Chapter 11

Contamination Migration, Characteristics, and Responses for the Edwards–Trinity Plateau Aquifer

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Introduction

The Edwards–Trinity Plateau (ETP) aquifer system consists of Cretaceous rocks that cover about 42,000 square miles in west-central Texas. The extent of the aquifer system and the study area are illustrated in Figure 11-1. The aquifer is comprised of saturated sediments of lower Cretaceous age Trinity Group (Trinity aquifer) which are overlain by saturated limestones and dolomites of Cretaceous age Fredericksburg and Washita Groups (Edwards aquifer). The water from the aquifer supplies all or part of the water needs for thirty-eight counties. Irrigation accounts for 70 percent of the total pumpage and 15 percent of the water is used to meet local municipal water demands (Ashworth, 1995; Barker and Ardis, 1992). The aquifer is potentially susceptible to contamination where the aquifer is unconfined and/or has development of joints, fractures, faults, or karstic solution features.

Vulnerability of the ETP Aquifer to Contamination

Using the DRASTIC model, the Texas Commission of Environmental Quality (TCEQ) has assigned a vulnerability rating of medium to the ETP aquifer (TCEQ 1999). The model includes characteristics that are important to all evaluations of groundwater contamination, including **D**epth to water, net **R**echarge, **A**quifer media, Soil media, Topography, Impact of vadose zone media, and hydraulic Conductivity of the aquifer (Focazio and others, 2002). This rating reflects the fact that karst aquifers are more vulnerable to contamination than many other types of aquifers (Vesper and others, 2003). Fractures promote higher groundwater velocities, less dilution along the flow paths, and less filtration of contaminants as compared to non-fractured strata; all of these features exacerbate groundwater contamination problems. The DRASTIC model rating does not reflect existing contamination and does not consider chemical characteristics; rather, it reflects the geology and hydrogeology of a region and represents that region's

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Figure 11-1: Edwards–Trinity Plateau aquifer, project study area, and cross-section trace A-A'-A".

susceptibility to groundwater contamination of all kinds. Clark (2000) developed a related analysis procedure for the Edwards (BFZ) aquifer recharge zone that incorporated hydrogeologic units, faults, caves and sinkholes, slopes, and soils within the context of a Geographic Information System. The method of Clark (2000) has not been applied to the ETP aquifer.

Under natural conditions, the ETP aquifer generally has high overall water quality with the exception of the northwest quadrant of the aquifer. Water quality in all of Upton and Reeves counties is generally poor. Areas within Ector, Midland, Glasscock, Reagan, Crockett, and Pecos counties also have poor water quality, including high natural total dissolved solids (TDS), sulfates, and chlorides (Texas Water Development Board [TWDB] March, 2003 water well database). Most groundwater contamination that has been identified in the ETP aquifer has been the result of human activity. There have been isolated cases of groundwater contamination that have posed problems to water resource managers that have been frustrated by the uncertainty regarding the movement of contaminants in the system.

In this document, "contamination" refers to any undesirable natural or anthropogenic chemical present in the water at concentrations exceeding a level of concern. A primary $\underline{\mathbf{m}}$ aximum $\underline{\mathbf{c}}$ ontaminant $\underline{\mathbf{l}}$ evel (MCL) is the highest level of a contaminant that is allowed

in drinking water, as per USEPA regulations. A secondary maximum contaminant level is a non-enforceable guideline for contaminants that cause cosmetic or aesthetic effects (such as taste and odor). For this document, these categories are combined and denoted by "MCL". The MCL provides a benchmark concentration with which to compare and ascertain if measurements are of environmental concern.

General Geology and Stratigraphy of the Study Area

A detailed summary of the depositional history, stratigraphy and structural evolution of the ETP Aquifer system can be found in Barker and Ardis (1996) and Walker (1979). The following description will present general characteristics of the ETP aquifer that are pertinent to this report.

The Edwards Plateau is a gently rolling upland that is locally incised by moderate-size streams. It is one of the largest karst (caves and other dissolution features) areas in the United States. The resistant rocks at the surface are thin to thick-bedded Cretaceous limestones with some dolomites and belong to the Edwards (Fredericksburg equivalent) Group. The rocks dip gently to the south and southeast (Elliott and Veni, 1994).

Underlying the Edwards Group carbonates are the Trinity Group formations (Figure 11-2) of the ETP aquifer. The formations include the Maxon Sand and the Glen Rose Limestone (minor water resources in study area) in the southern half of the study area and the basal Cretaceous sands (referred to in this report as the Antlers Sand) in the northern half of the study area (Barker and Ardis, 1996). The Antlers Sand is a major source of water for Ector, Midland, Glasscock, Sterling, Upton, Reagan, Irion, and Tom Green counties (Figure 11-1). The Antlers Sand is a fine to medium grained, cross-bedded, quartz sandstone interbedded with shales. Cementation of the sandstone varies from tightly cemented to friable (loosely cemented) sandstone (Walker, 1979).

The trace of cross-section A-A'-A" across the ETP aquifer is shown in Figure 11-1. This cross-section was constructed to provide a three dimensional perspective of the aquifer. Figure 11-2 illustrates the stratigraphic sequence and equivalent geologic formations that comprise the aquifer along the trace of this cross-section. The geographic distribution of Fredericksburg and lower Washita Groups rock units (Edwards and associated limestones) are illustrated in Figure 11-3 (Barker and Ardis, 1996).

Some of the Fredericksburg and lower Washita Groups (Edwards aquifer) rock units shown in Figure 11-3 have undergone dissolution (dissolving of carbonates or evaporites) to form karstic features like karren (surface features), sinkholes, solution channels (conduits), and caves. These karstic features dramatically influence the local groundwater flow directions, flow rates, and groundwater in storage. The permeability of the ETP aquifer system results mostly from tectonic factures and secondary porosity caused by selective leaching of evaporites and soluble carbonate constituents (Barker and Ardis, 1992).



Figure 11-2: Modified cross-section of K-K' and L-L' (from Barker and Ardis, 1996).



Figure 11-3: Location of TWDB wells in Antlers Sand and carbonate units within the Edwards Trinity Plateau aquifer (modified from Barker and Ardis, 1996).

The Fort Lancaster and Segovia formations are generally fossiliferous, thick-bedded to massive, and cherty limestones (Figure 11-3). The Fort Lancaster Formation (west) and Segovia Formation (east) occupy the highest elevations in the Edwards Plateau. They are generally unsaturated or contain only perched groundwater. However, the Fort Lancaster and Segovia formations, in addition to the Devils River and Salmon Peak formations, are important water-producing units in parts of Edwards, Kinney, and Val Verde counties (Barker and Ardis, 1996).

The Devils River Formation, an accumulation of carbonate sediment and reef debris, is in the southern half of the study area. The formation is "very permeable and porous," especially in middle and upper parts of the unit that contain collapse breccia or vuggy zones of leached rudists (Figure 11-3). South of the Devils River Formation, the Salmon Peak Formation is "moderately to very permeable" near the top, but the lower part is nearly impermeable, except where it is fractured (Barker and Ardis, 1996).

The Fort Terrett Formation provides most of the groundwater on the Edwards Plateau. The base of this formation may be the most permeable part of the Edwards Group limestones (Barker and Ardis, 1996). Most caves and intervals that have the greatest conduit development are along the contact between the Segovia and the underlying Fort Terrett formations. The formation becomes marly (clayey) to the west (Figures 10-2 and 10-3; Elliott and Veni, 1994). Overlying the Fort Terrett Formation is the Kirschberg Evaporite zone (Figure 11-2) which is highly permeable where it is brecciated. The high permeability is the result of post-depositional leaching and structural collapse (Barker and Ardis, 1996).

General Hydrogeology of Study Area

Figure 11-4 illustrates the regional groundwater gradient within the ETP aquifer. The groundwater is generally unconfined or semi-confined in the west and becomes progressively more confined toward the southeast (Barker and Ardis, 1996). The groundwater elevation contours were generated from the TWDB March 2003 water-well database using the most recent water levels (1995 to 2003, 661 wells with recent water levels). The groundwater flow directions and gradients are illustrated in Figure 11-4. The dominant regional groundwater flow directions are northwest to southeast for the western half of the study area. Whereas, groundwater flow directions are north to south or northeast to southwest in the eastern half of the study area (except in the eastern border of the study area where flow is again northwest to southeast). Higher groundwater gradients (>15 feet per mile) indicate regional discharge through Val Verde and Edwards counties.

Carbonate aquifers have three porosity elements: linear elements like channels, conduits, or caves; two-dimensional or planar elements such as bedding planes, joints, and faults; and the three-dimensional, primary porosity elements within the matrix of the limestone or dolomite (Worthington, 2003; White, 2003). Solution features can be stratigraphic, structural, and fabric influences on preferential dissolution of some areas of rock (Hovorka and others, 1998). The Edwards limestones are a good example of triple porosity (Klimchouk and Andrejchuk, 2003). Water moving through fractures, jointed



Figure 11-4: Regional groundwater flow directions and flow gradients.

rocks, solution channels or caves have much higher flow velocities. Water flow becomes turbulent at the higher velocities with flow rates that can exceed over a few thousand feet a day (Barton Springs/ Edward Aquifer Conservation District Report, 2003).

The greatest dissolution occurs where the water first enters the soluble rock and dissolution diminishes with flow distance. Karst porosity decreases in the down flow direction and flow coalesces into relatively few major conduits. Branching conduit patterns are the most common. The decrease of dissolution porosity with depth in karst aquifers is well documented by borehole data (Palmer, 2003).

The study area was divided into three areas to evaluate surface contamination potential (Figure 11-5). Geographical extents of the areas were based on formation (Figure 11-3) and flow direction and gradient (Figure 11-4). The northern area includes Ector, Midland, Glasscock, Sterling, Upton, Reagan, Irion, and Tom Green counties (Figure11-5). The dominant ETP aquifer water source for this area is the Antlers Sands with the regional groundwater flow from northwest to southeast and a low hydraulic gradient of 7 feet/mile (or 7 feet/5,280 feet = 0.001; Figure 11-4).



Figure 11-5: Cave distribution by county (Fieseler and others, 1978).

The central area includes Pecos, Brewster, Terrell, Crockett, Schleicher, Sutton, Menard, Concho, and Kimble counties. The Edwards and associated limestones are the dominant water supply in this area and groundwater flow patterns are generally northwest to southeast or north to south. Hydraulic flow gradients in the central area are from 7 to 13 feet per mile (or 0.001 to 0.002; Figure 11-4).

The southern area includes Val Verde, Edwards, Real, Kinney, and Uvalde counties. The Edwards and associated limestones are the dominant water supply in this area. This area has the steepest groundwater hydraulic gradient ranging from 11 to 17 or more feet/mile (0.002 to 0.003; Figure 11-4). Gradients as low as 0.001 formed the Mammoth Caves of Kentucky (Klimchouk and Andrejchuk, 2003).

Water-well information was obtained from the March 2003 TWDB database. The most recent (2000 to 2003, 262 wells) water-level measurements were compiled for each area in Table 11-1. Specific-capacity and pump test results from the TWDB water well database provide insights to the local aquifer hydrogeologic characteristics (relative well yields and groundwater flow rates) and are also compiled in Table 11-1.

Groundwater in the Antlers Sand occupies the interstices or pore spaces between the sand grains. Water flow through the sand grains is laminar. The porosity and permeability of

Table 11-1:	Recent average water	levels and specific	capacity of we	ells by area
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Area (aquifer source)	Number of Wells	Average depth to water from land surface	Average specific capacity gpm/ft/ # wells
North (Antlers Sand)	106	141 feet	1 gpm/ft / 57 wells
Central (Edwards)	78	211 feet	14 gpm/ft / 54 wells
South (Edwards)	29	163 feet	*14 gpm/ft / 151 wells

* State Well # 5456602 had a specific capacity of 4,000 gpm/ft, this well had a short pump test three hours) and was not used for the average specific capacity calculation.

the Antlers Sand (or ability of water to move through the formations) are dependent on degree of cementation, grain size, packing, and sorting. Extensive calcite cementing may retard groundwater movement and reduce storage. Movement in the Antlers Sand ranges from a few feet to many tens of feet per year (Walker, 1979).

The TWDB database has twenty-five pump tests results for the Antlers Sand (north area) with an average transmissivity (rate of flow through the aquifer) of 2,700 gpd/ft. The maximum calculated transmissivity for the Antlers Sand in the TWDB database is for State Well # 4426104, which is located in Upton County. The well was pumped at 300 gpm and had a draw down of 45 feet. Transmissivity, T, was estimated using the formula $T = Q/s \ge 1500$ (Driscoll, 1995) for an unconfined aquifer where Q is the pumping rate and s is the drawdown in the pumping well. The resulting transmissivity is 10,000 gpd/ft (gallons per day per foot).

Central area transmissivity data was unavailable for the Edwards and associated limestones. However, estimates of transmissivity from aquifer test and specific capacity data indicates most of the Edwards Plateau is less than 5,000 ft²/day (or 36,169 gpd/ft). The central areas maximum calculated transmissivity in the Edwards aquifer limestone is from State Wells # 5423203 (Schleicher County) and # 5505101 (Crockett County). Both wells have a specific capacity of 100 gpm/ft and have an estimated transmissivity of 150, 000 gpd/ft.

South area transmissivity data was unavailable for the Edwards and associated limestones. The south areas maximum transmissivity in the Edwards aquifer limestone is from State Well # 7033701 which is located in southern Val Verde County. The well has a specific capacity of 400 gpm/ft and has an estimated transmissivity of 600,000 gpd/ft.

Structural Influences on Groundwater Flow

The Edwards Plateau has remained largely undeformed since deposition with the exception of small folds and local dip changes that occur within fault zones. The units are nearly horizontal, dipping 0.25 to one degree to the southeast and southwest. Vertical jointing is the dominant fracture type of the region (Elliott and Veni, 1994). Structural control on karst development is very important. The relationship between lineaments and fractures in the Edwards, transmissivity and cave orientation has been studied by Wermund and others (1978) and Alexander (1990) (Hovorka and others, 1998).

Two major structural features may have influenced local fluid flow in the southern third of the study area: the Carta Valley Fault Zone and the Devils River Uplift. The Carta Valley Fault Zone trends east-west for about 75 miles from western Edwards County through central Val Verde County. The Carta Valley Fault zone is approximately one to five miles wide wrench-fault system consisting of high angle faults and fault grabens predominately oriented N 50 E. The zone is aligned along the northern faulted boundary of the Devils River Uplift. The Devils River Uplift is located in the southeast corner of Val Verde County and trends southeast into the northwest corner of Kinney County. The uplift forms a resistant buttress. Both structural features were active during the Cretaceous (Elliott and Veni, 1994).

During late Oligocene through early Miocene time (30 to 20 million years ago), largescale normal faulting created the Balcones Fault Zone east of the study area, resulting in intensive fracturing of the Cretaceous strata from the southwest (Medina County) to the northeast (Travis County). The strike (orientation) of these faults is N 50 to N 80 E (Wermund, 1978). The ETP aquifer in the study area was not impacted by this large-scale normal faulting and intensive fracturing of the Edwards aquifer, as was the Balcones Fault Zone (Barker and Ardis, 1996). The fractures in the study area appear to be related to regional uplift rather than local faulting and folding (Elliott and Veni, 1994). Four studies have investigated fractures, joints, and/or caves in the southern half of the study area. The relative locations of these studies are illustrated in Figure 11-5 and include Freeman (1968), Kastning (1983), Kunath (1995), and Wermund and others (1978). The dominant orientation for fractures, joints and linear caves in the southern portion of the study area is between N 10 to N 80 E with a less dominant trend bearing northwest. The fracture and joint orientations of the northern half of the study area are unknown. A list of the longest caves in Texas can be downloaded at http://www.cavetexas.org/.

Regional groundwater flow illustrated in Figure 11-4 suggest that groundwater flow in the central and eastern sections of the study area may be parallel or slightly oblique to the dominant northeast fracture patterns illustrated in Figure 11-5. This alignment of the regional groundwater flow direction with the dominant fracture joint orientation may allow for greater dissolution of the carbonates along the flow path. Groundwater flow in the western half of the study area appears to be oblique to the dominant northeast fracture and joint orientation (Figures 11-4 and 11-5).

Subjective Evaluation of Surface Contamination Potential

Table 11-2 is a subjective surface contamination decision matrix of the contamination susceptibility characteristics of the three areas (north, central, and south) developed by the authors. The subjective ranking is from 1 (least favorable to surface contamination) to 3 (most favorable to surface contamination) times a multiplier (subjective weighting of characteristics). Fracture orientation was left out since the orientation of fractures and joints in the north are unknown. The ranking of each characteristic is based on these assumptions:

Table 11-2:Subjective surface contamination decision matrix (rankings from 1 to 3
times multiplier; low scores indicate least likely for contamination)

Location	Multiplier	North	Central	South
Formation vertical susceptibility to contamination	Formation characteristics	Antlers Sand	Edwards Limestones	Edwards Limestones
	Score x 2	2	4	4
Ave. depth to water (Table 11-1)	Vertical travel distance	141 feet	211 feet	163 feet
· · · · ·	Score x 1	3	1	2
# of karst features (caves) (Figure 11-5)	Number of potential pathways	None	Minor to moderate	Abundant
	Score x 2	2	4	6
Hydraulic gradient (Figure 11-4)	Flow rate variable	7 feet/mile	7 to 11 feet /mile	> 15 feet/mile
	Score x 1	1	2	3
Maximum calculated transmissivity (see text)	Flow rate	10,000 gpd/ft	150,000 gpd/ft	600,000 gpd/ft
	Score x 2	2	4	6
Dilution potential (dispersion) # of karst features & max. Transmissivity (Figure 11-5 & text)	Relative abundance of groundwater to dilute contamination	Low	Moderate	High
(inguite in e to text)	Score x 2	6	4	2
Location Total score;	Multiplier	North	Central	South
Lower score is less likely for surface contamination		16	19	23

1) Vertical movement of contamination is probably more rapid through a fractured limestone than a cemented sandstone. Cemented sandstones are less favorable to vertical movement.

2) The shallower the water table, the less distance a contaminant has to travel vertically. Deeper water tables require more travel time.

3) The greater the number of karst features, the greater the probability of rapid vertical and horizontal movement of contamination. Less karst features create less pathways.

4) The greater the hydraulic gradient, the greater the potential for the formation of larger conduits in the karst aquifer (Klimchouk and Andrejchuk, 2003).

5) Higher transmissivities represent higher subsurface flow rates; contaminants would travel faster in the subsurface after contamination has occurred. Lower transmissivities would minimize contamination sub-surface distribution.

6) With abundant karst features and high transmissivities, the likelihood of dilution is higher which is more favorable for the dispersion of the contaminant.

The following is a brief summary of the surface contamination potential of each area:

North area - Surface contamination would probably reach the water table relatively slowly and remain localized; relatively minor dilution with existing groundwater.

Central area - Surface contamination could reach the water table and move down gradient rapidly; relatively moderate dilution with existing groundwater.

South area - Surface contamination could reach the water table and move down gradient very rapidly; moderate to high dilution with existing groundwater.

Table 11-2 is a subjective opinion of the ranking of available data and is not comprehensive enough (for example, it does not include soils, size of spill, chemical characteristics of contaminant, recharge rates, topography, and impact of vadose zone) and therefore should only be considered as a guide for regional surface contamination potential evaluations. Figure 11-6 illustrates a brief summary of each area.

Sources and Types of Potential Contamination

Groundwater contamination will depend not only on the intrinsic vulnerability of a groundwater resource, but also on the presence of contamination sources. Table 11-3 identifies examples of point and nonpoint sources as well as types of contamination possible in the Edwards Plateau.

Point sources are those that originate at a single location and can be either short-term releases (for example, spills) or long-term releases (for example, slow leaks). Nonpoint sources, on the other hand, are distributed over large areas. Point sources can be mitigated by elimination of the problem (for example, fixing a leak) or appropriate treatment before discharge. However, point sources that have gone unnoticed for a long period can result in widespread contamination of an aquifer as the pollutant moves with the groundwater. Nonpoint sources are minimized by changes in land practice (for example, reduced pesticide applications) and/or implementation of <u>b</u>est <u>m</u>anagement <u>p</u>ractices (BMPs; for example, installing a buffer zone along riparian corridors).

Documented Contamination in the ETP Aquifer

TCEQ and other agencies have collected and compiled data on groundwater contamination in the ETP aquifer, including:



Figure 11-6: Subjective evaluation of surface contamination potential of the Edwards Plateau aquifer.

Table 11-3: Possible sources and types of contamination in the ETP Aquifer

Potential Source	Type of Contamination	
Point Sources		
Failed septic tanks, failure at wastewater treatment plant	Sewage	
Dry cleaners, automotive repair	Chlorinated hydrocarbons (Dense Non-Aqueous Phase Liquids [DNAPLs])	
Oil wells, leaking storage tanks, pipeline	Petroleum hydrocarbons (Light Non-Aqueous Phase	
ruptures	Liquids [LNAPLs])	
Wood preservative	Arsenic	
Residues from explosives manufacture and testing	Perchlorate	
Metal fabrication and plating	Heavy metals	
Oil and water wells	TDS	
Nonpoint Sources		
Human and animal wastes; fertilizer	Nitrate	
Agriculture	Pesticides	
Naturally occurring	TDS, fluoride, iron, manganese, radionuclides	
Point and Nonpoint Sources		
Hormones, antibiotics, disinfectants	Pharmaceutical and personal care products (PPCPs)	

- Joint Groundwater Monitoring and Contamination Report-2002 Texas Groundwater Protection Committee (TGPC, 2003) reports releases of oil, crude oil, tetrachloroethene, benzene/toluene/ethylbenzene/xylene (BTEX), hydrocarbons, polychlorinated biphenyls (PCBs), chlorides, salt water, natural gas, chromium, methylene chloride, formaldehyde, and sulfates.
- Texas Water Quality Inventory–2000 (TCEQ, 2002): Includes 1996 data. Constituents with one or more samples exceeding the drinking water primary or secondary maximum contaminant level (MCL) include: nitrate, selenium, chloride, fluoride, iron, manganese, sulfate, dissolved solids, gross alpha radioactivity, and beta radioactivity. This report also documents releases and/or groundwater detections of chromium, gasoline, diesel, waste oil, jet fuel, BTEX, total petroleum hydrocarbons (TPH), volatile organic compounds (VOCs), lead, pesticides, nitrate, arsenic, NaCl, crude oil, natural gas, HCl, and sulfates.
- Texas Nonpoint Source Pollution Assessment Report and Management Program–1999 (TCEQ, 1999): Reports nonpoint source impaired groundwaters for the ETP Aquifer, including releases of pesticides; priority organics; nonpriority organics; metals; oil and grease; and salinity, TDS, and chlorides.
- **Hydrologic Atlas No. 3** (Hopkins, 1995): Documents naturally occurring waterquality constituent concentrations and exceedences above the MCL for 1988-1993.

Additional water quality-data can be obtained from the TWDB Water Information Integration and Dissemination (WIID) system at: http://wiiddev.twdb.state.tx.us/.

Fate and Transport of Chemicals in the Subsurface

Once a chemical is released into the soil, it will move under the influence of gravity and may be subject to one or more reactions. The behavior of a chemical in the environment is generally referred to as "fate and transport." The fate and transport of chemicals in the subsurface is controlled by a variety of physical, chemical, and biological processes. Irrespective of geology, there are two primary zones in the subsurface: the unsaturated (vadose) zone and the saturated zone. In the saturated zone, water fills all of the pore space between soil grains, that is, air pockets are absent. In the unsaturated zone, air is present in some of the pore spaces. While the mobility of chemicals may be markedly different in the unsaturated zone as opposed to the saturated zone, both share many of the same processes. In this section, the fate and transport processes most relevant to the ETP aquifer are reviewed.

Advection

Advection refers to the transport of dissolved chemicals by flowing groundwater. In a uniform porous media, water will travel vertically downward until it hits the water table and then move in the down gradient direction of the aquifer. In the ETP aquifer, fractures may create preferential flow paths that redirect groundwater flow. For this reason, local groundwater gradients are not reliable indicators of groundwater flow direction when fractures are present (Brassington, 1999). Large fractures are not required. Fractures of even a few centimeters across may govern groundwater flow (Wolfe and others, 1997). However, only interconnected fractures provide pathways for transport, hence merely

knowing the existence of fractures is not always sufficient to identify flow paths (USEPA, 1989; Pohll and others, 1999). In addition, assigning a representative hydraulic conductivity to a local area with fractures without knowledge of the interconnectivity of the fractures will increase the uncertainty associated with groundwater flow and contaminant transport evaluation (Focazio and others, 2002).

In part due to the difficulty in predicting flow paths and velocities, the Final Environmental Assessment of the Longhorn Pipeline did not incorporate actual estimates of groundwater transport but instead used a conservative estimate of 25 miles from the pipeline to denote areas with potential for contamination in the event of a pipeline leak (USEPA, 2000).

Dispersion

Dispersion refers to the mixing and spreading of dissolved chemicals due to local differences in groundwater velocity and direction (for example, around particles within a soil matrix or individual rock fractures within a fracture network (Focazio and others, 2002). Dispersion acts to increase the volume of contaminated water and decrease the contaminant concentration.

Diffusion

Diffusion is the molecular-scale transport of dissolved chemicals from areas of high concentration to areas of low concentration (Focazio and others. 2002). This process is negligible compared to dispersion in all but extremely low hydraulic conductivity strata. Hence, diffusion will not be discussed further.

Dissolution

Dissolution refers to the dissolving of a solid or liquid (that is immiscible with water) into water. It is controlled by the chemical's solubility and the characteristics of the water. Chemicals with high solubility will dissolved rapidly and will result in high concentrations in the groundwater. Chemicals with low solubility will remain in the pure phase longer and will be present in water at low concentrations. The dissolved fraction is subject to advection and dispersion by transport with groundwater.

<u>Sorption</u>

Sorption is a generic term referring to the attraction and adhesion of chemicals to solid surfaces and inside solid particles. Common examples include the sorption of hydrophobic organic chemicals (for example, petroleum) to soil organic matter and the sorption of metals to clays and other minerals. As dissolved chemicals move with groundwater, some fraction may temporarily (or, in some cases, permanently) attach to soil particles and stop moving. At a later time (based on concentration gradients) the sorbed chemicals may release from the soil particles, dissolve, and move again with the groundwater. The net result is that these chemicals are transported in the same direction as groundwater, but at a slower velocity. This behavior is termed retardation. Highly sorptive chemical/soil combinations may cause chemical transport to be many times slower than that of groundwater.

With regards to sorption to organic matter, this process is probably less important in the ETP aquifer than in other systems, due to low organic matter content. Indeed, in their model of flow and transport in the Barton Springs segment of the Edwards aquifer, Barrett and Charbeneau (1996) assumed an organic matter content of zero, which resulted in no retardation of the target chemical.

Biodegradation

Biodegradation is the decay of a chemical from one form to another, mediated by bacteria. This process often results in lower toxicity (for example, when petroleum hydrocarbons are degraded to carbon dioxide and water), but many exceptions occur (for example, when perchloroethylene degrades to the more toxic vinyl chloride). Biodegradation only occurs on the dissolved portion of chemicals. Due to the low content of natural organic matter in Edwards Plateau soils, it is expected that the native community of bacteria that might consume contaminants is present in lesser numbers than in other systems, resulting in slower biodegradation rates.

Volatilization

Volatilization is the transfer of a chemical from the liquid phase to the gaseous phase. This can occur from the chemicals pure phase to air (termed evaporation), or from chemicals dissolved in water to air. Volatilization is generally only significant in the unsaturated (vadose) zone and for chemicals with a high volatility (for example, VOCs).

Precipitation

In the subsurface environment, precipitation is the opposite of dissolution and refers to the creation of a solid from a combination of dissolved chemicals (positive and negative ions). Precipitation can retard the transport of chemicals much like sorption.

Properties of Chemical Classes

Chlorinated Hydrocarbons

Chlorinated hydrocarbons exist in the pure phase as dense non-aqueous phase liquids (DNAPLs, pronounced "dee-napl", "dense" refers to the fact that these chemicals are denser than water). An example is the solvent perchloroethylene (PCE, also known as tetrachloroethylene and tetrachloroethene) used in dry cleaning and metal degreasing. Chlorinated hydrocarbons have low solubilities, and therefore, when released to the subsurface, only a small portion dissolves at a time (Figure 11-7). The remaining DNAPL will transport downward through the vadose zone following fractures if present. The pure phase may get trapped in a dead-end fracture, or it may continue moving downward until it reaches the water table (the top of the aquifer). At this point, downward motion will be inhibited as the DNAPL pools on top of the water surface. If sufficient DNAPL is present, the weight of the DNAPL will overcome the surface tension in the water and will break through, allowing the DNAPL to continue moving downward until it may ultimately reach underlying (impermeable) bedrock. Once bedrock is reached, the DNAPL may follow the dip of the bedding planes, irrespective of the groundwater flow direction. The distance the DNAPL travels will be dependent on the initial size of the spill as residual DNAPL will be left behind in pore spaces and the



Figure 11-7: Illustration of DNAPL contamination (after Guarnaccia and others, 1997).

volume of the pure phase will consequently decrease as it is transported. Every location that the DNAPL passes will become a long-term source of groundwater contamination due to the low solubility and high toxicity of this class of chemicals. If sufficient DNAPL is present, the pure phase could transport through hundreds of meters of fractures over the course of several weeks (Wolfe and others, 1997).

The dissolved fraction of the chlorinated hydrocarbon will transport in the direction of groundwater movement. Ordinarily, it would sorb strongly to soil organic matter. However, the low concentration of organic matter will lessen this behavior in the Edwards Plateau soils. Under the right conditions, dissolved chlorinated hydrocarbons may also biodegrade slowly. This may be problematic, as with the degradation of PCE. While the original chemical (PCE) is toxic, one of the reaction products (vinyl chloride) is more toxic. Under certain conditions, an accumulation of vinyl chloride may result. A more detailed discussion of chlorinated hydrocarbon behavior in karst systems is provided in Wolfe and others (1997).

Petroleum Hydrocarbons

Petroleum hydrocarbons exist in the pure phase as light (that is, lighter than water) nonaqueous phase liquids (LNAPLs, pronounced "ell-napl"). Their behavior is similar to that of DNAPLs (Figure 11-7) except that upon reaching the water table they will not break through and continue moving downward. Rather, they will pool on the top of the water table and migrate laterally (and down gradient) depending on gravity and the presence of pores and fractures. Similar to chlorinated hydrocarbons, petroleum hydrocarbons have low solubility.

The likelihood of petroleum hydrocarbons reaching the water table in the pure phase depends, among other characteristics, on the volume of chemical released. Rose (1986, as cited in Brandes, 1999) estimated that a spill of 42,000 gallons or larger has a reasonable likelihood of reaching the water table in the unconfined ETP aquifer.

The dissolved portion will move in the direction of the groundwater, but more slowly due to retardation caused by sorption to organic matter. Again, the low level of organic matter in the Edwards Plateau soils and aquifer will lessen the effects of sorption, relative to many other systems. Petroleum hydrocarbons will slowly biodegrade in the groundwater, with the lower molecular weight constituents (that is, the lighter fraction) degrading more rapidly. There are no intermediate by-products of petroleum hydrocarbon degradation that are significantly more toxic than the parent compound(s).

<u>Metals</u>

Metals in karst aquifers can be grouped into three categories: (1) naturally occurring alkaline earth metals (mostly calcium and magnesium), (2) small concentrations of naturally occurring heavy metals (mostly aluminum, iron, and manganese), and (3) contaminant metals (Vesper and others, 2003). Contaminant metals are typically released to the environment in solid or dissolved form. Their behavior in the subsurface is highly dependent on the particular metal and reducing/oxidizing conditions. However, the following generalizations are possible. Dissolved metals will transport in the direction of groundwater, but may sorb (temporarily or essentially permanently) to certain minerals through ion exchange. Hence, the transport of metals is frequently controlled by pH and cation exchange capacity. For example, cadmium can exchange with adsorbed calcium, which is prevalent in the ETP aguifer, thereby binding the cadmium. In addition, metals hydroxides and carbonates can precipitate out in karst aquifers, thereby impeding their transport in narrow pores (but not stopping transport in fractures) (Vesper and others, 2003). Metals do not biodegrade, per se, but may be biologically converted to a form with a different (more or less) mobility and/or toxicity. Additional information on the transport of metals in groundwater can be found in USEPA (1999a, 1999b).

Iron and manganese are two naturally occurring heavy metals found in the ETP aquifer, sometimes at concentrations exceeding the secondary MCL.

<u>Nitrate</u>

Nitrate (NO₃) freely dissolves in water and transports, in both direction and velocity, with groundwater flow. Nitrate will not be converted to another chemical unless an anaerobic zone is encountered (rare in the ETP aquifer), in which case nitrate may be converted to

ammonia through the process of denitrification. Because of its characteristics, nitrate can be used as a tracer to identify flow paths and velocity if a discrete source is known.

Pesticides

Pesticides exhibit a range of solubility, sorption affinity, and biodegradability. Therefore, their mobility in the subsurface depends on the specific pesticide in question. Because of their application method, they are frequently distributed in small quantities across large areas rather than concentrated in a single location (as in a chemical spill).

<u>Perchlorate</u>

Perchlorate (ClO_4) is a soluble anion associated with ammonium perchlorate, which is used as rocket fuel. There is also evidence that perchlorate may be naturally occurring (TGPC, 2003). It has been detected in groundwater in several locations in the western United States, as well as the Ogallala, Dockum, and ETP aquifers around Midland (TGPC, 2003) and Lake Waco. The source of perchlorate in Texas is unclear. This contaminant has only received attention in the last several years and hence its health effects at low concentrations are highly uncertain. Research is being performed at several universities, including Texas Tech

(http://www.tiehh.ttu.edu/Research/Current_Research_Perchlorate.asp).

Radionuclides

Radionuclides dissolved in groundwater behave according their specific characteristics and are subject to ion exchange, adsorption, and bulk and surface precipitation (Pohll and others, 1999). Additional information on the transport of radionuclides in groundwater can be obtained at USEPA (1999a, 1999b).

Pathogens

In non-fractured systems, pathogens are rarely a problem in groundwater, due to long travel times and concomitant inactivation (death) of the organisms. However, due to higher flow rates and reduced filtration, pathogens may be an issue in localized areas of the ETP aquifer following wastewater system failures. A typical example would occur when a faulty septic system is located up-gradient and hydraulically connected to a water well. The presence of E. coli and certain other bacteria is indicative of human and/or animal waste in close proximity, as these bacteria rarely survive in the environment for more than a few weeks or months

(http://www.epa.gov/safewater/standard/montbl1.html). Other microorganisms (for example, Giardia lamblia, which occurs in the form of a protozoan cyst) can survive for considerably longer.

Pharmaceuticals and Personal Care Products (PPCPs)

PPCPs include a broad range of prescription and non-prescription drugs, antibiotics, preservatives, antiseptics, fragrances, and herbal remedies. Currently, there is little information available with regards to their environmental behavior and toxicological impact (particularly at low doses and in complex mixtures; Daughton and Ternes, 1999). However, they are being increasingly measured in wastewater treatment plant effluent and in the environment (Kolpin and others, 2002). Many of the compounds are resistant to degradation, have low volatility, and are polar, all of which promote aqueous transport.

Due to low population densities in the ETP aquifer, combined with the overall lack of high-density livestock operations (such as concentrated animal feeding operations, or CAFOs), PPCPs are unlikely to be a primary concern of water managers.

<u>Summary</u>

The variety of chemicals that may be released to the environment exhibit a wide range of behaviors. Hence, it is important to know the identity of the chemical(s) involved when investigating groundwater contamination, both from the point of view of predicting where a spill may migrate to and identifying where the contaminant in a well may have come from.

It is important to note that even those chemicals with very low solubility can exist in the aqueous phase at concentrations exceeding maximum contaminant levels (MCLs) or other regulatory criteria. Hence, a low solubility does not immediately eliminate a chemical from further consideration.

Suggestions for evaluating a contaminated well

Questions to be resolved when discovering contamination in a well:

- What is the contamination?
- Where is the contamination coming from?
- How long will the well be contaminated?
- Where else might the contaminant migrate to?

Low-cost tasks which can be accomplished that may provide answers.

- 1. Literature review of the site.
- 2. Literature review of the suspected contaminant(s).
- 3. Site visit.
- 4. Development of a conceptual model.

Examination and evaluation of existing data and information should include (Moore, 2002; Brassington, 1999):

- Location of aquifers and confining beds.
- Characteristics and location of recharge areas (for example, infiltration and irrigation).
- Characteristics and location of discharge areas (for example, springs, seeps, streams, and evapotranspiration).
- Site history and presence of nearby buildings, storage tanks, pipelines, and chemical sources.
- Maps of the area including wells, springs, streams, and vegetation using both topographic and aerial maps.
- Previous studies and drilling in the area.
- Geochemistry of groundwater in the area.
- Porosity and permeability of rock matrix.

- Geologic factors that control groundwater flow (for example, lithology, stratigraphy [fractures, dip, strike, and interconnectivity are particularly important], and topographic relief).
- An inventory of nearby wells from drillers logs, well owners, public agency files, and oil and gas exploration activities.
- Pumpage and irrigation information from nearby landowners.
- Historical soil boring information (for example, well logs) available to identify soil type, location, density, and orientation of fractures.

Information on some of these items, particularly fractures, requires substantial effort and may not be available.

Following review of site characteristics, the chemical contaminant should be identified (or at least characterized) to identify likely behavior in the subsurface, including:

- Whether or not the chemical may be naturally occurring.
- Retardation potential based on sorption to organic matter, ion exchange, or precipitation.
- Volatility.
- Solubility.
- Potential for transport in the pure phase (for example, is the pure phase a solid or liquid and, if liquid, is it more dense or less dense than water?).
- Biodegradability.
- Health impacts at different concentrations.
- Regulatory limits in soil and water.
- Potential sources of chemical (for example, oil and gas wells, dry cleaning, and storage tanks).

A site visit is important to identify characteristics that cannot be gleaned from literature sources. This visit should include, at a minimum, an investigation of:

- Soil and rock outcrops.
- Vegetation.
- Irrigation, infiltration, and drainage.
- Visible signs of fractures.
- Wells and other subsurface features.

Based on this information, a preliminary conceptual model of the system can be developed. A conceptual model is a qualitative description of the important characteristics controlling the behavior of target chemicals in a particular system. The conceptual model is used to document, prioritize, and communicate the important characteristics of a system so that fieldwork and analyses focus on the primary factors affecting contaminant transport. If sufficient groundwater head data exist, it may be possible to identify the hydraulic gradient and infer the groundwater flow direction. However, in fractured systems groundwater head is an unreliable indicator of groundwater flow direction.

The information gathered above and the conceptual model can be used to begin to isolate the location(s) of the contaminant source. If enough information is available, another site visit may be sufficient to identify the source. If not, additional data collection may be necessary, including groundwater monitoring wells, tracer tests, and other geophysical methods.

The duration of contamination will depend on the mass of chemical released and its persistence in the environment. Chemicals that are rapidly transported and/or degraded will dissipate more rapidly than those that are insoluble, highly sorptive, and/or difficult to degrade. The migration distance will be primarily dependent on the mass of chemical and its solubility. Strong sorption and high levels of biodegradation both act to retard and contain the spread of contaminant.

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