from 2 depths (28 and 29.1 m). Tritium concentration in perched ground water adjacent to Wink playa was  $1.8 \pm \text{ TU}$  (Mullican et al., 1994a).

Field ponding experiments showed preferential flow of water (fig. 22). Dyed pathways were found to a maximum depth of 1 m. These pathways included roots and root tubules and cracks between ped faces in the interplaya region. Beneath the playa the dyed areas had an approximately two-dimensional geometry and probably originated as desiccation cracks that formed as a result of shrink and swell.

## DISCUSSION

### Subsurface Water Movement in Playa Versus Interplaya Settings

The soil physics and soil water chemistry data collected in this study both indicate that playas act as focal points of recharge. High water contents, high water potentials, low chloride and carbonate concentrations, and high tritium concentrations all indicate high water fluxes beneath playas. Subsurface water fluxes beneath playas are much higher than those in interplaya settings because water ponds in playas. In the past, some researchers assumed that the Randall clay soils in the floors of playas prevented or minimized downward movement of water and much of the ponded water evaporated. However, the lack of chloride buildup in the ponded water (Wood and Osterkamp, 1987) and the soil physics and chemistry data in this study along with information on perched-aquifer water-table response to rainfall events (White et al., 1946) conclusively demonstrate that the ponded water infiltrates and recharges the underlying aquifers.

In contrast to the playa settings, subsurface water movement in undisturbed interplaya settings is much lower. This is supported by low water contents, low water potentials, and high maximum chloride concentrations in soil water and high carbonate content in the soil. The upward decrease in water potentials in the upper 5 to 10 m indicates net upward water movement in this zone. Below this zone, water potential data indicate downward movement of water. Water fluxes calculated from the chloride data range from 1 to 10 mm/yr.

### Importance of Preferential Flow

The soil physics and soil water chemistry data unequivocally show that subsurface water movement is focused beneath playas. The importance of preferential flow along cracks and root tubules is more difficult to determine. The ponding test results indicate that FD&C blue dye was concentrated along ped faces, root tubules, and shrink-swell cracks; therefore, flow along preferred pathways is critical for transport of an adsorbed tracer and, by analogy, of adsorbed contaminants. The ponding experiments showed that preferred pathways exist in both playa and interplaya settings. Shrink-swell cracks that develop in the Randall clay soil are critical for allowing water movement beneath the playa floors. For nonadsorbed tracers and nonadsorbed contaminants, matrix flow may be as effective as preferential flow, particularly beneath the

Randall clay. Furthermore, stratigraphic studies such as those described above have shown that potential preferred pathways such as soil fractures and root tubules are present throughout much of the Blackwater Draw and Ogallala.

#### Application of Unsaturated Zone Studies to Site Remediation

The results of the unsaturated flow studies have important implications for site remediation. In the natural system, playas act as focal points of recharge because water ponds ephemerally in playas. However, at the Pantex Plant, water was also ponded in ditches and therefore the ditches would also focus subsurface water movement. Contaminants should therefore be concentrated beneath playas and ditches in the unsaturated zone. The low rates of water movement in interplaya settings indicate that if surface contamination occurred in interplaya settings that were not subjected to ponding, these contaminants should be restricted to the shallow subsurface.

The two main options for remediation of the unsaturated zone are soil vapor extraction and bioremediation. These two options are not mutually exclusive because oxygen added during soil vapor extraction could enhance biodegradation. Volatile organic contaminants can be at least partially removed from the unsaturated zone by soil vapor extraction (venting). Key factors that may affect the suitability and efficiency of soil vapor extraction include: the vapor pressure of the chemical contaminant; grain size of the sediments because preferential pathways may play an important role in migration of contaminants in fine-grained sediments; water content of the sediments because volatile organic chemicals move up to 10,000 times faster in the gas phase than in the liquid phase; and the distribution of contaminants in the subsurface relative to air permeability of the sediments because restriction of volatile contaminants to zones of low air permeability would reduce the efficiency of the soil vapor extraction method.

Our studies indicate that water content of sediments beneath playas is quite high, which may be a limiting factor on the efficiency of the soil vapor extraction method. In addition, soils are relatively fine grained, which may also result in air from the venting operation being restricted to preferential pathways. Interplaya settings where leaking underground storage tanks are located or in landfills may be more readily remediated with soil vapor extraction. Numerical modeling would be required to predict the efficiency of soil vapor extraction and design of the remedial approach at these locations.

Our studies indicate that preferential flow is important, particularly with respect to contaminants that sorb onto sediments. These contaminants will likely be concentrated along and adjacent to preferred pathways. If these pathways are air filled, then soil vapor extraction may be successful in volatilizing contaminants and removing them from the subsurface.

### Unanswered Questions

Although the data described in the above studies indicate negligible water fluxes in undisturbed interplaya settings, low chloride concentrations beneath the chloride peak could result from preferential flow diluting chloride beneath the peak or from higher recharge in the past. The occurrence or significance of preferential flow in interplaya settings is important because it will help determine whether contaminants may be located in these areas. To evaluate the possibility of preferential flow beneath known or suspected contaminant sources, soil samples should be analyzed for bomb pulse tracers such as chlorine-36 and tritium. The presence of such tracers below the chloride peak would indicate whether preferential flow is important for moving water and contaminants in selected areas in interplaya settings.

Unsaturated zone studies described above concentrated on playa settings and on interplaya settings that were not subjected to ponding. A major source of potential contamination at the Pantex Plant is ditches that were ponded for long times. Our studies did not specifically address subsurface water flow beneath ditches. It is reasonable to assume that subsurface flow beneath ditches is similar to that beneath playas, with the exception that flow rates may be even higher beneath ditches because of the lack of Pullman clay soils. Detailed studies of water flow beneath ditches are an essential prerequisite for optimal remediation of the Pantex facility. Information about texture, water content, water potential, chloride concentration, bomb pulse tracer distribution and contaminant distribution is required. In addition, monitoring of water content and water potential would be required to understand the dynamics of subsurface water movement. These hydraulic and chemical parameters beneath ditches should be compared with similar data from areas adjacent to ditches to predict rates and locations of contaminant transport.

No information has been collected on unsaturated zone processes beneath the perched aquifer. This is a critical area of study because hydraulic and hydrochemical processes in this zone will greatly affect how rapidly contaminants are migrating from the perched aquifer to the underlying Ogallala aquifer. Important data include matric potential heads, water contents, water chemistry, tritium and chlorine-36 concentrations, and contaminant concentrations in water and soil samples.

## CONCLUSIONS

Evaluation of subsurface flow and solute transport is important in determining the distribution of contaminants in the unsaturated zone and is critical for development of an effective remediation strategy. Understanding flow and contaminant transport processes allows the subsurface distribution of contaminants to be estimated and also helps evaluate the rate of contaminant transport through the unsaturated zone.

Subsurface water movement is focused beneath playas, as evidenced by low carbonate content in the sediments, low chloride concentrations, high water content, and high water potentials. Low chloride concentrations indicate high water fluxes, which prevent chloride accumulation or flush out previously accumulated chloride. Low carbonate content is attributed to dissolution or nonprecipitation of carbonate as a result of high water fluxes. Water potentials were close to zero and suggest drainage of water under unit gradient (near saturated) conditions. In contrast, subsurface water movement in interplaya regions not subject to ponding is negligible as shown by low water contents, low water potentials, high carbonate content, and high maximum chloride concentrations. Calcic soils are abundant in interplaya settings. Maximum chloride concentrations at depths of 1 to 2 m in different profiles reflect concentration of chloride as a result of evapotranspiration. Water potentials increase with depth except in the shallow subsurface after rainfall, which results in an upward driving force for liquid water movement. Hydraulic and hydrochemical data from playa and interplaya settings are consistent and suggest that subsurface water movement is focused beneath playas and is negligible in interplaya settings.

Applied tracer experiments conducted in playa and interplaya settings indicate that preferential flow is important, particularly for transport of adsorbed contaminants. Preferred pathways occur in both playa and interplaya settings; however, ponded conditions in playa settings result in much more preferential flow than in interplaya settings.

The unsaturated zone studies conducted in this program provide the basic information required to evaluate different remediation approaches. Application and optimal design of a specific remediation approach will also rely heavily on the information on estimated distribution and rate of transport of contaminants provided by the unsaturated zone studies.



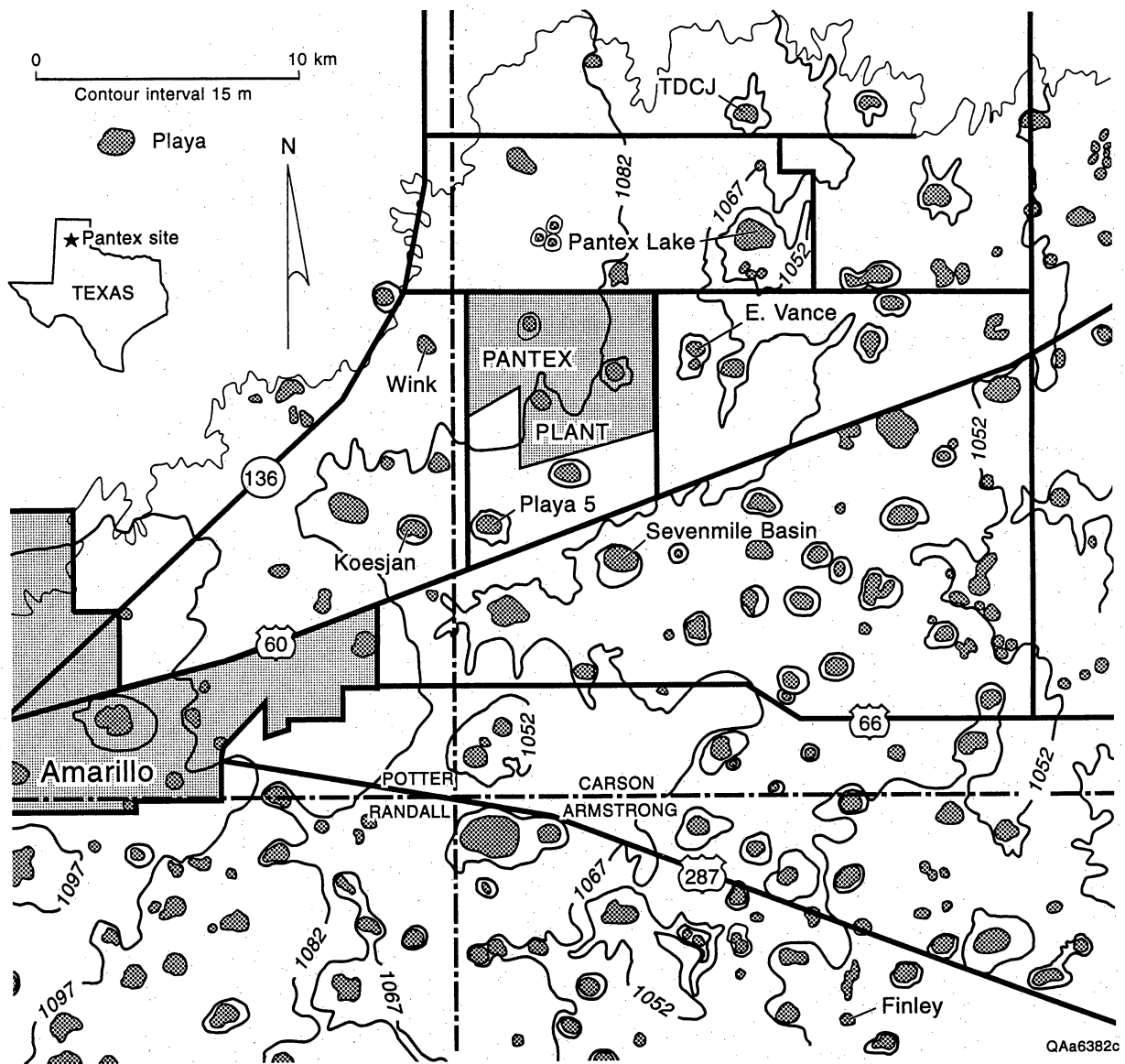


Figure 17. Location of the study area and sampled playas (TDCJ, Wink, E. Vance, Koesjan, Sevenmile Basin, Playa 5, and Finley).

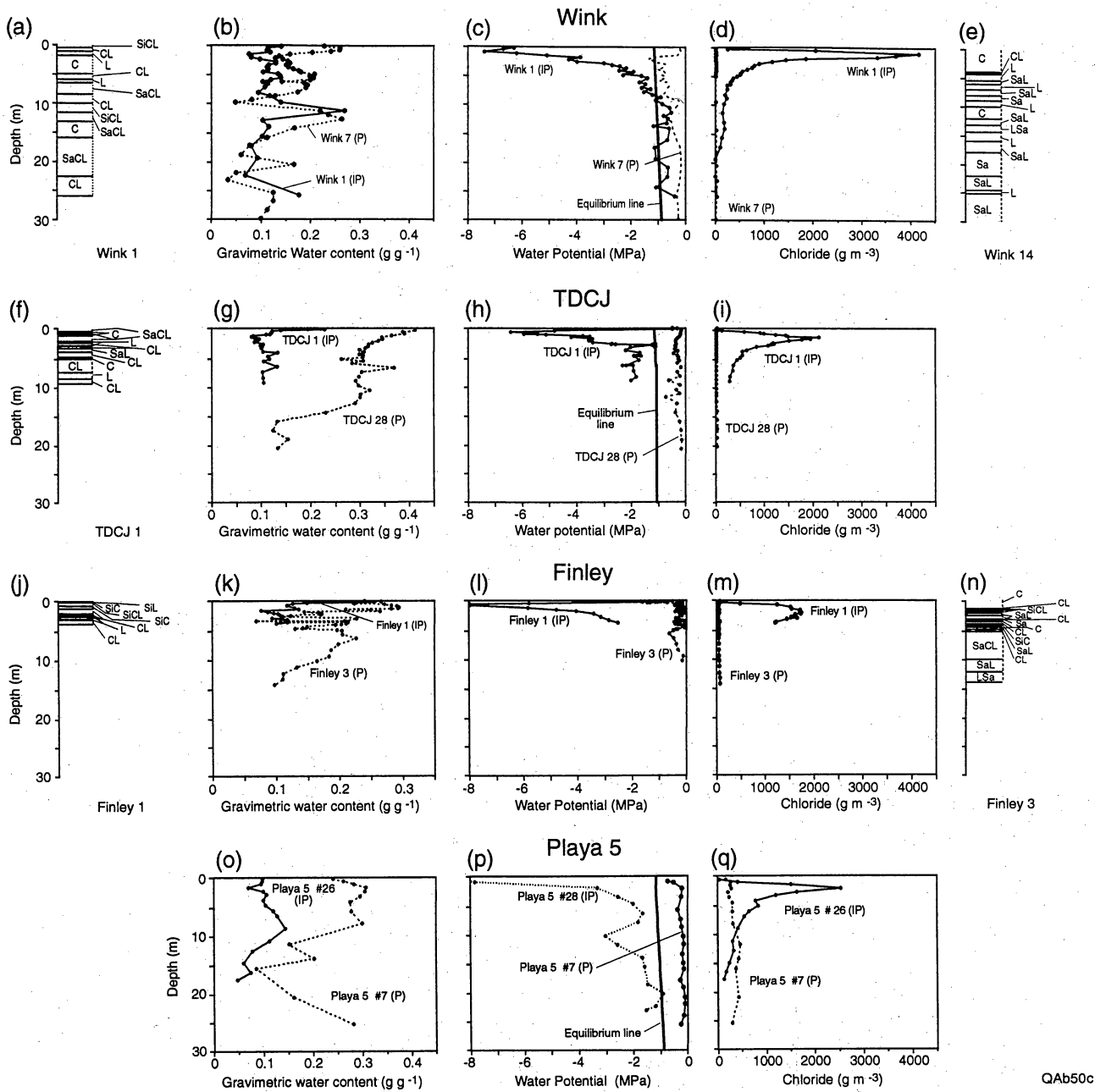


Figure 18. Profiles of texture, gravimetric water content, water potential, and chloride concentrations for boreholes in Finley, TDCJ, and Wink playa and adjacent interplaya settings.

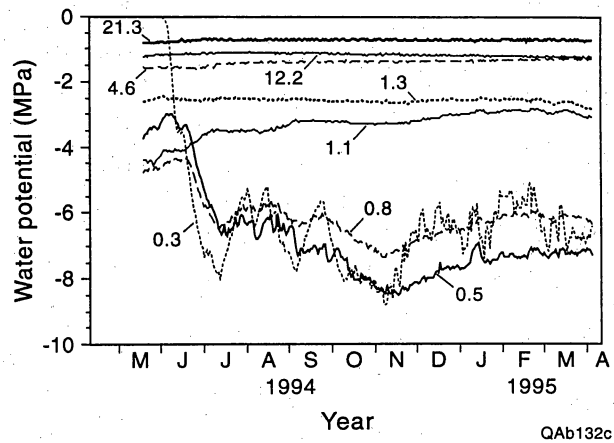


Figure 19. Field-monitored water potentials in an interplaya setting adjacent to Playa 5.

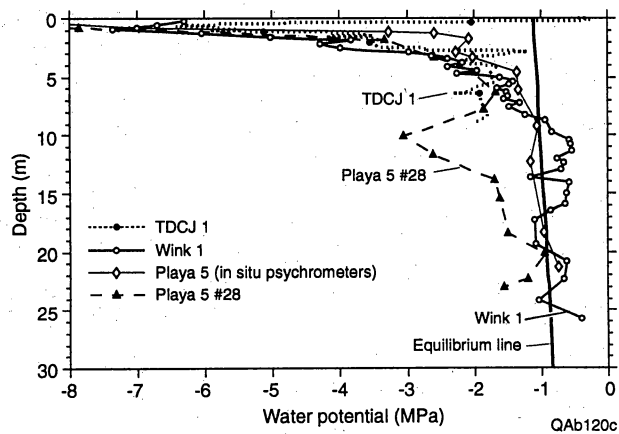


Figure 20. Comparison of field-measured water potentials adjacent to Playa 5 and laboratory-measured water potentials based on samples collected in interplaya settings adjacent to TDCJ, Wink, and Playa 5.

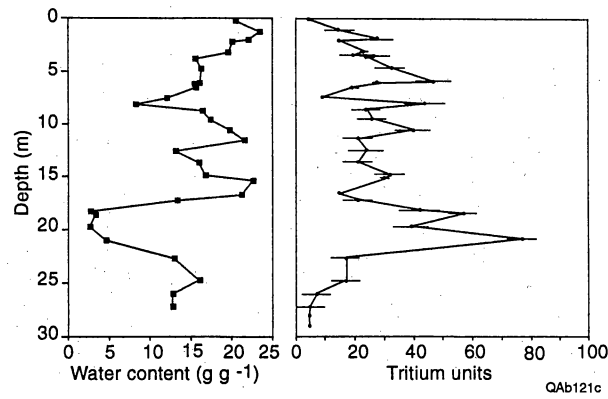


Figure 21. Vertical distribution of water content and tritium in a profile (Wink 13) beneath Wink playa.

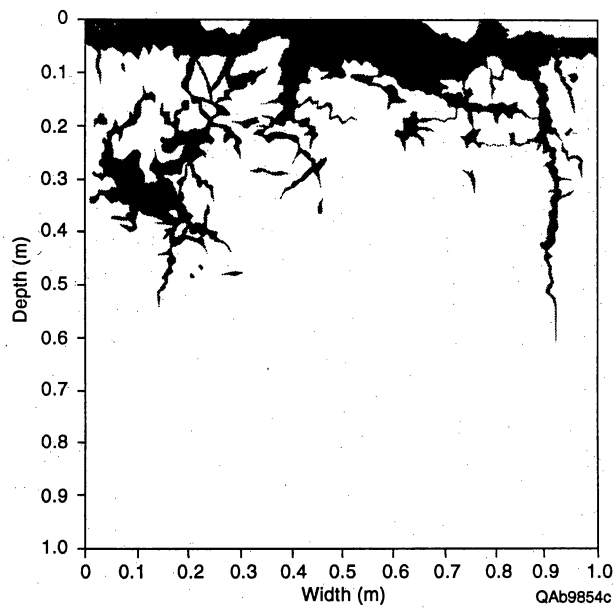


Figure 22. Delineation of preferential flow with FD&C blue organic dye in a trench dug through one of the ponded sections.

# Saturated-Zone Hydrology

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## PERCHED AQUIFER

### Introduction

Naturally occurring perched aquifers above the regional Ogallala (High Plains) aquifer are present locally throughout the Southern High Plains and underlie most of the Pantex Plant. Ground-water contaminants documented at the Pantex Plant are limited to the perched aquifer, with the exception of low levels of nitrate contamination in the Ogallala aquifer at Playa 5. There have been two perched aquifers delineated under the Pantex Plant and one to the west of the plant. The primary focus of this study is the perched aquifer, which extends from Playa 1 past the northern and eastern plant boundaries, to the southern edge of Zone 12, and to the west of Playa 2. In this summary, this hydrologic unit will be referred to as the main perched aquifer. Understanding the hydraulic properties, continuity, and areal extent of the main perched aquifer is critically important for the design of effective remediation strategies.

Perched aquifers form where the downward flux of recharge water is greater than the transmissivity of a stratigraphic horizon. This relationship may occur naturally, or it may result from human-induced artificial or enhanced recharge. Historical records for a domestic water well located immediately off-plant to the north document that the main perched aquifer predates the establishment of the Pantex Plant. The degree to which Pantex Plant activities have enhanced the size of the main perched aquifer has not been determined.

The stratigraphic horizons responsible for perched aquifers at the Pantex Plant are referred to as fine-grained zones. These fine-grained zones are not, however, impermeable to downward ground-water flow. In fact, the range in vertical hydraulic conductivities measured on samples collected from fine-grained zones illustrates that ground-water flow to the Ogallala aquifer is, to varying degrees, only temporarily slowed along the flow path. The following discussion summarizes our understanding of (1) ground-water flow through the main perched aquifer, (2) vertical flow through fine-grained zones, (3) the areal extent of perched aquifers in the region, (4) historical water-level fluctuations, and (5) results from numerical modeling of ground-water flow. Each of these topics is important to anyone concerned with remediation of the main perched aquifer and the fate of contaminants in ground water at Pantex.

## Hydraulic Parameter Measurements

Pumping tests are an important element of hydrologic characterization at the Pantex Plant. To date, three types of pumping tests have been performed to generate data needed to evaluate rates and physical controls on ground-water flow through perched aquifers. These are (1) multiwell pumping tests, (2) single-well pumping tests, and (3) slug tests.

### 11-14 Pond Multiwell Pumping Tests

Results from multiwell pumping tests conducted in wells located at the 11-14 pond significantly increased our understanding of the hydrogeology of perched aquifers at the Pantex Plant (Mullican and others, 1995). The mean transmissivity and hydraulic conductivity calculated for all four wells (PM-101, PM-102, PM-103, and PM-104), based on delayed yield analysis, were  $45.3 \pm 23.2 \text{ m}^2 \text{ d}^{-1}$  and  $10.3 \pm 5.4 \text{ m d}^{-1}$ , respectively. Based on these hydraulic conditions (assuming an effective porosity of 0.25 based on geophysical logs from nearby OM-105 and an average local hydraulic gradient of 0.0063), a ground-water velocity in the 11-14 pond area of  $0.26 \text{ m d}^{-1}$  was calculated. Lithologic descriptions from driller's logs and calculated transmissivity values for the four wells tested, which range over an order of magnitude, document the presence of significant local heterogeneities in the main perched aquifer.

### Single-Well Pumping Tests

In addition to the 11-14 multiwell pumping tests, results from six single-well pumping tests in perched aquifers at Pantex have been reported (Bureau of Economic Geology, 1992a). Wells tested include PM-19, PM-20, PM-38, PM-44, PM-45, and PM-106. All of these wells were tested with low-discharge sample pumps for relatively short periods (less than two hours).

With the exception of PM-106, the results of single well pumping tests are somewhat less accurate than the multiwell pumping tests due to the lack of significant stress to the aquifer. The transmissivity and hydraulic conductivity calculated for PM-106, based on the Theis recovery method, were  $3.0 \times 10^{-2} \text{ m}^2 \text{ d}^{-1}$  and  $2.1 \times 10^{-3} \text{ m d}^{-1}$ , respectively. The mean transmissivity and hydraulic conductivity for PM-19, PM-20, PM-38, PM-44, and PM-45, based on drawdown and recovery analyses, were  $5.3 \pm 4.3 \text{ m}^2 \text{ d}^{-1}$  and  $0.9 \pm 0.9 \text{ m d}^{-1}$ , respectively.

One additional single-well pumping test was attempted in a private well owned by Mr. C. Wink. This well is located immediately west of the Pantex Plant, is completed in a

perched aquifer that is probably not in communication with the main perched aquifer, and was reportedly drilled and completed in 1941, prior to any plant activities. At a low discharge rate, no definitive drawdown was observed.

### Slug Tests

Slug tests have been conducted in some of the perched-aquifer monitor wells as part of various RCRA Facility Investigations. The mean hydraulic conductivity for the nine wells tested by Radian (1994) was  $5.9 \pm 2.0 \text{ m d}^{-1}$ . Two other slug tests are reported by the U.S. Army Corps of Engineers (1992), but because the input parameters used to analyze the data are incorrect, the reported results are also spurious.

### Vertical Hydraulic Conductivity

The vertical hydraulic conductivity of fine-grained zones within and below perched aquifers is one of three primary factors controlling cumulative ground-water travel times along flowpaths to the Ogallala aquifer. Vertical hydraulic conductivity values were measured on 20 core samples from the fine-grained zone (Fryar and Mullican, 1995). Because a significant thickness of sediment 77.8 to 96.9 m overlies the main perched aquifer, values of vertical hydraulic conductivity obtained under ambient conditions may not be representative. For this reason, hydraulic conductivity was measured at both ambient and overburden conditions. Vertical hydraulic conductivity measurements on fine-grained sediments ranged from  $4.62 \times 10^{-6}$  to  $6.92 \times 10^{-9} \text{ cm s}^{-1}$  for ambient pressure conditions and from  $5.35 \times 10^{-7}$  to  $1.08 \times 10^{-9} \text{ cm s}^{-1}$  for overburden conditions (Fryar and Mullican, 1995). Traveltimes of ground water through fine-grained zones are controlled by (1) vertical hydraulic conductivity, (2) thickness of fine-grained zones, (3) thickness of the perched aquifer, and (4) effective porosity of fine-grained sediments. Figure 23 illustrates the fundamental relationships one can use to evaluate flow velocities through fine-grained zones in this setting, and figure 24 depicts results from figure 23 using a range in effective porosity. For example, if the perched aquifer thickness is 3.0 m, the fine-grained zone is 2.4 m thick, and if the vertical hydraulic conductivity of the fine-grained zone is  $1 \times 10^{-8} \text{ cm s}^{-1}$ , then time required for a water particle to move through the fine-grained zone would be approximately 100 yr.

## Potentiometric Surface

Potentiometric surface maps for perched aquifers in the Pantex region have undergone numerous modifications and refinements over the last 5 yr because of the ongoing addition of new water-level measurements. A well-defined potentiometric surface map can be used as a predictive tool to describe (1) the areal extent of an aquifer, (2) the direction of flow within the aquifer, and (3) possible recharge zones and boundaries influencing hydraulics.

During mapping of the potentiometric surface of perched aquifers, an understanding that localized ground-water mounds result from focused recharge beneath playas was used to interpolate certain contours in areas of sparse data. This interpolation is justified by observations that both physical and chemical data indicate that recharge is focused through playa basin floors (Scanlon and others, 1994).

### Areal Extent

There are three areas of perched ground water in the vicinity of the Pantex Plant (fig. 25). The main area of perched ground water extends from slightly south of the southern Pantex Plant boundary to some distance north of the plant. Incorporating water-level data from the recently completed wells (not shown on fig. 25 because surveys and water-level measurements were not yet available) along the eastern edge of the plant, the main perched aquifer is now known to extend east of the plant boundary. The main perched aquifer is not clearly defined to the west, but would appear to be continuous from Playa 1 to the southwest under Playa 2 and almost to the western plant boundary. There appears to be a discontinuity between the main perched aquifer and the perched aquifer present in the immediate vicinity of Playa 3. An additional area of perched ground water was documented to the west of the plant on the C. Wink farm.

The main perched aquifer appears not to extend beyond the plant boundaries to the south and west. A saddle or low occurs in the potentiometric surface between Playa 1 and the northern plant boundary; therefore, ground water in the main perched aquifer beneath Playa 1 could not flow to the north beyond the low in the potentiometric surface. Perched ground water from the eastern portion of the plant is moving to the east beyond the plant boundary. Based on physical hydrologic parameters, a conservative velocity of  $1.8 \text{ m d}^{-1}$  was calculated for flow from Zone 12 to the southeast, toward the plant boundary. Given this velocity and a travel distance of 1,372 m, a first arrival time at the plant boundary is approximately 2.1 yr.



## Controlling Hydraulics

Two characteristics of the potentiometric surface map important to the hydrogeologic characterization of perched aquifers at the Pantex Plant are the mounds under Playas 1, 2, and 3; the first unnamed playa north of Playa 1; and the high or nose on the potentiometric surface extending from Playa 1 south to Zone 12 (fig. 25). The mounds indicate that recharge to the aquifer is localized or focused, in these cases from playas collecting surface runoff and ditches carrying plant discharge water.

In the natural environment under current climatic conditions, negligible recharge is observed in interplaya areas. However, results from numerous studies across the Southern High Plains addressing the feasibility of artificial recharge (summarized in Mullican and others, 1994b) indicate that if the natural surface of interplaya areas is altered, then recharge can be greatly enhanced. The nose extending from Playa 1 south to Zone 12 was one of two primary lines of evidence reported to DOE (Bureau of Economic Geology, 1993b) indicating that contaminants present in the perched aquifer in the Zone 12 south area were probably the result of enhanced ground-water recharge through the drainage ditches and not from Playa 1. The second line of evidence was that conservative ground-water velocities and travel times over the interval of 1952–1989 were not sufficient for transport from Playa 1 to PM-20.

Barriers or no-flow boundaries are not suggested by the potentiometric surface map of the perched aquifer. Variable vertical hydraulic conductivity in fine-grained strata is suggested, however, by variations in spreading distances away from the point of recharge (playa). If recharge and horizontal hydraulic conductivity remain constant, then over areas of lower vertical hydraulic conductivity, the perched aquifer will spread farther away from the point of recharge. In other words, the gradient will be less in areas of lower vertical hydraulic conductivity and greater in areas of higher vertical hydraulic conductivity.

## Water-Level Fluctuations

Water-level fluctuations measured for the perched aquifer were used to (1) calculate barometric efficiency, (2) evaluate long-term trends in water levels, and (3) characterize the aquifer dynamics. Barometric efficiencies were calculated for the perched aquifer in four monitor wells (PM-19, PM-20, PM-38, and PM-45) using long-term water-level records and corresponding atmospheric-pressure records. The mean barometric efficiency, 0.96, is very close to unity and suggests that atmospheric-pressure changes are nearly 100 percent efficient at changing water levels in wells.

Water-level fluctuations in monitor wells PM-19, PM-20, and PM-38 (fig. 26a, 26b, and 26c) illustrate that (1) the perched aquifer is a dynamic hydrologic unit; (2) the magnitudes of water-level fluctuations are greater closer to Playa 1 than under Zone 12, south of Playa 1; (3) a significant volume of water is moving through the perched aquifer on an annual basis; (4) more than one complete cycle of decline and recovery has been documented in the two wells adjacent to Playa 1 during the period of record (1990–1994); and (5) if the current trend in declining water levels continues, the volume of perched ground water remaining for remediation may be significantly reduced naturally. For example, if the current declines in water levels in PM-19 and PM-38 are the result of reduced waste-water discharge to Playa 1 and thus represent a real reduction in water in storage, then the volume of water that has moved through the system under Playa 1 can be calculated. Based on an approximate surface area for Playa 1 of 108 acres, a decline in water level of approximately 1.5 m and an effective porosity of 0.25, the reduction of ground water in storage in the perched aquifer under Playa 1 is approximately 44 M gal. Water-level responses in PM-20, although based on a less complete data set, appear to be about half of those recorded in PM-19 and PM-38. This may result from (1) a loss in magnitude due to the difference in distance between Playa 1 and the wells; (2) differences in arrival times, such that the responses recorded in PM-19 and PM-38 have not yet arrived at PM-20; or (3) ground-water recharge at PM-20 from the overlying ditches masks any influence from Playa 1.

### Ground-Water Flow Models

A series of numerical models were constructed to evaluate hydrologic parameters controlling ground-water flow in the perched aquifer (Mullican and others, 1994a). The main thrust of this effort was to evaluate the sensitivity of a perched aquifer system to variations in hydrologic parameters such as recharge, hydraulic conductivity, and aquifer geometry.

### Data Set Summary

During model calibration, few parameters contained sufficient data to establish a truly deterministic numerical model. For example, results from only six widely spaced single-well pumping tests and two slug tests were available to evaluate horizontal hydraulic conductivity in the aquifer. A mean horizontal hydraulic conductivity of  $0.61 \text{ m d}^{-1}$  was used during initial model calibration. Data defining aquifer geometry were also limited, especially with respect to areal extent, saturated thickness, and thickness of the fine-grained zone. Sufficient data to

reasonably define the shape of the mound under Playa 1 were available from water-level measurements in several perched aquifer monitor wells. Geophysical logs from PM-106 were used to define a representative internal geometry for the perched aquifer. At the time of model construction, only four laboratory measurements of vertical hydraulic conductivity from fine-grained zone cores were available, ranging from  $2.1 \times 10^{-6}$  to  $6.9 \times 10^{-9}$  cm s<sup>-1</sup>.

Recharge was estimated using a playa-focused approach by concentrating the regional average rate of 6 mm yr<sup>-1</sup> to the area of the playa lakes (from Mullican and others, 1994b, c). Because playa lakes contain approximately 2.7 percent of the surface area in the region of the Pantex Plant, the effective natural recharge rate used during the simulations was 219 mm yr<sup>-1</sup>. No recharge was applied to the model in interplaya areas.

## Results

Sensitivity analysis of numerical ground-water flow models in perched aquifers in the Pantex Plant region indicated that the three primary hydrologic parameters controlling ground-water flow are (1) rate and spatial distribution of recharge, (2) vertical hydraulic conductivity of fine-grained strata causing the perching above the Ogallala aquifer, and (3) horizontal hydraulic conductivity of the perched aquifer (Mullican and others, 1994a).

The primary control on vertical transport of ground water is the vertical hydraulic conductivity of fine-grained strata above the Ogallala aquifer. Model results indicate that a range in vertical hydraulic conductivity from  $1 \times 10^{-6}$  to  $1 \times 10^{-9}$  cm s<sup>-1</sup> will cause perching at the scale encountered in the area of the Pantex Plant, with the best agreement between simulated and observed potentiometric surfaces occurring when a vertical hydraulic conductivity of  $5 \times 10^{-8}$  cm s<sup>-1</sup> is used. It should be noted that this value matches well with later analyses reported by Fryar and Mullican (1995). Figure 27 illustrates the relationship between vertical hydraulic conductivity of the fine-grained zone, radial distance from the point of recharge, and percentage of recharge water moving through the fine-grained zone. For example, if the vertical hydraulic conductivity is set at  $1 \times 10^{-8}$  cm s<sup>-1</sup>, 100 percent of the ground water will move through the fine-grained zone after moving less than 1.6 km radially away from the point of recharge.

If recharge is held constant, the degree of mounding on the potentiometric surface is controlled by the horizontal hydraulic conductivity of the aquifer. The lower the hydraulic conductivity, the greater the mounding, the higher the hydraulic conductivity, the less mounding will develop.

## OGALLALA AQUIFER

Investigations of the Ogallala aquifer were conducted at two scales: a regional scale over the 11 counties that make up the northeastern segment of the Southern High Plains and at a site-specific scale within Carson County. The focus of these investigations was to (1) understand the rates and controls on recharge to the Ogallala aquifer; (2) determine directions and rates of ground-water flow in the Ogallala aquifer, both in a steady-state and in the current transient state; and (3) construct steady-state and transient numerical ground-water flow models of the Ogallala aquifer.

### Recharge – A Review

The hydrologic characterization of the Pantex Plant requires an understanding of the rates and controls on both natural and artificial recharge to the Ogallala aquifer. As part of this effort, an extensive literature was compiled (Mullican and others, 1994b). Most of these studies, dating back to Johnson (1901), designated playas as the primary focal point of recharge to the Ogallala aquifer or as one of several possible areas of recharge. Recently, Scanlon and others (1994) provided chemical and physical data from the region of the Pantex Plant, which illustrates that under current climatic conditions, negligible recharge is occurring in natural interplaya areas and that natural recharge is focused in the floors of playas and the immediately surrounding sediments.

### Potentiometric Surface

#### Regional Trends

Numerous studies (for example, Nativ, 1988) have documented that regional ground-water flow in the Ogallala aquifer beneath most of the Southern High Plains of Texas and eastern New Mexico is to the southeast. However, in the northeastern segment of the Southern High Plains (this study area) ground-water flow is predominantly to the east-northeast. This shift in flow direction results from the east and northeast slope of the Southern High Plains and the Canadian River valley to the north.

## Historical Changes

To evaluate historical changes in the potentiometric surface of the Ogallala aquifer in the study area, a series of five potentiometric surface maps were constructed for the time periods 1927–1949, 1950–1959, 1960–1969, 1970–1979, and 1980–1991 (Bureau of Economic Geology, 1992b). At a regional scale, there are three primary trends illustrated by this set of maps. The dominant feature is the development through time of an extensive cone of depression centered over the Carson County Amarillo well field to the north and northeast of the Pantex Plant. Declines in the Ogallala water table in the center of the Carson County Amarillo well field exceed 46 m. The expansion of this cone of depression has lowered Ogallala water levels beneath the Pantex Plant.

A more subtle feature is the regional decline in the potentiometric surface owing to other ground-water withdrawals. Although the amount of decline is variable across the study area, most of the region has experienced a 10 to 25 ft (3 to 8 m) decline in the Ogallala water table. The third trend through time is the increasing complexity to the potentiometric surface. This is the result of both an increasing number of wells (thus water-level measurements) available with each successive map and also the variable rates of withdrawal and storativity of the aquifer.

## Ground-Water Flow Models

Previous models of ground-water flow through the Ogallala aquifer, used primarily for water-resource evaluations, utilized spatially uniform recharge. The data base of geologic, geomorphic, hydrologic, hydrochemical, and pedologic information is extensive, however, supporting the hypothesis that, in the natural undisturbed environment on the Southern High Plains, recharge is focused through playas. If the modeling goal is simply to evaluate ground-water resources, then spatially uniform recharge is acceptable because it does not violate the mass balance of the system. If the modeling goal is to evaluate contaminant transport in an environment where focused or preferential recharge is dominant, as is the case in this area, then spatially uniform recharge is invalid. This is because focused recharge occurs at significantly higher velocities than those associated with spatially uniform recharge and thus contaminant velocities will also be higher.

We analyzed the sensitivity of the “predevelopment” or steady-state ground-water flow system in response to three different recharge scenarios. These were (1) spatially uniform recharge, where equal recharge was applied throughout the model area; (2) zonal recharge, where recharge rates were varied on the basis of regional surface geologic units; and

(3) modified zonal or playa recharge: where playas are present (where the Blackwater Draw Formation is present at the surface), recharge is focused through the playas, and where playas are absent (where the Ogallala Formation is present at the surface), recharge is applied at a uniform rate. Next, a ground-water flow model was developed that represented current or transient conditions for the area. The transient model was used to evaluate particle velocities in the Ogallala aquifer in the immediate area of the Pantex Plant.

### Steady-State Model Results

Three different conceptual models were used during this study of ground-water flow in the Ogallala aquifer. Model results using spatially uniform recharge varied by area and by rate of recharge. The best agreement was achieved in the area where the Blackwater Draw Formation is present at the surface using a recharge rate of  $6 \text{ mm yr}^{-1}$ . However, the model underpredicts hydraulic heads using this rate in areas where the Ogallala Formation is present at the surface. Using a spatially uniform recharge rate of  $9 \text{ mm yr}^{-1}$  resulted in good agreement between observed and simulated heads where the Ogallala Formation is present but underpredicted heads where the Blackwater Draw Formation is exposed.

A zonal approach was used so that recharge rates could be varied according to the geologic unit exposed at the surface. In this series of simulations, the best agreement was achieved using a recharge rate of  $6 \text{ mm yr}^{-1}$  where the Blackwater Draw Formation is present and a rate of  $9 \text{ mm yr}^{-1}$  where the Ogallala Formation is exposed.

The agreement between observed and simulated systems was as good as or slightly better with the modified zonal or playa recharge scenario as with the spatially uniform or zonal methods. The best fit achieved with the modified zonal or playa recharge scenario used a focused recharge rate through the playas of  $219 \text{ mm yr}^{-1}$  (based on a regional rate of  $6 \text{ mm yr}^{-1}$  focused through playas, which in this area covers 2.7 percent of the surface. In regions where playas are absent, a uniform recharge rate of  $9 \text{ mm yr}^{-1}$  was used. A statistical comparison of the results from various recharge scenarios is presented in Mullican and others (1994b, c). The results from this modeling effort illustrate that focusing all of the recharge through the playas where they are present is viable numerically. Therefore, the model may be used to support various field and laboratory observations of focused recharge through playa lake basins (for example, Scanlon and others, 1994). Although playas cover only 2.7 percent of the surface where playas are present (where the Blackwater Draw Formation is present at the surface), model results indicate they are a plausible route for all of the recharge water in this area.

## Transient Model Results

To represent or model the Ogallala aquifer under current conditions, the amount of ground water removed to meet agricultural, municipal, industrial, and domestic needs between 1960–1990 (when significant declines in the water table were recorded) had to be determined and then incorporated into the numerical simulations. Therefore, the main difference between steady state and transient models was the addition of water wells to withdraw ground water to the transient model for a specified period of time.

Best agreement between observed and simulated heads throughout the modeled time period was achieved using a combination of known (783) and simulated (1,453) well locations sufficient to withdraw the required volume of ground water for each time period (Mullican and others, in press).

The calibrated transient model was then used to evaluate particle velocities in the area of the plant. Particles were placed in the aquifer at the various points of recharge (the playas) and then tracked through time to evaluate the flowpath and time interval required for the particle to reach the termination point. Results were dependent on the effective porosity applied to the system. In figure 28, for example, if an effective porosity of 0.25 is used, then the shortest traveltime from any playa to either the plant boundary or an existing well would be 67 years.

## APPLICATION OF SATURATED ZONE INVESTIGATIONS TO REMEDIATION

Three major results from perched aquifer investigations are directly applicable to remediation efforts. First, ground-water flow is radial away from mounds under playas and away from noses in the potentiometric surface under ditches. Any efforts to capture ground water in the perched aquifer will require an understanding of the local gradient because there is no uniform direction or gradient. Second, the fine-grained zones are not impermeable. Several lines of evidence document the variable nature of flow through these stratigraphic horizons. Therefore, it must be understood that, for a considerable period of time, potentially contaminated ground water has been exiting the perched aquifer and moving down toward the Ogallala aquifer. Third, if pump and treat is considered as a method of remediation, it must be understood that the main perched aquifer at the Pantex Plant is not a homogeneous hydrologic unit, and an efficient application of pump-and-treat remediation may not be possible.

Investigations of the Ogallala aquifer have provided two primary areas of information applicable to remediation efforts. First, ground-water withdrawals in the local area have significantly altered the potentiometric surface of the aquifer in the region of the Pantex Plant,

such that ground-water flow in the Ogallala aquifer now is to the north-northeast as a result of drawdown in the water table caused by the Carson County Amarillo well field. The second area relates to modeling results for velocities and traveltimes in the Ogallala aquifer at the plant. For example, the traveltimes from Playa 1 and Playa 3 (closest points of recharge to the Ogallala aquifer) to the northern edge of the plant are conservatively in excess of 60 yr.

## RECOMMENDATIONS FOR FUTURE WORK/UNANSWERED QUESTIONS

There are some elements of the saturated zone hydrology for which data sets are inadequate to effectively evaluate remediation alternatives. The following are areas where additional data should be acquired to insure successful remediation.

### Pumping Tests

All existing perched aquifer monitor wells should be tested at discharge rates and for time periods sufficient to stress the aquifer. Successful, cost-efficient remediation will be dependent on a clear understanding of the spatial variability and heterogeneity of hydrologic properties controlling ground-water flow in perched aquifers.

### Tracer Tests

There are multiple sites at the Pantex Plant where tracer tests in the perched aquifer could be initiated. These tests would provide critical information with respect to contaminant transport that is needed to develop a more deterministic fate and transport model.

### Vertical Hydraulic Conductivity Tests

The vertical hydraulic conductivity of fine-grained zones is one of three primary controls on ground-water flow in the perched aquifer. All future monitor wells should be sampled and analyzed for vertical hydraulic conductivity of fine-grained sediments. A clear understanding of the spatial variability of vertical hydraulic conductivity would be beneficial to the evaluation of remediation strategies.



## Fate and Transport Modeling

Deterministic fate and transport models of ground-water flow and contaminant transport for both the perched and Ogallala aquifers, based on sufficient data sets for critical parameters, are crucial for the successful evaluation, implementation, and tracking of remediation strategies. As part of this effort, the viability or optimization of certain remediation strategies such as pump and treat can be evaluated.

## Ground-Water Resource Modeling on the Ogallala Aquifer

Existing steady-state and transient ground-water flow models should be used to evaluate the long-term impact of ground-water withdrawal in the region by the Carson County Amarillo well field, the Pantex Plant, and the agricultural community.

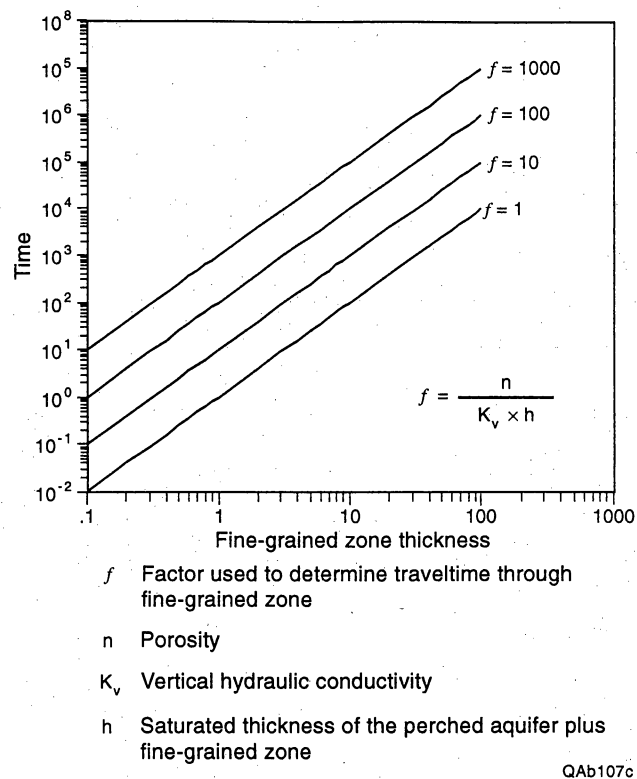


Figure 23. Fundamental relationships used to quantify ground-water flow velocities through fine-grained zones. To calculate traveltimes through a fine-grained zone (1) determine  $f$  (2) determine position of  $f$  on graph, (3) move along  $f$  line to fine-grained zone thickness, and (4) read traveltimes from y-axis.

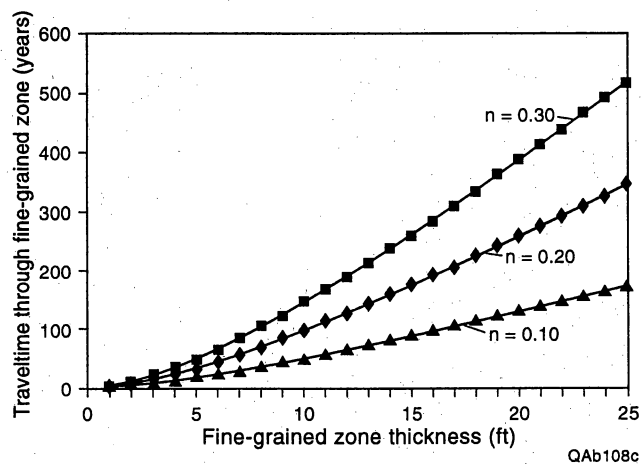


Figure 24. Graph illustrating varying traveltimes through a 3.0-m-thick fine-grained zone with a vertical hydraulic conductivity of  $1 \times 10^{-8} \text{ cm s}^{-1}$  at probable effective porosities.

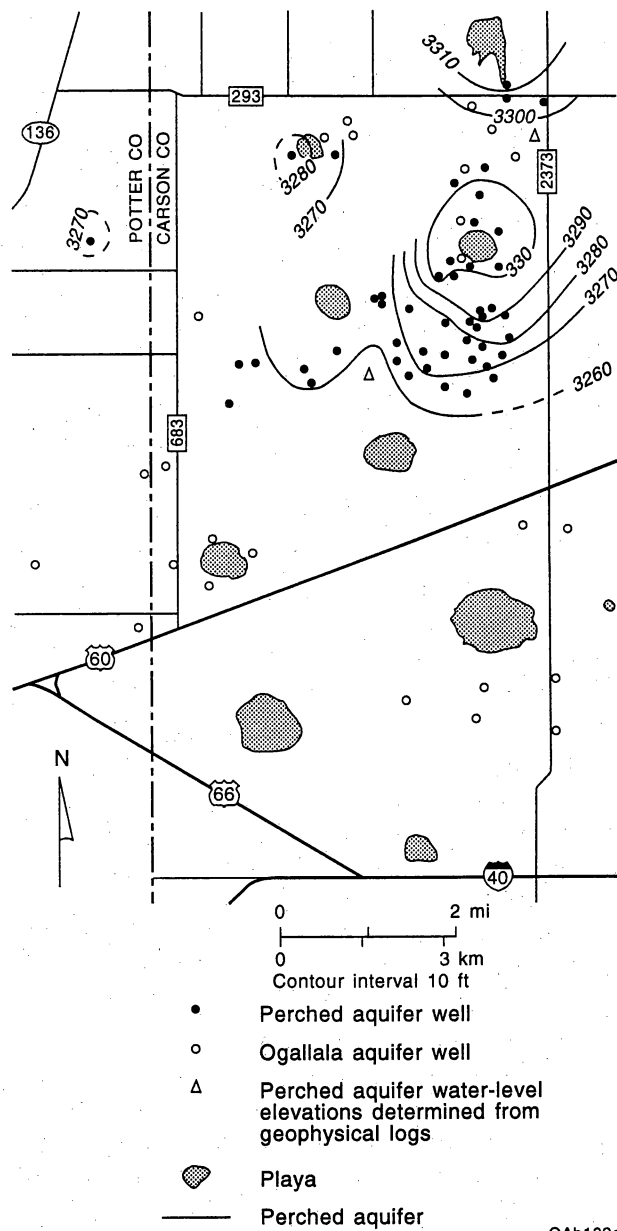


Figure 25. Potentiometric surface map of perched aquifers in the region of the Pantex Plant. Map does not include new wells drilled and completed along east boundary of plant.

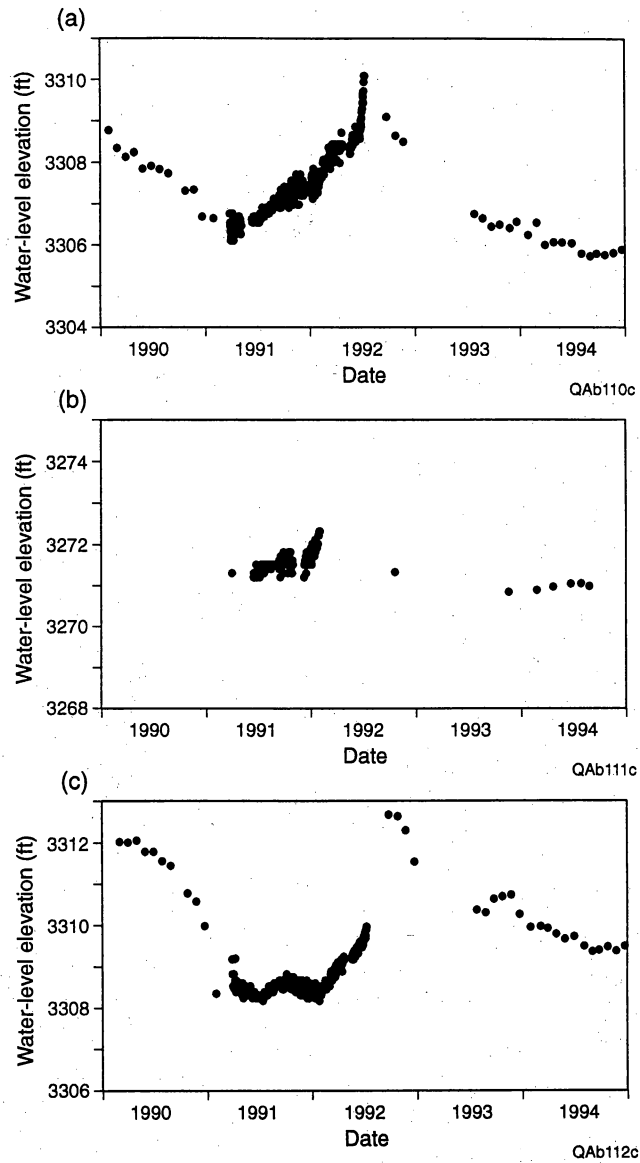


Figure 26. Water-level fluctuations in (a) PM-19, (b) PM-20, and (c) PM-38. Data from March 1991 through May 1992 collected using transducers and dataloggers. All other data collected during monthly monitoring using wire-line probe.

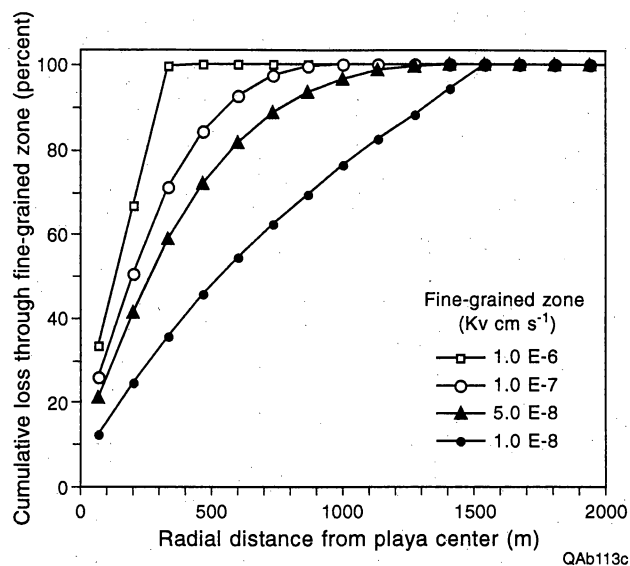


Figure 27. Graph illustrating percentage of ground-water flow through a fine-grained zone at increasing distance away from playa center.

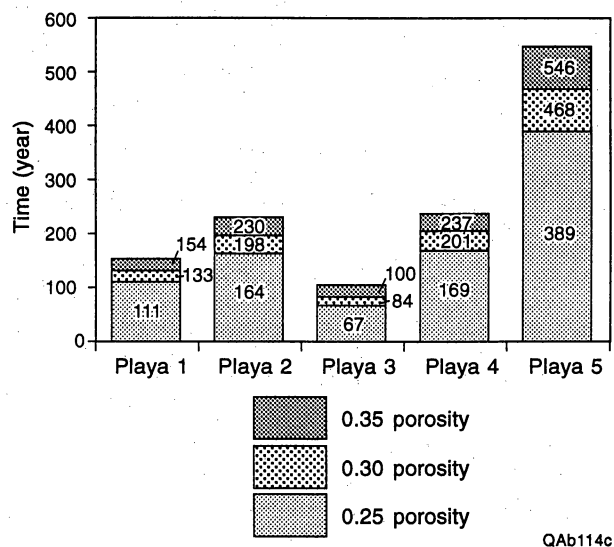


Figure 28. Graph illustrating traveltimes from the point of recharge at the different playas to the plant boundary at three probable effective porosities.

# Inorganic Hydrochemistry

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## INTRODUCTION

Knowledge of subsurface contaminant transport is needed for selection and application of remediation technologies and evaluation of remediation efforts. In turn, knowledge of sources and rates of recharge and of reactions governing ground-water quality is important for understanding subsurface contaminant transport, and characterizing the ionic and isotopic composition of ground water is important for delineating sources and rates of recharge and reactions. Therefore, we sampled 34 wells in the vicinity of the Pantex Plant (fig. 29) for major and minor ions, 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 wells (2 offsite, 8 onsite) in perched aquifers above the Ogallala aquifer, and 1 offsite well in the Permian-age Quartermaster Formation below the Ogallala aquifer. In addition, interest in  $\text{NO}_3^-$  as a possible product of high-explosive degradation and as a contaminant associated with waste-water discharge to Playa 5, upgradient from the Pantex Plant, led us to analyze sediment samples from Playa 5 and four other playa basins. Methods of sample collection and analysis are detailed in Fryar and Mullican (1993) and Fryar and others (1995a, b).

## RESULTS

As illustrated on the Piper diagram (fig. 30), which represents the relative concentrations of major cations and anions in  $\text{meq L}^{-1}$ , ground water in the study area is predominantly of a Ca-Mg- $\text{HCO}_3$  composition. This result is consistent with the findings of Nativ (1988) for the Ogallala aquifer in the northern half of the Southern High Plains.  $\text{Ca}^{2+}$  concentrations are highest in 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, are  $>20 \text{ mg L}^{-1}$  in 8 of 10 perched-aquifer wells sampled and in 3 of 23 Ogallala-aquifer wells sampled. In only five wells are  $\text{NO}_3^-$  concentrations greater than the regional average of  $14 \text{ mg L}^{-1}$  determined

by Anderson and Bernstein (1983). The highest  $\text{Cl}^-$  ( $>190 \text{ mg L}^{-1}$ ) and  $\text{NO}_3^-$  concentrations occur within the Ogallala aquifer  $<1,000 \text{ m}$  downgradient from Playa 5. Concentrations of Si are lowest in the perched aquifers ( $10.1$  to  $15.8 \text{ mg L}^{-1}$ ), highest ( $18.6$  to  $27.5 \text{ mg L}^{-1}$ ) in the Ogallala aquifer upgradient from (south and southwest of) the Pantex Plant, and  $13.8$  to  $19.4 \text{ mg L}^{-1}$  beneath the Pantex Plant.

$\delta\text{D}$  and  $\delta^{18}\text{O}$  are relatively enriched, and  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) is relatively depleted in the perched aquifers adjacent to playas; the opposite is true of the main perched aquifer in interplaya areas.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  results indicate that both perched and Ogallala ground waters fall between the local summer and winter meteoric water lines (MWLs), which were calculated from data for Amarillo International Airport (Nativ, 1988) (fig. 31). Other stable isotopes ( $\delta^{11}\text{B}$ ,  $\delta^{15}\text{N}$ , and  $\delta^{34}\text{S}$ ) do not appear to vary systematically along flowpaths in either the perched aquifers or the Ogallala aquifer.  $\delta^{15}\text{N}$  appears to vary inversely with  $\text{NO}_3^-$  concentration, although the most enriched value of  $\delta^{15}\text{N}$  and the highest  $\text{NO}_3^-$  concentration both occur in well FPOP-MW-06.

Because of the likelihood of mixing of waters of different ages in unconfined aquifers (Dutton, 1995), tritium ( $^3\text{H}$ ) and  $^{14}\text{C}$  provide relative, rather than absolute, ground-water ages. Those radioisotopes decay at different time scales, with half-lives of  $12.43 \text{ yr}$  for  $^3\text{H}$  and  $5,568 \text{ yr}$  for  $^{14}\text{C}$ . Prior to 1952, tritium ( $^3\text{H}$ ) concentrations in precipitation were probably 3 to 10 tritium units (TU) (Hem, 1985; Robertson and Cherry, 1989). From 1952–1963, atmospheric nuclear testing by the U.S. and the U.S.S.R. resulted in much greater  $^3\text{H}$  concentrations in precipitation ( $>2000 \text{ TU}$  at Ottawa, Ontario). As an aside, it should be noted that even these values are well below the drinking-water standard for  $^3\text{H}$ , which is  $2.0 \times 10^{-5} \mu\text{Ci mL}^{-1}$  ( $6,300 \text{ TU}$ ). 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 greater than approximately 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 the perched aquifers are highest adjacent to and south of Playa 1 ( $>9 \text{ TU}$ , maximum  $44.4 \text{ TU}$  for PM-38). In the Ogallala aquifer, levels  $>1 \text{ TU}$  have been detected in six wells south and southwest of the Pantex Plant, including the two downgradient monitoring wells 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. Although the source of  $^3\text{H}$  cannot be proven, our results and those of Argonne National Laboratory (ANL) (1994) (with one exception:  $60 \text{ TU}$  for PTX08-1009) fall within the range of 0 to  $45 \text{ TU}$  (corrected for decay to 1994) observed regionally in the Ogallala aquifer by Nativ (1988). These results suggest that  $^3\text{H}$  observed in wells on or near the Pantex Plant is likely to have originated at least in part from fallout from atmospheric testing outside of Texas.

$^3\text{H}$  concentrations in the perched aquifer near Playa 1 and in the Ogallala aquifer near Playa 5 probably represent mixing and infiltration of water pumped from the Ogallala aquifer and runoff from modern precipitation. Trends in  $^{14}\text{C}$  are similar to those of  $^3\text{H}$ : the highest  $^{14}\text{C}$  abundances (>85 percent modern C [pmc]), and the youngest waters, in the perched aquifers occur adjacent to Playa 1 and the C. Wink playa. In the Ogallala aquifer,  $^{14}\text{C}$  abundances decline from >50 pmc south of Sevenmile Basin and southwest of Playa 5 to 24 to 45 pmc beneath the Pantex Plant.

Extractable  $\text{NO}_3^-$  concentrations in playa sediments are typically greatest within 1 m of land surface, with secondary peaks at greater depths. Within 1.0 and 3.4 m of land surface, respectively,  $\text{NO}_3^-$  concentrations in the floor and annulus of Playa 5 are greater than those in similar geomorphic settings at the TDCJ playa, which currently receives return flow from irrigation, and the Finley playa, which receives no return flow (fig. 32). The maximum  $\text{NO}_3^-$  concentration is  $719.7 \text{ mg kg}^{-1}$  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  $24.5 \text{ mg kg}^{-1}$ .

## DISCUSSION

Simulations using the computer program NETPATH (Plummer and others, 1991) indicate that the major-ion composition of ground water in the study area may reflect evaporation and reactions in the vadose zone. Plausible reactions include (1) dissolution of soil carbonate (comprised of calcite [ $\text{CaCO}_3$ ]),  $\text{CO}_2$  gas, feldspars, sepiolite, and palygorskite; (2) precipitation of smectite; and (3) ion exchange involving  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . We find that the shifts toward lower  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations and more enriched  $\delta^{13}\text{C}$  values of DIC with distance away from Playa 1 cannot be explained by reactions within the perched aquifers and may reflect different recharge regimes, as also suggested by ANL (1994). Elevated levels of  $^3\text{H}$  and  $^{14}\text{C}$  in perched ground water adjacent to playas, and mounding of the perched water table beneath Playa 1 and the next playa north (Fryar and Mullican, 1995), indicate younger waters and focused recharge beneath playas. Romanak and others (1993) indicated that increased partial pressures of  $\text{CO}_2$  (which would result in elevated  $\text{HCO}_3^-$  concentrations) are associated with greater microbial activity in the vadose zone beneath playas. Reaction-path modeling using NETPATH suggests that depleted  $\delta^{13}\text{C}$  (DIC) values in perched ground water beneath playas may be associated with dissolution of  $\text{CO}_2$  generated by microbial oxidation of organic carbon (OC).



Recharge to the perched aquifers beneath interplaya areas can be attributed in part to focused infiltration beneath ditches. The presence of plumes of contaminants such as Cr, TCE, and RDX beneath Zones 11 and 12 (for example, Radian Corporation, 1994) and the "noses" on the perched water table in that area (Fryar and Mullican, 1995) provide evidence of infiltration beneath ditches to which waste water was discharged. Enhanced recharge beneath both ditches and playas is evidenced by  $\text{Cl}^-$  concentrations in perched ground water that are typically greater than background levels in the Ogallala aquifer. Enrichment of  $\text{Cl}^-$  suggests that water pumped from the Ogallala aquifer for Pantex Plant use and discharged to ditches and playas was subjected to partial evaporation before or during infiltration. However, the coincidence of  $\delta^{18}\text{O}$  versus  $\delta\text{D}$  plots with local MWLs suggests that evaporation is limited. For most wells in which contaminants or elevated levels of  $\text{Cl}^-$  have been detected,  $^3\text{H}$  concentrations (including data of ANL [1994]) are  $>1$  TU. This coincidence indicates that water pumped from the Ogallala aquifer, with in situ  $^3\text{H}$  concentrations  $<1$  TU, may mix with tritiated precipitation at land surface.

In contrast, wells in the main perched aquifer between playas and away from ditches, including PM-44 and PTX10-1007 and -1008 (the latter two sampled by ANL but not by BEG), appear to be uncontaminated, with concentrations of  $\text{Cl}^-$  and  $^3\text{H}$   $\leq 21$  mg  $\text{L}^{-1}$  and  $\leq 1.2$  TU, respectively. Vadose-zone hydraulic and hydrochemical data from the vicinity of the Pantex Plant indicate that negligible natural recharge currently occurs in interplaya settings (Scanlon and others, 1994). 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. The most depleted values of  $\delta\text{D}$  ( $-57$  to  $-46\%$ ) and  $\delta^{18}\text{O}$  ( $-7.1$  to  $-6.5\%$ ) in perched ground water include both uncontaminated and contaminated interplaya wells (ANL, 1994). Those values overlap the range of, and in contaminated wells may reflect,  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of water pumped from the Ogallala aquifer.  $\delta^{13}\text{C}$  values in contaminated and uncontaminated perched ground water in interplaya areas are also similar, and may be controlled by dissolution of isotopically enriched caliche. 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  $\text{CaCO}_3$ .

Focused recharge to the Ogallala aquifer upgradient from the Pantex Plant is associated in part with waste water 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  $>11$  mg  $\text{L}^{-1}$ , respectively). Two of these wells 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, 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 (1994a).

$\text{NO}_3^-$  concentrations in ground water may be controlled by intrinsic denitrification (coupled to oxidation of OC) in the vadose zone. Evidence for denitrification is provided by (1) declines in  $\text{NO}_3^-$  concentrations in soil extracts with depth, (2) counts of denitrifying bacteria in playa sediments, (3) values of  $\delta^{15}\text{N}$  of soil gas depleted relative to atmospheric  $\text{N}_2$ , and (4) relatively enriched values of  $\delta^{15}\text{N}$  accompanying relatively low  $\text{NO}_3^-$  concentrations in ground water (Fryar and others, 1995a, b). The depletion of  $\text{O}_2$  and the presence of high  $\text{CO}_2$  and  $\text{CH}_4$  in soil gas (Romanak and others, 1993) suggest microbial processes beneath playas that would include denitrification. However,  $\text{NO}_3^-$  contamination of the Ogallala aquifer adjacent to Playa 5 suggests that denitrification may only partially reduce  $\text{NO}_3^-$  in waste water discharged to playas. Denitrification may be limited by the amount of bioavailable organic carbon, or it may be slower than the downward solute flux (Fryar and others, 1995a).

#### APPLICATIONS TO REMEDIATION

Hydrochemical results indicate that contaminant migration to the perched aquifers in interplaya regions away from playas and ditches (such as in the vicinity of leaking underground storage tanks; for example, Woodward-Clyde, 1993) is likely to be slow and may be negligible. Conversely, contaminant migration at points of focused recharge, such as playas and ditches, may be relatively rapid, if not limited by reactions such as sorption and biodegradation. Although  $^3\text{H}$  concentrations  $>1$  TU indicate the occurrence of post-1952 recharge, recharge may have occurred more recently: for example, the discharge of waste water, which is now detectable in the Ogallala aquifer, to Playa 5 probably began between 1968 and 1975 (Bureau of Economic Geology, 1993a). Therefore, to minimize further leaching of contaminants to the perched aquifers, remediation of contamination in the vadose zone adjacent to playas and ditches should be given priority over remediation of contamination elsewhere in the vadose zone.

Evidence of leakage downward from the perched aquifers to the Ogallala aquifer indicates that continued monitoring of water quality in Ogallala-aquifer wells is appropriate, even though contamination of the Ogallala aquifer beneath the Pantex Plant has not been detected.

Additionally, evidence of mixing suggests that concentrations of contaminants reaching the Ogallala aquifer could be potentially limited by dilution.

In ground water, relatively enriched  $\delta^{15}\text{N}$  values, relatively low  $\text{NO}_3^-$  concentrations, and dissolved oxygen concentrations  $>3.24 \text{ mg L}^{-1}$  indicate that the existence of anaerobic conditions conducive to denitrification in the vadose zone does not preclude the influx of atmospheric  $\text{O}_2$ . Oxygenated water may percolate through macropores while the clayey soil matrix remains anaerobic. Dissolved  $\text{O}_2$  and contaminants such as  $\text{Cr(VI)}$  and chlorinated solvents could diffuse from macropores into the soil matrix and there be reduced by microbial oxidation of sediment OC. Subsequently, residual concentrations of contaminants might diffuse back out of the soil matrix if 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 in playas or occasional releases of waste water to ditches, could lead to reduction of  $\text{O}_2$  and contaminants within macropores. These pulses might subsequently be displaced by oxygenated pulses of infiltrating rainwater or reoxidized by atmospheric  $\text{O}_2$  diffusing laterally inward. In either of these scenarios, which are not mutually exclusive, reducing conditions are spatially and temporally variable. Both variable geochemical conditions and heterogeneous hydraulic properties may impair the efficiency of vadose-zone remedial strategies, such as soil-vapor extraction or amended biodegradation, that involve withdrawing contaminants or delivering nutrients.

#### UNANSWERED QUESTIONS AND ADDITIONAL NEEDED RESEARCH

Adsorption of contaminants onto solids in the perched aquifers can affect the efficiency of pump-and-treat remediation. Both  $\text{Cr(VI)}$  (in anionic form) and organic compounds such as TCE and RDX are prone to adsorption (onto Fe oxyhydroxides and sediment OC, respectively [Cherry and others, 1984]). Although we have estimated retardation coefficients for RDX transport within the perched aquifer from literature values (Bureau of Economic Geology, 1995), site-specific data are lacking. We recommend collecting and preserving (freezing) core samples from perched-aquifer sediments during the drilling of future wells. Measurements of the fractions of Fe oxyhydroxides and of sediment OC, and of the surface areas of those phases and of the bulk sediment, should be made on those cores. Adsorption of contaminants onto sediments should be quantified in the laboratory over the ranges of contaminant concentrations observed in perched ground water. By conducting these analyses, estimates of the effectiveness of adsorption as a mechanism that inhibits contaminant transport and affects the efficiencies of some remediation technologies (such as pump and treat) may be achieved.

Information on vertical variability in ground-water compositions is needed to establish the exact locations of contaminants (critical to any remediation effort) and the extent of solute mixing. Because monitoring wells at Pantex are commonly screened over tens of feet, wellbore dilution during pumping may underpredict actual contaminant concentrations and overpredict the vertical extent of contamination. We recommend installing strings of passive (dialysis) samplers (Ronen and others, 1986), spaced at narrow intervals (for example, every 0.3 m), in monitoring wells from which the dedicated pumps will have been pulled. Because these wells are pumped every one to three months, whereas the time necessary for equilibration should be on the order of one week, passive sampling should be possible without major disruption of existing monitoring schedules. In addition, we recommend delineating vertical variability in the composition of water in the unsaturated zone beneath the main perched aquifer by collection of extracts from core samples and analyses for major solutes and contaminants.

We also recommend additional delineation of the extent of waste-water contamination of the Ogallala aquifer emanating from Playa 5. Although contamination beneath Playa 5 does not appear to have resulted from Pantex Plant activities (Bureau of Economic Geology, 1993a), the  $\text{Cl}^-$  and  $\text{NO}_3^-$  plume, unless hydraulically contained by pumping, is likely to migrate toward the Plant's production wells. In addition, information on solute transport within the Ogallala aquifer that can be derived from this plume is relevant to predicting potential contaminant transport within the Ogallala aquifer onsite. Currently, only two monitoring wells downgradient from Playa 5 intercept this plume.

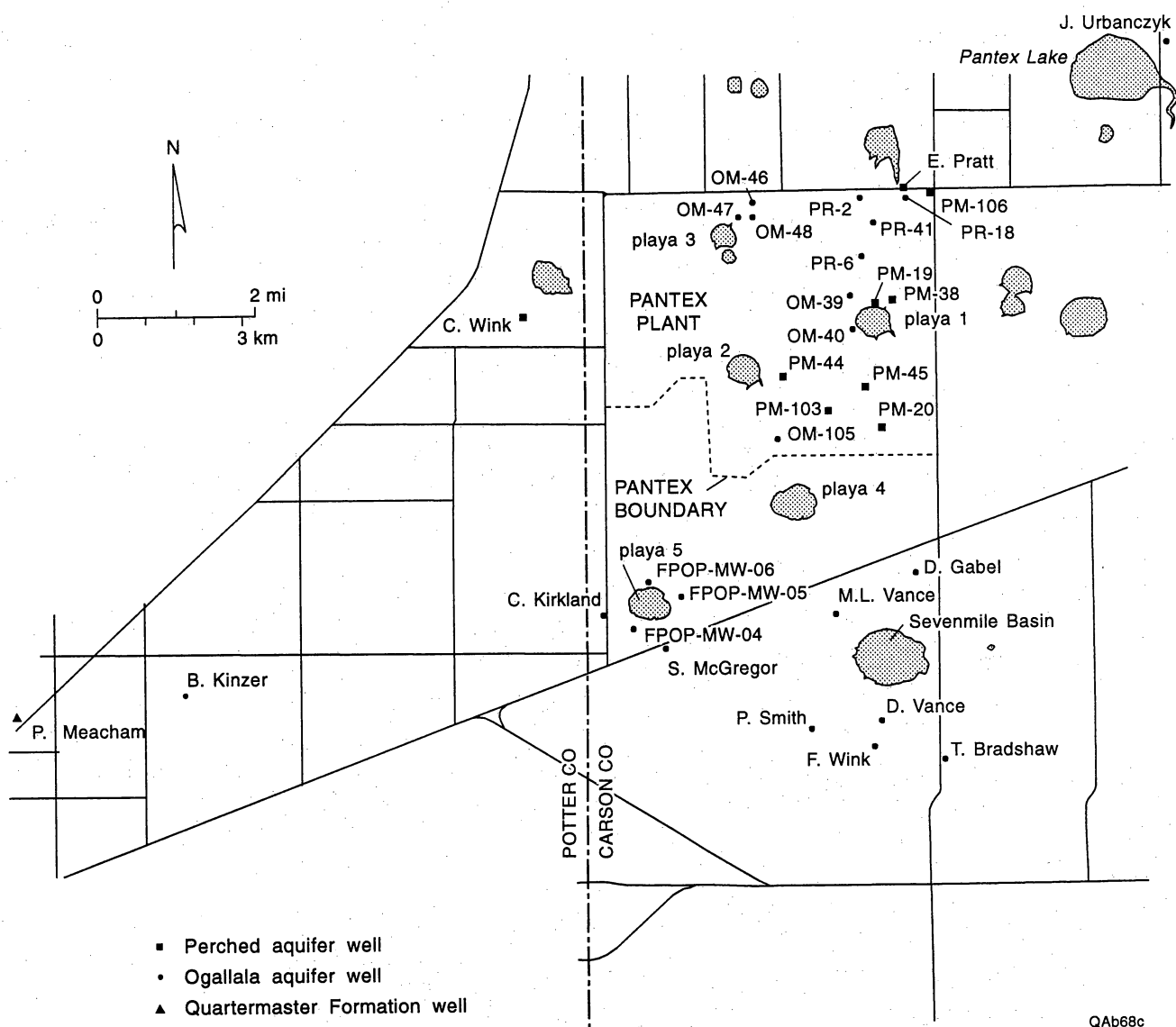


Figure 29. Location map of wells sampled by the Bureau of Economic Geology in the area of the Pantex Plant. Landowners and/or tenants of private properties are indicated.

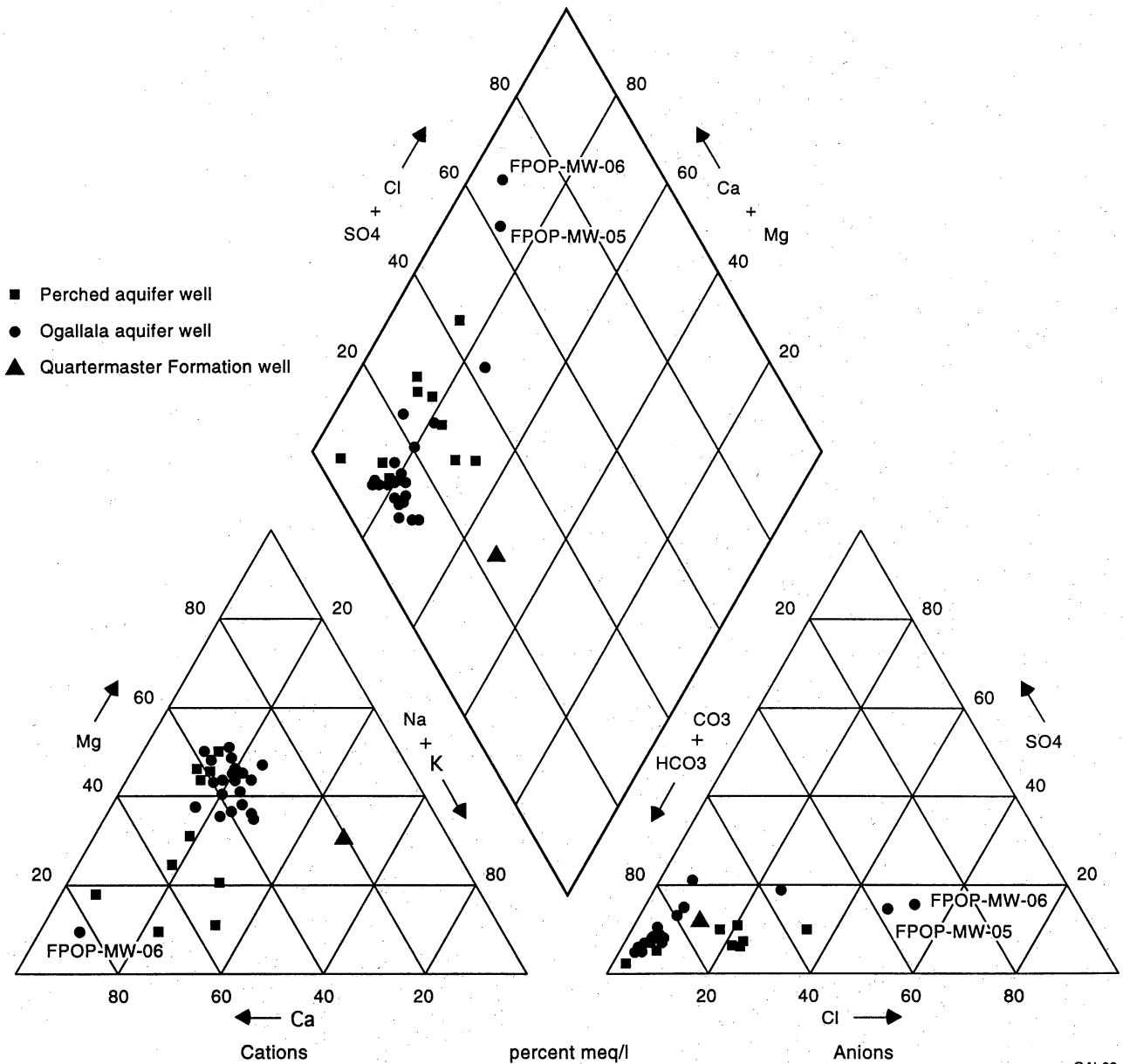


Figure 30. Piper diagram representing relative concentrations (in meq L<sup>-1</sup>) of major ions in ground water. The most recent data are plotted for wells sampled on more than one occasion.

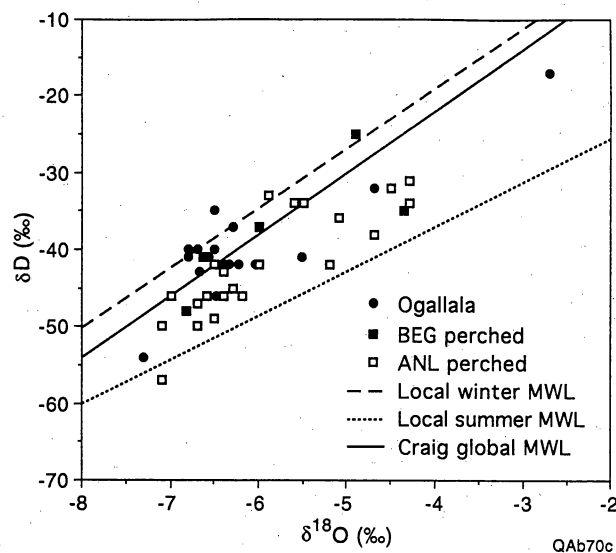


Figure 31. Relative abundances of deuterium in ground water plotted versus relative abundances of oxygen-18 (‰ standard mean ocean water [SMOW]). Note that 1992 BEG data, for which  $\delta D$  values may be in error, are not plotted. Local meteoric water lines (MWLs) calculated using data from Appendix 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.

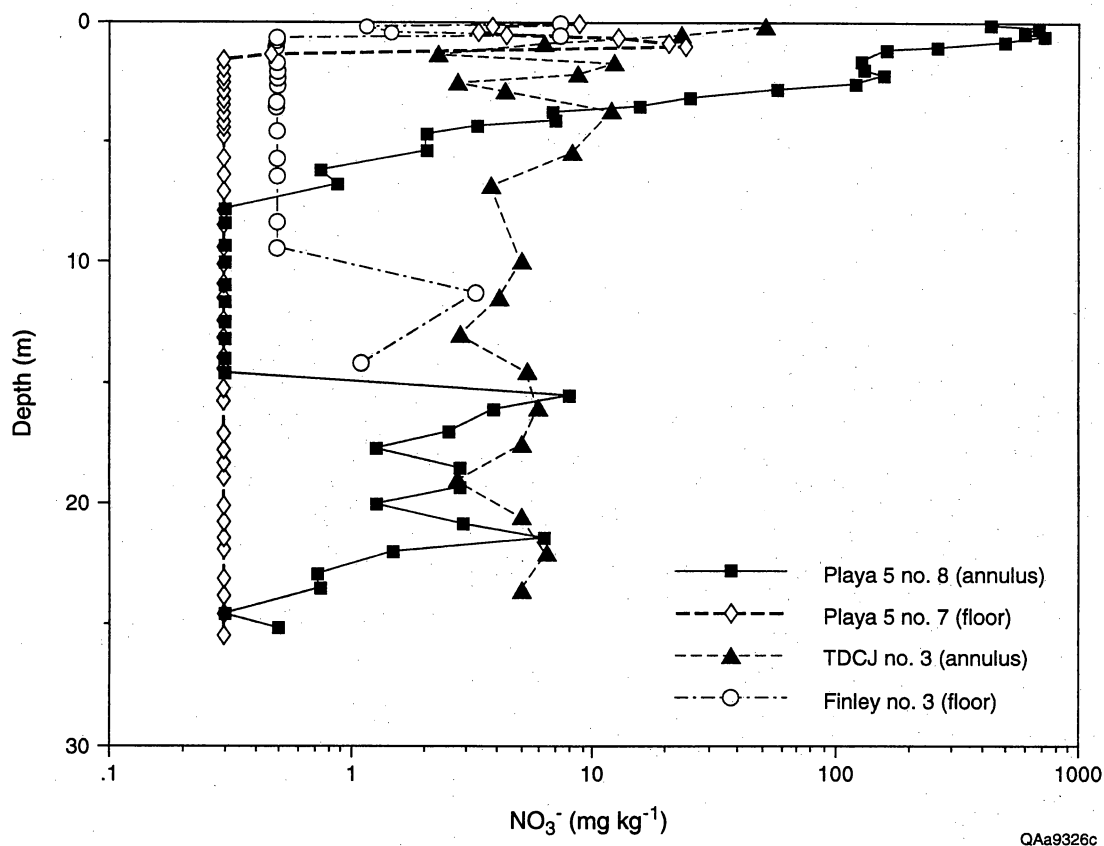


Figure 32. Extractable nitrate concentrations in playa sediment samples as a function of depth in selected boreholes. Geomorphic setting of each borehole is given in parentheses. Concentrations reported as below detection limit are plotted as equal to detection limit.

# Geochemical Controls on Organic Contaminants in the Vadose Zone

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## INTRODUCTION

This project examined some of the geochemical controls on the fate and transport of organic contaminants in the vadose zone under the ditches and playas of the Pantex facility. Chemically, the vadose zone can be viewed as a collection of phase boundaries representing the interfacial regions of solid matrix, pore waters, pore gases, and free organic compounds. The mobility of an organic contaminant through the unsaturated zone therefore will be controlled by interfacial processes, such as volatilization, evaporation, sorption, partitioning, and dissolution. These abiotic processes can result in both retardation and enhancement of the movement of organic contaminants. In addition, many organic compounds in natural aquatic systems can act as carbon substrate for native microbial populations and are therefore subject to transformation or mineralization via enzyme catalyzed biologic systems. These biotic processes often act to limit the linear mobility of the contaminant but can occasionally increase the solubility of some compounds or increase the toxicity of others.

The potential for organic contaminant transport through the subsurface was characterized by examining the sorption and desorption at mineral surfaces, gas-transport phenomena, partitioning to soluble and insoluble natural organic materials, the potential for biodegradation, and the controlling geochemical environment beneath wetland playas. Each of these aspects are summarized below.

### Vapor-Phase Sorption Equilibria

Contaminants discharged into the ditches and playas at Pantex facility must cross a very thick unsaturated zone before entering a water-bearing strata. In this type of environment, volatile contaminants can be transported via free-phase infiltration, dissolved aqueous phase infiltration, or vapor-phase diffusion and advection. In a vapor-phase system, like the aqueous phase, transport velocity will be a function of the permeability, tortuosity, advection-diffusion potential, and retardation by sorption. This project element examined the sorption of volatile organic contaminants on playa soils.



The sorption of volatile organic compounds (VOCs) onto playa soils was characterized using benzene, toluene, and trichloroethylene (TCE) as model sorbates in a batch-type, headspace testing method across a range of vapor pressures. Three primary soils collected from different depths from Playa 1 were used as representative material for these experiments and were analyzed for inorganic and organic carbon content and specific surface area (table 4). Water vapor sorption isotherms were established for these playa soils to determine the relationship between relative humidity and moisture content. VOC sorption was measured as a function of partial pressure, moisture, temperature, organic carbon content, and surface area.

Table 4. Critical parameters for soils used in the experiments.

Sampling Site	Soil Type	Surface Area	Percent organic C
P1O4 A (0"~1'2")	clay silt	73.30 m <sup>2</sup> /g	0.66
P1O4 B (1'5"~2'4")	silt	59.51 m <sup>2</sup> /g	0.14
P1O4 C (2'7"~3'6")	silt	52.89 m <sup>2</sup> /g	0.08

Water adsorption by playa soils fits a type III or type V isotherm and as such does not provide information on monolayer coverage. At low moisture contents (<~2 percent), VOC sorption isotherms fit a BET model (fig. 33). Monolayer coverage ranged from 26.31 mg/g to 21.38 mg/g for benzene. Because the moisture content exceeds 60-percent humidity (2 percent), sorption capacity is greatly reduced, and the isotherm type changes from BET-type to a Freundlich isotherm with a  $1/n \sim 1$  (fig. 33). At higher moisture contents, sorption follows a linear-type isotherm directly related to the fraction of soil organic carbon ( $f_{oc}$ , with the log  $K_{oc}$  for benzene ranging from 1.92 to 2.56 as the  $f_{oc}$  decreases from 0.66 to 0.08 percent. The heats of sorption  $DH_a$  are all less than 10 kcal/mol, suggesting low-energy physisorption or partitioning interactions.

Monolayer capacity for different compounds correlates well with the surface area of dry soils; soils with higher surface areas also have higher monolayer capacities. The difference in molecule cross-sectional area between calculated and theoretical values for a specific compound indicates that the packing arrangement onto soil minerals may not be simple hexagonal close packing. Sorption capacities of compounds with net exothermic heats of sorption such as benzene decreased as temperature increased.

Table 5. Sorption constants for benzene on playa soil. Kf = Freundlich coefficient at 0, 1, and 3 percent moisture contents; Kd = linear sorption constant at 30 percent moisture content (corrected for solubility in water); Koc = partition constant accounting for soil organic carbon; and DHa = heat of adsorption (kcal/mol).

Soil	Kf (0%)	Kf (1%)	Kf (3%)	Kd	Log Koc	DHa
P104A	660	280	1.68	0.544	1.92	-9.41
P104B	630	236	0.79	0.357	2.41	-9.47
P104C	553	139	0.40	0.293	2.56	-9.26

The results of this study suggest that volatile organic contaminants will strongly sorb to soils at very low moisture contents, such as that encountered in surface soils during the summer. Moisture content at depths greater than a few centimeters, however, is high enough and the fraction of organic carbon is low enough to keep VOC sorption relatively low and vapor-phase concentrations high. In this type of system, VOC compounds will be transported in the vapor-phase by diffusion along concentration gradients, or be advected along pressure gradients, with little retardation. At very high moisture contents or saturated conditions, vapor-phase transport is limited by the lack of air-filled porosity, and volatile organic contaminants will dissolve into the aqueous phase according to their individual Henry's Law constants. In this environment, transport will be by aqueous-phase advection and diffusion barely retarded by limited sorption and partitioning.

#### Geochemical Controls on High-Explosives Transport

The objective of this study is to examine the interaction of soil, water, and explosives and how their properties interact to control movement of explosives contamination through onsite sediments. Water samples from onsite monitoring wells were analyzed for specific high-explosives (HE) residues, including 2,4,6-TNT, RDX, and HMX. TNT degradation products such as nitrotoluenes and nitrobenzenes were also examined. Soil samples from playas, interplaya areas, and drainage ditches were characterized for their geochemical properties, such as organic carbon content and surface area. Experiments were then performed to quantify HE sorption with varying soil and water types.

Water samples collected from perched-zone monitoring wells near work zones and Playa 1 contain measurable RDX up to 85 ug/l (ppb). HMX concentration in soils collected from the Zone 12 ditch ranged up to 1,106 ppm, whereas RDX was found up to 63 ppm. TNT was not

detected in any soil. Soil inorganic carbon (carbonate) contents ranged from 2 to 50 percent by weight, with the lowest values found in playa sediments. Organic carbon was found to range from 500 to 4,500 ppm (0.05 to 0.45 percent), with the highest values from the playas, whereas surface areas range from 20 to ~80 m<sup>2</sup>/g.

Sorption capacity experiments were performed with various water types and explosive compounds on soils collected from the Pantex site. A soil with low organic carbon and high inorganic carbon has been compared to a soil with midrange organic carbon and low inorganic carbon. Solutions used for these experiments are purified water with HMX, RDX, or TNT. Freundlich sorption coefficients for TNT range from 1.0 to 2.8 on the latter soil type. RDX sorption coefficients are near 0.7 to 0.9 and are less dependent on soil type. Experiments with increasing ionic strength waters show an increase in TNT sorption probably owing to salting-out. Waters with ionic strengths as low as 0.002 N result in a measurable increase in TNT sorption.

These experiments show that organic carbon content and surface area share control over adsorption capability of the collected soils; in low *foc* soils, sorption is low and controlled by mineral surface areas, whereas in high *foc* environments, sorption is more favorable and primarily controlled by *foc*. Waters with higher ionic strengths favor TNT sorption to the solid phase, whereas increasing temperature favor solution-phase dissolution. TNT adsorption is greater than RDX, an inverse relationship to their solubilities and contrary to theory. This suggests that TNT may interact directly with the soil surface via pi-bonding or via relatively strong Coulombic interactions, in contrast to the weaker "hydrophobic" bonding of RDX and HMX.

In the upland ditch environments, sorption capacity is at a minimum and mobility is highest, especially when high-volume low ionic strength runoff waters are in the ditch system. Here, TNT and HMX are most likely to sorb, whereas RDX will be relatively mobile. In the playas, however, where soil organic carbon *and* soil surface area are maximal, explosive mobility is minimal, and surface binding is favored. Because both *foc* and surface area decrease with depth, mobility increases with increasing depth beneath both playas and ditches for all compounds, but less for TNT.

#### Geochemical Controls on High-Explosive Desorption from Soils

The Pantex facility has a 50-yr history of discharging dissolved and particulate HE residues into the ditches and playas, and this class of organic contaminants may represent the primary source of contamination at the facility. HMX and RDX have been detected at fairly high concentrations in the soils near the Zone 11 and 12 ditches and at the burning ground, and dissolved RDX has been detected in the perched water beneath Zone 12 and Playa 1. The

movement of HE residues through the unsaturated zone will be controlled by the infiltration rate, aqueous-phase solubility, interactions with other dissolved organic carbon substances, and sorption-desorption kinetics and equilibria. This project element investigated HE solubility, interactions with DOC and SOC, and the desorption equilibria from contaminated ditch soils.

Desorption equilibria and dynamics on playa and interplaya soils were examined for HMX, RDX, and TNT at various temperatures and solution compositions using contaminated soils from the Pantex facility. Compound solubilities were also determined in DI H<sub>2</sub>O at five temperatures. The resulting data were used to determine enthalpies of desorption and solution of HMX and RDX. Uncontaminated playa soils were extracted to isolate the humic fraction and fulvic fractions, and the desorption and solubility experiments were repeated in a fulvic acid solution. The fulvic acid fraction was also used in an experiment to determine if there is formation of charge transfer complexes between it and HMX. The fulvic and humic acids were analyzed by <sup>1</sup>H-NMR (liquid) and <sup>13</sup>C-NMR (solid state), respectively. The humic fraction was used to determine the presence or absence of charge transfer complexes between it and HMX and RDX.

Desorption isotherm constants, solubilities, and critical thermodynamic constants for HMX, RDX, and TNT in H<sub>2</sub>O are summarized in table 6. Representative desorption isotherms are presented in figures 34 and 35. Enthalpies of desorption and solubility for HMX differ by about 3 kcal/mol, indicating partitioning and/or hydrophobic interaction of the compound and the soil. UV-V in different experiments does not indicate the formation of a charge transfer complex between HMX and playa fulvic acid. Further, the desorption and solubility experiments in fulvic acid do not indicate any greatly enhanced desorption or solubility of HMX as opposed to experiments run in DI H<sub>2</sub>O.

Table 6. HE solubility and sorption parameters in DI H<sub>2</sub>O. Solubility is expressed in mg/l, K<sub>f</sub> is the Freundlich coefficient, and DH is expressed in kcal/mol.

Compound	Solubility (295±K)	DH Solution	K <sub>f</sub> Desorp	DH Desorp
HMX	3.34	13.1	0.24	16.0
RDX	63.0	8.3	0.11	—
TNT	106	6.7	—	—

NMR analyses of the fulvic acid fraction indicate a largely aliphatic character and a pronounced absence of electron-donating aromatics and carboxylics. Conversely, the humic acid fraction exhibits roughly equal amounts of aliphatic, aromatic, and carboxylic

functionalities, indicating that the humic acid fraction is the predominant component of soil organic carbon involved in interactions with HMX and RDX.

This study found that soils from the Zone 12 ditch were contaminated by both sorbed and particulate HMX, but primarily sorbed RDX. Sorbed HMX and RDX readily desorb in water, with equilibrium concentrations approaching 75 percent of their aqueous solubilities. Because the solubility of RDX and TNT is much greater than HMX, these compounds are more readily transported in the aqueous phase, while HMX is more likely to be retained on the solid phase. The sorption interaction is primarily partitioning to the soil organic carbon, but there is also mineral-surface sorption. There is no detectable interaction between HMX and playa-soil-derived DOC, and neither solubility nor the desorption behavior of HMX is influenced by DOC concentration.

### Gas Transport in a Playa Subsurface

Vapor-phase transport of volatile contaminants and the mineralized by-products of biodegradation is influenced by many of the same factors that control fluid movement in the subsurface, that is, permeability, porosity, tortuosity, and temperature. Gas can move through the vadose zone via diffusion, as well as by advection under temperature or barometric pressure gradients, depending on the geological controls at that location.

To examine permeabilities (both vertical and horizontal) for flow characterization and tortuosities for diffusion characterization, an uncontaminated analog site, located a few miles northwest of the facility, was chosen because of onsite security restrictions. Several gas wells were installed to a maximum depth of 14 m, most to a depth between 1.8 and 5.5 m. Three types of experiments were performed: (1) continuous monitoring of pressures at several depths in several wells compared with atmospheric pressure variations to give information on the minimum vertical permeability of a large area around a well; (2) steady-state air injection tests (back pressures between 1.5 and 2.5 atmospheres) and monitoring of pressure changes in monitoring wells within a 2-m radius to calculate both vertical and horizontal permeabilities in a more restricted area around the well, but for each of the layers; and (3) transient analysis of tracer tests (injection of ethylene and propane) to measure air tortuosities.

The data was analyzed using both analytical and numerical computer models. It was found that pore spaces below 6 m are not well connected to the surface (probably owing to a wetting front at a depth of 6 to 9 m). This effect was observed to be greatly enhanced immediately after a major precipitation event, when elevated surface moisture contents eliminate vertical gas exchange even at very shallow depths, leaving only horizontal pathways available for gas exchange. Air permeabilities are very anisotropic and considerably enhanced by cracks and root

channels under dry conditions (from 16 to 1 D as opposed to a matrix permeability of 20 md). Also, air tortuosities are 25 to 50 percent higher than expected. The high vertical permeability owing to fractures and the large differential pressures raise the possibility of contaminant *advection*, via barometric or temperature-induced pressure gradients, in contrast to the usual assumption of diffusion for vapor-phase transport. In this environment, therefore, volatile contaminants may be transported much faster than would be expected by diffusion only.

### Spatial and Temporal Variations in Soil Gas Composition

The purpose of this project component is to characterize unsaturated-zone geochemical and biogeochemical processes in the unsaturated zone beneath ephemeral wetland playas.

Soil gas around onsite and offsite playas was analyzed for nitrogen, carbon dioxide, methane, and oxygen in the field from more than 50 locations ranging in depth from 0.6 to 14 m below land surface. Samples were collected from the playa basin slope, lake annulus, and playa floor regions and compared over a 4-yr period. A subset of gas samples was also analyzed for argon:nitrogen ratios and stable carbon and oxygen isotopic ratios.

In the playa slope area, vadose-zone concentrations of carbon dioxide range from 0.1 to 1 percent, with little depth-related variation. Concentration increases in the spring owing to root respiration and decreases in the winter. Methane was not detected, oxygen concentrations are >20 percent, and the  $\text{CO}_2 + \text{O}_2$  versus  $\text{N}_2$  ratio is consistent with a simple one-step carbon oxidation model.

In the annulus area, oxygen concentration varies from 0 to 19 percent, whereas methane varies from 0 to 2.2 percent. Carbon dioxide ranges from ~1 to 15 percent, with concentration increasing with depth to ~5 m, then decreasing with depth to 14 m. Carbon dioxide concentration did not vary with season but did vary with the presence or absence of water in the playa. Enriched  $\text{d}^{13}\text{CCO}_2$  is correlated with the presence of methane. Under dry conditions, carbon dioxide concentration varies from 1 to 5 percent, but under wet conditions, carbon dioxide concentrations generally increase in the annulus area. In addition, when the playa is saturated and oxygen concentration is low, methane is detected in the playa vadose zone, whereas under dry conditions, no methane is detected.  $\text{CO}_2 + \text{O}_2$  versus  $\text{N}_2$  ratios are lower than expected for a simple carbon oxidation model, suggesting a multistep carbon oxidation, oxygen consumption, and carbonate dissolution process that can result in nitrogen concentrations >90 percent.

Under the playa floor, carbon dioxide concentrations range from 1 to 5 percent, increasing when the playa holds water. Concentration increases to 4.5 m and then decreases to 14 m. Methane was not detected from playa floor wells, but these points can only be sampled under

completely dry conditions when methane is not detected at any location. Spatial variations in soil-gas  $\delta^{13}\text{CCO}_2$  (-13 to -26 per mil) imply less communication with atmospheric  $\text{CO}_2$  toward the playa center.

The elevated  $\text{CO}_2$  concentrations at depth are attributed to microbial oxidation of organic matter in the playa subsurface. Under wet conditions, water and carbon recharges into the vadose zone immediately beneath the playa, supplying substrate, nutrients, and moisture to the native microorganisms but limiting vertical gas permeability. Microbial carbon oxidation produces carbon dioxide as it consumes oxygen, and with the limited vertical diffusion of oxygen, anaerobic conditions can be attained, producing methane from either fermentation or bicarbonate methanogenesis. The carbon dioxide concentration in the vadose zone represents an equilibrium condition between gas phase, liquid phase, and consumption by carbonate dissolution. Under dry conditions, microbial oxidation still proceeds, producing carbon dioxide, but the high vertical permeability, rapid diffusion rates, and barometric effects quickly vent carbon dioxide out and keep oxygen in, maintaining low  $\text{CO}_2$  concentrations and constant aerobic conditions (fig. 36).

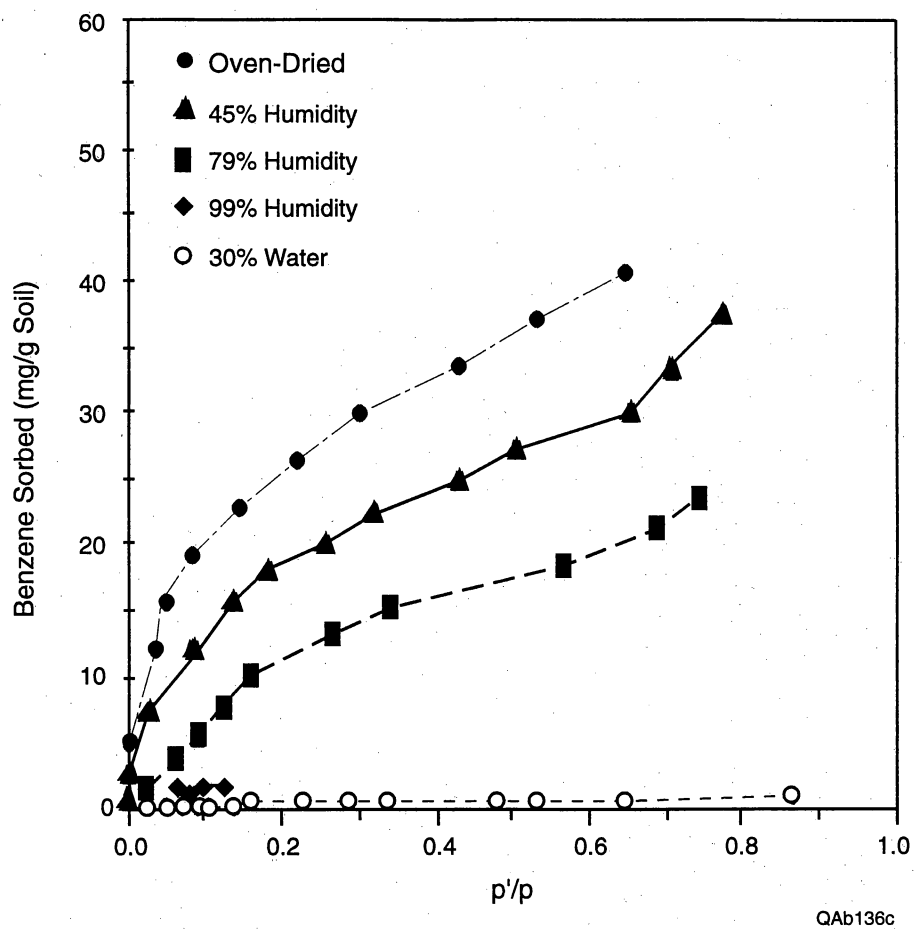


Figure 33. Benzene sorption isotherm on Playa 1 soil as a function of moisture content at 25° C.



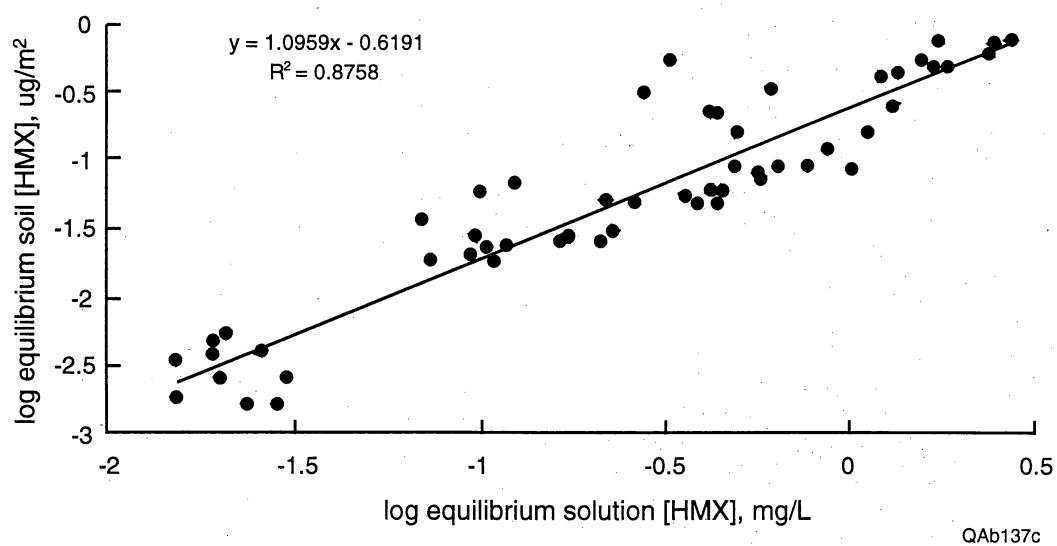
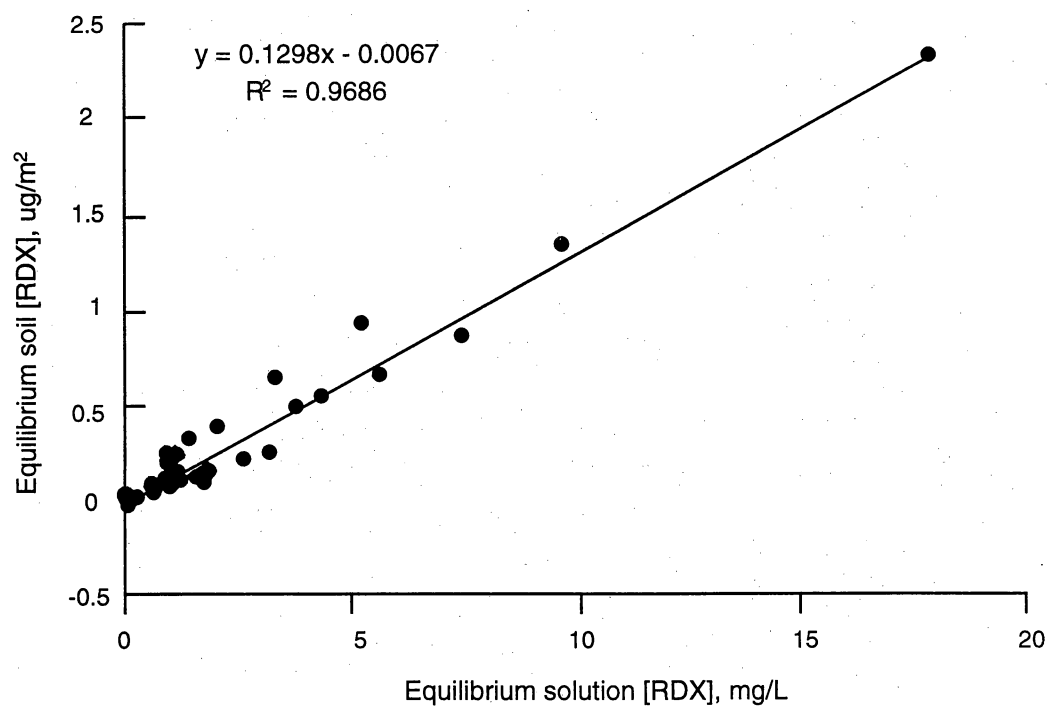


Figure 34. Desorption isotherm for HMX off soils collected from the Zone 12 East Ditch.



QAb139c

Figure 35. Desorption isotherm for RDX from soils collected from the Zone 12 East Ditch in distilled water at 25° C.

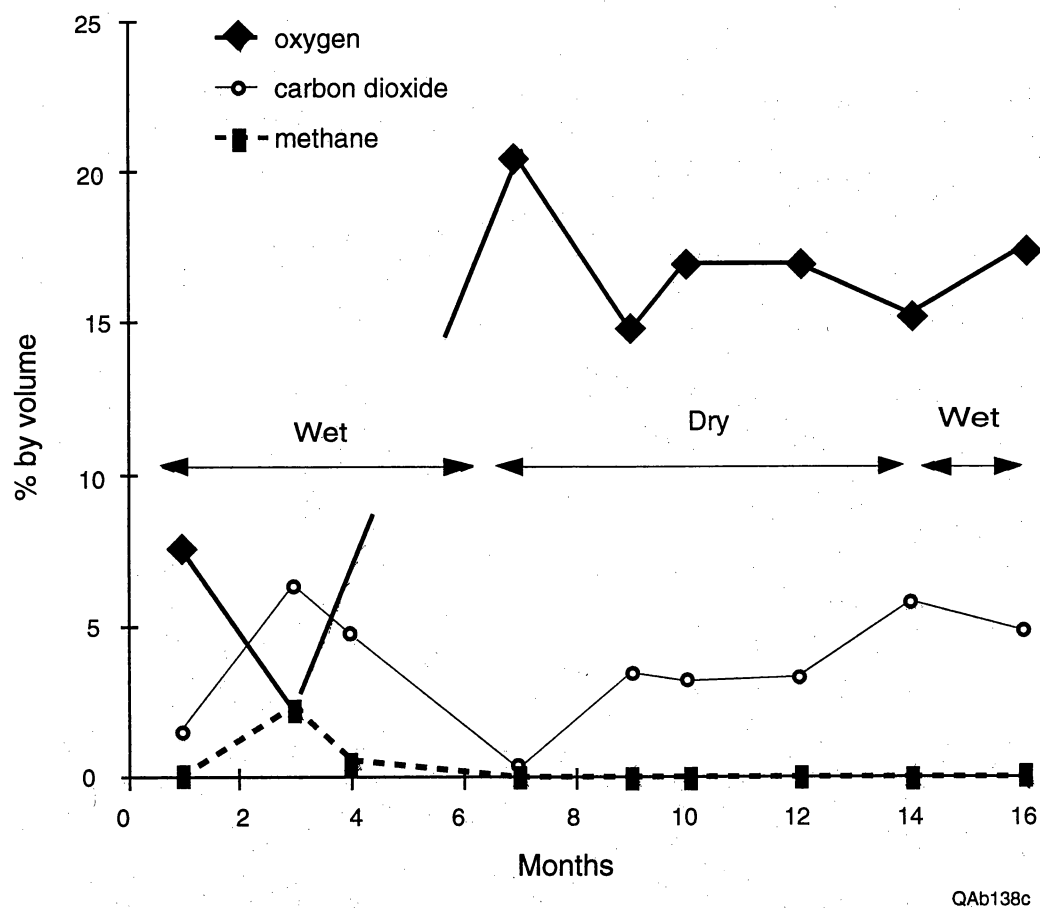


Figure 36. Gas concentrations in percent at TDCJ playa plotted over time. A qualitative description of the moisture condition of the playa is shown.

## Chromium Sorption Studies

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Chromium contamination has been documented at concentrations ranging from 0.1 to 9.5 mg/L in the perched aquifer beneath Zone 12. Chromium sources were likely from cooling tower blow down or from plating waste discharges. Because chromium is known to exist in the perched aquifer well above natural levels, it is certain that this heavy metal has been mobile both through the unsaturated zone and in the perched aquifer. As a heavy metal cation, chromium is known to sorb to soils and may be retarded as it moves through the porous media. The nature of the sorption process in the subsurface soils directly affects the selection of possible remediation alternatives. In this task area, samples of subsurface soil horizons were analyzed for characteristics that affect chromium solute transport.

The subsurface materials used in this study were selected from the core recovered by the Bureau of Economic Geology from well BEG-PTX No. 2, located south of Playa 2 and west of Zone 11. This site does not have any man-made chromium contamination, so any chrome presence would be due to natural background. After visual inspection of the core and evaluation of the geologic logs, sections of core were removed from six lithological units. The first column of table 7 shows the depths below land surface for each sample. The upper four samples were well above the perched aquifer. The sample at 313 ft was within the saturated zone of the perched aquifer. The deepest sample was taken from beneath the perched aquifer. The purpose in selecting samples from various depths was to determine possible differences in vertical chromium transport through the various layers.

Table 7 summarizes the results of the laboratory analyses. The second, third, and fourth columns were derived from a grain-size analysis, which combined sieve and hydrometer techniques. Clay and silt are combined in the second column because both can contribute to sorption effects. Cation exchange capacity (CEC) was measured with the ammonium saturation method. It is interesting that the highest CEC was found within the perched aquifer material. The Toxicity Characteristic Leaching Potential (TCLP) test (EPA SW 846-1310) was used to determine the leachable natural chromium contents for the soils. The numbers in the fifth column are within typical ranges for undisturbed soils. Cr concentrations were analyzed by flame and graphite furnace atomic absorption spectrophotometry as required. Batch equilibrium sorption tests were performed to determine the values of the coefficient and exponent for a simple Freundlich isotherm fit for each soil. Ogallala ground water from the Pantex Plant water supply system was used for the base solution in these tests because that water was the primary

transport liquid for the Cr in waste waters at the plant. It is recognized that as a cation, Cr(III) or Cr(VI) will be sorbed as ion exchange. However, the presence of large concentrations of calcium and magnesium dominates the cation exchange as represented by simple mass-action law exchange. The Freundlich isotherm gives a simple relation that can be used in transport modeling for the low Cr concentrations of interest.

The final phase of the Cr studies is currently underway. In this phase, one-dimensional soil columns are being used to determine the actual transport parameters in effect as the water flows. The soil columns are each 25 cm in length and 2.54 cm in diameter. One column is constructed from each soil type. The columns are carefully packed with the soil, then slowly saturated with the baseline Ogallala water. During the flow tests, a continuous injection of concentrations of 5 mg/L of both bromide, as a conservative tracer, and chromium in the Ogallala water solution are passed through the columns. Samples are collected at the effluent end of the columns. Ion chromatography is used for the bromide analysis, whereas the chromium is analyzed as previously described. The apparent transport parameters will be fitted through use of the USGS Method of Characteristics solute transport model (Konikow and Bredehoeft, 1978) as modified by Goode and Konikow (1989) for sorptive transport.

Table 7. Preliminary analyses of core samples from BEG-PTX No. 2.

Sample depth (ft)	Percent clay-silt	Percent sand	Percent gravel	Cation exchange capacity (meq/g)	TCLP chromium (mg/kg)	Freundlich S (ppm) = coefficient	Isotherm a C(ppm) <sup>b</sup> exponent
18	57	41	2	26.5	0.16	0.82	0.92
55	36	60	4	21.4	0.30	0.75	0.73
95	25	69	6	9.6	0.42	0.84	0.69
151	37	62	1	8.0	0.54	0.86	0.94
313	17	74	9	39.3	0.18	1.0	1.1
346	36	63	1	4.6	0.25	0.85	1.3

## Surface Water Hydrology Study

*by David Thompson, Ph.D., P.E., and Alan Reedüer  
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The objective of the surface-water analysis at the Pantex plant was estimation of infiltration through bed sediments of five study playa lakes. The period of record for this analysis was 1952 through 1991. Estimates of infiltration required development of a detailed hydrologic budget for each study playa.

A hydrologic budget is an expression of mass balance in a hydrologic context. That is, the algebraic sum of inflow and outflow volumetric discharge rates must be equal to the time rate of change of volumetric storage in a control volume, in this case a playa lake. This concept leads to an accounting of the distribution of water within a playa lake. Inputs to the lake are watershed runoff, direct precipitation, and anthropogenic discharges. Outputs from the lake are infiltration through bottom sediments, evaporation, and anthropogenic withdrawals.

To achieve this part of the project objective, surface-water hydrologic analysis at the Pantex Plant comprised several activities: installation of instrumentation and data collection, selection and calibration of a surface-water hydrologic model, operation of the calibrated model to generate watershed runoff to instrumented playa lake basins, operation of the model to generate watershed runoff to playa lake basins with no instrumentation, and calculation of hydrologic budgets for the five study playa lakes.

Instrumentation and data collection were for the sole purpose of providing data to calibrate and validate a hydrologic model. The hydrologic model was used to compute watershed runoff to playa lakes. Six rain gauges were installed to measure the spatial distribution of precipitation falling on the site. One of these was a tipping bucket rain gauge used to measure temporal distributions of precipitation; the remaining five rain gauges were of the total catch variety. Eight v-notch weirs were installed at selected subcatchments at Playas 1 and 2.

Records of stages at these structures were made using either pressure transducers or sonic sensors. Discharges were computed using stage-discharge curves developed using scale models of the weirs operated in the Texas Tech University, Civil Engineering Department fluid mechanics laboratory. Two additional pressure transducers were used to record stage in the two monitored playas. Additional data were taken from the meteorologic tower operated by Pantex personnel and from the Agricultural Research Service facility located at Bushland, Texas.

Instruments were installed in 1991, and data were collected for this part of the project through 1993. Although instruments were operational for a period of about three years, few significant runoff events were recorded. Simply put, this resulted from the natural semiarid

nature of site climate and was compounded by the fact that fewer than normal storm events occurred. However, a sufficient number of runoff events were recorded to allow calibration of a hydrologic model. More events would increase the confidence in modeling results, but they simply were not available.

Computation of long-term hydrologic budgets requires an accounting of soil moisture for accurate estimates of evapotranspiration. Therefore, a continuous-simulation hydrologic model is required. A continuous-simulation model uses a hydrologic budget to account for all portions of the hydrologic cycle. This is in contrast to a storm-event model, which focuses strictly on those hydrologic components important during a storm event. Storm-event models are generally used when considering flooding events; continuous-simulation models are used when all components of the hydrologic cycle are considered important.

Because of the relative simplicity of the hydrologic system at the Pantex Plant, a relatively simple continuous-simulation model was required. The U.S. Army Corps of Engineers Storage-Overflow-Runoff-Model (STORM), although not specifically developed for semiarid hydrologic systems, is a simple model that uses hydrologic technology appropriate for surface-water hydrologic modeling at the Pantex Plant. The soil-moisture accounting system in STORM is based on the Soil Conservation Service curve number method, which is widely accepted in practice.

STORM was calibrated by adjusting its parameters until model output was in general agreement with site measurements. Because runoff volume is most important in estimating playa lake infiltration, no attempt was made to model storm-runoff hydrographs. During STORM calibration, it was discovered that a single curve number could not be used to model all events. Therefore, measured were divided into two data sets, those with relatively large curve numbers and those with relatively low curve numbers, and calibration was completed. For the two study playas, the range of low curve number was from 66 to 79. This suggested that a reasonable lower bound for curve numbers at the site is around 65. The range of high curve numbers was from 79 to 89. This suggested that a reasonable upper bound for curve numbers is about 89. A reasonable middle value and one suggested by examination of site land use is about 78 or 79. This is considered the most likely value of the curve number.

STORM was then operated for all five study playas using meteorologic data taken from National Weather Service archives for Amarillo, Texas. Treatment plant discharges to Playas 1 and 5 were estimated from water usage records and discharge permits. The period of record for these simulations was from 1952 through 1991. The model was operated using three values for the curve number: 65, 79, and 89. These values were chosen as representative of the range of

values likely to be reasonable for this site. Therefore, a range of possible runoff volumes, hence infiltration volumes, was considered. These values served to provide watershed runoff to study playas.

A model, WaterBalance, was developed for modeling study playas. It was developed using the same conservation of mass statement (hydrologic budget) discussed previously in this report. WaterBalance uses watershed runoff, precipitation, and evaporation estimates, along with playa bathymetry, to distribute hydrologic inputs to infiltration and evaporation. In the process, it tracks playa stage (water-surface elevation). Infiltration is modeled using two values for infiltration capacity: a lower value (stage three) for that portion of the playa bed covered with water (hence with a lower potential infiltration) and a higher value (stage two) for that portion of the playa bed not covered with water. It is assumed that incoming runoff must cross the high-infiltration capacity bed before reaching the wetted pool.

A variety of estimates of infiltration capacity were available for modeling. A lower bound for infiltration capacity is the saturated hydraulic conductivity of the soil. Estimates of soil saturated hydraulic conductivity are available from Soil Conservation Service soil maps. In addition, several ring infiltrometer measurements were conducted on soils in or near the study playas. Ring infiltrometers measure infiltration capacity of soils over very small areas. The scaling of these point measurements to watershed scale is difficult at best. However, ring infiltrometers provide input as to the size of infiltration capacity over larger areas. In addition, records of playa stage for Playas 1 and 2 were used to provide estimates of infiltration capacity over wetted areas of study playas.

Because of uncertainty associated with infiltration capacity and runoff curve number, a matrix of possibilities was constructed. The matrix had runoff curve numbers on one axis and combinations of stage two and stage three infiltration capacity on the other axis. Playa infiltrating area was the third axis of the matrix. WaterBalance was operated for each cell in the matrix and total playa infiltration was tabulated. After examination of the results, many entries were eliminated as physically unrealistic. This left a range of possibilities of infiltration. Results of these analysis are summarized in table 8. Because modeling results are still under review, these values should be considered tentative and subject to revision.

Table 8. Total Infiltration for the period of record 1952–1991 (volumes in acre-inches).

Basin	Playa 1	Playa 2	Playa 3	Playa 4	Playa 5
Minimum	116,000	113,000	52,000	163,000	333,000
Maximum	301,000	273,000	107,000	302,000	835,000



Although the range of values appears quite large, it is likely that the actual infiltration through playa bed sediments is within this range. Furthermore, the range of values is reasonable given the data available for operating the models. This infiltration has the potential to transport solutes through unsaturated materials to the perched aquifer beneath the Pantex site.

## Nutrients in a Wetland Receiving Wastewater

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### ABSTRACT

Wetlands may be used to remove or store nutrients from runoff and waste water. The objective of this project was to evaluate the fate of waste water received in a playa lake wetland at the Department of Energy Pantex facility near Amarillo, Texas. Playas are small, ephemeral lakes that serve as catchments for surface runoff in this semiarid region. Soil and plant parameters were evaluated seven times during a 2-yr period in areas dominated by cattail (*Typha domingensis*) or pink smartweed (*Persicaria pensylvanicum*). The nutrients measured were nitrogen, phosphorus, copper, iron, manganese, and zinc. Copper, Fe, and Mn soil nutrient concentrations were significantly greater in soils beneath the cattail than the smartweed. On the basis of the nutrient accumulations, it appears that this wetland functions quite well as a sink for added nutrients from the waste-water treatment facility and runoff water.

### INTRODUCTION

Wetlands have been recognized as an accepted means of absorbing nutrients, as well as chemical contaminants, from runoff and waste waters (Tilton and Kadlec 1979; Dierburg and Brezonik, 1983). However, wetland application of waste water may not always be a responsible practice. The capacity of a wetland to remove or store excessive nutrients and other pollutants is highly dependent on its individual characteristics such as plant nutrient composition, vegetation species, and hydrology.

There are thousands of relatively shallow, circular wetlands known as playa lakes on the Southern High Plains. These small ephemeral water bodies average 6.3 ha in surface area (Bolen et al., 1989), with depths ranging from several centimeters to 20 m (Traweek, 1981). Playas annually collect 250,000 to 370,000 ha-m (2 to 3 million acre-ft) of water (Ward and Huddleson, 1972), which is estimated at 89 percent of all surface runoff within the region (Clyma and Lotspeich, 1966). In the Texas Panhandle, approximately 30 playas are utilized for

municipal waste-water treatment, with an additional 40 being used for treatment of feedlot runoff (T. Nisbet, Texas Natural Resource Conservation Commission, personal communication, 1993).

Awareness of environmental concerns in playa lakes goes back to the 1960's. At that time, the main environmental concern was the use of playas for runoff catchment from cattle feedlots. Current concerns are the use of playas in municipal waste-water treatment schemes. Pantex, producing ammunition for World War II and currently disassembling the U.S. nuclear arsenal, presents a unique situation. Conventional high explosives and those used to implode nuclear weapons are high in nitrogen. Those high nitrogen wastes are transmitted to the playa via the waste treatment facility.

The objective of this study was to determine the effects on vegetation and soil components of a playa receiving secondarily treated waste water from the U.S. Department of Energy Pantex facility. Soil and plant samples were analyzed for total N, total P, Cu, Fe, Mn, and Zn.

## EXPERIMENTAL

The playa lake wetland is located at the U.S. Department of Energy Pantex facility in Carson County, Texas, approximately 27 km northeast of downtown Amarillo. This playa basin soil is classified as a Randall clay (fine, montmorillonitic, thermic Typic Haplustert) and occupies an estimated 37 ha in a 1,069 ha rangeland/cropland watershed of relatively flat topography. Hydrologic characteristics of the playa, particularly runoff, vary annually with weather variation and waste-water additions. Average annual Carson County precipitation is 560 mm and varies from 250 to 1,070 mm, with most of the runoff in the spring or summer. The vegetational composition of the playa wetland can be divided into two communities. The center of the basin is dominated by cattail (*Typha domingensis*), with the annulus perimeter occupied by pink smartweed (*Persicaria pensylvanicum*).

Plant and soil samples were collected on 20 May, 1 July, 18 August, 20 November 1992, and 18 May, 1 July, 19 August 1993. These dates corresponded with early growth of the hydrophytic plants, a midgrowth stage, a late growth stage, and a nongrowing or senescent stage that represented a transition between the two growing seasons. A minimum of 10 replicated samples from each of the two predominant vegetation types was collected. Living and dead aboveground tissues were harvested from 0.5- by 0.5-m-square quadrats. Total concentrations of N and P were determined on Kjeldahl digests of the dried ground material. Total N concentrations were quantified on a Technicon TRAACS 800 Autoanalyzer (U.S. Environmental Protection Agency [EPA], 1983). Total P was determined using an EDTA extraction and a

Brinkmann PC 800 Colorimeter (with 620 filter) according to Hons et al. (1990). Copper, Fe, Mn, and Zn were determined with a Perkin-Elmer Plasma 40 Emission Spectrometer (Lindsay and Norvell, 1978).

Soil samples were collected with a soil probe (I.D. = 2.2. cm) to a depth of 60 cm. Cores 0 to 30 cm and 30 to 60 cm were placed in 475 mL acid-washed glass jars, purged with nitrogen gas, capped with plastic screw-on covers, and refrigerated pending chemical analyses. All soil samples were analyzed for TN, extractable P, Cu, Fe, Mn, and Zn. Samples were Kjeldahl digested for TN (U.S. EPA, 1983). Concentrations of extractable P were measured similar to Hons et al. (1990). Copper, Fe, Mn, and Zn were determined using the DTPA extraction method of Lindsay and Norvell (1978)

## RESULTS AND DISCUSSION

Pantex Playa 1 is a wetland that normally receives surface runoff from the surrounding cropland and rangeland. The nutrients entrained in this runoff are supplemented with a maximum 650,000 gallons per day (gpd) of waste water. The vegetation in a playa normally consists of hydrophytic plants, but the presence of cattails is uncommon. Only those playas that receive supplemental water, as in the case of those that receive municipal waste water or feedlot runoff, will produce cattails. Throughout this study, the cattail area located in the playa basin had more ponded water than did the smartweed area. Water depth varied daily, and on several occasions water depth changes were observed during sample collection as water was discharged from the waste-water treatment plant aeration pond.

The environmental concerns are the fate of additions of nitrogen and other elements from the waste-water treatment facility and the runoff from adjoining rangeland and cropland. Based on information in table 9, there are only minimal waste-water additions of Cu, Fe, Mn, and Zn added annually. The added nitrogen (1,890 kg) is dispersed throughout the 37 ha of the playa. Sweeten (1991) reported yearly runoff losses of 0 to 1.12 kg of nitrogen per hectare from rangeland, or 1.1 to 11.2 kg/ha from cropland. Because the land surrounding Pantex Playa 1 is a mixture of cropland and rangeland and is approximately 1,000 ha in area, the natural runoff would annually contribute approximately 5,000 kg nitrogen. If the Pantex playa was surrounded entirely by cropland, as are many High Plains playas, more than twice the nitrogen could be added to the playa. Sweeten (1991) reported annual phosphorous runoff losses of 0 to 4.5 kg/ha for cropland and 0 to 0.3 kg P/ha for rangeland. Natural runoff would annually contribute 2,000 kg P/yr to Pantex Playa 1 (table 9). These natural additions of N and P exceed that contributed from waste water.

Table 9. Waste-water concentration and annual elemental additions.

Element	Waste water Concentration <sup>1</sup>	Quantity added/year	
	mg/l	Waste water <sup>2</sup>	Runoff <sup>3</sup>
		----- k g / y r -----	
N	2.1	1890	5000
P	N/A	N/A	2000
Cu	0.01	9	- -
Fe	0.32	288	- -
Mn	0.013	11.7	- -
Zn	0.031	27.9	- -

<sup>1</sup>U.S. Environmental Protection Agency, 1993

<sup>2</sup>650,000 gal/d × 365 d/yr × 3.785 l/gal × concentration/l

<sup>3</sup>1,000 ha × 5 kg/ha for N or 2 kg/ha for P (after Sweeten [1991])

To evaluate the fate of these added nutrients, soil samples were collected. Stewart et al. (1994) reported playa N and P data from a beef feedlot and a dairy lot. Total soil N in the top 30 cm was 1.1 kg N/m<sup>2</sup> and 1.9 kg N/m<sup>2</sup> for beef and dairy lots, respectively. They also reported phosphorus contents of the top 30 cm to be 0.4 kg P/m<sup>2</sup> and 1.1 kg P/m<sup>2</sup> for beef and dairy lots, respectively (Stewart et al., 1994). Measured soil nitrogen and phosphorus data for the wetland (table 10) show similar values. Other soil nutrients (Cu, Fe, Mn, and Zn) are also presented in table 10. Soil contents of Fe and Mn in 1992 and 1993, and Cu in 1992, were significantly influenced by vegetation type. These soil nutrient levels may have been impacted by the larger amounts of detritus being cycled into the soil throughout the more productive areas of the playa.

Differences between soil nutrient and metal concentrations with depth were also quantified. Concentrations in the 30 to 60 cm depth tended to be lower than in the 0 to 30 cm depth (table 11). Copper, Mn, and Zn were always significantly less in the second depth both of the study years. Nitrogen and P were significantly lower in different years (N in 1992, P in 1993). Iron was not significantly different in either year. Because Fe is a natural constituent of clay minerals, it has a relatively high soil concentration. The limited addition waste water Fe added would not be expected to significantly change its status. The Cu, Mn, and Zn results were expected because the rate of exchange at the soil surface typically plays an important role in the chemistry of submerged soils. Surface soils would be anticipated to have the higher levels in

Table 10. Mean soil nutrient concentrations in the upper 30 cm and significant differences for two vegetation types during different years of study.

Parameter	Year	Vegetation type	
		Smartweed	Cattail
		g/m <sup>2</sup>	
TN	1992	1520	1600
	1993	507	468
Extractable P	1992	293	250
	1993	468	429
Cu	1992	0.36	0.42*
	1993	0.22	0.23
Fe	1992	4.7	13.3***
	1993	14.0	19.5***
Mn	1992	0.82	2.1*
	1993	1.4	1.9*
Zn	1992	0.40	0.41
	1993	0.25	0.21

\* Means differ significantly at alpha = 0.05 level using ANOVA.

\*\*\* Means differ significantly at alpha = 0.001 level using ANOVA.

the upper soil layer because of a higher proportion of organic material compared to the deeper soils, which do not receive the same magnitude of influence from plant litter and microorganisms.

Significant chemical changes occurred within the soil system throughout the growing season. Although seasonal patterns were difficult to distinguish, mainly owing to differences between years, these changes indicate that a relatively high rate of chemical exchange occurred in the playa soils. The (1) status of organic material; (2) the reduction of intensity and fluctuation due to site-specific hydrology, turbulence, and soil temperature; and (3) assimilation capacity of the playa related to past disposal practices are likely to have been the primary influences related to this observation.

The mean aboveground nutrient concentrations for cattail and smartweed are presented in table 12. Significant differences were observed between the smartweed and cattail aboveground tissue concentrations for P, Cu, Fe, and Mn. Total P and Fe concentrations in the smartweed biomass were significantly greater (1-percent level) than cattail for both 1992 and 1993. Copper was significantly greater at the 5-percent level in both 1992 and 1993, whereas Mn was only greater (5-percent level) in 1992. These results indicate that tissue concentration of nutrients in vegetation is an important consideration in wetland waste-water treatment.

The quantity of the aboveground elements accumulated by the cattail (table 13) was significantly greater than the smartweed owing to yield differences. Cattail yielded 979 g/m<sup>2</sup> in 1992 and 800 g/m<sup>2</sup> in 1993. Smartweed yields were 314 and 285 g/m<sup>2</sup> for 1992 and 1993, respectively. Because cattail production is relatively high, approximately three times that of smartweed, total assimilation of the measured parameters was considerably larger for cattail compared to smartweed. These yield differences show the importance of vegetation species.

Although a detailed nutrient mass balance is beyond the scope of this paper, insight into the internal compartments involved in the playa's nutrient budget will be briefly discussed. In general, processes that affect the chemical dynamics of a wetland are most closely linked to the import and export of elements through water. However, since playas are closed drainage basins, the impact of atmospheric as well as internal physical and chemical processes is appreciable. Positive relationships between surface water and vegetation and/or soil components of the playa were not observed on a spatial or short-term temporal scale. In part, this observation could be due to the fact that cattail does not exchange elements directly with water during senescence; they may not have been added to the litter or incorporated into the soil for several months or longer. Therefore, exchanges from the vegetation to the water or soil may not have been readily distinguished. On the basis of these findings, the Pantex wetland seems to function very well as a sink for the added nutrients from the waste-water treatment facility and natural surface runoff.

Table 11. Whole playa soil nutrient concentrations and significant differences for two soil depths during different years of study.

Parameter	Year	Soil depth (cm)	
		0–30	30–60
		g/m <sup>2</sup>	
TN	1992	1560	898*
	1993	1330	702
Extractable P	1992	355	316
	1993	382	343**
Cu	1992	0.37	0.24*
	1993	0.36	0.23
Fe	1992	17	7.4
	1993	19	8.2
Mn	1992	12	5.1*
	1993	14	5.5**
Zn	1992	0.43	0.16***
	1993	0.43	0.20***

\* Means between depths differ significantly at alpha = 0.05 level.

\*\* Means between depths differ significantly at alpha = 0.01 level.

\*\*\* Means between depths differ significantly at alpha = 0.001 level.



Table 12. Comparison of mean nutrient concentrations in aboveground biomass from the Pantex playa between two vegetation types.

		Vegetation type	
Parameter	Year	Smartweed	Cattail
mg/kg			
TN	1992–1993	9,700	9,200
TP	1992–1993	2,500	2,000**
Cu	1992–1993	31	25*
Fe	1992–1993	870	380*
Mn	1992	350	240*
	1993	210	200
Zn	1992	130	120
	1993	70	50

\* Means between vegetation types differ significantly at  $\alpha = 0.05$  level.

\*\* Means between vegetation types differ significantly at  $\alpha = 0.01$  level.

Table 13. Comparisons of average total nutrients in aboveground biomass between two vegetation types.

Parameter	Year	Vegetation type	
		Smartweed	Cattail
		mg/m <sup>2</sup>	
TN	1992	3,000	9,000 ***
	1993	2,800	7,400 ***
TP	1992	790	2,000 ***
	1993	710	1,600 ***
Cu	1992	10	24***
	1993	8.8	20***
Fe	1992	270	370***
	1993	250	300***
Mn	1992	110	230***
	1993	60	160***
Zn	1992	40	120***
	1993	20	40***

\*\*\* Means between vegetation types differ significantly at  $\alpha = 0.001$  level.

## Waste-Water Discharges to Drainage Ditches

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The primary objectives of this phase of the study were to (a) develop a waste generation history for the operations conducted at the Pantex facility since it was reactivated in 1951 through the late 1980's, (b) correlate the waste generation history with the quantities and qualities of waste water generated over time, and (c) estimate the potential infiltration rates through the soils of the earthen ditches that carried waste water from the various facilities on the Pantex site from 1951 to the late 1980's. Since the late 1980's, waste streams (liquid and solids) generated in the actual production activities at Pantex have been reworked to greatly reduce current discharges. Waste waters that were previously released to the drainage ditch system either have been treated to meet discharge standards or have been collected and shipped to an approved offsite disposal site.

Past and ongoing investigations at the Pantex site have identified the presence of organic and inorganic contaminants in the soils and subsurface ground water at several locations. The sources of these contaminants are not always obvious. Proper description of these sources requires identification of the individual facilities that were potential generators, as well as the duration and intensity of the generation period. The timing of the waste discharges affects the mobility and possible chemical transformations of the contaminants in the water and soil. This document is the first attempt to compile descriptions of as many of the facilities' waste generation histories as is possible with current information. In addition, it became apparent during the study that the infiltration capacities of the drainage ditches determined the fate of much of the waste discharges.

An attempt has been made to reconstruct the types, amounts, and duration of waste-generating activities that took place at the various facilities involved with known hazardous waste materials. The typical releases of pollutants at the Pantex facility have consisted of the following broad material classes associated with the production facilities:

- air emissions (gases and particulates) from vaporized solvents, fuel combustion processes required for plant production activities, and disposal and testing of high explosives (HE);
- liquid and solid disposal to the soils adjacent to the generating facilities;
- waste-water discharges to the facility sewer system or to the drainage ditch network that contained solvents and dissolved or suspended HE from different source buildings where casting and processing of HE occurred prior to assembly into weapon systems; and
- solid wastes that have been buried at various locations onsite, some of which may allow infiltration and leaching.

In addition to the actual production of the weapons systems, the infrastructure that supported these activities had to be examined for its impacts on pollutant production and emissions. These infrastructure components included (a) storage facilities for raw materials and fuel; (b) steam and compressed air production; (c) laboratory work; (d) facility support operations, cleanup, and maintenance; and (e) water supply for cooling water, production facilities, cafeteria, and sanitary use.

The first two objectives were realized using an iterative document review and rewrite process. After an initial review of existing documents, interviews were conducted with Pantex personnel, selected because of their plant experience and tenure, to obtain information about previous plant activities. A preliminary draft was prepared from interview notes and resubmitted for comments from both those interviewed as well as others with knowledge about the historical plant operations. The collected comments were then incorporated into a second draft and resubmitted for additional comments. Each time the corrected draft has been resubmitted, it has evoked comments and corrections that have been essential in developing a history of plant facilities. Estimates of infiltration rates, the third objective, were obtained by conducting replicated double-ring infiltrometer tests at various points along the channels of the unlined waste-water drainage ditches and in the ephemeral playa lake basins that received periodic inputs of storm-water drainage and effluent waste waters from Zones 11 and 12.

The Pantex facility was originally one of the government-owned, contractor-operated ordnance plants that was built after World War II started. Construction started in May 1942, and the plant started production on September 17, 1942 (Murphy, 1993). Production was maintained during the remaining years of World War II. In Zones 9, 10, and 11, TNT (2-methyl-1, 3, 5-trinitro-benzene) and RDX (research and development explosive) were mixed in various combinations to prepare castable HE for use in the various weapons assembly operations conducted at the plant. Materials produced at the plant consisted of 500-lb bombs, fragmentation bombs, 105 howitzer shells, incendiary flares, TNT pellets, ammonium nitrate, and other explosive devices. Zone 12 was completed at the end of World War II; no use was made of this facility during World War II. The entire facility was essentially shut down on VJ day (September 2, 1945).

In 1951, the United States Army reclaimed the northern half of the plant, and in 1952, production of atomic weapons began. Production of nuclear weapons has continued to the present. Today, the focus of operations at the plant is in the disassembly of nuclear weapons. The HE used during the 1950's were primarily mixtures of TNT and nitramine-based RDX and HMX (high-melting explosive). The main HE that were melt-cast were TNT and a 60/40 mixture of RDX and TNT called Composition B, Comp B3, or Comp B.

Operations conducted at the Pantex facility since reactivation through the late 1980's consisted primarily of taking components produced at other DOE sites and assembling these into the desired weapons system. The interview process helped identify the sites (building or facility areas) where the various production and support activities were conducted, the production wastes generated, and the pathways used in production waste disposal.

Even though no information was obtained on the number of weapons produced per day, the length of the production run for each weapon system, or the amounts of wastes identified per weapons system produced, assumptions can be made to obtain an estimate of the primary waste streams involved. For example, after reactivation in 1951, rejected explosive components were taken to the burn ground where they were burned or detonated rather than buried in a landfill or thrown out on the ground surface as practiced during the World War II period. Also, many of the larger particles of explosive generated during machining of the explosive components prior to weapons assembly were removed from the waste-water streams and taken to the burn ground for disposal. These practices thus reduced the potential for long-term impacts on the ground water from leachate produced from buried or improperly disposed of HE. Solvents used in production during the period of interest had several fate pathways: (a) volatilized at the point of use, (b) collected and taken to the burn ground where they either were burned or poured into disposal pits to infiltrate or volatilize, (c) released with waste water to volatilize or infiltrate into the subsurface, or (d) reused. The possible fates of suspended and dissolved solids in production waste waters became the primary concern of the study. Estimates of the average and maximum waste-water flows from the various buildings at the Pantex facility to the ditch system or to leach pits are shown on table 14.

The primary conveyance channels were the two ditches that carried both process flows and storm-water runoff northward toward Playa 1. The West Ditch carried process flows from Zone 11 from synthesis of small experimental batches of HE as well as from explosive machining operations. Additionally, waste water discharged to the sewer collection system from other buildings supporting the production facilities at Pantex that are on the sewer system also eventually entered the West Ditch as treated effluent. The waste waters released to the East Ditch were primarily from weapons production processes in Zone 12. The amounts of waterborne wastes would have been much more if the HE had been synthesized onsite rather than resulting from material manufactured offsite and formed into weapon systems in Zone 12. Using estimated process flow volumes, the East Ditch could have carried a flow of about 224,000 to 314,000 gpd, whereas the West Ditch could have carried flows of from 66,000 to 95,000 gpd.

Synthesis of new explosive materials was and is conducted at Pantex in Bldg. 11-36. Generally, this was been done in small batches rather than in production amounts as shown by the average daily flow of 1,000 gpd to the West Ditch in Zone 12. The composition of

Table 14. Estimates of past wastewater flow from various buildings.

Building number	Playa watershed	Primary flow destination	Maximum daily flow [gpd]	Average daily flow [gpd]
11-17	Playa 1	leach pit	2,400	960
11-20	Playa 1	Ditch - WZ 12	315	150
11-36	Playa 1	Ditch - WZ 12	25,000	1,000
11-44a	Playa 1	Ditch - WZ 12	70,000	65,000
11-50	Playa 2	Ditch	2,400	1,440
12-4	Playa 1	Sewer	5,600	2,800
12-5	Playa 1	Sewer		
12-5B	Playa 1	Storm Runoff		
12-9	Playa 1	Sewer	2,400	960
12-10	Playa 1	Storm Runoff		
12-17	Playa 1	Ditch -EZ 12	134,000	111,000
12-18	Playa 1	Sewer		
12-19	Playa 1	Ditch - EZ 12	100,000	75,000
12-21	Playa 1	Ditch - EZ 12		
12-24	Playa 1	Bldg. 12-43	77,000	35,500
12-35	Playa 1	Storm Runoff		
12-41	Playa 4	Ditch	4,500	neg.
12-43b	Playa 1	Ditch	80,000	38,000
12-43A	Playa 1	Storm Runoff		
12-44E	Playa 1	Storm Runoff		
12-59	Playa 1	leach pit	2,400	960
12-67	Playa 1	Storm Runoff		
12-68	Playa 1	Sewer		
12-73	Playa 1	Bldg. 12-43	5,000	1,000
12-81	Playa 1	Sewer		
16-1	Playa 2	Sewer		

a Filters water from Bldgs. 11-20 and 11-36

b Filters water from Bldgs. 12-24 and 12-78

waste waters generated here over the period of interest would have been similar to those at other locations where HE were manufactured.

The formation of explosive elements used in the various weapons systems occurred in Bldgs. 12-17 and 12-19 that both drain into the East Ditch. The components formed there were taken to machining facilities in both Zones 11 and 12 for final shaping prior to their assembly into the weapon system. By far, the largest amounts of water generated at both Bldgs. 12-17 and 12-19 were from water-curtain dust filtration units used to control dust and to provide point-source fume removal for solvent vapors. Three such units have been used in Bldg. 12-17 since the 1950's, and two others have been used in Bldg. 12-19E since the 1960's. These systems use "point-source" ventilation hoods located close to the contaminant source point to draw dust- and solvent-laden air through a baffled reservoir, causing highly turbulent mixing of the air and water. The water droplets "wash" the dust and some of the water-soluble solvents from the inlet air stream. The washed air is exhausted to the atmosphere. The constant flow of

air allows the rapid evaporation of some of the solvents that might have been captured in the wash water. Originally, the system had level controls to maintain the water level for the optimum contact with the incoming polluted air stream. Make-up water was added continuously, and the overflow waste water was dumped into the ditch system leading to Playa 1 until 1986 or 1987. The waste water flow rate from each filtration unit until this time was approximately 25 gal per minute; the unit ran continuously 24 h per day (approximately 36,000 gpd) for about 360 days per year. The remaining wastewater flows from these two buildings consist of flows of coolant water from machining operations (primarily Bldg. 12-17), wash water from building cleanup, and condensate from the building's air conditioning units. The primary contaminant class in the waste waters discharged from these two buildings during the period of interest was solvents.

The flows shown on table 14 for the two filter buildings (Bldgs. 11-44 and 12-43) were due to process waste waters from machining operations in Zones 11 and 12 (primarily Bldg. 12-24). Water was used as the coolant during machining operations, directed under pressure through a 1.27-cm diameter nozzle to the explosive assembly mounted on the machine tool. Initially, the resultant waste water from the machining operations and its load of HE particles flowed through pipes or troughs to the building drains located along the walls of the bay, through the building walls, into a concrete flume that flowed parallel to the outside building wall to empty into the ditch system. Later, the spent cooling water and its entrained load of HE particles were flushed into drainage ways that conveyed the flow to the two filter buildings for further treatment. The primary contaminants from these two facilities were suspended and dissolved explosives.

The chromium that has been detected in ground waters underlying Zone 12 in recent field investigations probably came from the three-story-high cooling tower that was located to the east of Bldgs. 12-17 and 12-19 and adjacent to the northeast confluence of the building drains from both buildings. The cooling tower was used in support of operations in these buildings and operated from the time of reactivation until 1964; it was demolished in the late 1960's. Effluents from the cooling tower operations could have consisted of overflow from the cooling water reservoir, leakage through the containment reservoir, air-blown droplets of the cooling water during tower operations, and "blow-down" water used to lower the dissolved solids content of the coolant. The latter wastewater, that had been conditioned with compounds (possibly containing chromates, sulfuric acid, and sodium hydroxide salts), was discharged directly to the ground surface in the vicinity of the tower. The disposition of the portion of the blow-down water that did not evaporate could have been to either infiltrate into the soil or flow into part of the ditch system just a few meters west of the tower facility and on into the East Ditch system. The amount of leakage and of water discharge per blown-down event, the concentration of chemical species in the water, and the number of times that blow-down

events occurred per day at the tower sites are not known.

There is an interest in estimating the amounts of waste water that could have infiltrated through the soil material in the unlined ditch system and in the playa lake beds over the period from reactivation of the Pantex site to the late 1980's since waste waters from the various operations conducted at Pantex were discharged daily. Infiltrometer tests were conducted to determine the rates of Stage I infiltration (rate of infiltration during the first minute after water is applied), Stage II infiltration (infiltration rates during the transition period from Stage I to Stage III), and Stage III infiltration (the steady-state infiltration rate that results when the soil profile is near saturation). The tests were conducted using a metal inner ring (128-mm diameter) and an outer ring made from plastic pipe (205-mm diameter) in groups of three at each test site. Infiltration tests were conducted in September 1991 at three test sites in Playas 2, 3, and 4 (three infiltrometers were installed 5 m apart from each other at each site) and at three test sites in the East Ditch drainage system. In March 1994, a more extensive infiltration study was conducted at 21 sites in the Pantex drainage ditch systems serving Zones 11 and 12.

In the September 1991 playa lake studies, an infiltrometer was placed in a flooded section of the East Ditch about 30 m upstream of Playa 1. No change in water level occurred during a week-long test. The other three playas that all contained no ephemeral water during the test period exhibited different infiltration characteristics. Playa 3, with its sedge grass vegetation typical of wet soils, exhibited the lowest infiltration rates for Stage I (11.5 m/d) and for Stage II (range of 0.028 to 0.59 m/d for the nine sites). Playa 2, located to the west of Bldg. 16-1, exhibited a variety of different vegetation types among the three test areas where the infiltrometers were placed. The data that was obtained for a site in the southwest part of the playa basin in a stand of sunflowers showed high levels of infiltration in both Stage I (99.5 m/d) and Stage II (range of 0.13 to 34.9 m/d for the nine sites). Playa 4 exhibited an infiltration pattern midway between the other two playa lakes for Stage I (35.6 m/d) and Stage II (0.041 to 10.6 m/d).

The two ditch locations that were investigated during 1991 consisted of a triplicate setup in a tributary ditch just outside the fence and to the northeast of Bldg. 12-110 and a location on the East Ditch about 200 m to the south of Washington Drive. The average Stage I infiltration rates were 9.18 m/d for the three tributary ditch locations and 9.6 m/d at the East Ditch location. The Stage II rates were 1.25 m/d for the tributary ditch, whereas the three locations in the East Ditch exhibited an infiltration rate that ranged from 0.45 m/d to 2.16 m/d. These are high infiltration rates but not unreasonable for the time period used in the tests.

Infiltration data was obtained for 21 sites in March 1994. At several sites in the East Ditch area, Stage I infiltration was very rapid, and little reduction in this rapid rate was observed in a



2-h period. The amount of water that infiltrated in a 10- to 20-minute period after the two days of water application was used to estimate the Stage III rates. The values obtained for those sites would thus be conservatively low and not reflect the true amount of water that could have been infiltrated during a comparable time period if inundation of the infiltrometer had been maintained throughout the test period in those units.

Infiltration studies made in the East Ditch over a 44- to 48-h period showed infiltration rates ranging from 0.018 to 0.488 m/d for the four locations along the bottom of the main channel. The average infiltration rate for the test sites in the East Ditch was 0.228 m/d. If one ignores the contribution of the location some 200 m south of the Washington Drive, three infiltrometer locations in the bottom of the East Ditch in the secure area conservatively exhibited total infiltration rates ranging from 0.25 to 0.31 m/d. This ditch, approximately 3.6 to 4.5 m below the original land surface, was constructed in the late 1940's and has been in use since the Pantex facility was reactivated. From the short-term study that was conducted, it is highly probable that the ditch area itself has been a major sink for the waste waters discharged by the buildings located to the west of the ditch.

It is interesting to note that at a site in the bottom of the East Ditch just south of the culvert on Washington Drive, the average total infiltration rate was the eighth lowest (0.024 m/d) of the 21 values obtained. The values at this site more closely resembled the values obtained in the shallow ditches constructed in the Pullman soils in Zone 11 and in shallow waste-water ditches flowing from Bldgs. 12-17, 12-19, etc. in Zone 12. The permeability of these soils in the 0.3- to 1.17-m depth is less than 0.0015 m/h according to Soil Conservation data used for this category of soil. Only 4 of the 14 shallow ditch sites in these areas exhibited infiltration rates higher than the 0.0015 m/h value. Ten of the sites were lower than the reference soil value.

If the width of the wetted sector of the bottom of the East Ditch bottom was 1.5 m during the period of interest, the amount of water infiltrated per day from the confluence of the drainage ditch from Bldg. 12-43 to the culvert under Washington Drive could have been as high as 99,000 gpd. Perhaps half of the daily flows of waste waters, suspended solids, and various soluble waste components that were entrained in flows entering the East Ditch from sources along the eastern edge of Zone 12 would end up in Playa 1; the suspended solids would have been deposited in both the ditch and the playa. The remainder of the flow would have infiltrated the channel soils and percolated downward through the vadose zone.

In the ditches that were constructed in the upper Pullman soil profile in both Zones 11 and 12, 13.3 m<sup>3</sup> of water per m<sup>2</sup> of channel bottom would have percolated through the ditch bottom per year if flows were constant during the 40 yr of operation of the Pantex facility. In the channel of the East Ditch, however, the amounts that would have infiltrated into channel

soils would have been  $87.6 \text{ m}^3$  of water per year per  $\text{m}^2$ . This flow rate would have been sufficient to have made an impact on the ground water in the perched aquifer underlying the Pantex area.

During dry weather, the West Ditch could not have carried water to Playa 1. The average of three infiltration tests conducted in March 1994 in the bottom of this ditch (just to the west of the culvert under the boundary road separating Zone 11 from Zone 12 and about 545 m from Bldg. 11-44) exhibited an average long-term infiltration rate of 0.163 m/d. This value is large enough for all discharged water to be lost to infiltration within the ditch. It is improbable that the ditch leading from this area carried water from processing operations to Playa 1 during dry weather operations.

The following conclusions were drawn from the study of the production activities that took place during the period from reactivation of the Pantex facility in 1951 to the late 1980's when management of the plant wastes was improved:

1. The primary production activities at the Pantex facility (melt-pour and pressing) were the formulation of explosive components from explosive materials produced offsite and machining of these units prior to assembling them into the finished weapon system. These activities produced relatively little dissolved and suspended solids in waste waters that were generated compared with that which would have been generated if the primary mission of the plant had been to produce explosive materials onsite.

2. The majority of the waste waters from the production of facilities and their supporting operations were generated on the east side of the plant site, flowed into the East Ditch system, and either infiltrated into the ditch soils or flowed into Playa 1.

3. Waste water from explosive synthesis facilities in Zone 11 produced relatively small amounts of waste water that entered the ditch system, but most infiltrated into the channel soils rather than flowing to Playa 1.

4. Plating operations and blow-down water from a cooling tower located on the east side of Zone 12, in effect from the time of reactivation until 1964, probably produced the heavy metal releases that have been detected in recent field investigations.

5. Disposal of other wastes—fuels, paint pigments, etc.—was done similarly to practices used by other industries of the period.

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