

Sources—Quality of Recently Recharged Water in the High Plains Aquifer

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Chapter 1. Sources—Quality of Recently Recharged Water in the High Plains Aquifer

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Introduction

The quality of ground water depends on the quality of water recharging the aquifer and the hydrologic and biogeochemical processes that affect it along flow paths from recharge to discharge areas. The quality of water recharging aquifers varies with land use/land cover (Nolan and Stoner, 2000; Gilliom and others, 2006; Zogorski and others, 2006); therefore, HPGW studies designed to assess the quality of recently recharged water were stratified on the two land-use categories hypothesized to have the largest effect on recharge water quality relative to natural conditions: agriculture and urban. Recently recharged water, as used in this report, refers to ground water that was recharged during the past ~50 years, as indicated by tritium concentrations in ground water greater than 0.5 tritium unit (TU) at the time of sampling in 2000 through 2004. Agricultural activities occurred over substantially more High Plains land area than urban development (38 and 3 percent, respectively, in 2000). Thus, this chapter focuses on the quality of ground-water recharge beneath agricultural lands. The effect of urbanization on ground-water quality was examined as part of the HPGW study (Pope and others, 2002; Clark and others, 2007), but those types of effects are not considered to be substantial at the regional scale of this assessment.

Recharge under natural conditions is minimal across much of the semiarid High Plains (Scanlon and Goldsmith, 1997; Scanlon and others, 2005; McMahon and others, 2006); therefore, the application of irrigation water to cropland is thought to be an important driving force for the movement of agricultural chemicals from the land surface to the water table. Thus, the agricultural land-use studies targeted irrigated cropland. Recharge beneath nonirrigated cropland could be comparable to that beneath irrigated cropland (Scanlon and others, 2005), but fertilizer and pesticide application rates on the predominant nonirrigated crop in the High Plains (wheat) typically are less than on the predominant irrigated crop (corn) (Blumenthal and Sander, 2002; Shapiro and Wortmann, 2003; Bernards and others, 2007). About 30 percent of the High Plains agricultural lands are irrigated, with ground water providing most (97 percent) of the water used for that irrigation (Qi and others, 2002a; Maupin and Barber, 2005).

The connection between chemical use at the land surface and the quality of recently recharged ground water would be costly to measure across the entire High Plains aquifer. Therefore, areas considered to be representative of the most intensively irrigated parts of the High Plains were selected for detailed study to provide a basis for extrapolating the results to unmonitored areas of the aquifer. In this chapter, data collected in representative irrigated areas and in rangeland control sites (unsaturated-zone sites) are used to explore the relations between land use/land cover and ground-water quality at the water table. Additional processes that control the movement of water and chemicals from the land surface to the water table, such as climate variability, also are discussed.

Study Design

Data from the land-use and unsaturated-zone well networks were used to assess and explain the quality of recently recharged ground water in irrigated areas of the High Plains (table 4 and fig. 18). The unsaturated-zone studies were considered to be an important component of the HPGW design because of the effect thick unsaturated zones (fig. 12) could have on chemical storage and transit times between land surface and the water table. Details of the study designs, sample collection, and sample analysis can be found in Bruce and others (2003), Stanton and Fahlquist (2006), and McMahon and others (2003, 2006), and are briefly presented in the following paragraphs.

Agricultural Land-Use Studies

Agricultural land-use wells were installed in the following hydrogeologic units: Plio-Pleistocene deposits of eastern Nebraska (NHP); Ogallala Formation in Kansas, Oklahoma, and New Mexico (CHP); and the Ogallala Formation in Texas (SHP). Those areas represent some of the most intensively irrigated parts of the High Plains (fig. 18). The NHP study area is the smallest of the three study areas, but it had the largest percentage of irrigated cropland within the counties containing land-use wells (table 5), followed by the SHP and CHP study areas. The dominant crops grown in the NHP study area in

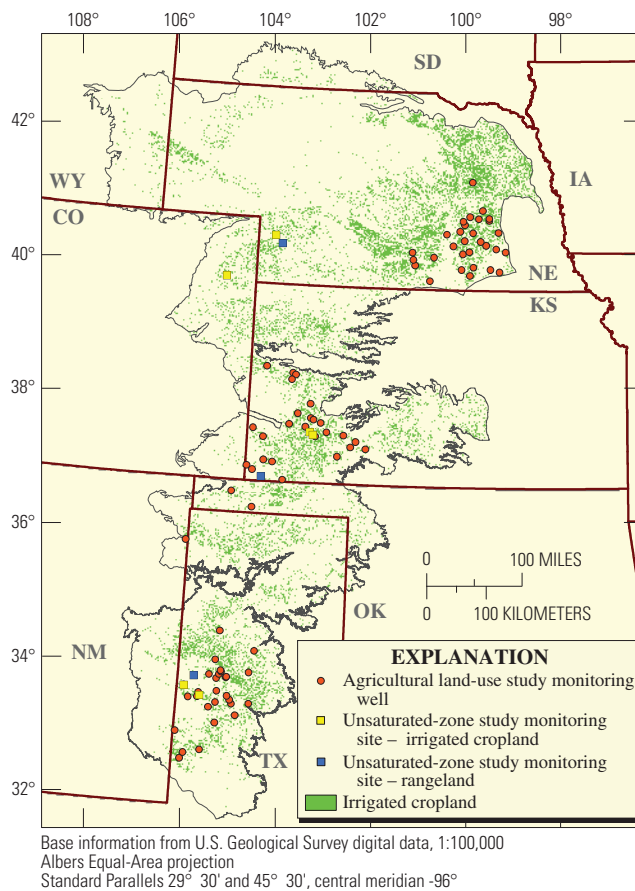


Figure 18. Distribution of irrigated cropland in the High Plains aquifer area, nominal date 1992 (Qi and others, 2002a), location of unsaturated-zone study monitoring sites, and location of monitoring wells for the agricultural land-use studies.

Table 5. Land-use/land-cover and population statistics for the High Plains counties containing agricultural land-use study wells.

[Land-use data for 2002 (U.S. Department of Agriculture, 2002); Human population data for 2000 (U.S. Census Bureau, 2000a); Crop and animal-population data for 2002 (U.S. Department of Agriculture, 2002)]

Region	Land use/land cover, as a percentage of county areas			Population		
	Nonirrigated cropland	Irrigated cropland	Primary irrigated crop	Humans	Cattle and calves	Swine
Northern High Plains	35	46	Corn/soybeans	142,607	633,080	658,067
Central High Plains	47	15	Corn	132,893	1,753,463	1,074,090
Southern High Plains	42	28	Cotton	371,347	945,443	3,584

2002 were corn and soybeans (table 5). In the CHP study area, corn was the dominant crop, whereas cotton dominated in the SHP study area. In each study area, monitoring wells were installed at 30 randomly selected locations. One of the SHP wells was dry at the time of sampling so water-quality data are available for only 29 wells in that study area. Wells were constructed with 10-ft-long screens with the top of the screen placed about 5 ft below the water table to intercept recently recharged ground water. Selection of well locations was subject to these additional criteria:

- Next to a field that had been irrigated for at least 20 years
- Depth to water less than 200 ft
- The direction of regional ground-water flow beneath the irrigated field was toward the well site
- Crops grown in the targeted field were primarily corn and soybeans in the NHP, corn in the CHP, and cotton in the SHP
- Well not located near surface-water bodies, irrigation wells, or other potential sources of contamination
- Well not located in a water-gathering topographic depression in the land surface

Because of these criteria, the final location chosen for installing monitoring wells could be within a 4-mi radius of the randomly selected location. Water samples were collected once from the wells in the NHP in the summer of 2004, once from the wells in the CHP in the summer of 2000, and once from wells in the SHP in the winter of 2003. The samples were analyzed for the properties and constituents listed in table 4. Analyses were done at USGS laboratories in Menlo Park, Calif.; Denver, Colo.; Lawrence, Kan.; and Reston, Va. (see Bruce and others, 2003, and Stanton and Fahlgquist, 2006, for details related to analytical procedures and quality-assurance data).

Unsaturated-Zone Studies

Nine sites were selected for monitoring the movement of water and chemicals between the land surface and water table (fig. 18). Two irrigated sites and one rangeland site were located in each of the NHP, CHP, and SHP subregions. The NHP and CHP sites targeted irrigated corn overlying the Ogallala Formation, and the SHP site targeted irrigated cotton overlying the Ogallala. Each site consisted of a water-table monitoring well and instruments installed at different depths within the unsaturated zone to monitor matric potentials and water and gas chemistry. The wells and instruments in the unsaturated zone were sampled multiple times between 2000

and 2005 for analysis of the properties and constituents listed in table 4. Analyses were done at USGS laboratories in Menlo Park, Calif.; Denver, Colo.; Lawrence, Kan.; and Reston, Va. (see McMahon and others, 2003, 2006 for details).

Hydrogeologic Setting

Thickness and composition of sediments in the unsaturated zone contribute to controlling water and chemical movement to the water table. Median depth to the water table at the land-use study wells was shallowest in the NHP (85 ft) and significantly deeper in the CHP and SHP study areas (about 151 and 153 ft, respectively) (table 6). Regional variability in depths to water in the High Plains aquifer results from regional differences in climate, soils, land use, and ground-water withdrawals. Where withdrawals greatly exceed recharge, large declines in water levels occur and increase the overall thickness of the unsaturated zone (fig. 14). In general, declines have been largest in the SHP and smallest in the NHP.

The NHP agricultural land-use study was located in the Plio-Pleistocene deposits of southeastern Nebraska. Those sediments are composed primarily of sand and gravel of fluvial origin but also include loess, paleosols, and glacial till. In that area, layers of loess in the unsaturated zone may limit the movement of percolating water to the water table. Ground-water recharge in the area is estimated to be about 20 percent of mean annual precipitation, which is equivalent to 4 to 6 in/yr (Dugan and Zelt, 2000).

The CHP and SHP agricultural land-use study areas are defined by the areal extent of the saturated Ogallala Formation in those regions. The formation is generally described as being composed of interbedded sand, gravel, silt, and clay deposited by fluvial processes. The sediments are poorly sorted and generally unconsolidated, but in some locations are cemented by calcium carbonate and, to a lesser degree, silica. Cemented zones are more common near the land surface and were thickest in the SHP. The Tertiary-age sediments can be overlain by Quaternary-age deposits (alluvial gravel, dune sand, and loess deposits). Those deposits are less extensive than the Ogallala Formation, but where saturated, are considered to be part of the High Plains aquifer. The CHP and SHP study areas have flat to gentle slopes and soil texture that is sufficiently coarse to allow moderate to high infiltration rates. Recharge rates across these two study areas are estimated to be about 3 percent of mean annual precipitation, which is equivalent to about 0.25 to 2 in/yr (Dugan and Zelt, 2000). In the SHP and diminishing northwards into the CHP, playas dot the landscape and are thought to be important topographic features for capturing rainfall and irrigation runoff and focusing it as recharge to the underlying ground water (Wood and Sanford, 1995; Scanlon and Goldsmith, 1997).

Chemical Characteristics of Recently Recharged Water Beneath Irrigated Cropland

Water-quality results for the three agricultural land-use studies are reported by Bruce and others (2003) and Stanton and Falhquist (2006). The following discussion focuses on selected water-quality properties and constituents and provides an overview of the status of water quality in the High Plains aquifer beneath irrigated cropland.

Tritium

Water samples from the land-use study wells were analyzed for tritium to estimate the relative residence time of water in the aquifer. Tritium is a radioactive isotope of hydrogen with a half-life of about 12.3 years. It is an excellent tracer of water movement because it substitutes for stable hydrogen isotopes in the water molecule. Because tritium is radioactive, its concentration in ground water decreases over time through radioactive decay. In general, tritium in ground water originates from precipitation. Before the onset of atmospheric testing of nuclear weapons in 1953 (prebomb), the tritium content of precipitation in the Central United States probably ranged from about 3 to 8 TU (Kaufman and Libby, 1954; Thatcher, 1962). As a result of radioactive decay, ground water derived from precipitation that fell before 1953 would have contained no more than about 0.5 TU when the land-use wells were sampled in 2000 to 2004. The tritium content of precipitation increased substantially after the onset of atmospheric nuclear weapons testing but has slowly decreased from its peak in the early 1960s. Even with the variability in tritium content of precipitation over time, ground water totally derived from precipitation that fell since 1953 (postbomb) contained more than 0.5 TU in 2000 to 2004.

The majority of samples in each study area contained some recent recharge, as indicated by tritium concentrations greater than 0.5 TU (fig. 19). The percentage of samples containing tritium concentrations greater than 0.5 TU systematically decreased from north to south in the High Plains (NHP—90 percent; CHP—77 percent; and SHP—59 percent), which is consistent with the increases in mean annual air temperature (which could decrease recharge through increased evapotranspiration) and depth to water from north to south (figs. 12 and 19), and generally indicates that transit times of water from land surface to the water table were longer in the SHP than the NHP.

Dissolved Solids

The dissolved-solids content of ground water is an important factor to consider when assessing the suitability of a water supply for a variety of uses. Elevated concentrations

of salt in ground water might make it unusable as a drinking-water supply, unusable to farmers for irrigation and livestock, or unusable for industrial uses. Dissolved-solids concentrations in ground water beneath the irrigated cropland generally increased from north to south in the High Plains (fig. 19). Concentrations in the SHP were significantly ($p < 0.001$, Mann-Whitney and Kruskal-Wallis tests) larger than concentrations in the NHP and CHP (table 6).

In undisturbed ground-water flow systems, concentrations of dissolved solids typically increase with depth in the aquifer as water/rock interactions dissolve minerals in the aquifer matrix. A comparison of results from the land-use studies and the major-aquifer studies in which they were nested shows that concentrations of dissolved solids in recent recharge beneath the irrigated cropland were significantly ($p < 0.001$, Mann-Whitney test) larger than the concentrations deeper in the aquifer in the CHP and SHP and equal to the concentrations deeper in the aquifer in the NHP. The data imply that conversion of native grassland to irrigated cropland has altered the chemistry of recharge to the aquifer by increasing dissolved-solids concentrations.

Dissolved Oxygen

Some chemicals of environmental concern in the aquifer, such as nitrate, may be reduced to less oxidized forms by naturally occurring micro-organisms under suboxic to anoxic conditions. Microbial reduction of those chemicals is beneficial because it may convert the chemicals into less soluble or less toxic forms. Reducing conditions, however, also may lead to the mobilization of toxic elements like arsenic or nuisance elements like iron. In oxygenated ground water, micro-organisms may oxidize some chemicals, such as atrazine, ultimately to carbon dioxide (McMahon and others, 1992). The role of dissolved oxygen in microbial processes and ground-water chemistry makes measuring its distribution in ground water important if the fate of potentially harmful chemicals is to be understood.

Samples from all the land-use study wells were oxic (dissolved oxygen concentration greater than or equal to 0.5 mg/L; McMahon and Chapelle, in press) (fig. 19). Median oxygen concentrations ranged from 6.5 to 6.7 mg/L and were not significantly ($p = 0.679$) different between the study areas (table 6). Oxic conditions in ground water beneath irrigated cropland in the High Plains are not conducive for nitrate degradation but they are conducive for degradation of some other chemicals like atrazine.

Major Ions and Trace Elements

The primary ionic constituents contributing to dissolved solids in ground water are sodium, potassium, calcium, magnesium, bicarbonate, chloride, sulfate, and in some cases nitrate and/or fluoride. Relative proportions of those constituents in samples from the land-use study wells are shown

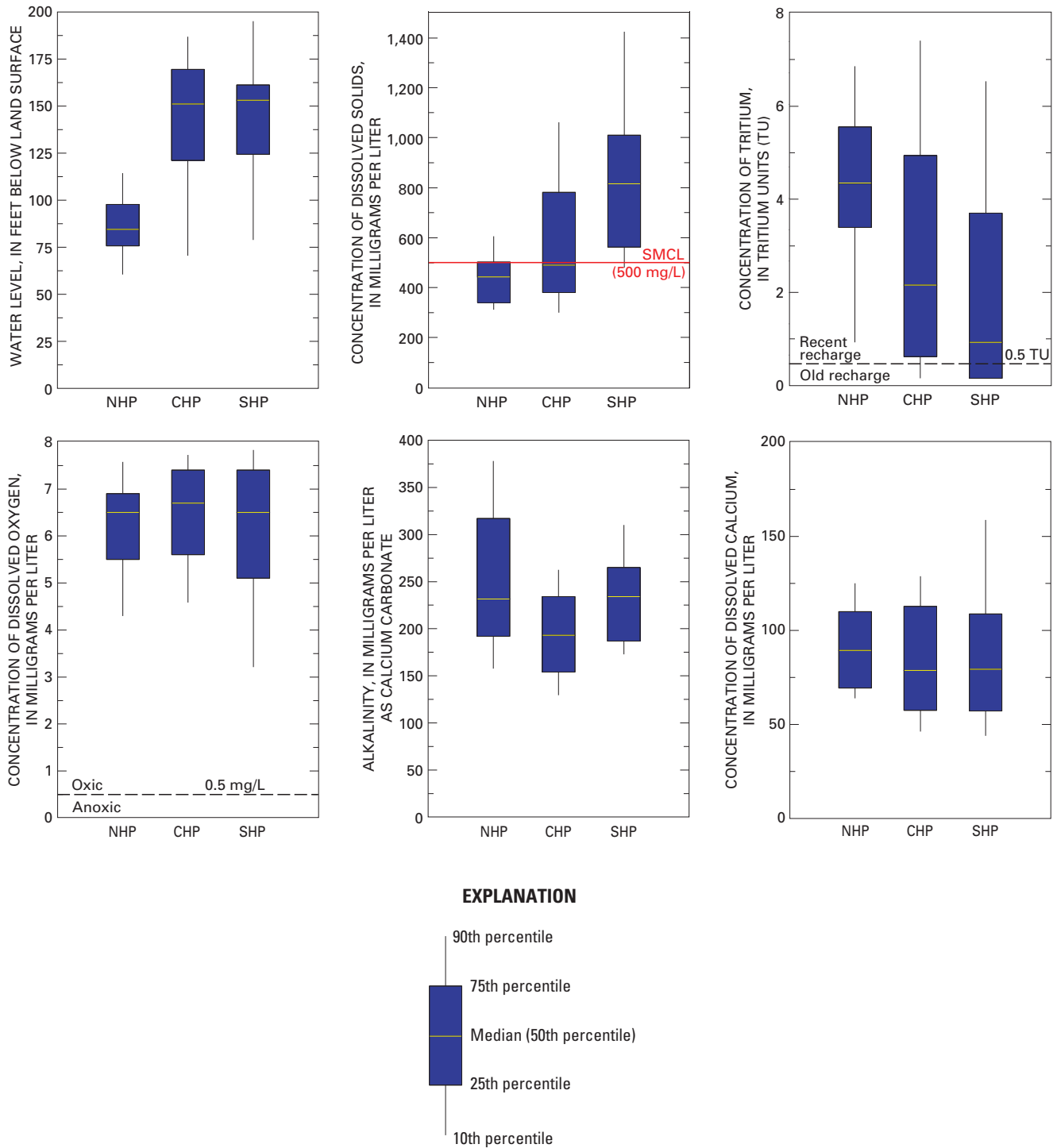


Figure 19. Distribution of water levels and concentrations of dissolved solids, tritium, dissolved oxygen, alkalinity, selected major ions and nutrients, arsenic, and uranium in water samples collected from the northern (NHP), central (CHP), and southern (SHP) High Plains agricultural land-use study wells, 2000–2004.

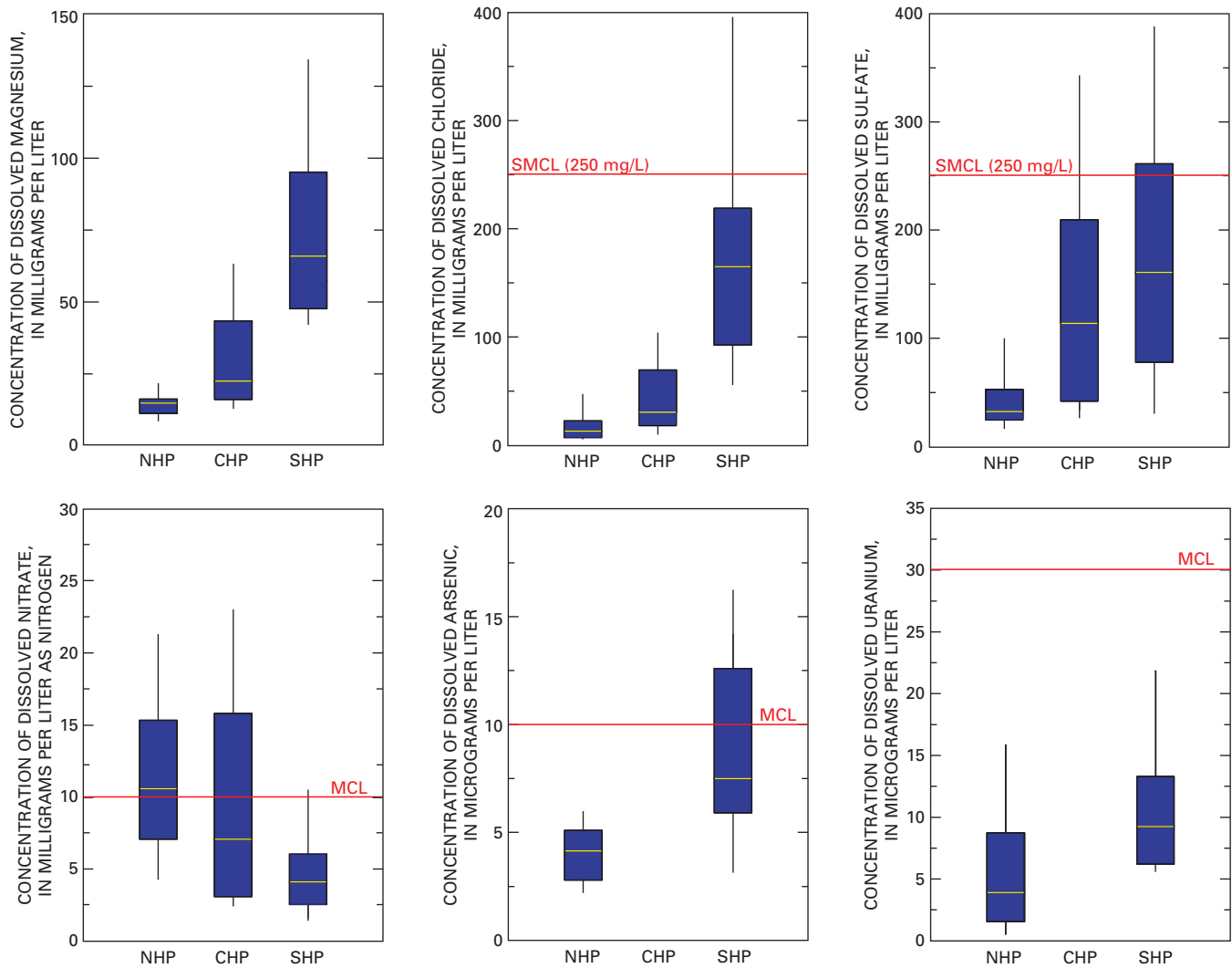


Figure 19. Distribution of water levels and concentrations of dissolved solids, tritium, dissolved oxygen, alkalinity, selected major ions and nutrients, arsenic, and uranium in water samples collected from the northern (NHP), central (CHP), and southern (SHP) High Plains agricultural land-use study wells, 2000–2004.—Continued

graphically in figure 20. Water from the NHP was mostly dominated by calcium and bicarbonate. Water from the CHP and SHP generally contained no dominant cation or anion. A cation or anion is referred to as dominant if it accounts for more than 60 percent of the total cationic or anionic charge. The major-ion data indicate that sodium, magnesium, chloride, and sulfate were important contributors to the significant increase in dissolved solids from north to south in the High Plains (table 6 and figs. 19 and 20). Those constituents can have natural and anthropogenic sources in the High Plains and are discussed later in this chapter.

Concentrations of arsenic and uranium were significantly ($p < 0.001$) larger in samples from the SHP than in samples

from the NHP (table 6 and fig. 19). Trace-element data were not collected for the CHP land-use study. Thirty-eight percent of the SHP arsenic samples exceeded the 10 $\mu\text{g/L}$ MCL, whereas none of the NHP samples exceeded the standard. Seven percent of the NHP uranium samples exceeded the 30 $\mu\text{g/L}$ MCL, whereas 3 percent of the SHP samples exceeded the MCL.

Nitrate

Nitrite plus nitrate concentrations in samples from the land-use study wells decreased significantly ($p = 0.001$) from north to south in the High Plains (table 6 and fig. 19). Median

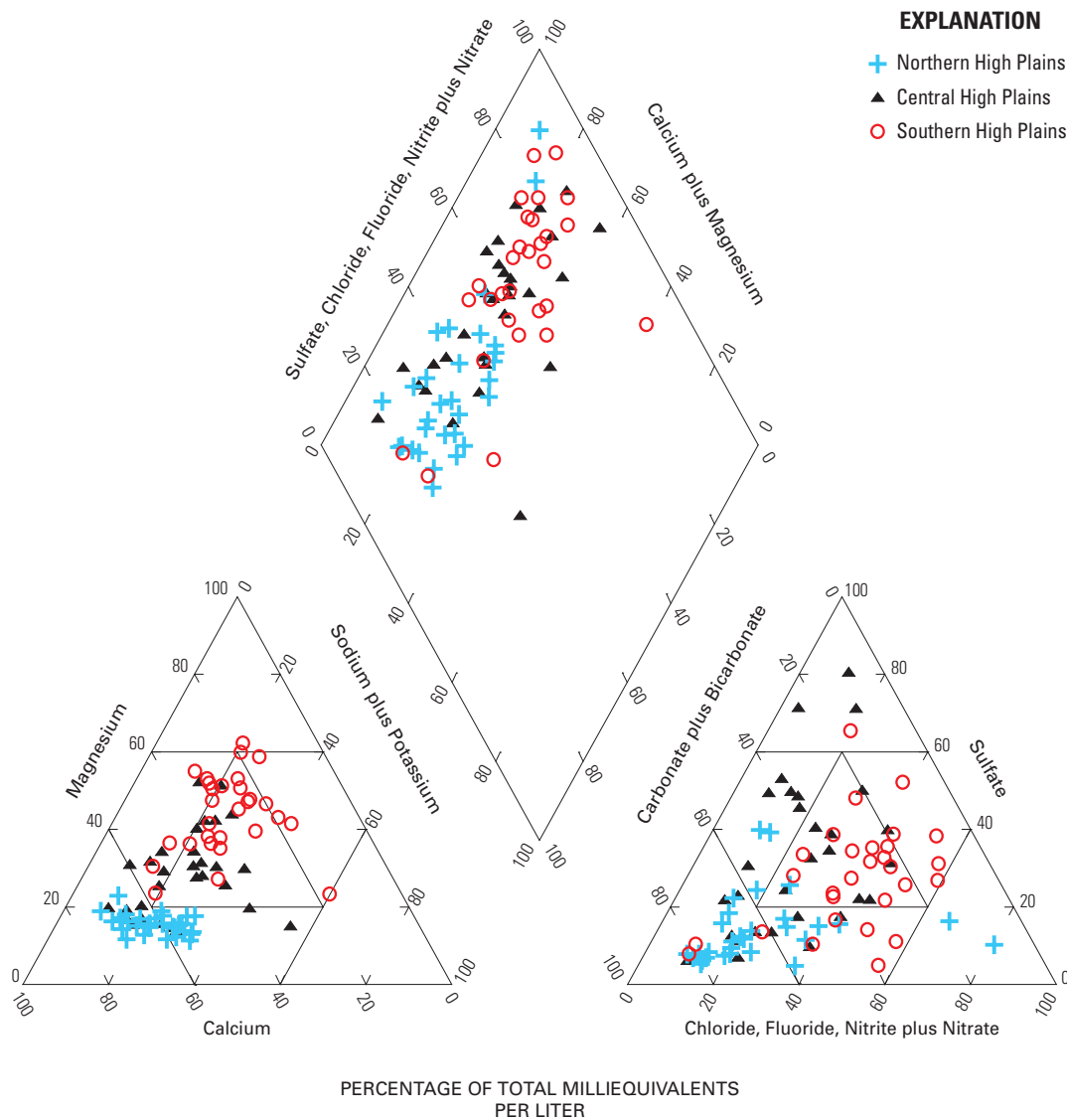


Figure 20. Trilinear diagram showing relations between major ions in water samples collected from the northern, central, and southern High Plains agricultural land-use study wells.

Table 6. Summary of water levels and concentrations of dissolved solids, tritium, dissolved oxygen, alkalinity, selected major ions and nutrients, arsenic, and uranium in water samples collected from the northern, central, and southern High Plains agricultural land-use study wells.

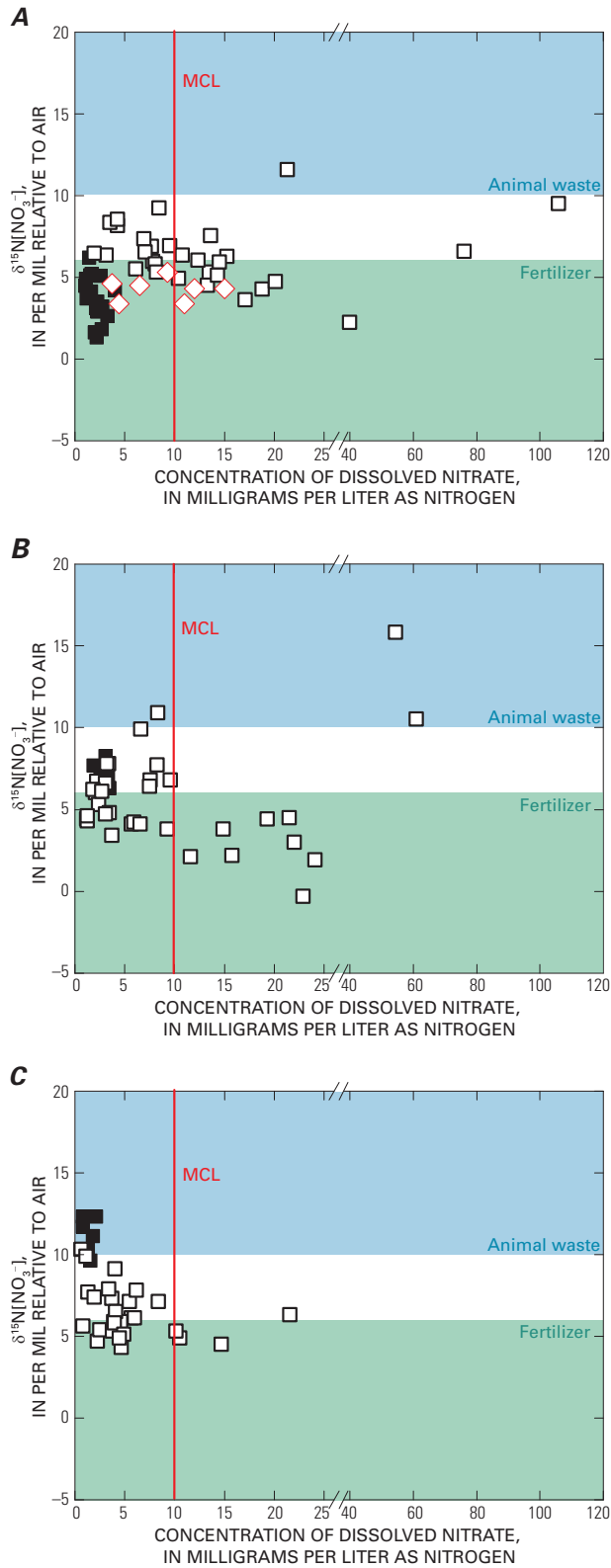
[USEPA, U.S. Environmental Protection Agency; H, variable is significantly larger than in the other study areas; L, variable is significantly smaller than in the other study areas; M, variable is in between those in the other study areas. If two groups have the same letter, values for that variable are not significantly different between the two groups; --, variable not significantly different than those in any of the other study areas; <, less than; N, nitrogen; n.s., no standard has been established; TU, tritium units; mg/L, milligrams per liter; µg/L, micrograms per liter; CaCO₃, calcium carbonate; *, Mann-Whitney test used]

Parameter	p-value (Kruskal-Wallis test)	Northern High Plains n=30		Central High Plains n=30		Southern High Plains n=29		USEPA drinking-water standard/type of standard
		Median	Kruskal-Wallis test result	Median	Kruskal-Wallis test result	Median	Kruskal-Wallis test result	
Water level (ft below land surface)	< 0.001	84.6	L	151.2	H	153.2	H	n.s.
Dissolved solids (mg/L)	< .001	442	L	491	L	814	H	500/secondary
Tritium (TU)	.009	4.2	H	2.2	--	0.9	L	n.s.
Dissolved oxygen (mg/L)	.679	6.5	--	6.7	--	6.5	--	n.s.
Alkalinity (mg/L as CaCO ₃)	.020	232	H	193	L	234	H	n.s.
Sodium (mg/L)	<.001	31.4	L	31.4	L	59.4	H	n.s.
Potassium (mg/L)	.001	6.9	--	5.4	L	9.1	H	n.s.
Calcium (mg/L)	.417	89.4	--	78.8	--	79.4	--	n.s.
Magnesium (mg/L)	<.001	14.8	L	22.4	M	65.9	H	n.s.
Chloride (mg/L)	<.001	13.2	L	30.9	M	165	H	250/secondary
Sulfate (mg/L)	<.001	32.4	L	114	H	160	H	250/secondary
Nitrite+nitrate (mg/L as N)	.001	10.6	H	7.0	--	4.1	L	10/primary
Arsenic (µg/L)	<.001*	4.1	L	No data		7.5	H	10/primary
Uranium (µg/L)	<.001*	3.9	L	No data		9.2	H	30/primary

nitrite plus nitrate concentrations in samples from the NHP and SHP were 10.6 and 4.1 mg/L as N, respectively. The median nitrite concentration in samples from each land-use study well network was less than 0.01 mg/L as N; therefore, concentrations of nitrite plus nitrate consisted almost entirely of nitrate and will be referred to as such for the remainder of this chapter. Nitrate can be derived from natural processes (such as mineral weathering, decay of organic material, and atmospheric deposition) or from anthropogenic sources (such as septic tank effluent and agricultural sources like commercial fertilizers and animal waste). Although nitrate is present naturally in ground water, elevated concentrations generally can be attributed to humans. The maximum background concentration of nitrate representing natural sources in most High Plains ground water is less than or equal to about 4 mg/L as N (Litke, 2001; Becker and others, 2002; McMahan and others, 2004a,b; McMahan and Böhlke, 2006). Ninety, 60, and 55 percent of the samples from the NHP, CHP, and SHP wells, respectively, exceeded the background nitrate concentration. The data show that conversion of native grassland to irrigated

cropland has altered the chemistry of recharge to the aquifer by increasing nitrate concentrations.

Measurements of the stable nitrogen isotope composition of nitrate have been widely used to assess sources of nitrate in ground water because some important nitrate sources like fertilizer and animal waste can have distinctly different isotopic signatures (Kreitler, 1979; Heaton, 1986; Kendall, 1998). Interpretation of the nitrogen isotope data can be complicated by several factors, particularly isotopic fractionation as a result of microbially mediated nitrate reduction. That process generally is not substantial in young, oxic ground water, which is the case for most of the land-use study wells. In that case, it may be possible to use nitrogen isotopes to identify important sources of nitrate in ground water. Nitrogen isotope measurements for the three land-use studies are plotted in figure 21. In each subregion, many of the samples with the largest nitrate concentrations plot within the fields commonly associated with fertilizer or animal waste sources. Several other samples, however, plot between those two fields, indicating that they could be from other sources or represent mixtures of nitrate



EXPLANATION

Ground-water sample

- Agricultural land-use sample
- Paleorecharge sample (McMahon and Böhlke, 2006)
- ◇ Water-table sample (Nebraska Panhandle) (Steele and others, 2005)

Approximate range in nitrogen isotopic compositions of source material (Kreitler, 1979; Heaton, 1986; Kendall, 1998)

- Animal waste
- Fertilizer

MCL = Maximum Contaminant Level (U.S. Environmental Protection Agency, 2006)

from fertilizer and animal waste. These results are discussed in more detail in the next section of this chapter.

Pesticides

Concentrations of all detected pesticide compounds in water samples from the land-use study wells are shown in figure 22. (Reporting levels varied over time and not all compounds were analyzed for each subregion.) Atrazine was the only pesticide compound detected that exceeded its MCL and these were both in the CHP. Ten pesticide compounds that were analyzed in each subregion and that had comparable detection frequencies are shown in figure 23. At least one of those pesticide compounds was detected in 67 percent of the NHP samples as compared to 70 and 21 percent in the CHP and SHP samples, respectively. Atrazine or its metabolite deethylatrazine were the most commonly detected pesticide compounds in each subregion when compared against a common assessment level of 0.016 µg/L (fig. 23). The types of detected pesticide compounds generally were consistent with the crops grown and typical agricultural practices for each subregion.

Pesticide compounds were detected most frequently in ground water that also contained tritium concentrations greater than 0.5 TU or nitrate concentrations greater than the background concentration of 4 mg/L as N (fig. 24), supporting the interpretation that those samples are associated with recent agricultural recharge. For example, 71 to 100 percent of the samples that contained at least one pesticide compound also contained tritium concentrations greater than 0.5 TU.

Factors Affecting the Quality of Recently Recharged Water Beneath Irrigated Cropland

As described in the previous section of the chapter, the chemistry of recently recharged ground water beneath irrigated cropland was not uniform across the High Plains. Several

Figure 21. Nitrogen isotope composition of nitrate as a function of nitrate concentration in water samples collected from the (A) northern, (B) central, and (C) southern High Plains agricultural land-use study wells.

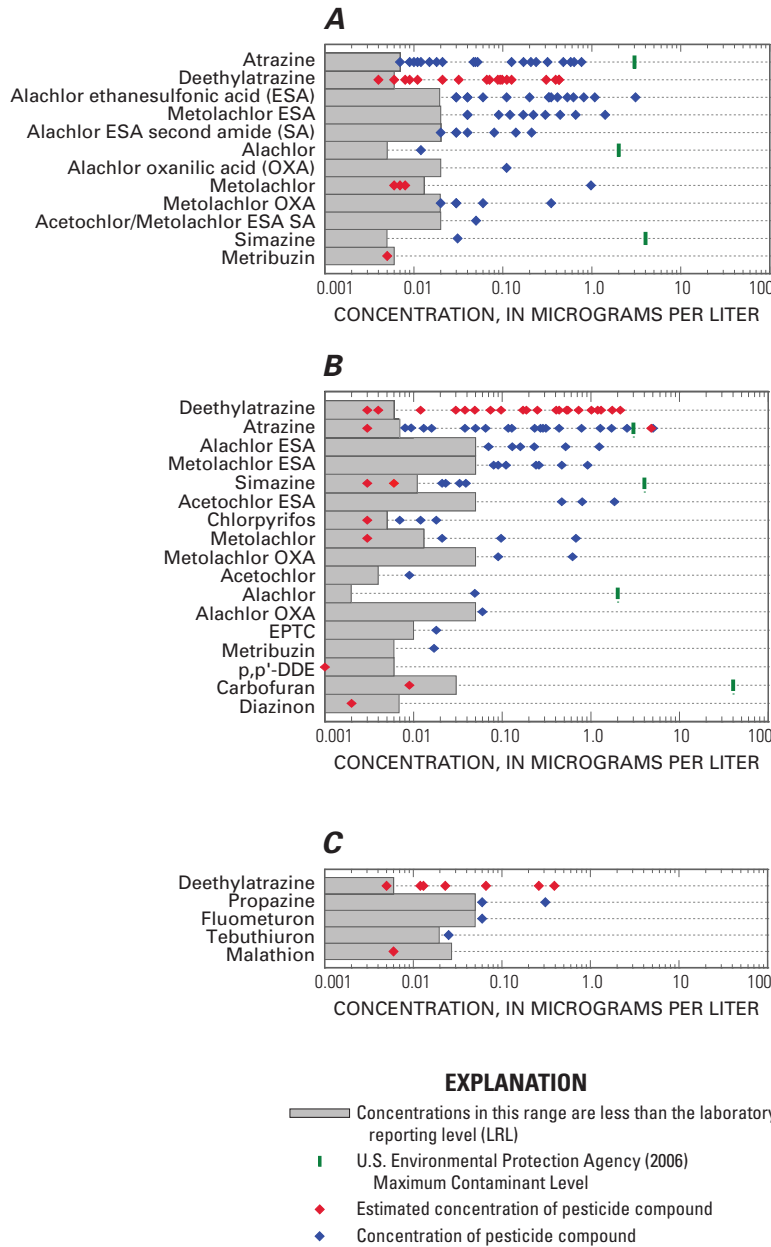


Figure 22. Concentrations of detected pesticide compounds in water samples collected from the (A) northern, (B) central, and (C) southern High Plains agricultural land-use study wells, listed in order of decreasing number of detections in each subregion.

factors that may be responsible for the observed regional differences in recharge chemistry are discussed in this section of the chapter.

Chemical and Water Use

The general north-to-south decrease in nitrate concentrations and frequency of pesticide-compound detections in

ground water beneath irrigated cropland is generally consistent with patterns of chemical use in those regions. Fertilizer-plus-manure application rates were larger in the NHP study area than in the CHP and SHP (fig. 25), and total average pesticide application rates in the NHP study area were about twice as large as those in the CHP and SHP study areas (table 7). Irrigation water use on cropland in the CHP and SHP areas was larger than in the NHP (fig. 26), which could promote chemical movement from the land surface to the water table,

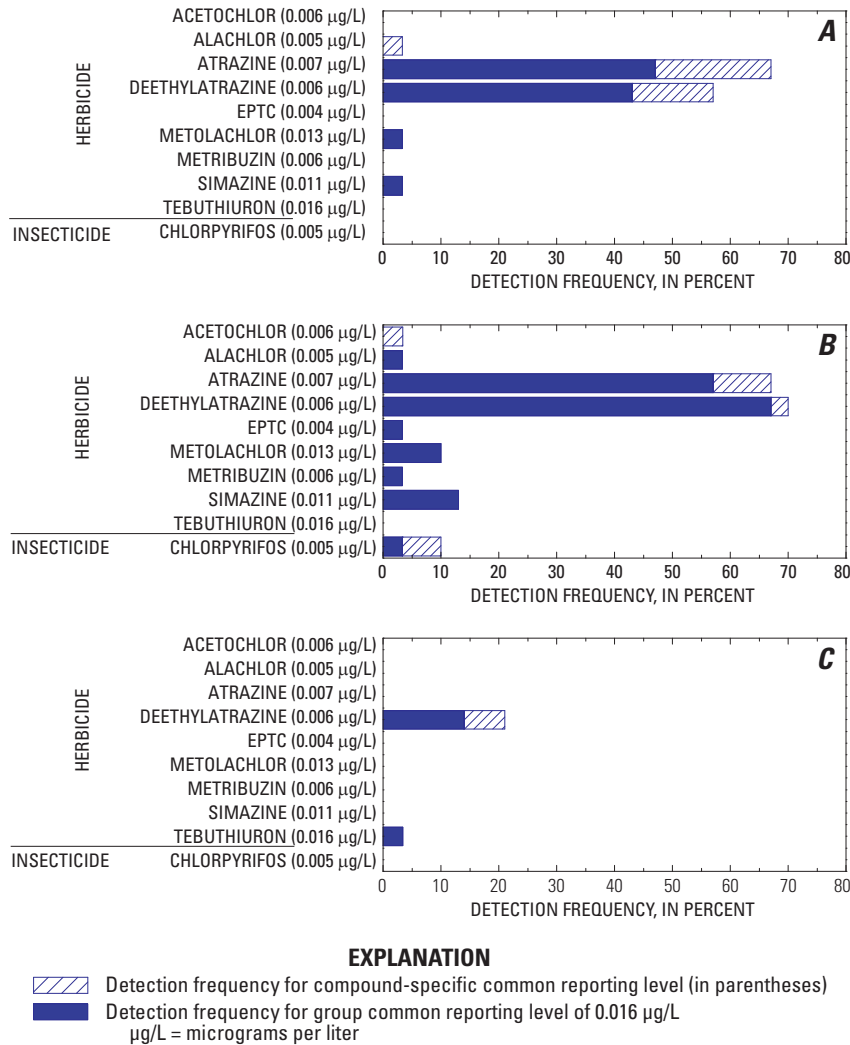


Figure 23. Frequency of pesticide-compound detections in water samples collected from the (A) northern, (B) central, and (C) southern High Plains agricultural land-use study wells. For compounds that were analyzed in each subregion and were detected at least once in any subregion.

but natural recharge was larger and depths to the water table were smaller in the NHP study area than in the CHP and SHP study areas, which could result in shorter transit times from land surface to the water table. Stanton and Fahlquist (2006) concluded that the combination of smaller depths to water, greater precipitation and recharge, and larger fertilizer-plus-manure and pesticide application rates in the NHP compared to the SHP was primarily responsible for the differences in nitrate and pesticide concentrations in ground water beneath irrigated cropland in those two subareas.

The water-use data in figure 26 provide insight as to the extent of irrigation water use, but they do not indicate whether spatial patterns of irrigation have changed over time. Understanding how irrigation has varied spatially over time in the High Plains is important because conversion of native

grassland to cropland and subsequent agricultural activity can alter the chemistry of recharge to the aquifer. Qi and others (2002a) used satellite imagery (nominal date 1992) to determine the location of irrigated cropland across the entire High Plains area and compared those findings to maps of irrigated cropland based on 1980 satellite imagery from Gutentag and others (1984). That comparison showed that the location of irrigated cropland had shifted from areas where there were large ground-water level declines to areas where ground-water levels were static or increasing (fig. 27). That shift may have required the conversion of rangeland to cropland, which could change recharge in those areas. A recent study (Perry, 2006) examined the effect of irrigation practices on water use within the Kansas High Plains and concluded that water use had not changed over the period 1991–2003. The data also show that

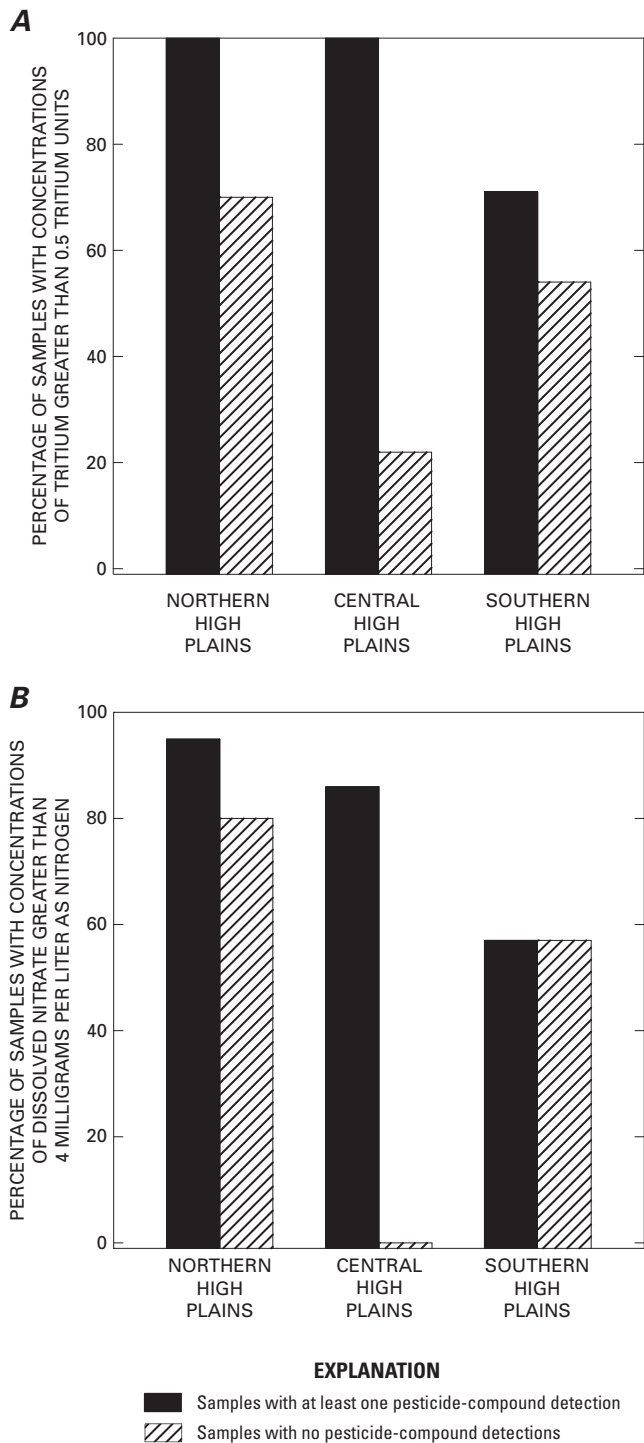


Figure 24. Percentage of samples from the agricultural land-use study wells with concentrations of (A) tritium greater than 0.5 tritium units and (B) dissolved nitrate greater than 4 milligrams per liter as nitrogen, for samples with and without pesticide-compound detections

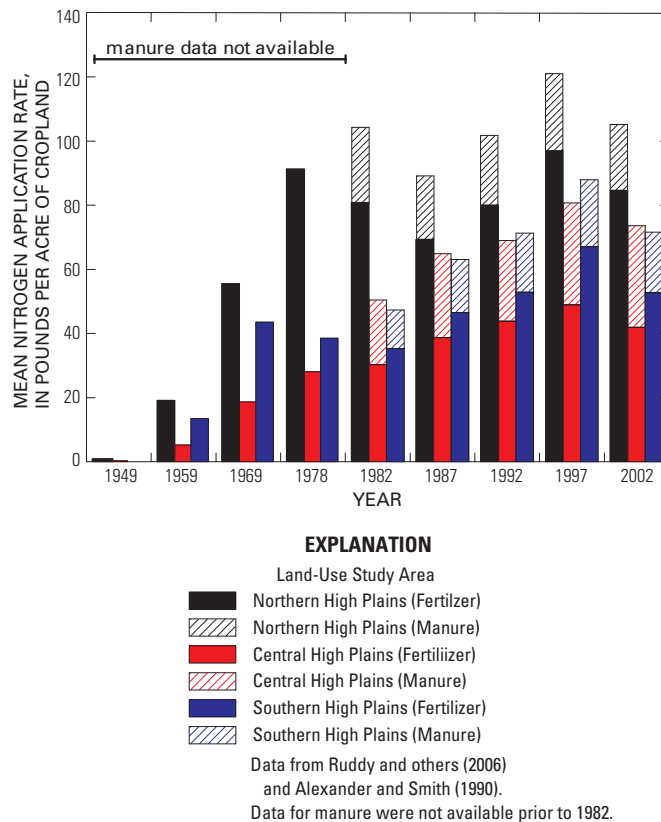


Figure 25. Fertilizer and manure (as nitrogen) application rates in the High Plains counties containing agricultural land-use study wells for the years 1949 to 2002, normalized to the total cropland acreage in the counties.

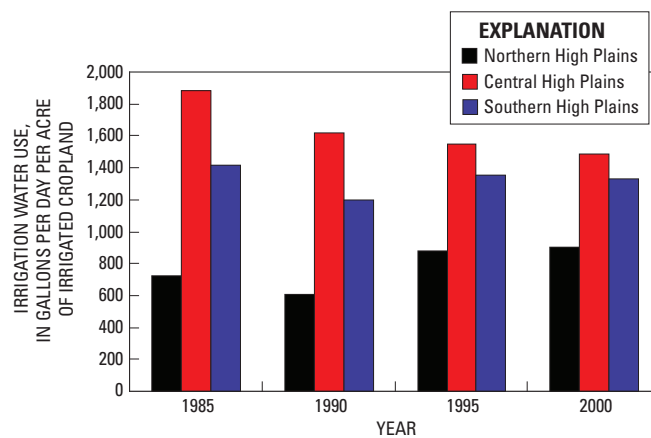


Figure 26. Irrigation water use per acre of irrigated cropland in the High Plains counties containing agricultural land-use study wells for the years 1985, 1990, 1995, and 2000. Data from the U.S. Geological Survey (variously dated) and from the U.S. Department of Agriculture (1999, 2002).

Table 7. Ten most frequently applied pesticides in the High Plains counties containing agricultural land-use study wells.

[Pesticide application rates on crops were estimated from Gianessi and Marcelli (2000) and county-level information on harvested crops in the 1997 Census of Agriculture (U.S. Department of Agriculture, 1999); lb/acre, pound per acre; a.i., active ingredient]

Northern High Plains land-use study area		Central High Plains land-use study area		Southern High Plains land-use study area	
Pesticide	Average amount applied to cropland (lb/acre of a.i.)	Pesticide	Average amount applied to cropland (lb/acre of a.i.)	Pesticide	Average amount applied to cropland (lb/acre of a.i.)
Atrazine	0.46	Atrazine	0.27	Trifluralin	0.17
Metolachlor	.44	Metolachlor	.13	Malathion	.09
Acetochlor	.18	2,4-D ¹	.12	2,4-D ¹	.09
Glyphosate ¹	.18	Glyphosate ¹	.08	Atrazine	.08
Alachlor	.08	Alachlor	.03	Pendimethalin	.07
Cyanazine	.06	Butylate	.02	Sodium chlorate ¹	.06
Pendimethalin	.06	Dicamba ¹	.02	Metolachlor	.05
2,4-D ¹	.06	Acetochlor	.02	Ethephon ¹	.05
Terbufos	.05	Carbofuran	.01	Glyphosate ¹	.04
Carbofuran	.05	Cyanazine	.01	Tribufos ¹	.03
TOTAL	1.62	TOTAL	.71	TOTAL	.73

¹Not analyzed in samples collected as part of this study.

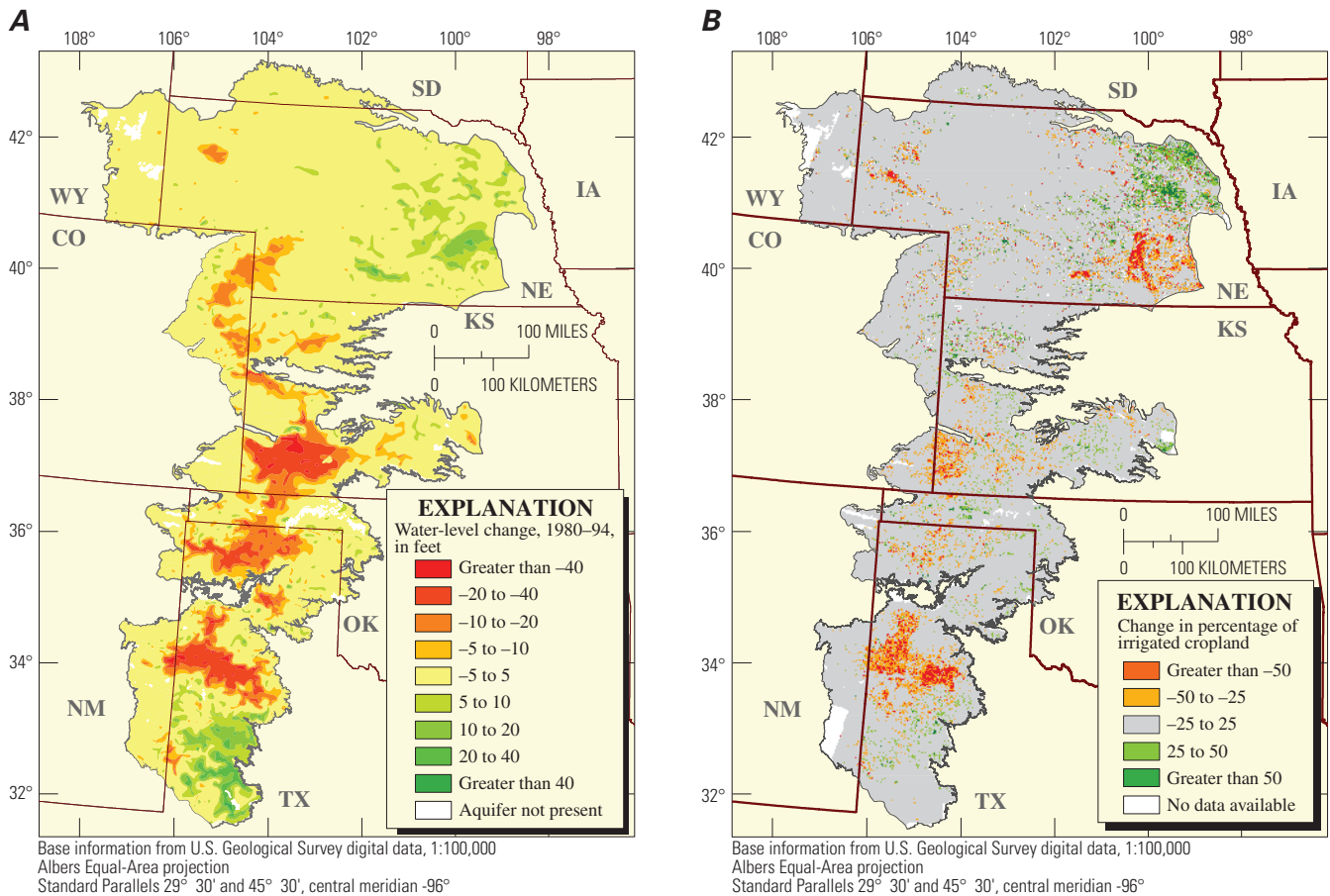


Figure 27. Water-level changes and change in percentage of irrigated cropland from 1980 to 1994 (Qi and others, 2002a).

increased efficiency of irrigation systems has enabled the development of more water-intensive crops to be grown on more irrigated acres. Thus, irrigated agriculture was occurring over more and different lands with about the same amount of water use.

Chemical Storage in the Unsaturated Zone

Elevated concentrations of dissolved solids in recharge beneath irrigated cropland could be derived from agricultural fertilizers and soil amendments containing minerals and trace elements that, when applied at land surface, can dissolve and move downward to the water table. Furthermore, oxidation of reduced nitrogen fertilizer produces protons that may react with soil or aquifer minerals to further increase the concentration of dissolved solids in ground water (Böhlke, 2002). Chloride concentration profiles measured at the unsaturated-zone sites in the SHP illustrate one example of how the application of agricultural chemicals at the land surface has increased the mass of dissolved solids moving to the water table (fig. 28). The data in figure 28A show chloride concentrations in sediment and ground water beneath irrigated cotton that was not amended with potassium chloride, and the data in figure 28B show chloride concentrations beneath irrigated cotton that was amended with potassium chloride. The subsoil chloride mass at the site in figure 28B is about 2.5 times larger than the mass at the site in figure 28A. Those data indicate that application of agricultural chemicals at the land surface can increase the salt load moving to the water table.

Not all elevated concentrations of subsoil chloride at the unsaturated-zone sites were from agricultural sources. For example, subsoil chloride and tritium data from one of the NHP irrigated sites show that a large chloride peak was located below the tritium mass that represented recent irrigation return flow (fig. 29). Because of its position in the unsaturated zone relative to irrigation return flow, the chloride peak is interpreted to represent natural chloride that was displaced downward by irrigation return flow. The occurrence of natural subsoil salt deposits in the High Plains, including perchlorate salts, has been previously reported (Scanlon and Goldsmith, 1997; McMahon and others, 2003; Walvoord and others, 2003; Scanlon and others, 2005; Rajagopalan and others, 2006). Mobilization of natural subsoil salt deposits by irrigation return flow also has been previously proposed (Stonestrom and others, 2003; Scanlon and others, 2005; McMahon and others, 2006; Rajagopalan and others, 2006). The data in figure 29 support that interpretation and indicate that about 80 percent of the subsoil chloride mass beneath that irrigated field may be from natural sources.

Natural subsoil chloride deposits in the High Plains probably were derived from long-term evaporative concentration of chloride in atmospheric deposition near the base of the root zone in rangeland settings, a process that is dependent on climate, vegetation, topography, and soil type. There was a positive correlation between subsoil chloride mass and mean

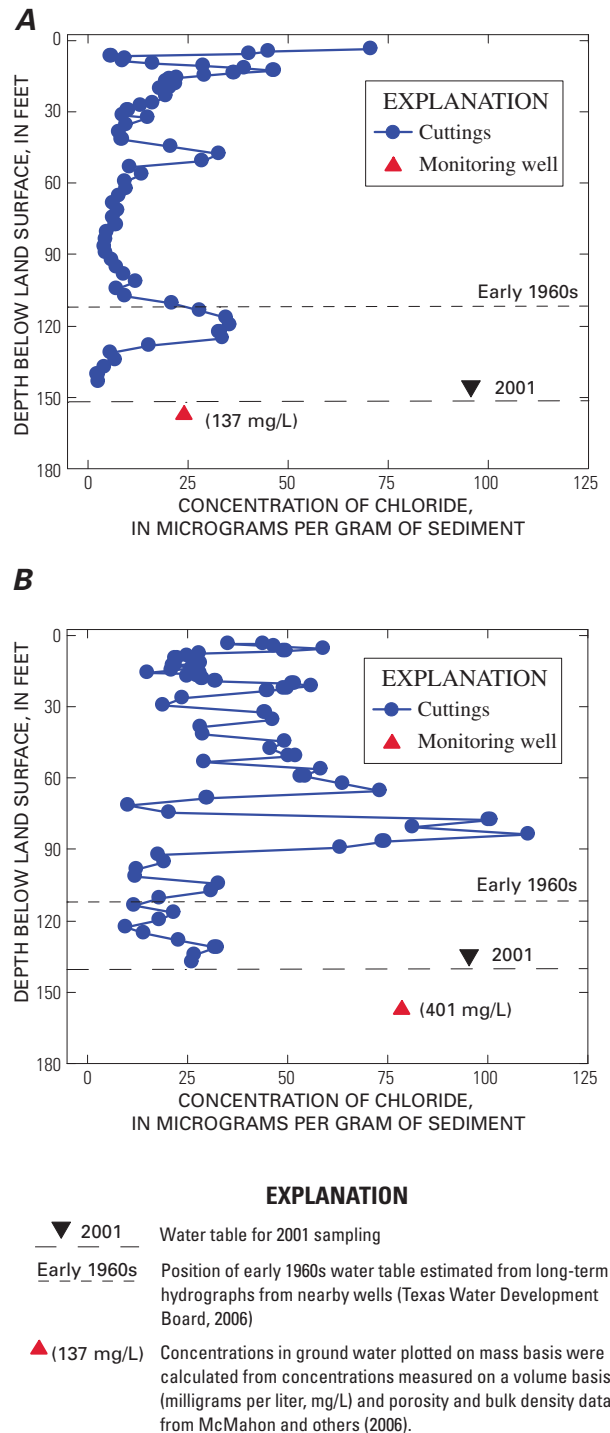


Figure 28. Concentrations of chloride in unsaturated-zone sediment and in ground water from irrigated cotton sites in the southern High Plains that (A) were not and (B) were amended with potassium chloride.

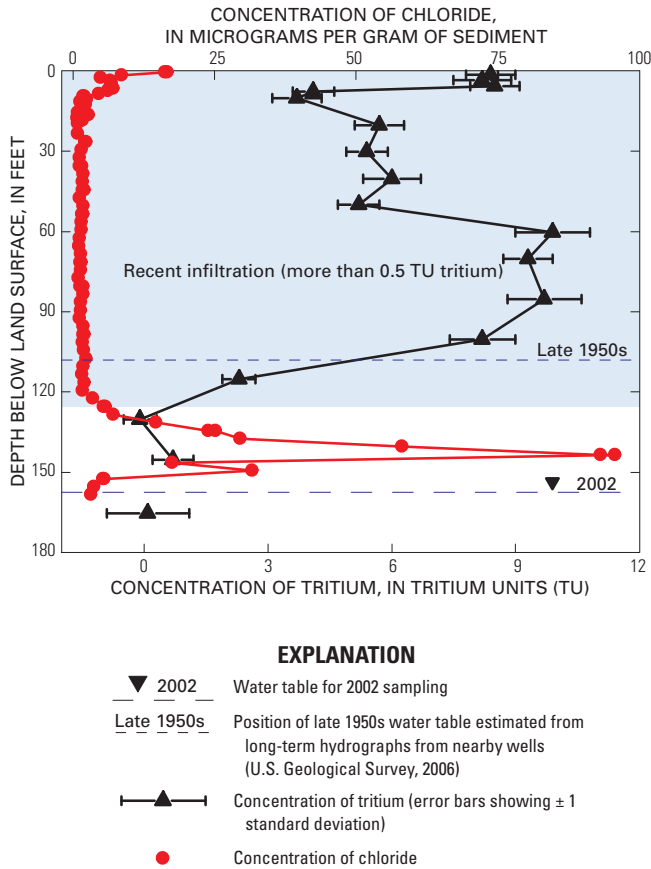


Figure 29. Concentrations of chloride and tritium in unsaturated-zone sediment beneath irrigated corn in the northern High Plains.

annual air temperature and an inverse correlation between unsaturated-zone water flux and mean annual air temperature among the three rangeland unsaturated-zone sites (fig. 30). Warmer air temperatures tend to increase evapotranspiration and reduce recharge, both of which could result in the accumulation of atmospheric chloride in the unsaturated zone. The increase in rangeland chloride mass from north to south implies that conversion of rangeland to irrigated cropland could result in larger ground-water chloride concentrations in the SHP aquifer than in the NHP aquifer if that chloride was transported to the water table by irrigation return flow. Water-potential data from the unsaturated zone beneath rangeland and irrigated cotton in the SHP show that application of irrigation water at the land surface can reverse the direction of water movement in the unsaturated zone from predominantly upward (rangeland site) to predominantly downward (irrigated site) (fig. 31), a process that could result in the downward movement of natural subsoil salt deposits. Chloride concentrations in water samples from the SHP land-use study wells were significantly ($p < 0.001$) larger than those from the NHP wells (table 6), but relating those concentrations to the chemistry of the overlying unsaturated zone is complicated by long

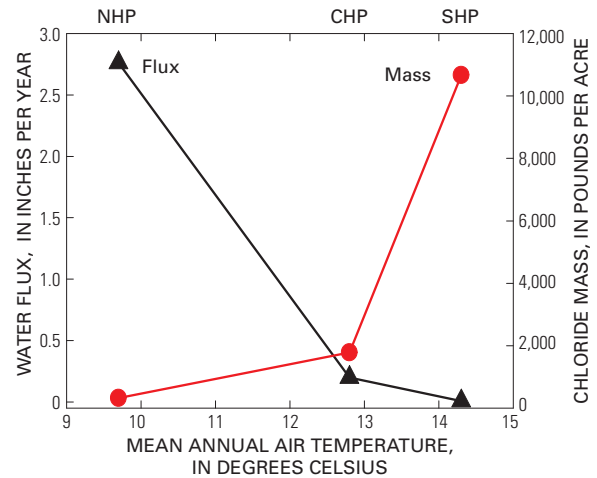


Figure 30. Chloride mass and water flux in the unsaturated zone beneath rangeland as a function of mean annual air temperature (1971–2000). Temperature data are from weather stations in Imperial, Nebraska; Elkhart, Kansas; and Muleshoe National Wildlife Refuge, Texas (High Plains Regional Climate Center, <http://www.hprcc.unl.edu/>, 2007; Southern Regional Climate Center, <http://www.srcc.lsu.edu/>, 2007).

chemical transit times through the unsaturated zone (discussed later in this chapter), chloride contributions to ground water from upgradient recharge areas, and possible chloride sources in underlying bedrock (Nativ, 1988; McMahon and others, 2004b).

Large subsoil nitrate deposits from agricultural and natural sources also occurred in the High Plains (Boyce and others, 1976; McMahon and others, 2003; Walvoord and others, 2003; McMahon and others, 2006). Figure 32 shows nitrate concentrations in unsaturated-zone sediment beneath rangeland and irrigated corn at the NHP unsaturated-zone sites. About 25 times more nitrate mass was stored in the subsoil at the irrigated site than was stored at the rangeland site, which is consistent with the much larger N application rate at the irrigated site compared to the rangeland site (McMahon and others, 2006). As a result, more nitrate was likely to be transported to the water table at the irrigated site than at the rangeland site, as indicated by nitrate concentrations in water at the water table at those two sites (fig. 32).

These findings are particularly relevant in light of the current (2007) interest in the production of ethanol from corn. The increased demand for corn has resulted in an increase in the acreage of U.S. farmland planted in corn (U.S. Department of Agriculture, 2007). The application of nitrogen and water to corn in the High Plains also apparently stimulated nitrous oxide gas production in the unsaturated zone. Nitrous oxide is of environmental concern because it acts both as a greenhouse gas and as an agent in the destruction of stratospheric ozone (Cicerone, 1987). Its concentration has been increasing in the

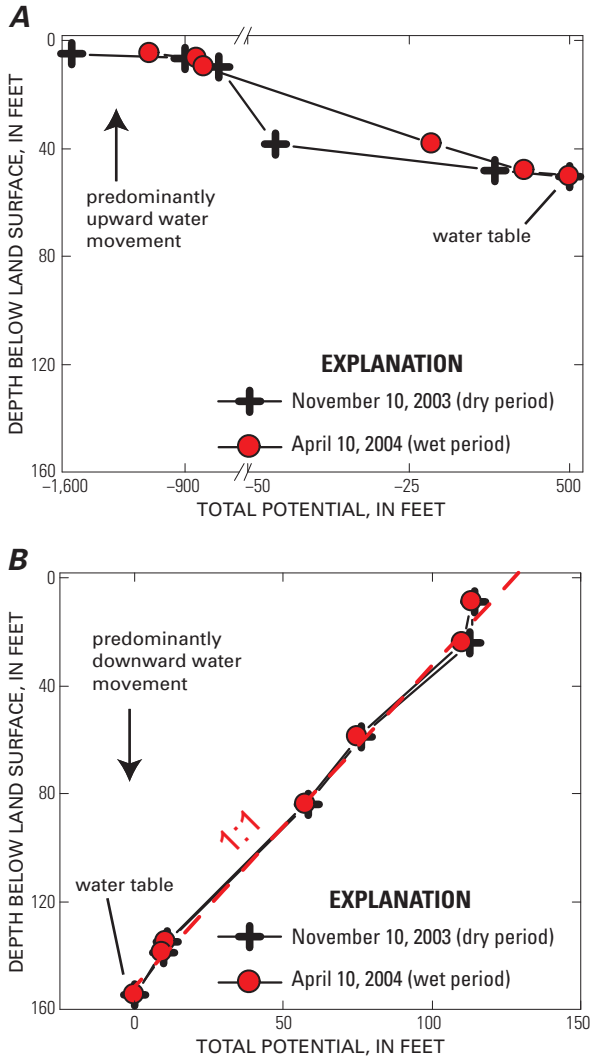
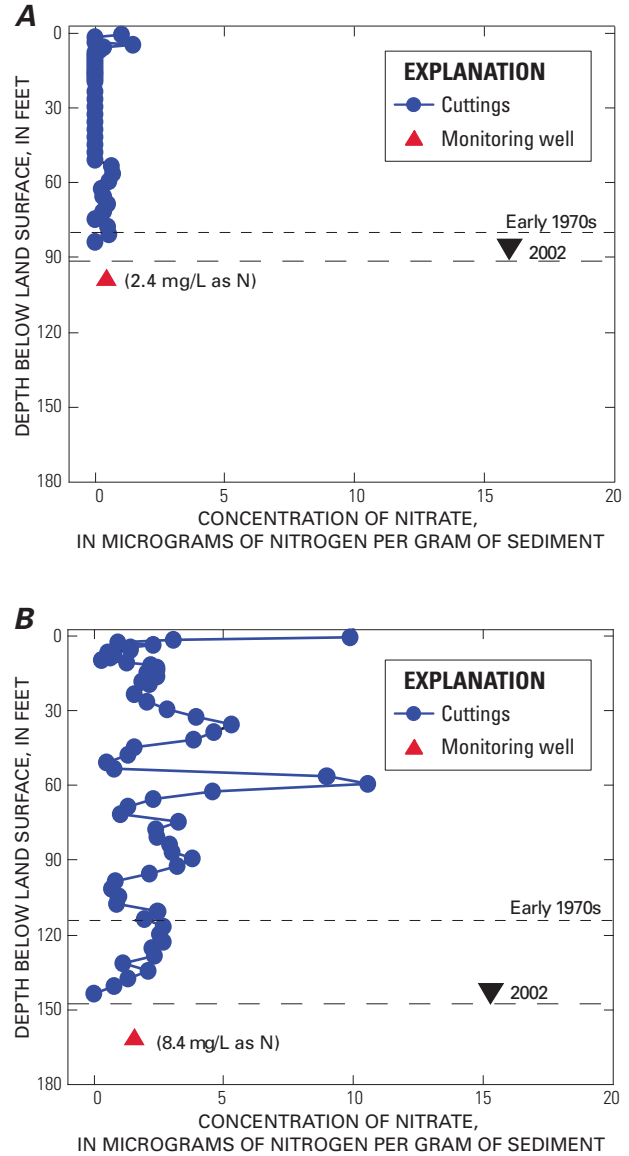


Figure 31. Profiles of total (matric plus gravimetric) potential measured on November 10, 2003, and April 10, 2004, in the unsaturated zone beneath (A) rangeland and (B) irrigated cotton in the southern High Plains. The dashed line with 1:1 slope represents a gradient of one, consistent with gravity-driven flow below the root zone. Note the break in the x-axis scale at the SHP rangeland site.



EXPLANATION

- ▼ 2002 Water table for 2002 sampling
- Early_1970s Position of early 1970s water table estimated from long-term hydrographs from nearby wells (U.S Geological Survey, 2006)
- ▲ (24 mg/L as N) Concentrations in ground water plotted on mass basis were calculated from concentrations measured on a volume basis (milligrams per liter as nitrogen, mg/L as N) and porosity and bulk density data from McMahon and others (2006).

Figure 32. Concentrations of nitrate in unsaturated-zone sediment and in ground water beneath (A) rangeland and (B) irrigated-corn sites in the northern High Plains.

atmosphere by about 0.24 percent/year for the last 25 years or so. Fluxes of nitrous oxide to the atmosphere from the rangeland sites ranged from near 0 to about 0.2 pound N_2O -N/acre/year (0 to 0.2 kg N_2O -N/hectare/year) (Weeks and McMahon, 2007). In contrast, nitrous oxide fluxes from the NHP irrigated corn sites ranged from about 2 to 5 pounds N_2O -N/acre/year (2 to 6 kg N_2O -N/hectare/year), about 25 times larger than the fluxes from rangeland (Weeks and McMahon, 2007).

Figure 33 shows nitrate concentrations and $\delta^{15}N$ values for nitrate in unsaturated-zone sediment beneath rangeland and irrigated corn at CHP unsaturated-zone sites. The downward movement of some nitrate peaks at irrigated sites relative to control sites in arid and semiarid regions has been interpreted as mobilization of naturally accumulated nitrate by irrigation return flow (Stonestrom and others, 2003; McMahon and others, 2006). The largest nitrate peak at the irrigated-corn site moved downward by about 35 ft relative to the peak at the rangeland site. Values of $\delta^{15}N$ associated with the peak nitrate concentrations at both sites were virtually indistinguishable from each other and within the range of values associated with natural soil N. In contrast, $\delta^{15}N$ values for nitrate above the peak at the irrigated site ranged from -0.5 to 0.2 per mil and are similar to values for N in fertilizer and in nitrogen-fixing plants. The data indicate that irrigation return flow did mobilize natural nitrate beneath the corn site. If that interpretation is correct, then about 60 percent of the subsoil nitrate mass at the irrigated corn site was from natural sources.

Despite the apparent mobilization of natural nitrate in the unsaturated zone by irrigation return flow, other isotopic data indicate that large concentrations of natural nitrate probably have not reached the water table yet. Stable isotope values for nitrate in recent recharge in the CHP and SHP land-use study areas were, for the most part, distinctly different from those of paleorecharge when viewed in the overall regional context (fig. 21). In each of those regions, nitrate in recent recharge with the largest concentrations apparently was derived primarily from sources other than natural N. The most likely sources are fertilizer and animal waste (yielding nitrate with relatively low and high $\delta^{15}N$ values, respectively) applied to those fields during their modern irrigation history. The data show that natural subsoil nitrate reservoirs, if originally present beneath those irrigated fields, apparently have not reached the water table yet or may have only a transient effect on ground-water quality when mobilized by irrigation return flow. In the NHP, there was considerable overlap in the $\delta^{15}N$ values for nitrate in paleorecharge and modern recharge (fig. 21). As a result, contributions of natural nitrate to large ground-water nitrate concentrations cannot be ruled out on the basis of those N isotope data.

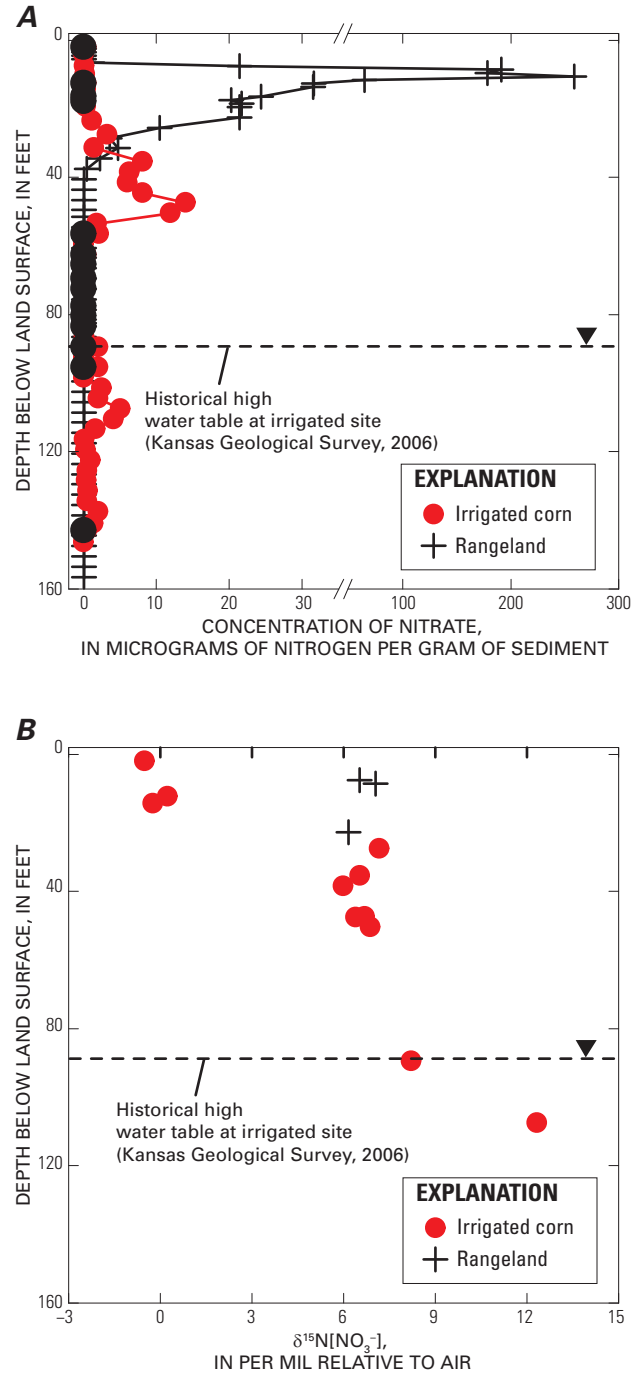


Figure 33. (A) Concentrations of nitrate and (B) the nitrogen isotopic composition of nitrate in unsaturated-zone sediment beneath rangeland and irrigated-corn sites in the central High Plains.

Chemical Transit Times in the Unsaturated Zone

One reason for the apparent absence of large concentrations of natural nitrate in ground water beneath irrigated cropland in the High Plains, despite its apparent mobilization by irrigation return flow in some areas, may be long chemical transit times through the unsaturated zone. This may also explain the general north-to-south decrease in the frequency of pesticide detections in ground water in the High Plains (figs. 22 and 23). In both cases, the chemicals may still be moving to the water table. Advective chemical transit times through the unsaturated zone at the unsaturated-zone sites were calculated using equation 1 and water-flux estimates that were based on either chloride mass balance or tritium profiles (McMahon and others, 2006):

$$t = \frac{\theta \times z}{q} \quad (1)$$

where t is the advective chemical transit time (years), θ is the depth-weighted average volumetric water content in the unsaturated zone, z is the depth to the water table (feet), and q is water flux in the unsaturated zone (feet/year). Assump-

tions associated with the use of equation 1 include that flow was one-dimensional and vertically downward, that θ was at steady state, and that chemical movement was conservative (McMahon and others, 2006). Chemical transit times through the unsaturated zone beneath irrigated cropland ranged from 49 to 373 years (table 8). Lateral spreading of water in the unsaturated zone would result in even longer transit times. Chemical transit times beneath irrigated corn (median = 84 years) were significantly shorter ($p < 0.01$) than the transit times beneath irrigated cotton (median = 245 years), which is consistent with greater pesticide detection frequencies in the NHP and CHP compared to the SHP (figs. 22 and 23). This difference is largely a reflection of the larger water fluxes beneath the irrigated corn sites rather than a thinner unsaturated zone (table 8). Although the chemical transit times are only approximations, they exceeded the irrigation period at all of the study sites (28 to 46 years). Those long transit times imply that agricultural chemicals should not have reached the water table. Indeed, this appears to have been the case at some of the unsaturated-zone sites, where elevated concentrations of tritium, chloride, nitrate, or pesticide compounds in the unsaturated zone did not appear to have reached the water

Table 8. Advective chemical transit times to the water table at the unsaturated-zone monitoring sites

[Water flux estimates based on tritium profiles at all sites except the rangeland sites in Kansas and Texas. The chloride mass-balance approach was used at those sites. Transit times at the Kansas and Texas rangeland sites represent chloride mass-balance ages]

Parameter	Northern High Plains			Central High Plains			Southern High Plains		
	Rangeland, Chase County, Nebraska	Irrigated corn, Perkins County, Nebraska	Irrigated corn, Yuma County, Colorado	Rangeland, Morton County, Kansas	Irrigated corn, Finney County, Kansas	Irrigated corn, Finney County, Kansas	Rangeland, Bailey County, Texas	Irrigated cotton, Cochran County, Texas	Irrigated cotton, Cochran County, Texas
Water flux (foot/year)	0.23	0.33	0.36	0.016	0.18	0.13	0.0007	0.10	0.056
Depth to water table (feet)	82 to 92	110 to 146	107 to 156	164	91 to 150	56 to 150	49	103 to 147	112 to 138
Depth-weighted volumetric water content	0.240	0.253	0.258	0.092	0.101	0.113	0.148	0.128	0.151
Advective chemical transit time (years)	86 to 96	84 to 112	77 to 112	2,000	51 to 84	49 to 130	10,500	132 to 188	302 to 373

table (fig. 29 – chloride and tritium). Ground water at the other irrigated sites contained some combination of elevated tritium, chloride, nitrate, and pesticide compound concentrations (McMahon and others, 2006). The discordant finding of long chemical transit times beneath irrigated cropland and the presence of agrichemicals at the water table is not readily explained by a simple model of matrix flow through the unsaturated zone, and it implies that fast and slow paths for water and chemical movement were present in the unsaturated zone. This concept is discussed in more detail later in this chapter.

Climate Variability

Hydrologic responses to interannual and interdecadal climate variability have important implications for ground-water resource sustainability, yet are poorly documented and not well understood in most regional aquifer systems. The influence of interannual to interdecadal climate variability on ground-water levels, deep infiltration events, and downward displacement of subsoil chemical reservoirs in the High Plains was investigated by Gurdak and others (2007a). Variability in precipitation and ground-water-level time-series data was partly coincident with known climate cycles, such as the Pacific Decadal Oscillation (PDO) (10- to 25-year recurrence interval), North American Monsoon System (NAMS) (6 to 10 years), and the El Niño/Southern Oscillation (ENSO) (2 to 6 years). Most of the variance in the precipitation time-series was attributed to >PDO (greater than 25 years) and PDO periods, capturing 51 to 64 percent and 23 to 78 percent of the variance, respectively (Gurdak and others, 2007a). Those findings indicate the importance of lower-frequency climatic forcings, with lesser controls by NAMS and ENSO, on precipitation variability across the High Plains. The strength of correlation between >PDO and PDO periods and precipitation variability is consistent with the findings from McCabe and others (2004) that indicate that most of the variance in drought frequency across the conterminous United States is attributed to lower frequency climatic forcings.

Although water-level fluctuations in the High Plains aquifer are dominated by seasonal irrigation pumping, climatic variability within ground-water level hydrographs also was identified. PDO-like variations in ground-water levels accounted for most of the total climate-related variance at the NHP (67 to 87 percent) and SHP (94 to 96 percent) sites, while accounting for only 23 to 35 percent of the variance at the CHP sites, similar to results for the precipitation time-series. The precipitation and water-level time-series were lag correlated, which could be an indication of the importance of interannual to interdecadal climate variability on recharge in the High Plains (Gurdak and others, 2007a).

Even though lower-frequency climate forcings such as PDO may exert major controls on unsaturated-zone water fluxes and aquifer recharge in the High Plains, annual climate variability also can be important. Total potential profiles

measured at one of the SHP unsaturated-zone sites in 2001–05 indicate that a relatively large wetting front moved to a depth of 24 ft below land surface during an unusually wet period in 2004 (fig. 34). Such wetting-front movement had not been observed at the 24-ft depth prior to that time. The propagation of those wetting fronts indicates predominantly pistonlike, or matrix flow, which is one possible mechanism for chemical movement through the unsaturated zone to the water table. The onset of deep infiltration in SHP unsaturated zones appears to have coincided with particularly large total monthly precipitation from June to December 2004, especially the near record-setting precipitation during November 2004. Total precipitation recorded at the rangeland unsaturated-zone site was 350 percent of average for that month. The National Oceanic and Atmospheric Administration (2006) reported similar record precipitation across much of the SHP for November 2004: Lubbock, Tex., 937 percent of average; and Amarillo, Tex., 597 percent of average. Wetting fronts such as those observed at the SHP irrigated site in figure 34 could

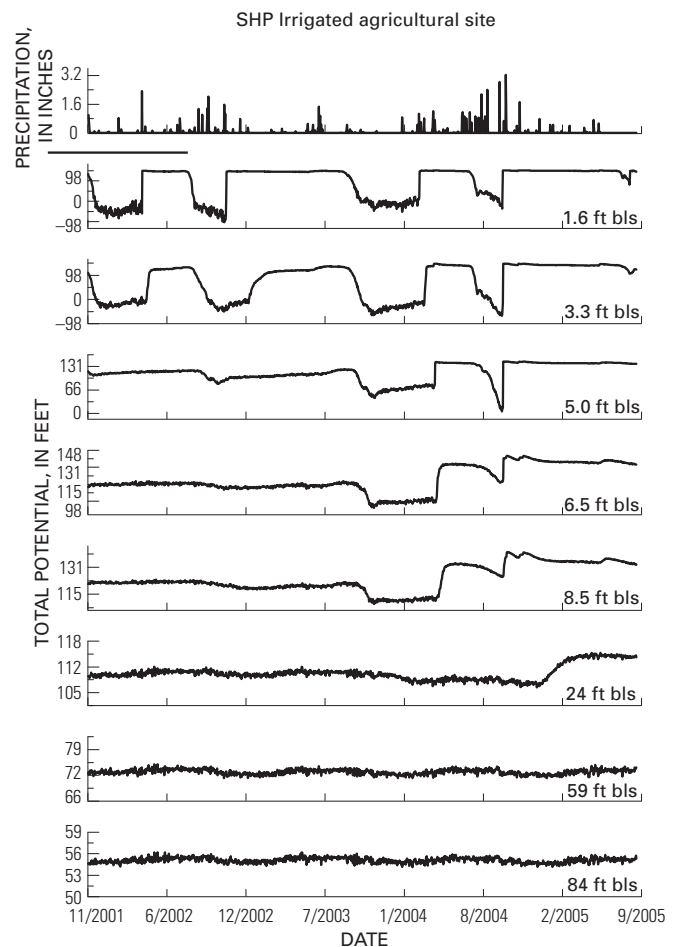


Figure 34. Daily precipitation and total (matric plus gravimetric) potential for selected depths below land surface (bls) as a function of time beneath irrigated cotton in the southern High Plains.

be important for moving chemicals in the shallow subsurface into deeper parts of the unsaturated zone, where hydraulic gradients are consistently downward to the water table. The study of Gurdak and others (2007a) illustrates the importance of longer frequency climatic variations on long-term groundwater-level fluctuations and aquifer sustainability but also implies that shorter frequency climatic events could influence water and chemical fluxes in the unsaturated zone.

Conceptual Models for Chemical Transport from Land Surface to the Water Table

Conceptual models for chemical transport from land surface to the water table in the High Plains were developed on the basis of data from the land-use and unsaturated-zone studies and the processes discussed in the previous section of the chapter (fig. 35). Nitrate transport is represented in the models because large reservoirs of nitrate exist in the subsoil beneath rangeland and irrigated cropland and because nitrate is perhaps the most common contaminant in High Plains ground water (Litke, 2001; Pope and others, 2001; Bruce and others, 2003; Stanton and Fahlquist, 2006). The models highlight the importance of fast and slow paths for nitrate transport in the unsaturated zone. Fast paths are most likely to occur beneath topographic depressions in the land surface in which surface runoff from irrigation or precipitation would collect. Playas in the SHP are a good example of this geomorphic feature (Wood and Sanford, 1995; Scanlon and Goldsmith, 1997). Fast paths also could occur through wellbore leakage and through cracks, burrows, fissures, and other soil structural features. Slow paths may occur in fine-grained sediments or beneath flat terrain, and possibly in other environments, with evapotranspiration further restricting water movement in both settings. Superimposed on these models is annual, interannual, and interdecadal climate variability that could alter precipitation, evapotranspiration, runoff, and recharge patterns in both settings.

Fast paths beneath rangeland would result in relatively small accumulations of nitrate mass in the subsoil and small concentrations of nitrate in ground water because periodic flushing would prevent the buildup of large concentrations of nitrate in the unsaturated zone and because of small N inputs at the land surface. The rangeland unsaturated-zone site in the NHP is considered to be an example of this component of the conceptual model (fig. 32A). Slow paths beneath rangeland would result in large accumulations of nitrate mass in the subsoil, in part because of evaporative concentration near the base of the root zone over long periods of time (Walvoord and others, 2003). The rangeland unsaturated-zone site in the CHP is considered to be an example of this component of the conceptual model (fig. 33). Slow paths beneath rangeland would likely result in the smallest ground-water nitrate concentrations because of the lack of recharge in that setting

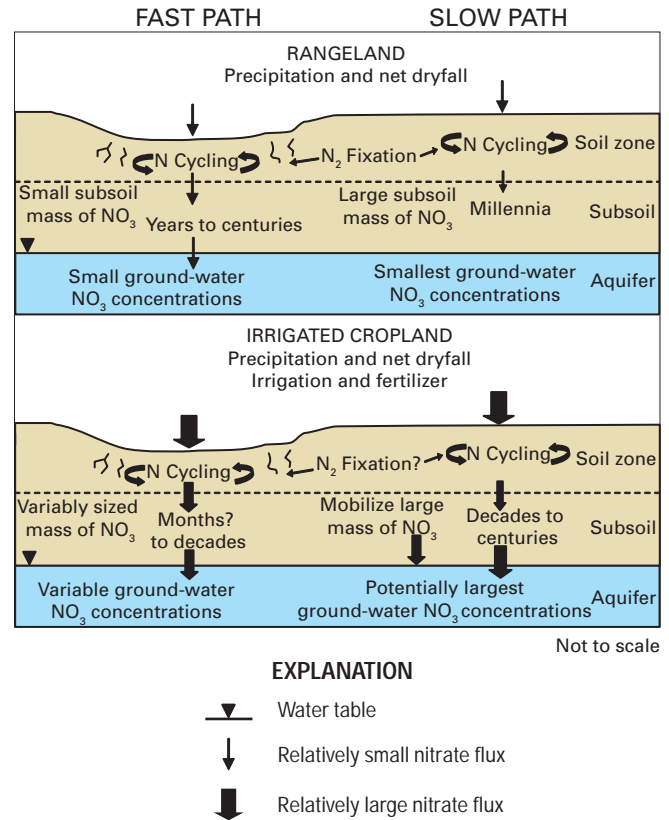


Figure 35. Conceptual models for nitrate (NO_3^-) transport from land surface to the water table beneath rangeland and irrigated cropland in the High Plains.

(see the upward total potential gradient for the rangeland site in fig. 31A). Fast paths beneath irrigated cropland apparently were not represented among the unsaturated-zone sites, but they could result in subsoil nitrate mass and ground-water nitrate concentrations of variable size, depending on N application rates. Those pathways for chemical transport may be responsible for the occurrence of many ground-water contaminants that were detected in the land-use and unsaturated-zone studies. In contrast, slow paths beneath irrigated cropland, which the data from some of the unsaturated-zone sites may represent, could mobilize nitrate mass from agricultural and natural sources (see fig. 33 for an example) and possibly produce the largest ground-water nitrate concentrations when those nitrate reservoirs eventually reach the water table. The conceptual models presented in figure 35 are related to the Wood and Sanford (1995) and Scanlon and Goldsmith (1997) models for recharge to the SHP aquifer and to previous models for preferential chemical transport in the unsaturated zone (as summarized by Nieber, 2001), but they extend the concepts of Wood and Sanford (1995) and Scanlon and Goldsmith (1997) to other areas of the High Plains, and they extend the preferen-

tial transport concepts to thick unsaturated zones in the High Plains.

Areas of the High Plains containing fast paths for chemical transport to the water table may be a small part of the total High Plains area. For example, Wood and Sanford (1995) estimated that about 50 percent of the recharge to the SHP aquifer occurred through playa basin floors that occupied about 6 percent of the total land area. Presumably, a much larger fraction of the land area was dominated by slow paths. This study indicates that substantial chloride and nitrate mass resided in the subsoil beneath some rangeland and cropland dominated by slow paths in the High Plains. Implications of those findings with respect to water quality in the aquifer are important because they indicate that the amount of chemical mass reaching the aquifer could increase with time as chemicals beneath this larger area reach the water table because of ongoing irrigation, conversion of rangeland to cropland, or climate change. Furthermore, long transit times in the unsaturated zone may delay future improvements in water quality that would result from implementation of best management practices.

Extrapolation of Results to Unmonitored Areas of the Aquifer

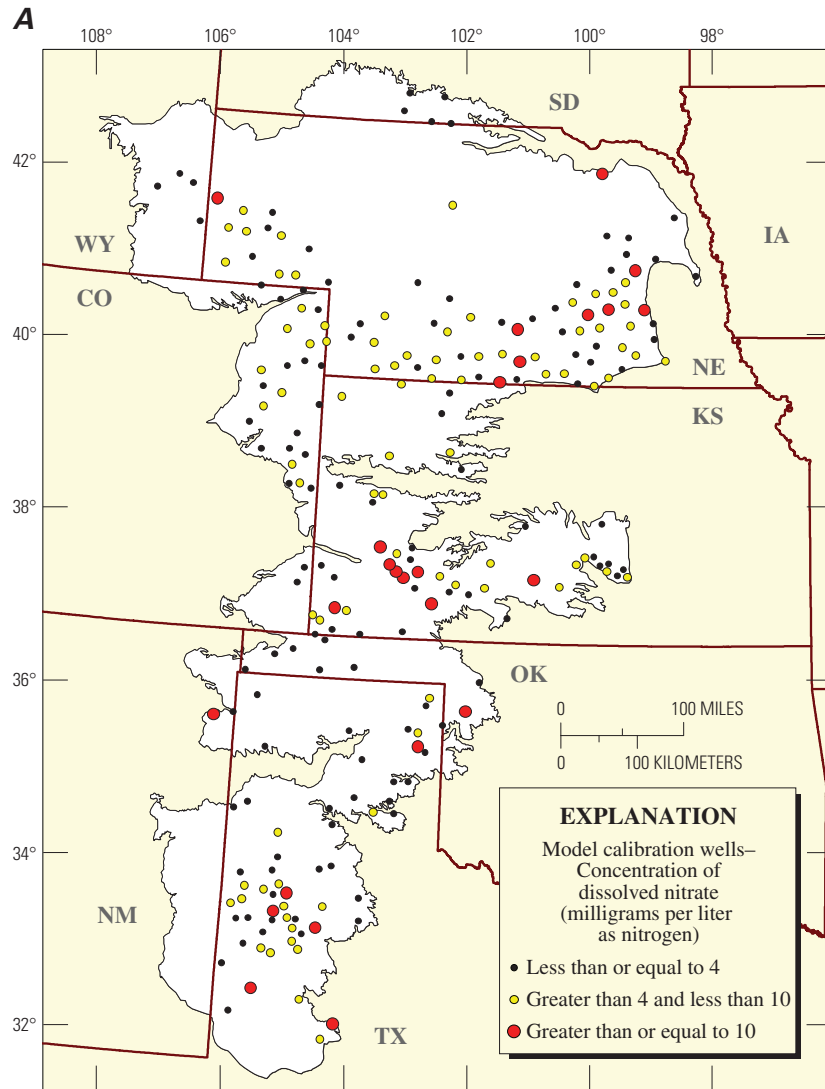
Measured concentrations of nitrate in ground water were used as a basis for extrapolating and predicting the occurrence of nitrate concentrations greater than 4 mg/L as N in recently recharged ground water in unmonitored areas of the aquifer. As discussed previously in this chapter, 4 mg/L as N is considered to be the maximum background concentration in the aquifer. Thus, concentrations exceeding 4 mg/L as N would be indicative of aquifer vulnerability to contamination from anthropogenic nitrate. Statistical relations between nitrate concentrations in water from existing well networks and important controlling factors such as percent agricultural land, soil type, soil organic-matter content, depth to water table, and unsaturated-zone lithology were developed using logistic regression models (Gurdak and Qi, 2006). The spatial distributions of those controlling factors are known for the entire High Plains area, thereby allowing for extrapolation of regression-model results to the entire aquifer area.

Details of the study design, data selection, sample analysis, model calibration and validation, and map construction can be found in Gurdak and Qi (2006), Qi and Gurdak (2006), and Gurdak and others (2007a). The general study design and methods are described as follows. Ground-water flow and particle-tracking simulations were run using the program Visual MODFLOW 2.8 (Waterloo Hydrogeologic, 1999) to define depth criteria for selection of wells that intercepted recently recharged ground water and to delineate the shape of the contributing areas for each well. All relevant ancillary data in electronic format were compiled for these wells, which include water-quality, anthropogenic, and hydrogeologic data.

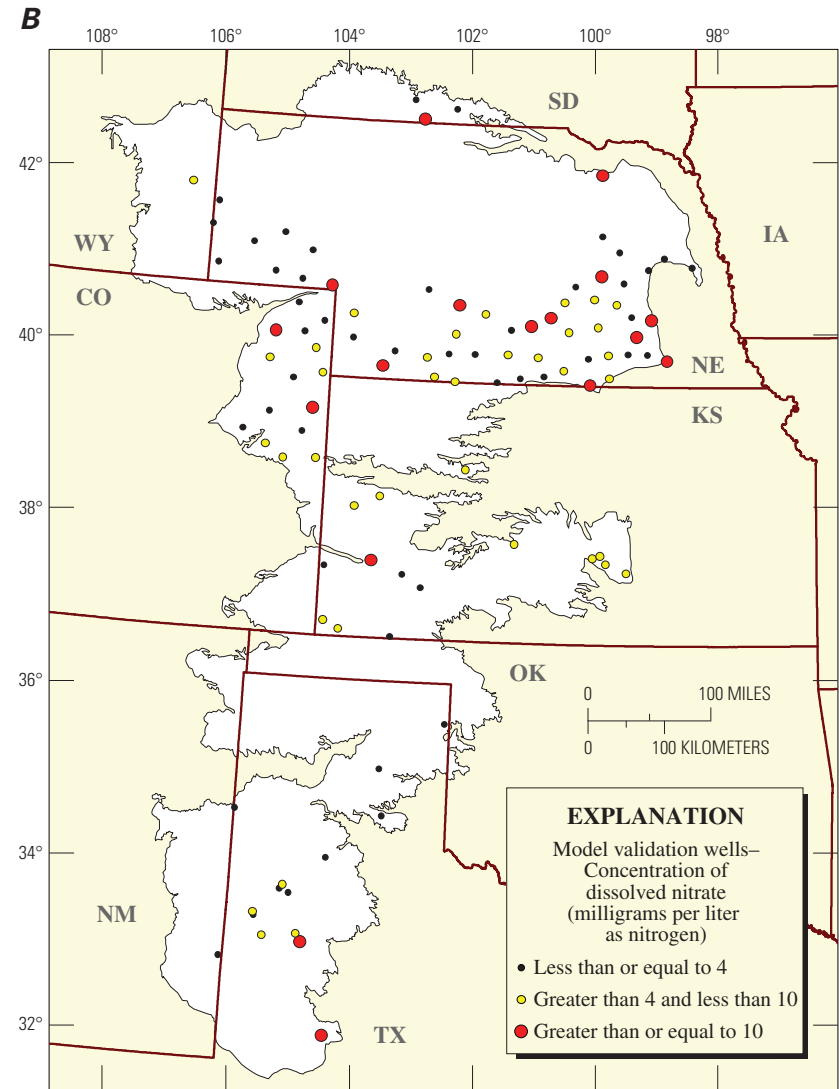
The anthropogenic and hydrogeologic data were available in electronic map format from a variety of sources and were developed specifically for use as explanatory variables during the statistical modeling. Using a geographic information system (GIS) and previously defined contributing areas, anthropogenic and hydrogeologic data were extracted for each well. By using multivariate logistic regression analysis (SAS 8.02) (SAS Institute, 1999), several preliminary multivariate models with various combinations of explanatory variables were constructed and evaluated. The two models (one for the NHP and one for the CHP and SHP) that best predicted the occurrence of nitrate concentrations greater than 4 mg/L as N in recently recharged ground water were selected on the basis of statistical significance, model fit, and predictive ability. Independent sets of nitrate data from recently recharged ground water were used for model calibration and validation (fig. 36). Coefficients of the explanatory variables from the final multivariate models were entered into the GIS, and a map was created using map-algebra techniques showing the probability of detecting nitrate concentrations greater than 4 mg/L as N in recently recharged ground water across the entire High Plains study area (fig. 37).

Results of the final multivariate analysis indicated excellent calibration for both models (r^2 values from 0.891 to 0.910). Explanatory variables included the percentage of nonirrigated agriculture, percentage of irrigated agriculture, organic matter in the soil, depth to the water table, and average percentage of clay in the unsaturated zone. The spatial distributions of those controlling factors are shown in figure 38. Gurdak and Qi (2006) discuss in detail the reasons why those factors appear to control aquifer vulnerability to nitrate contamination. The final multivariate models were validated to evaluate predictive ability. Using the subset of validation wells, predicted probabilities were calculated with the final models and compared to observed detections of nitrate exceeding 4 mg/L as N. The validation shows good predictive ability, with an $r^2 = 0.834$ and negligible systematic bias (Gurdak and Qi, 2006).

According to the vulnerability analysis (fig. 37), most (53 percent) of the aquifer area has less than a 40 percent predicted probability of containing recently recharged water with nitrate concentrations greater than 4 mg/L as N. Those areas are in northwestern and north-central areas of the NHP, the central and southern areas of the CHP, and a band across the north-central part of the SHP. Less agricultural land is present in those areas of the NHP, and relatively thick unsaturated zones may help protect the CHP and SHP aquifer in those areas of relatively low predicted vulnerability. Approximately 21 percent of the study area has relatively high (greater than 60 percent) predicted probabilities of containing recently recharged water with nitrate concentrations greater than 4 mg/L as N. Those areas generally are located in the southwestern, southern, and eastern areas of the NHP, the eastern arm of the CHP, and the central and southern areas of the SHP. Those areas tend to have higher densities of agricultural land and shallower depths to water table. The most vulnerable areas (greater than 80 percent) are scattered across the eastern and



Base information from U.S. Geological Survey digital data, 1:100,000
Albers Equal-Area projection
Standard Parallels 29° 30' and 45° 30', central meridian -96°



Base information from U.S. Geological Survey digital data, 1:100,000
Albers Equal-Area projection
Standard Parallels 29° 30' and 45° 30', central meridian -96°

Figure 36. Nitrate concentrations in water from wells used to calibrate and validate the High Plains nitrate vulnerability models (modified from Gurdak and Qi, 2006). The data are from this study and from Litke (2001).

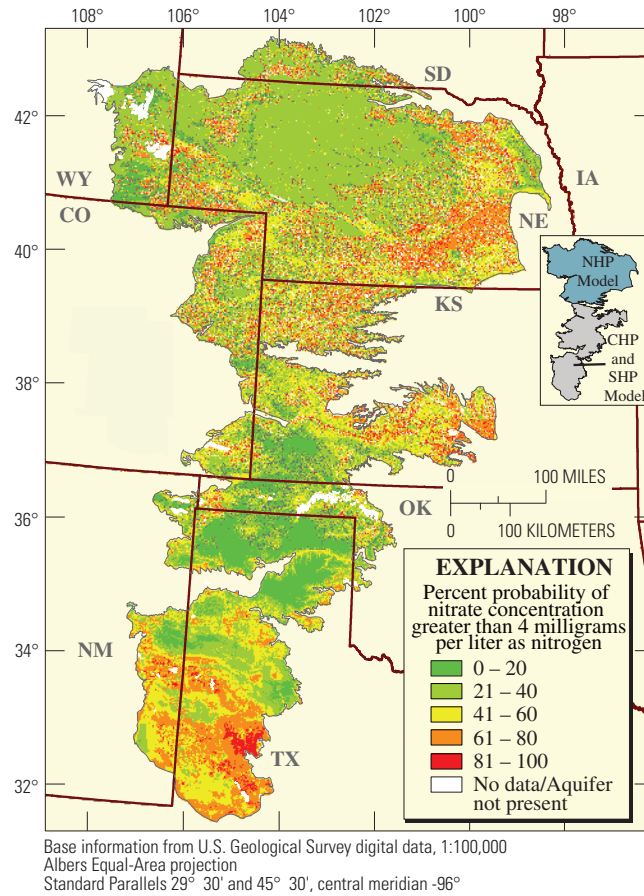


Figure 37. Probability of detecting nitrate concentrations greater than 4 milligrams per liter as nitrogen in recently recharged water in the High Plains aquifer (modified from Gurdak and Qi, 2006).

southern areas of the NHP and the southern areas of the SHP. Those areas generally have high percentages of agricultural land, shallow depths to water, and little organic matter or clay in the unsaturated zone.

Nitrate concentrations in water from the agricultural land-use study wells were compared to the predicted probabilities of elevated nitrate concentrations. Although the models show reasonably good predictive ability ($r^2 = 0.656$), there was a systematic underprediction of the observed percentage of nitrate concentrations greater than 4 mg/L as N. Underprediction by the models may result from the fact

that they do not explicitly incorporate possible preferential flow mechanisms in the unsaturated zone like the fast paths discussed previously in this chapter (fig. 35). Nevertheless, the models do incorporate many of the important factors controlling nitrate concentrations in recently recharged ground water. Thus, the probability map represents a tool for assessing the chemistry of recharge in unmonitored areas of the High Plains. Moreover, output from these types of predictive models can be used to identify potentially vulnerable areas for enhanced monitoring and protection.

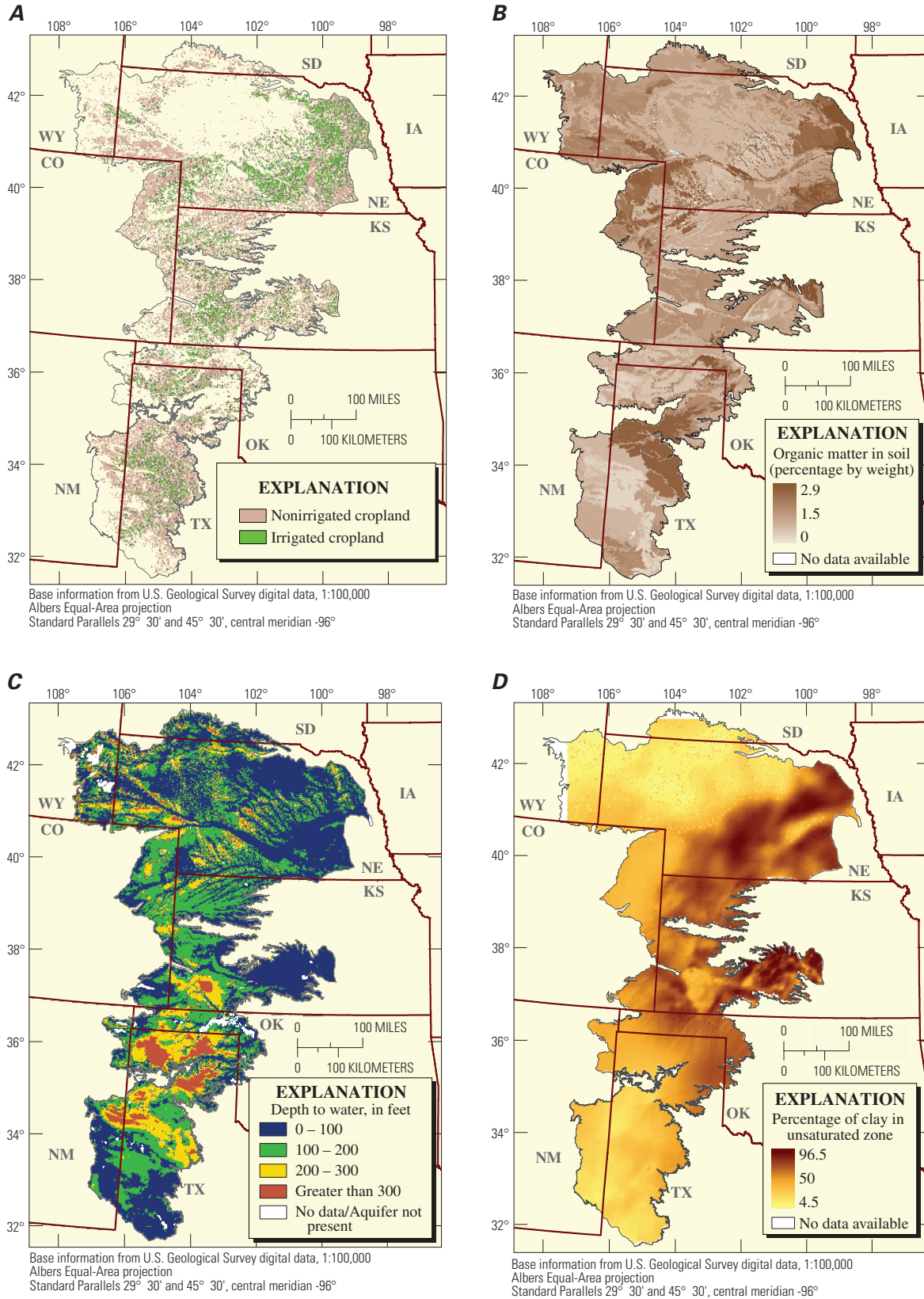


Figure 38. Spatial distribution of factors controlling elevated nitrate concentrations (greater than 4 milligrams per liter as nitrogen) in recently recharged water in the High Plains aquifer—(A) Irrigated and nonirrigated cropland; (B) organic matter in the soil; (C) depth to the water table; (D) percentage of clay in the unsaturated zone (Gurdak and Qi, 2006).