Transport—Linking the Chemistry of Recharge and the Used Resource in the High Plains Aquifer

Chapter 2 of

Water-Quality Assessment of the High Plains Aquifer, 1999–2004

By Peter B. McMahon and John Karl Böhlke

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Contents

Figures

39–41. Maps showing:

42–56. Graphics showing:

Table

Chapter 2. Transport—Linking the Chemistry of Recharge and the Used Resource in the High Plains Aquifer

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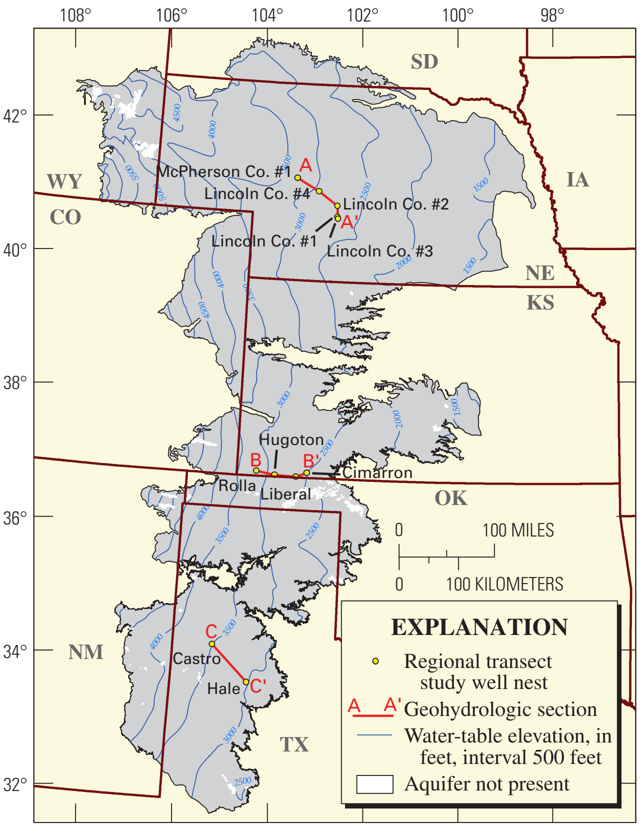
Introduction

In Chapter 1, it was shown that dissolved solids, nitrate, pesticides, and some other chemical constituents were present in relatively large concentrations near the water table in some land-use settings in the High Plains. Such large concentrations could limit the use of that water for human consumption or irrigation. Domestic, public-supply, and irrigation wells in the High Plains aquifer generally are not screened near the water table; therefore, the chemistry of the used resource may result from more than just recharge chemistry. The strength of the connection between the chemistry of recharge and the used resource is controlled by multiple processes, including temporal variability in recharge chemistry, ground-water residence time, mixing of water from different sources, and biogeochemical reactions occurring along flow paths to the wells; yet, those processes have not been documented systematically in the High Plains. In this chapter, data from the regional transect studies are used to examine those and other processes that affect the chemistry of water as it moves along flow paths from recharge areas to points deeper in the aquifer to better understand the connection between the chemistry of recharge and the used resource.



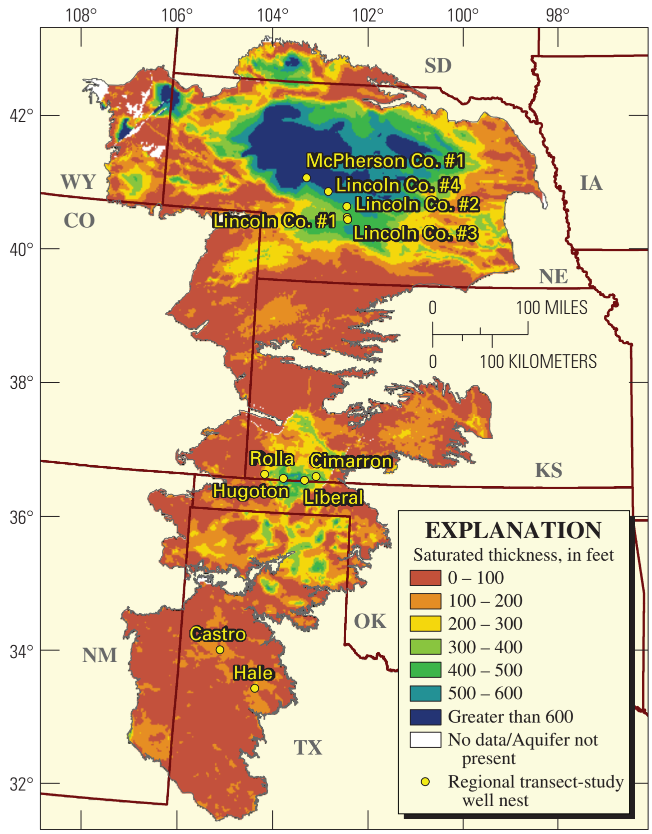
Base information from U.S. Geological Survey digital data, 1:100,000
Albers Equal-Area projection
Standard Parallels 29° 30' and 45° 30', central meridian -96°

Figure 39. Water-table elevations in the High Plains aquifer, 2000, and locations of the regional transect study well nests. (V.L. McGuire, U.S. Geological Survey, written commun., 2002).

Study Design

Regional transects consisting of two to five nested-well sites were established in the NHP, CHP, and SHP. Details of the study design, sample collection, and sample analysis can be found in McMahon and others (2004a, 2004b) and McMahon and others (2007). In general, each transect was oriented parallel to the regional water-table gradient in an area of the aquifer with some of the largest saturated thicknesses (figs. 39 and 40). The transect lengths ranged from about 55 to 70 mi. Saturated thicknesses among the transects increased from south to north from about 0 to 200 ft in the SHP, to 230 to 520 ft in the CHP, to 370 to 750 ft in the NHP. At each nested-well site, two to four short-screen monitoring wells were completed at different depths between the water table and base of the aquifer (fig. 41). Thus, each transect encompassed multiple flow paths along the regional water-table gradient. The deepest wells at the Cimarron (CHP) and Hale (SHP) sites were screened in sediments underlying the aquifer to examine the chemistry of water that might enter the aquifer from underlying geologic units. Construction details for the wells are listed in table 9.

The wells were installed from 1999 to 2003 and the samples were collected from 1999 to 2004. Water samples from the wells were analyzed for field properties, major ions, nutrients, trace elements, pesticides, isotopes (hydrogen, boron, carbon, nitrogen, oxygen, sulfur, strontium), and dissolved



Base information from U.S. Geological Survey digital data, 1:100,000
Albers Equal-Area projection
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Figure 40. Saturated thickness of the High Plains aquifer, 2000, and locations of the regional transect study well nests. (Modified from McGuire and others, 2003).

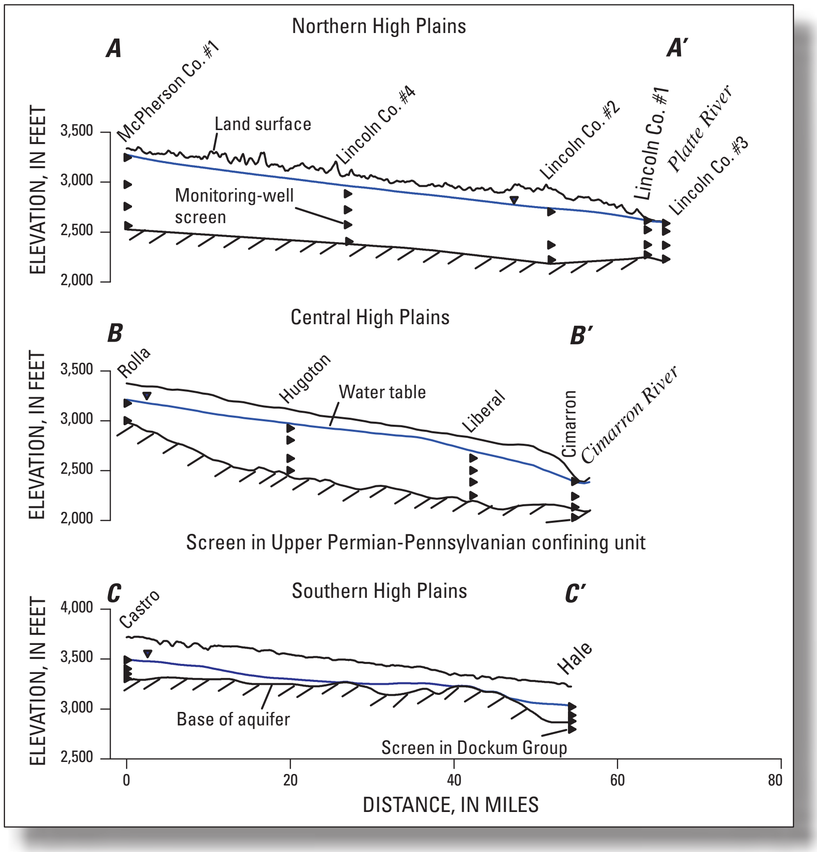


Figure 41. Geohydrologic section along each regional transect. Map locations of the sections are shown in figure 39.

Table 9. Construction details for the regional transect wells.

[All depths are in feet below land surface; casing and screen for all wells are made of threaded, flush-joint, Schedule 40 or Schedule 80 polyvinyl chloride (PVC) with a diameter of 2.0 or 2.5 inches; screen openings are 0.020 inch wide; --, not measured]

Site identification	Well name	Con-struction date	Elevation of land surface (feet)	Depth to base of High Plains aquifer (feet)	Depth to water at time of sampling (feet)	Total depth of hole (feet)	Total depth of well (feet)	Depth of screened interval (feet)	Depth of screen midpoint below water table at time of sampling (feet)
Northern High Plains									
405937100183504	Lincoln County #1-25	4/17/02	2,633	380	13	420	25	15 to 25	7
405937100183503	Lincoln County #1-119	11/13/02	2,633	380	14	275	124	109 to 119	100
405937100183502	Lincoln County #1-270	11/13/02	2,633	380	13	275	275	260 to 270	252
405937100183501	Lincoln County #1-370	4/17/02	2,633	380	13	420	375	360 to 370	352
410944100192104	Lincoln County #2-255	4/20/02	2,929	770	209	260	260	245 to 255	41
410944100192102	Lincoln County #2-590	11/18/02	2,929	770	210	600	600	580 to 590	375
410944100192101	Lincoln County #2-760	4/20/02	2,929	770	209	800	765	750 to 760	546
405745100174504	Lincoln County #3-30	11/5/02	2,614	395	7	260	35	20 to 30	18
405745100174503	Lincoln County #3-110	11/5/02	2,614	395	7	475	115	100 to 110	98
405745100174502	Lincoln County #3-250	11/5/02	2,614	395	7	260	255	240 to 250	238
405745100174501	Lincoln County #3-390	11/5/02	2,614	395	7	475	395	380 to 390	378
412213100425304	Lincoln County #4-195	5/14/03	3,075	700	104	730	200	185 to 195	86
412213100425303	Lincoln County #4-359	5/15/03	3,075	700	108	371	364	349 to 359	246
412213100425302	Lincoln County #4-510	5/16/03	3,075	700	108	525	515	500 to 510	397

Table 9. Construction details for the regional transect wells.—Continued

[All depths are in feet below land surface; casing and screen for all wells are made of threaded, flush-joint, Schedule 40 or Schedule 80 polyvinyl chloride (PVC) with a diameter of 2.0 or 2.5 inches; screen openings are 0.020 inch wide; --, not measured]

Site identification	Well name	Construction date	Elevation of land surface (feet)	Depth to base of High Plains aquifer (feet)	Depth to water at time of sampling (feet)	Total depth of hole (feet)	Total depth of well (feet)	Depth of screened interval (feet)	Depth of screen midpoint below water table at time of sampling (feet)
				Northern High Plains—Continued					
412213100425301	Lincoln County #4-695	5/14/03	3,075	700	108	730	700	685 to 695	582
413336101101004	McPherson County #1-45	5/24/02	3,326	775	8	800	50	35 to 45	32
413336101101003	McPherson County #1-330	11/23/02	3,326	775	21	560	340	320 to 330	304
413336101101002	McPherson County #1-550	11/23/02	3,326	775	21	560	555	540 to 550	524
413336101101001	McPherson County #1-770	5/24/02	3,326	775	22	800	780	760 to 770	743
				Central High Plains					
370402101394402	Rolla-193	5/25/99	3,361	399	179	400	198	173 to 193	4
370402101394401	Rolla-366	5/26/99	3,361	399	180	400	371	356 to 366	181
370130101180904	Hugoton-140	6/19/99	3,112	635	133	320	145	120 to 140	–3
370130101180903	Hugoton-313	6/18/99	3,112	635	154	320	318	303 to 313	154
370130101180902	Hugoton-495	6/15/99	3,112	635	172	640	500	485 to 495	318
370130101180901	Hugoton-617	6/14/99	3,112	635	175	640	627	607 to 617	437
370033100534204	Liberal-160	5/7/99	2,814	576	117	325	165	140 to 160	33
370033100534203	Liberal-319	5/6/99	2,814	576	149	325	324	309 to 319	165
370033100534202	Liberal-436	5/3/99	2,814	576	147	583	441	426 to 436	284
370033100534201	Liberal-570	4/30/99	2,814	576	147	583	581	560 to 570	418
370434100405204	Cimarron-65	5/23/99	2,534	345	56	341	70	45 to 65	–1

Table 9. Construction details for the regional transect wells.—Continued

[All depths are in feet below land surface; casing and screen for all wells are made of threaded, flush-joint, Schedule 40 or Schedule 80 polyvinyl chloride (PVC) with a diameter of 2.0 or 2.5 inches; screen openings are 0.020 inch wide; --, not measured]

Site identification	Well name	Construction date	Elevation of land surface (feet)	Depth to base of High Plains aquifer (feet)	Depth to water at time of sampling (feet)	Total depth of hole (feet)	Total depth of well (feet)	Depth of screened interval (feet)	Depth of screen midpoint below water table at time of sampling (feet)
Central High Plains—Continued									
370434100405203	Cimarron-210	5/20/99	2,534	345	54	441	215	200 to 210	151
370434100405202	Cimarron-336	5/22/99	2,534	345	54	341	341	326 to 336	277
370434100405201	Cimarron-436	5/19/99	2,534	345	55	441	441	396 to 436	361
Southern High Plains									
342313102174404	Castro-241	4/28/01	3,716	430	231	390	246	231 to 241	5
342313102174403	Castro-330	4/24/01	3,716	430	231	497	335	320 to 330	94
342313102174402	Castro-380	4/27/01	3,716	430	231	390	385	370 to 380	144
342313102174401	Castro-427	4/23/01	3,716	430	231	497	432	417 to 427	191
335028101365004	Hale-255	5/14/01	3,226	410	238	409	260	245 to 255	12
335028101365003	Hale-340	5/3/01	3,226	410	239	498	345	330 to 340	96
335028101365002	Hale-400	5/13/01	3,226	410	239	409	405	390 to 400	156
335028101365001	Hale-490	5/2/01	3,226	410	238	498	495	460 to 490	237

gases (helium, neon, dinitrogen, argon, oxygen, methane). Water levels in most of the wells were measured monthly for at least 12 months. Water levels and specific conductance were measured continuously in the two deepest wells at Hale (SHP). Those two wells were screened on either side of the contact between the SHP aquifer and the underlying Dockum Group (fig. 41), and so the water-level and specific-conductance data were used to evaluate water movement across that boundary.

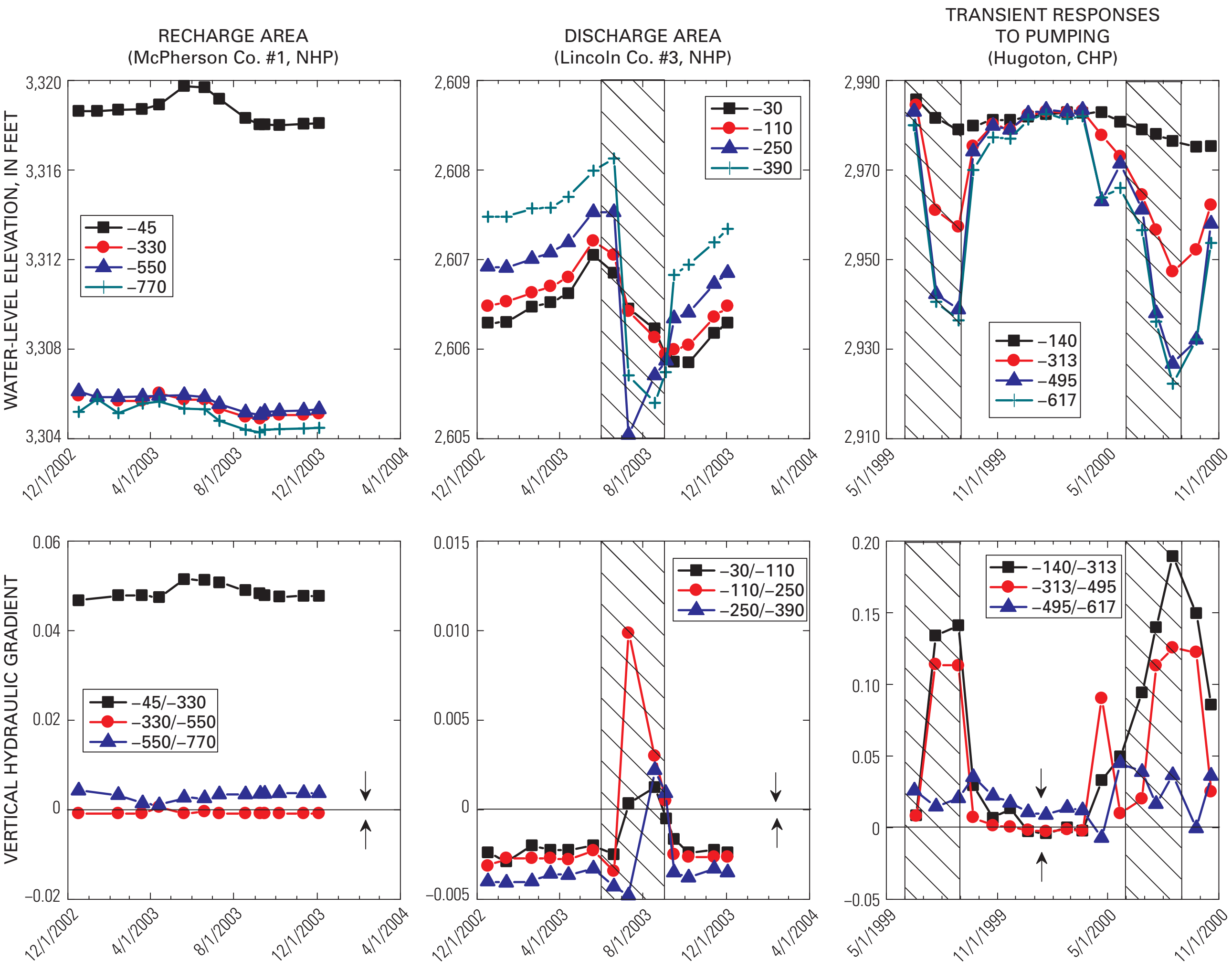
Vertical Gradients in Hydraulic Head, Water Chemistry, and Ground-Water Age

In this section, vertical gradients in hydraulic head, water chemistry, and ground-water age are presented for each transect as a basis for later discussions of water/rock interactions, mixing, and redox processes occurring along flow paths, and temporal variability in recharge chemistry.

Vertical Gradients in Hydraulic Head

Vertical gradients in hydraulic head provide useful information on vertical directions of ground-water flow. Three general patterns in vertical hydraulic gradient were observed at the transect sites; downward gradients associated with recharge, upward gradients associated with discharge, and transient responses to nearby pumping wells (fig. 42). Hydraulic gradients plotted in figure 42 were calculated as the difference in water-level elevation between adjacent shallow and deep well pairs, divided by the vertical distance between the well-screen midpoints. Positive gradients indicate the potential for downward water movement in the aquifer.

An example of temporal stability in water levels and hydraulic gradients in a recharge area is shown for the McPherson Co. #1 site in the NHP. That site is in an area with relatively little ground-water pumping. As a result, the water levels and gradients exhibited little change over time. A relatively large downward gradient persisted throughout the measurement period between the well nearest the water table (McPherson Co. #1–45) and the next deepest well. Downward gradients near the water table probably exist in most upland



EXPLANATION

▨	General irrigation period from June 1 to September 1
↓	Positive gradients indicate potential for downward water movement
↑	Negative gradients indicate potential for upward water movement
■ –45/–330	Numbers beside symbols refer to the individual well nest, with the smallest number indicating the shallowest well.
NHP =	Northern High Plains
CHP =	Central High Plains

Figure 42. Water levels and vertical hydraulic gradients at selected regional transect sites.

areas of the High Plains, indicating that chemicals leached to the water table in those areas have the potential to move deeper into the aquifer. Vertical gradients decreased substantially with depth below the water table at that site, indicating that the potential for vertical water movement diminished with depth.

Natural discharge areas in the High Plains are located primarily in the valleys of major rivers like the Platte and Republican Rivers in the NHP and the Arkansas and Cimarron Rivers in the CHP. In the SHP, natural discharge occurs primarily at springs along the eastern escarpment (Luckey and others, 1986). An example of temporal variability in water levels and hydraulic gradients in a discharge area is shown for the Lincoln Co. #3 site in the NHP (fig. 42), in the Platte River valley. During most of the measurement period, there was an upward gradient from near the base of the aquifer to the water table. Upward gradients at the base of the aquifer in regional discharge areas could have important implications for water quality in the aquifer because they could allow mineralized water from underlying geologic units to enter the aquifer. At Lincoln Co. #3, irrigation pumping in the valley during the summer caused a reversal in the gradient (fig. 42). That gradient reversal also could have important implications for water quality because it could allow river water to enter the aquifer in that area.

Another example of transient responses of water levels and hydraulic gradients to pumping is shown for the Hugoton site in the CHP (fig. 42). An irrigation well within 0.5 mi of that site was screened in the lower half of the aquifer. During the 1999 and 2000 irrigation seasons, water levels in the deepest transect well (Hugoton-617) dropped by at least 40 ft, resulting in large downward hydraulic gradients. The maximum downward gradient at the water table at that site is about four times larger than the downward gradient at McPherson Co. #1, an undeveloped site. Seasonal development of large downward gradients over many years could be an important mechanism for drawing recent recharge deeper into the aquifer more quickly than it would under undisturbed flow conditions. Similarly, a large decrease in water level near the base of the aquifer could enhance upward movement of mineralized water from underlying geologic units.

Vertical Gradients in Water Chemistry

Concentrations of some important water-quality constituents exhibited systematic changes with depth below the water table. For example, concentrations of dissolved oxygen systematically decreased with depth below the water table (fig. 43). Oxygen concentrations in recharge probably have remained relatively constant over time because of the atmospheric source for oxygen; therefore, the decrease in oxygen concentrations with depth indicates that oxygen reduction occurred along flow paths in the aquifer. Concentrations of dissolved nitrate and total pesticide compounds also decreased with depth below the water table in each High Plains region, particularly in the upper half of the aquifer (fig. 43). The decrease in nitrate and pesticide concentrations with depth in the upper half of the aquifer could be indicative of increasing concentrations in recharge over time and (or) degradation along flow paths in the aquifer. It is likely that nitrate concentrations in recharge did increase over time in some areas of the High Plains because land applications of fertilizer and manure nitrogen increased over time (fig. 25). On the other hand, the decrease in oxygen concentrations with depth could have produced geochemical conditions in the aquifer suitable for denitrification. Understanding the relative importance of changing source strength and biogeochemical reactions in the aquifer is necessary for assessing vulnerability of the deep ground water to anthropogenic contaminants like nitrate and pesticides.

Dissolved-solids concentrations in undisturbed aquifers usually increase gradually with depth below the water table as the residence time of ground water increases and water/rock interactions progress. For example, concentrations of dissolved solids at the Lincoln Co. #4 site (NHP) increased from 118 mg/L near the water table to 263 mg/L at the base of the aquifer (fig. 44). Agricultural activity at the land surface can increase the concentration of dissolved solids in recharge above what would be expected under natural conditions, resulting in a reversed gradient in dissolved-solids concentrations near the water table (fig. 44). Natural upwelling of brackish ground water at the base of the aquifer in regional discharge areas can cause large increases in dissolved-solids concentrations with depth below the water table (fig. 44). Thus, agricultural inputs and natural upwelling of brackish ground water have the potential to substantially alter the quality of ground water. Concentrations of dissolved solids for the entire HPGW data set generally decreased with depth in the vicinity of the water table (fig. 43), illustrating the effect of widespread agricultural activity in the High Plains on overall recharge chemistry in the aquifer.

Concentrations of dissolved arsenic and uranium generally decreased with depth below the water table in the SHP, but the concentration-depth trends were more variable in the CHP and NHP (fig. 43). Both arsenic and uranium could be derived from anthropogenic (pesticides/fertilizers) and natural (mineral) sources. Furthermore, natural sources of arsenic and uranium could be mobilized by anthropogenic activity. For example, phosphate or sulfate applied to agricultural fields could displace natural arsenate adsorbed to sediment surfaces (Welch and others, 2000). Jurgens and others (2005) reported that high-bicarbonate recharge water in agricultural areas near Modesto, California, leached uranium from sediments. General trends of decreasing arsenic and uranium concentrations with depth below the water table in the SHP and NHP (for uranium) could be consistent with the interpretation that anthropogenic sources or processes produced elevated concentrations of those trace elements in recharge. In contrast, general trends of increasing arsenic (NHP) and uranium (CHP) concentrations with depth below the water table could be consistent with the interpretation that those trace elements could also be derived naturally from sources along flow paths in the aquifer.

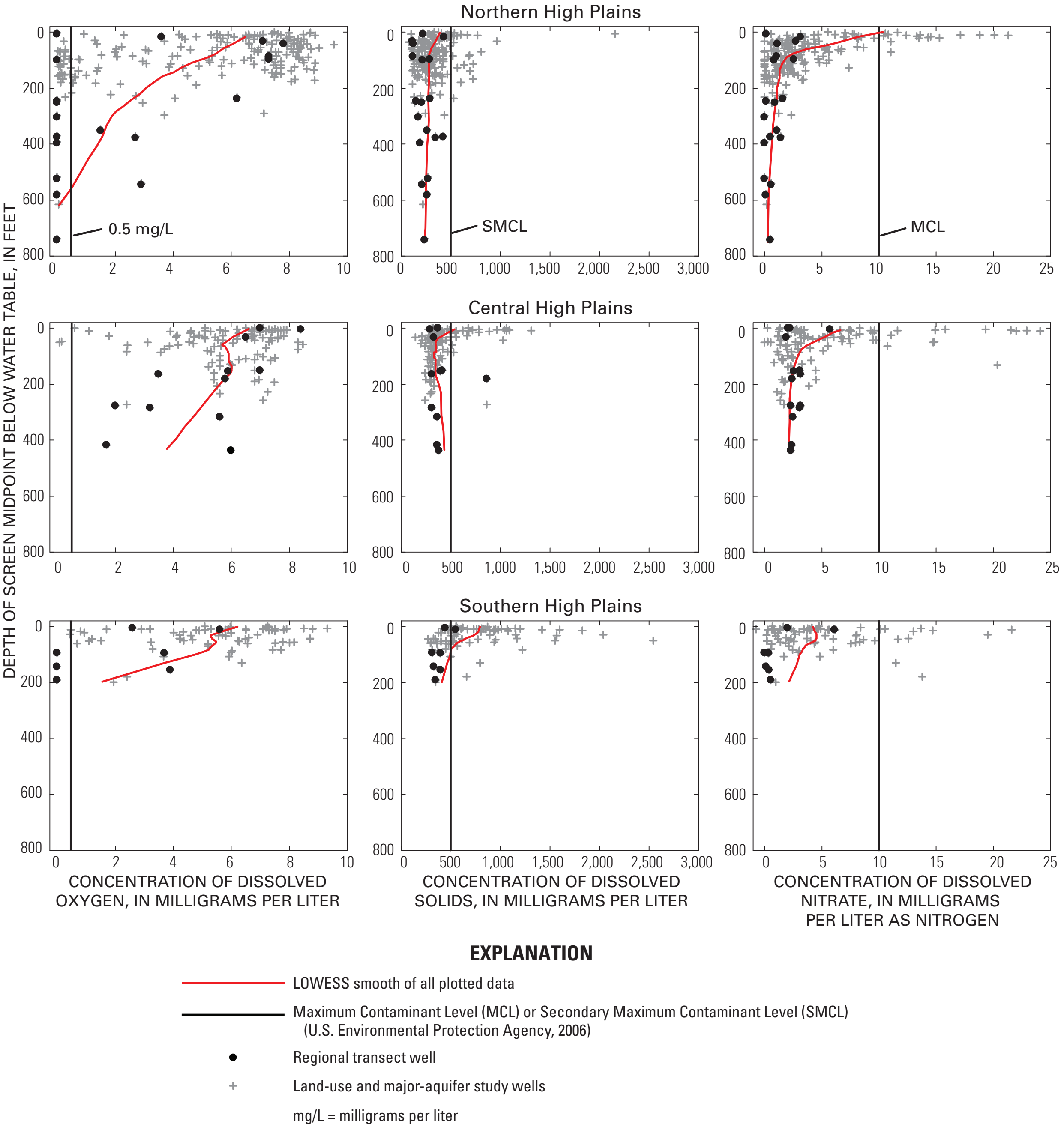


Figure 43. Concentrations of selected water-quality constituents as a function of well-screen depth below the water table.

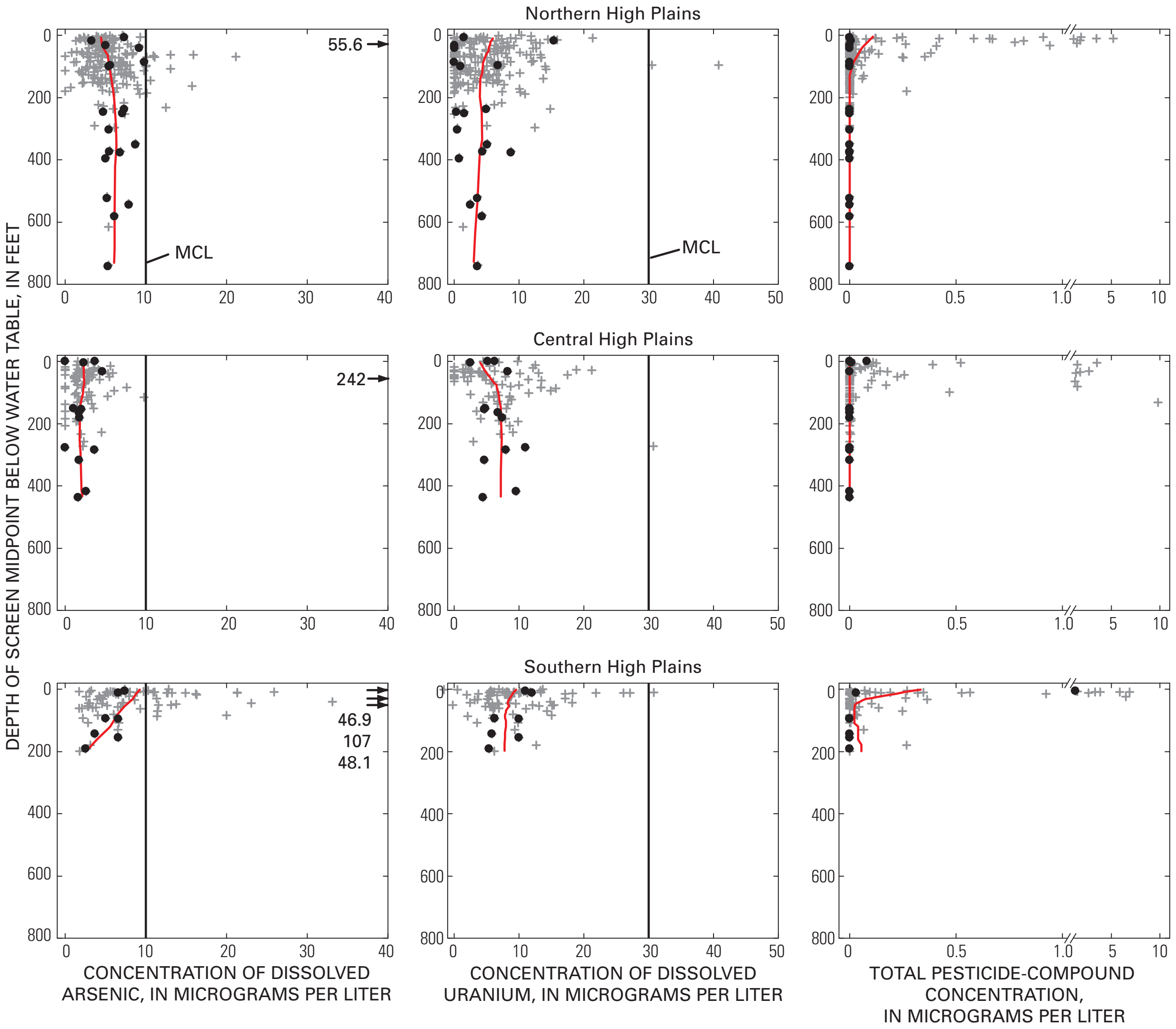


Figure 43. Concentrations of selected water-quality constituents as a function of well-screen depth below the water table.—Continued

Spalding and others (1984) reported chemical and isotopic evidence for uranium leaching along flow paths in an area of the NHP in western Nebraska, whereas large amounts of uranium also may be introduced to alluvial aquifers in this region by irrigation with uranium-bearing surface water (Verstraeten and others, 2001; Böhlke and others, 2007). The potential complexity of arsenic and uranium sources in the High Plains, as well as their sensitivity to changes in redox chemistry in aquifers, make it difficult to understand links between the trace-element chemistry of recharge and produced water.

Vertical Gradients in Ground-Water Age

The apparent age of water from the regional transect wells was characterized as modern or old, according to the tritium content of the samples. Modern ground water (less than 50 years old) was defined as water containing more than 0.5 TU of tritium. Old ground water was further characterized by using the radiocarbon content of dissolved inorganic carbon in ground water to estimate its age. Radiocarbon ages were adjusted for carbon sources and sinks along flow paths by using chemical and isotopic data from the wells, as previously reported for the High Plains aquifer (McMahon and others, 2004a,b; McMahon and others, 2007).

Two general types of vertical gradients in apparent ground-water age were observed at the regional transect sites. Ground-water ages systematically increased with depth below the water table in areas with relatively small amounts of pumping for irrigation or water supply (fig. 45*A*). In areas with relatively large amounts of pumping for irrigation or water supply,

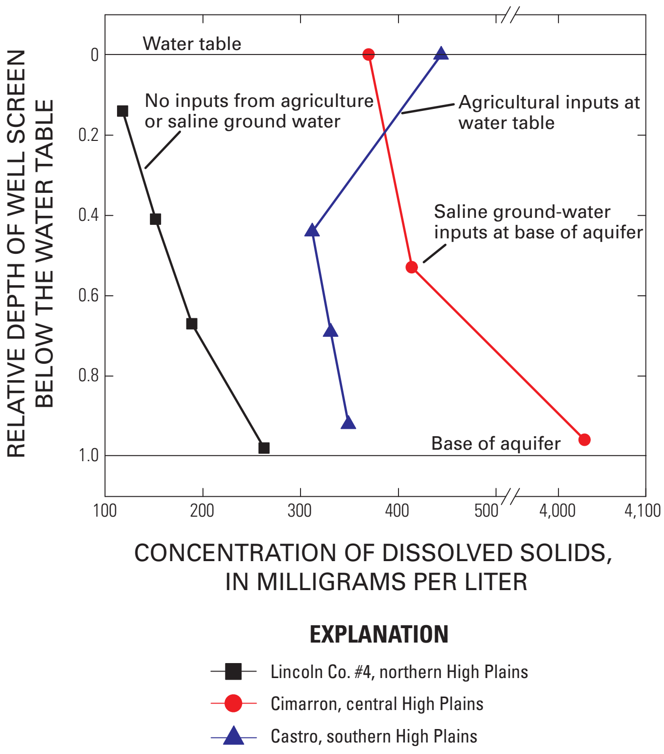


Figure 44. Concentrations of dissolved solids in selected regional transect wells.

ground-water ages increased with depth below the water table to a point below which ages did not increase further with depth (fig. 45*B*). The very small or nonexistent age gradients at depth in the developed areas are most likely the result of vertical mixing of water in the aquifer by pumping wells or leakage down long well screens, which would tend to flatten any preexisting steep age gradients. At the Hugoton (CHP) and Castro (SHP) sites shown in fig. 45*B*, vertical mixing may have affected at least 50 to 65 percent of the saturated thickness of the aquifer. Better resolution of the ground-water age profile between the two shallowest wells at each of those sites is needed to more fully evaluate the vertical extent of mixing.

Ground water recharged more than 50 years ago accounted for at least 44 to 95 percent (median 70 percent) of the water in the aquifer at the transect sites. Better resolution of the ground-water age profile between the two shallowest wells at each transect site is needed to more accurately determine the depth to the interface between modern and old ground water. Apparent ground-water ages at the base of the aquifer at the 11 transect sites ranged from about 3,400 (SHP) to 15,600 (NHP) years (McMahon and others, 2004a, b; McMahon and others, 2007). This age information indicates that most of the water in the High Plains aquifer at the transect sites consisted of old ground water that was recharged prior to the onset of modern anthropogenic activity in the region.

Old ground water was not unexpected in the aquifer because of its saturated thickness and because recharge rates in the semiarid High Plains region are small (Luckey and others, 1986; Dugan and Zelt, 2000; McMahon and others, 2007). Ground-water ages appeared to increase exponentially with depth at the sites that were relatively unaffected by well pumping (fig. 45*A*). Downward decreases in vertical hydraulic gradient (fig. 42, McPherson Co. #1) also are consistent with exponential age distributions if hydraulic conductivities do not decrease systematically downward. Thus, an exponential age-distribution model was used to estimate long-term average recharge rates at those sites (Cook and Böhlke, 2000). Calculated recharge rates at the two sites in fig. 45*A* are 0.02 ft/yr in the CHP and 0.05 ft/yr in the NHP. Cooler air temperatures in the NHP compared to the CHP (fig. 2), which would reduce evapotranspiration, probably contribute to the larger recharge rate at the NHP site. This finding is consistent with results from the unsaturated-zone studies discussed in Chapter 1, which indicated that unsaturated-zone water fluxes and chemical transit times to the water table decreased from north to south in the High Plains (fig. 30 and table 8). The estimated recharge rates at the regional transect sites are two to three times smaller than recharge rates assigned to the same areas of the aquifer in a model of ground-water flow developed in the USGS RASA Program (Luckey and others, 1986). Others have reported apparent discrepancies between flow-model-derived recharge rates constrained only by hydraulic-head data and those that were also constrained by ground-water age distributions (Sanford and others, 2004; McMahon and others, 2004a).

Processes Affecting the Chemistry of Water in the Aquifer

A variety of chemical, physical, and biological processes can alter the chemistry of water as it is moves along flow paths from recharge areas to points deeper in the aquifer. Chemical processes could include mineral dissolution and precipitation and ion exchange, which are referred to here as water/rock interactions. Physical processes could include mixing water from different sources as a result of natural or anthropogenic processes. Biological processes could include microbially mediated reduction of oxygen, nitrate, and sulfate, which are referred to here as reduction-oxidation (redox) processes. In this section, water/rock interactions, mixing, and redox processes that affect the chemistry of water along flow paths in the High Plains aquifer are discussed.

Water/Rock Interactions

Water/rock interactions occurring along flow paths from recharge areas to the regional transect wells were evaluated using a mass-balance approach and the geochemical reaction codes NETPATH and PHREEQC (Plummer and others, 1994; Parkhurst and Appelo, 1999), as discussed in detail by McMahon and others (2004a, b) and McMahon and others

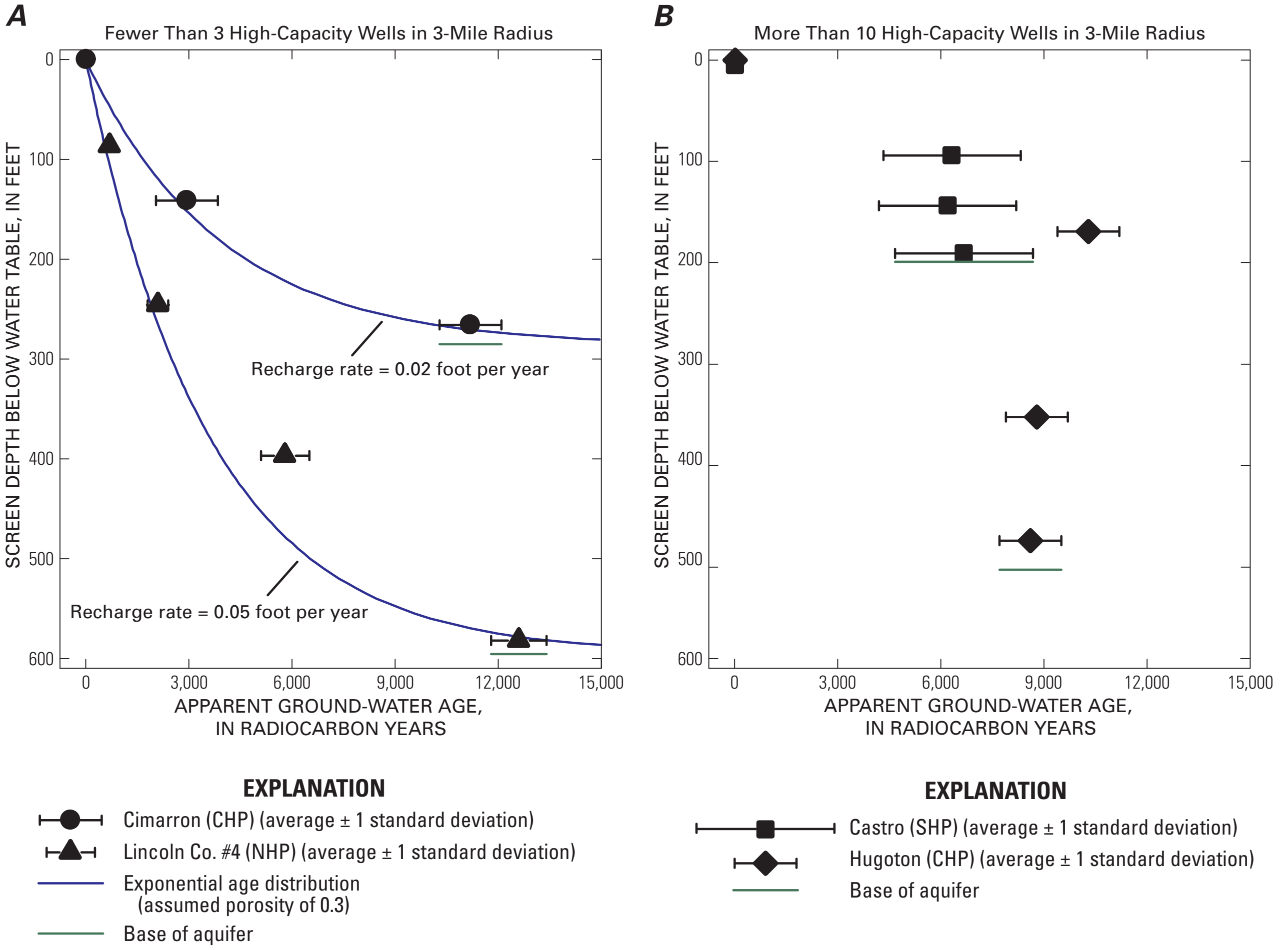


Figure 45. Ground-water age as a function of well-screen depth below the water table in areas of the High Plains aquifer with relatively (*A*) small amounts and (*B*) large amounts of pumping for irrigation and public water supply.

(2007). Although the models were constrained by mineralogic data, isotopic data, and mineral saturation indices, it is not likely that the mass-balance results represent unique solutions. Uncertainties in the delineation of flow paths, compositions of dissolving and precipitating mineral phases, and temporal variability in recharge chemistry, among other things, all contribute to uncertainty in model output. Nevertheless, the mass-balance model results are consistent with the available chemical, isotopic, and mineralogic data and provide useful information regarding possible water/rock interactions. In general, the primary water/rock interactions identified by the mass-balance models are carbonate and silicate mineral dissolution, precipitation of kaolinite and silica, and cation exchange. Specific reactions, and their relative importance in terms of mass balance, varied among the flow paths in each transect and between transects.

Along the NHP regional transect, concentrations of dissolved calcium and inorganic carbon were correlated and increased in roughly a 1:3 mole ratio, which is qualitatively consistent with calcite and sodium plagioclase dissolution in the presence of carbon dioxide (fig. 46) (McMahon and others, 2007). Calcite and sodium plagioclase were identified using X-ray diffraction analyses as being common mineral phases in NHP aquifer sediments. Production of carbon dioxide could result from oxidation of sedimentary organic carbon coupled to the reduction of oxygen, nitrate, sulfate, or other electron acceptors. Redox reactions are discussed in more detail in the section "Redox Processes."

In contrast to conditions in the NHP, concentrations of calcium decreased with increasing concentrations of inorganic carbon at the SHP transect sites. Concentrations of dissolved sodium and inorganic carbon were correlated, however, and increased in approximately a 2:1 mole ratio, which is qualitatively consistent with calcite dissolution and calcium-for-sodium ion exchange (McMahon and others, 2004b). Calcite also was identified as a common mineral phase in SHP aquifer sediments.

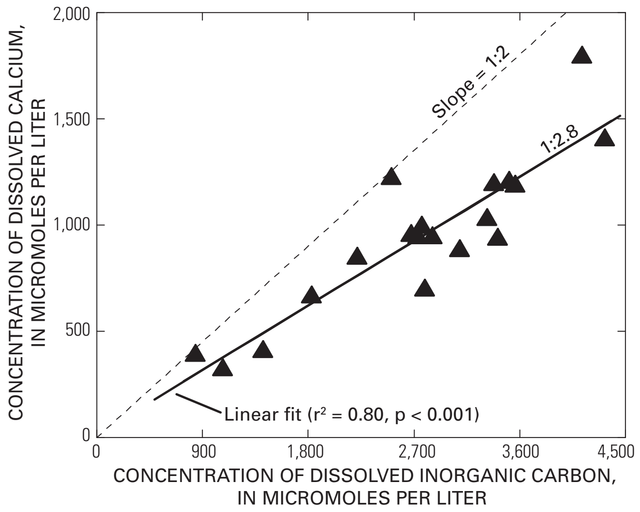


Figure 46. Concentration of dissolved calcium as a function of the concentration of dissolved inorganic carbon in samples from regional transect study wells in the northern High Plains.

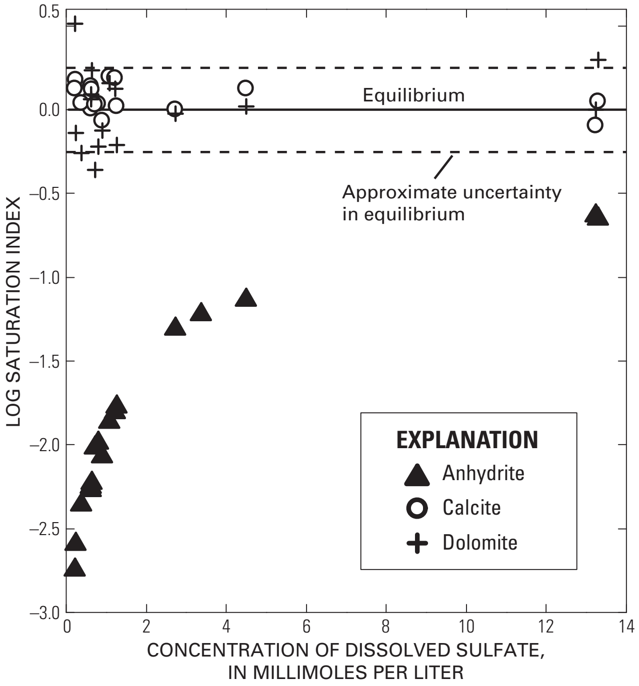


Figure 47. Mineral saturation indexes as a function of the concentration of dissolved sulfate in samples from regional transect study wells in the central High Plains.

Dedolomitization was an important reaction along flow paths in the CHP regional transect, according to the mass-balance models (McMahon and others, 2004a). Samples from the transect wells in the CHP were essentially in equilibrium with respect to calcite and dolomite across a range of sulfate concentrations, whereas the samples approached equilibrium with respect to anhydrite (and gypsum) with increasing sulfate concentrations (fig. 47). During dedolomitization, anhydrite dissolution adds calcium to solution, thereby supersaturating the water with respect to calcite. In order for the water to remain in equilibrium with respect to calcite, that mineral must then precipitate. During the process of calcite precipitation, inorganic carbon concentrations and pH values decrease, resulting in dolomite undersaturation and dissolution (Plummer and others, 1990). Calcite was identified as a common mineral phase in CHP aquifer sediments, and dolomite and anhydrite were identified as common mineral phases in sediments immediately underlying the aquifer. Although dolomite and anhydrite were not detected in CHP aquifer sediments as a part of this study, previous studies did report their presence in CHP aquifer sediments (Smith, 1940).

Reactions such as those described above tend to increase concentrations of dissolved solids in water as it moves along flow paths from recharge areas to points deeper in the aquifer. In addition to contributing major constituents such as calcium, sodium, inorganic carbon, sulfate, and silica to solution, those reactions may also contribute trace elements to solution if they are present in the dissolving mineral phases. For example, pyrite commonly contains arsenic, and its dissolution in the presence of oxygen, or other oxidants such as nitrate (Postma and others, 1991; Böhlke and others, 2002), could be a source of arsenic in solution (Welch, 2000; Smedley and Kinniburgh, 2002). Chemical and isotopic data indicate that pyrite dissolution may have occurred along flow paths in the NHP and SHP. The data in figure 48 for the NHP indicate that $\delta^{34}S$ values for sulfate generally decreased with increasing sulfate concentrations along flow paths from recharge areas. Pyrite commonly is a source of ^{34}S-depleted sulfur (Krouse and Mayer, 2000); therefore, those data are consistent with the interpretation that pyrite dissolution occurred in the NHP. In both the NHP and SHP, the water samples with the largest arsenic concentrations also contained O_2, which could indicate that pyrite oxidation was a source of arsenic in the aquifer. Other potential arsenic sources are discussed in Chapter 3.

Mixing

Mixing of ground water with surface water or with ground water from geologic units underlying the High Plains aquifer, and vertical mixing of water within the aquifer because of well pumping or leakage through long well screens, all have the potential to influence water quality in the aquifer. Chemical and isotopic data indicate that ground-water/surface-water mixing occurred in the Platte River valley at the Lincoln Co. #3 (NHP) transect site. Concentrations of dissolved strontium in water from the transect wells located north of the river in the Sand Hills increased as water moved

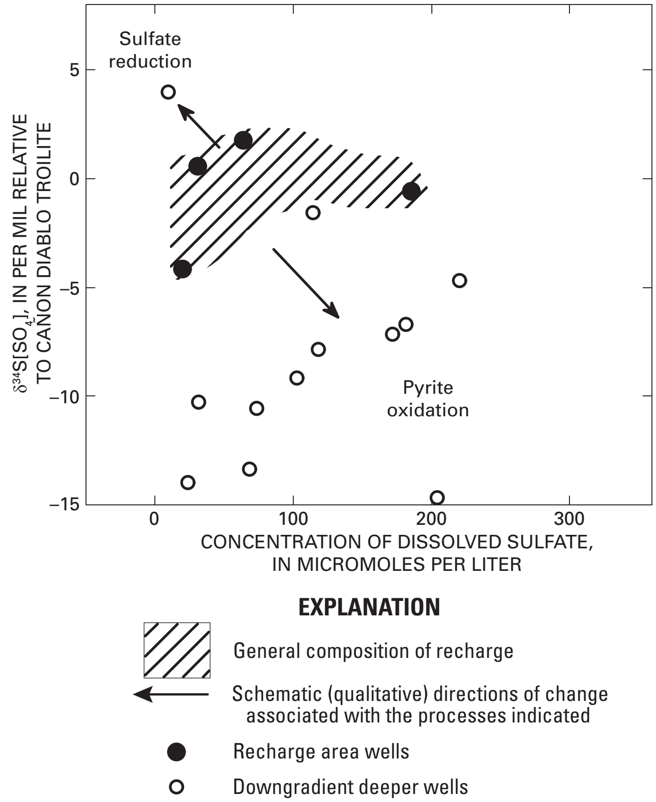


Figure 48. Sulfur isotopic composition of sulfate as a function of the sulfate concentration in samples from regional transect study wells in the northern High Plains

from recharge areas to points deeper in the aquifer (fig. 49). A similar pattern was observed at the Lincoln Co. #3 site south of the river, except for the shallowest well at that site (fig. 49), which is screened in Platte River alluvial sediments (see reference to alluvial systems in table 3 and fig. 10*A*). Water from the alluvial well plots along a mixing line between regional ground water and water from the Platte River, indicating that water from the alluvial well may contain about 30 percent river water. That mixing could be important from a water-quality standpoint because concentrations of dissolved solids in the river were about 2.5 times larger than their concentrations in regional ground water. Although the Lincoln Co. #3 site is located in a regional discharge area and hydraulic gradients at that site indicate a potential for upward ground-water movement to the river during most of the year (fig. 42), irrigation pumping in the summer reversed the gradients and apparently induced the flow of river water into the aquifer. Bank storage during floods is another mechanism that could cause ground-water/surface-water mixing, but that process is likely to occur less frequently and be of shorter duration than seasonal pumping for irrigation.

Ground-water/surface-water mixing probably is a common occurrence in major river valleys of the High Plains because the alluvial sediments are important sources of water for irrigation and public supply. Extensive well pumping in alluvial sediments could induce flow of river water into the aquifer (fig. 49). Whittemore (2000a, b) showed that irrigation pumping near the Arkansas River in southwestern Kansas caused a plume of river water containing elevated sulfate concentrations to infiltrate into the CHP aquifer. Emmons and Bowman (2000) reported that pumping public-supply wells in the Platte River alluvial aquifer near Grand Island, Nebraska, induced flow of surface water containing elevated pesticide concentrations into the aquifer. Substantial introduction of surface water into alluvial aquifers also occurs in areas receiving surface-water irrigation. The North Platte River alluvial aquifer in parts of western Nebraska is recharged primarily by infiltration of river-derived water beneath unlined canals (low nitrate, high uranium) and beneath the irrigated fields (high nitrate, high uranium) (Verstraeten and others, 2001; Böhlke and others, 2007).

Mixing also occurred between water in the aquifer and water from underlying geologic units at some of the transect sites in the CHP and SHP. In the CHP, halite-dissolution brines with dissolved chloride concentrations up to 35,000 mg/L were present in geologic units underlying the aquifer. Estimates of mixing based on concentrations of dissolved

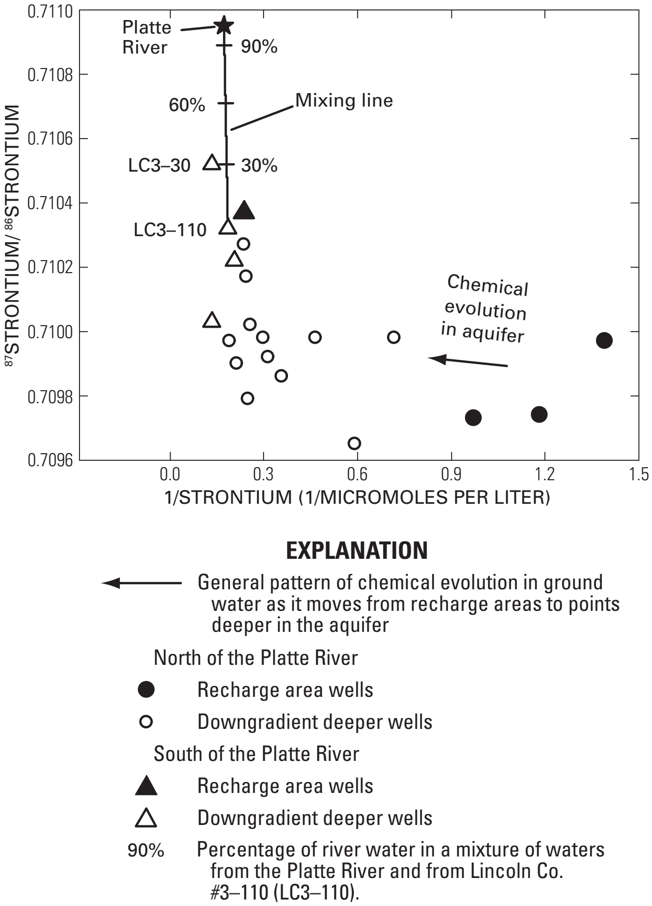


Figure 49. Strontium isotope ratios as a function of inverse strontium concentrations in samples from regional transect study wells in the northern High Plains.

bromide and chloride indicate that about 5 percent of the water at the base of the aquifer in the regional discharge area of the Cimarron River valley was derived from the brine (fig. 50) (McMahon and others, 2004a). About 20 percent of the water in the confining unit directly beneath the aquifer apparently was derived from brine sources. In the SHP, upward leakage of water from rocks of Cretaceous age contributed as much as 8 to 17 percent of the water in the aquifer on the basis of mass-balance calculations (McMahon and others, 2004b).

Pumping from wells has the potential to increase mixing between waters in the aquifer and underlying geologic units. As discussed previously, irrigation pumping at the Hugoton site (CHP) caused large declines in hydraulic head near the base of the aquifer (fig. 42). Large declines in head at the base of the aquifer could allow water to enter the aquifer from below, depending on preexisting heads in the underlying geologic unit, even though the site is not located in a regional discharge area. Hydraulic heads and specific conductance were monitored at the Hale regional transect site (SHP) to examine in more detail the relation between pumping from the aquifer and hydraulic gradients across the bottom of the aquifer. Irrigation pumping produced water-level declines of about 15 ft near the base of the aquifer relative to the maximum water levels that occurred in the spring prior to the start of irrigation season (fig. 51*A*). Water-level elevations in wells screened near the bottom of the aquifer remained higher than elevations in the underlying Dockum Group throughout the period of record, with the difference in head between the two units reaching a maximum of about 17 ft near the end of the winter in 2005 and a minimum of about 2 ft near the end of the irrigation season in 2004. These data indicate that there was no potential for advective movement of water from the underlying

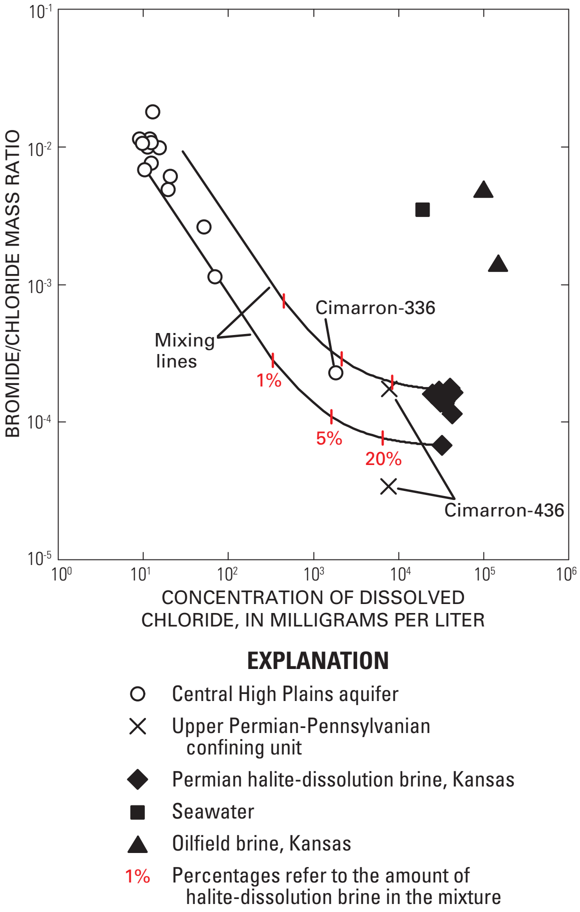


Figure 50. Bromide/chloride mass ratio as a function of the chloride concentration in samples from regional transect study wells in the central High Plains. Data for halite-dissolution brines in south-central Kansas are from Whittemore (1993) and data for seawater and oilfield brines in southwestern Kansas are from Whittemore (1984).

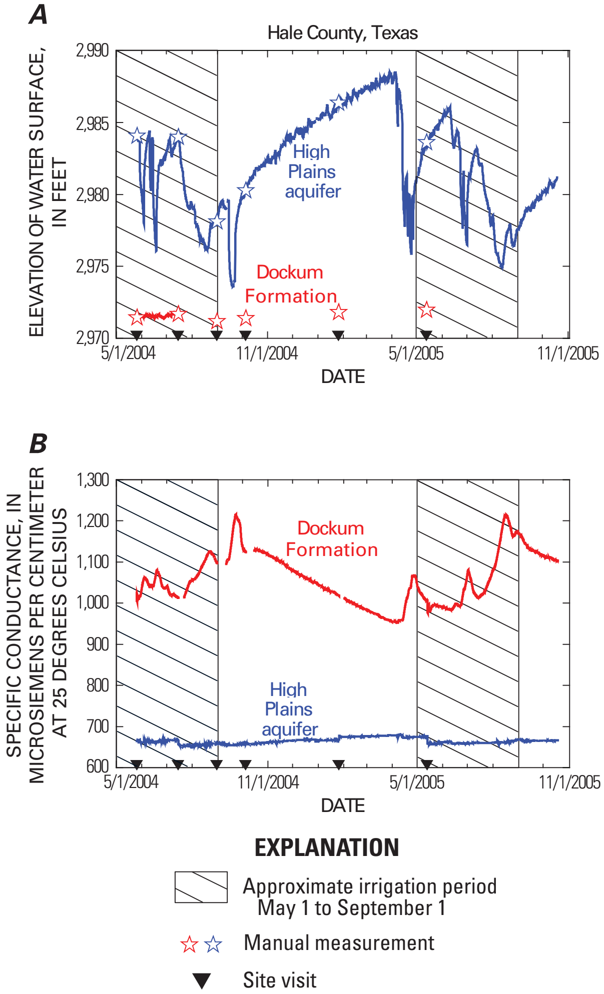


Figure 51. (*A*) Water-level elevation and (*B*) specific conductance as a function of time near the bottom of the southern High Plains aquifer (regional transect well Hale–400) and near the top of the underlying Dockum Group (regional transect well Hale–490).

geologic unit into the aquifer at this location during the period of record, however, that could change if water levels in the SHP continue to decline (McGuire, 2007).

Water in the Dockum Group had larger specific-conductance values than water in the aquifer, and values for water from the Dockum Group appeared to increase with decreasing head differences between the two units (fig. 51*B*). Those data indicate that the downward hydraulic gradient at that site may have suppressed the upward movement of brackish water in the Dockum Group. The chemistry of water at that site is not well characterized, but one water sample from the Dockum Group contained 1,900 mg/L of sodium, 4,200 mg/L of chloride, 1,100 µg/L of dissolved iron, and 12 µg/L of arsenic (McMahon and others, 2004b). Movement of that type of water into the aquifer could impair its use for irrigation and drinking.

Vertical gradients in apparent ground-water age at the transect sites that were relatively undisturbed by well pumping indicate that ground water at those sites was temporally well stratified and that most of it was recharged prior to the development of substantial anthropogenic activity in the High Plains (during the past ~50 years) (fig. 45*A*). Such steep age gradients are consistent with the small recharge rates in natural rangeland settings overlying the Ogallala Formation (Chapter 1). Thus, anthropogenic contaminants entering the aquifer from the land surface should not have traveled very far below the water table in those areas. Nevertheless, data indicate that contaminants originating at the land surface commonly were found in water from domestic and public-supply wells screened relatively far below the water table (Chapter 3). The most likely explanation to account for anthropogenic contaminants at depth is that well pumping or leakage through long well screens moved them deeper into the aquifer than they would have moved under natural hydraulic gradients (Burow and others, 2005; Landon and others, 2007; Clark and others, 2007). Irrigation and public-supply wells are considered to be more important than domestic wells for vertically redistributing contaminants in the aquifer because they pump at higher volumes, pump for longer periods of time, and generally have longer well screens (Bruce and Oelsner, 2001; Clark and others, 2007). In general, the occurrence of anthropogenic contaminants in water from the domestic and public-supply wells (Chapter 3) appears to depend not only on source factors (Chapter 1) but also on transport processes such as mixing caused by pumping wells (this Chapter).

Redox Processes

Micro-organisms in natural systems, which catalyze many redox processes, compete for limited resources. Because of this competition they tend to favor redox reactions that generate the maximum amount of available energy. Those microbial processes that couple the most efficient electron donors to the most efficient electron acceptors have a competitive advantage. Dissolved and particulate organic carbon are commonly the most abundant electron donors available in ground-water systems (Thurman, 1985), although some reduced forms of nitrogen, iron, sulfur, and possibly other species could be important electron donors in some cases (Engstrom and others, 2005; Straub and others, 1996; Kolle and others, 1985). There is similar variability in the kinds and amounts of available electron acceptors. Dissolved oxygen produces the most energy per mole of organic carbon oxidized than any other commonly available electron acceptor, and thus it is used preferentially by subsurface micro-organisms. Because ground-water systems can be isolated from the atmosphere, however, dissolved oxygen tends to be consumed along aquifer flow paths. Under anoxic conditions, the next most energetically favorable, naturally available electron acceptor is nitrate, followed by manganese-(IV), iron-(III), sulfate, and finally carbon dioxide. This order of preferential electron acceptor utilization—oxygen> nitrate> manganese (IV)> iron (III)> sulfate> carbon dioxide—is referred to as the ecological succession of terminal electron accepting processes (Chapelle and others, 1995).

The extent of progression through this sequence is primarily dependent on the availability of electron acceptors and electron donors in the aquifer. Water from 87 percent of the major-aquifer study wells was oxygen reducing, assuming that a dissolved-oxygen concentration of 0.5 mg/L represents the lower limit of the predominance of that redox process (Chapelle and others, 1995; McMahon and Chapelle, in press). The NHP had the largest percentage of water samples from major-aquifer study wells (20 percent) with dissolved oxygen concentrations less than 0.5 mg/L, and the CHP had the smallest percentage (4 percent). Overall, those oxic conditions are indicative of the relatively small supply of electron donors in the aquifer, such as sedimentary organic carbon and iron and sulfide minerals, to support other redox processes.

Although water in the aquifer was mostly oxic, anoxic redox processes also may have occurred in the aquifer to a limited extent. For example, about 2 and 5 percent of the major-aquifer study samples collected during this study could be indicative of local manganese-(IV) and iron-(III) reducing conditions, respectively, on the basis of measured dissolved oxygen, manganese, and iron concentrations. Locally reducing conditions, possibly associated with finely disseminated organic matter in the aquifer or at clay/sand interfaces, are known to occur in heterogeneous sedimentary aquifers (Murphy and Schramke, 1998; McMahon and others, 1999). Chemical and isotopic data from the transect wells indicate that nitrate and sulfate (fig. 48) reduction also were locally important in the aquifer. Nitrate reduction also may be important at larger scales in some of the hydrogeologic units. In particular, the Sand Hill eolian deposits and the Plio-Pleistocene deposits may have sufficient nitrate-reduction potential to represent an important attenuating mechanism for nitrate contamination in deeper parts of the aquifer where most public-supply wells are screened (McMahon and others, 2005; McMahon and others, 2007). Of the various anoxic redox processes, nitrate reduction may have the most importance with respect to linking the chemistry of recharge and the used resource in the High Plains because of large nitrate loading at the water table from agricultural lands (fig. 25) and because nitrate is one of the most common contaminants in water produced from domestic, public-supply, and irrigation wells (Chapter 3).

Stable nitrogen and oxygen isotopic data for nitrate in water samples from the transect wells support the interpretation that nitrate reduction occurred along flow paths in the aquifer. Nitrate in samples from each transect exhibited varying amounts of enrichment in ^{15}N and ^{18}O that define trends which are characteristic of nitrate reduction (fig. 52). Those results are important because they indicate that nitrate reduction did occur in this largely oxic aquifer. The question becomes whether the extent and rate of nitrate reduction are large enough to substantially attenuate nitrate contamination from anthropogenic sources.

Denitrification reaction progress in the aquifer was evaluated by comparing measured nitrate concentrations to reconstructed nitrate concentrations in the samples at the time they were recharged. Denitrification is a nitrate-reducing mechanism by which nitrate is reduced to dinitrogen gas (N_2) (Korom, 1992). Denitrification coupled to the oxidation of organic carbon produces N_2 and bicarbonate.

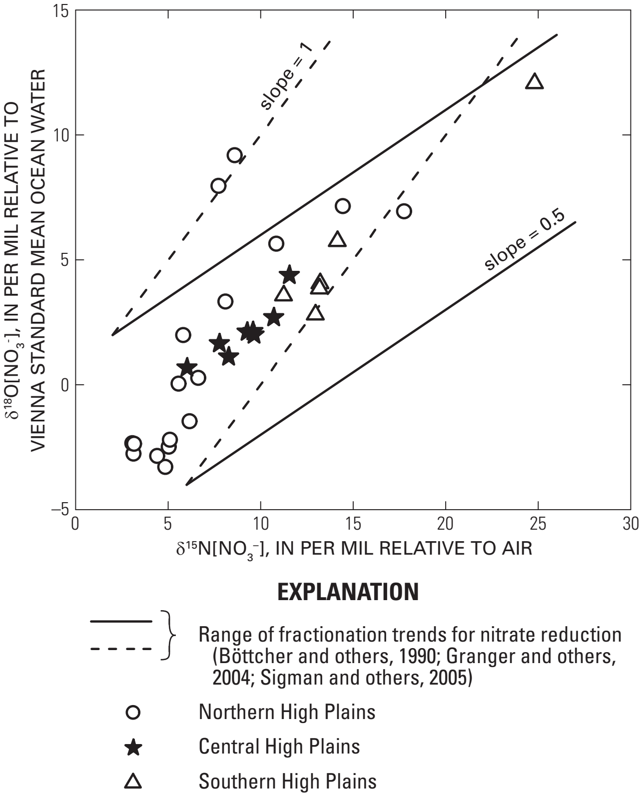


Figure 52. Measured δ18O and δ15N values for nitrate in samples from the regional transect study wells.

$$4NO_3^- + 5C + 3H_2O = 2N_2 + 5HCO_3^- + H^+ \qquad (1)$$

In some environments, denitrification may be coupled to the oxidation of sulfide minerals instead of, or in addition to, organic carbon (Postma and others, 1991; Böhlke and others, 2002), which produces N_2 and dissolved sulfate.

$$6NO_3^- + 2FeS_2 + 2H_2O = 3N_2 + 2FeOOH + 4SO_4^{2-} + 2H^+ \qquad (2)$$

Both the initial concentration and the initial isotopic composition of nitrate in recharge were reconstructed by combining data for reactant nitrate and product N_2 gas in denitrified ground-water samples (Heaton and others, 1983; Böhlke and others, 2002; McMahon and others, 2004a,b; McMahon and Böhlke, 2006). Thus, denitrification reaction progress for each sample was calculated using equation 3,

$$f = 1 - \frac{[NO_3^-]_{\text{measured}}}{[NO_3^-]_{\text{initial}}}, \qquad (3)$$

where f is denitrification reaction progress, $[NO_3^-]_{\text{measured}}$ is the measured concentration of nitrate in the sample, and $[NO_3^-]_{\text{initial}}$ is the concentration of nitrate in the sample at the time of recharge. Values of f ranged from 0 (no denitrification) to 1 (fully denitrified) for the transect-well samples (fig. 53), with median values for the NHP, CHP, and SHP of 0.67, 0, and 0.57, respectively. Those values of f indicate that denitrification reaction progress in the aquifer was spatially variable but generally not sufficient to completely remove the nitrate initially present in most samples.

Apparent rates of denitrification were estimated on the basis of increases in concentrations of produced N_2 and on ground-water ages along flow paths from the water table to deeper wells at the transect sites. Increases in produced N_2 concentrations with depth at the transect sites indicate that many of the samples underwent some denitrification. Calculations of apparent denitrification rates assume denitrification began after oxygen concentrations were reduced to about 2 mg/L or less (McMahon and others, 2004a, b), which typically occurred between the shallowest and second shallowest transect wells. Apparent denitrification rates in the aquifer ranged from less than 7×10^{-5} to 4×10^{-3} mg N/L/yr on the basis of this approach (McMahon and others, 2004a,b; 2007). Those rates are slow compared to the rates reported for some other aquifer systems (fig. 54), and they attest to the general lack of nitrate-attenuating capacity in the High Plains aquifer. Those slow denitrification rates have important implications with respect to nitrate concentrations in ground-water recharge that exceed the drinking-water standard (fig. 21). At such slow denitrification rates, it would take between 250 to 14,000 years to lower nitrate concentrations by 1 mg/L as N. The results highlight the importance of managing land use in the High Plains to minimize nitrate concentrations in recharge.

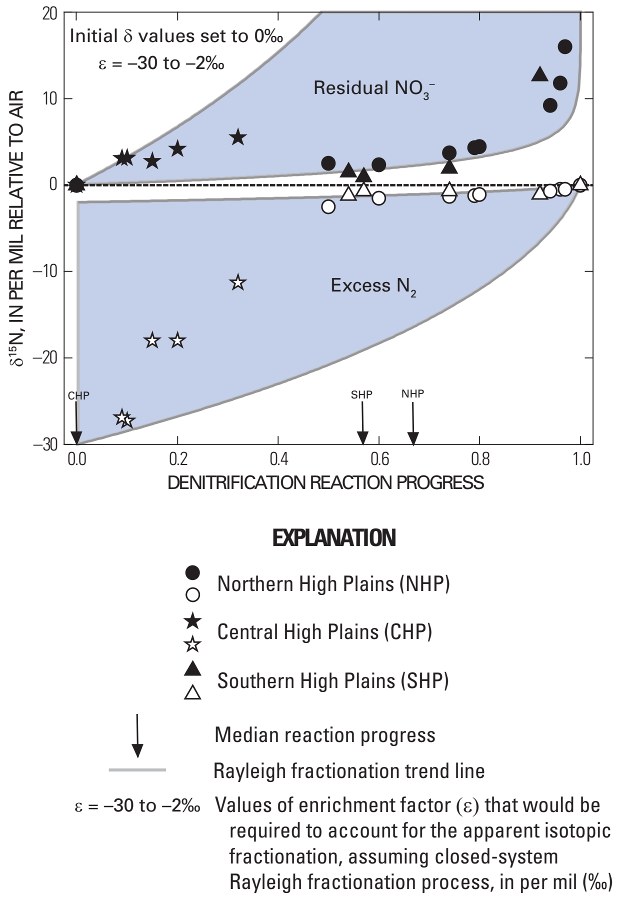


Figure 53. Values of $\delta^{15}N$ as a function of denitrification reaction progress. Initial δ values were set to zero in order to compare data from each transect. Residual nitrate (NO_3^-) and excess nitrogen gas (N_2) were determined for each sample and are denoted by the closed and open symbols, respectively.

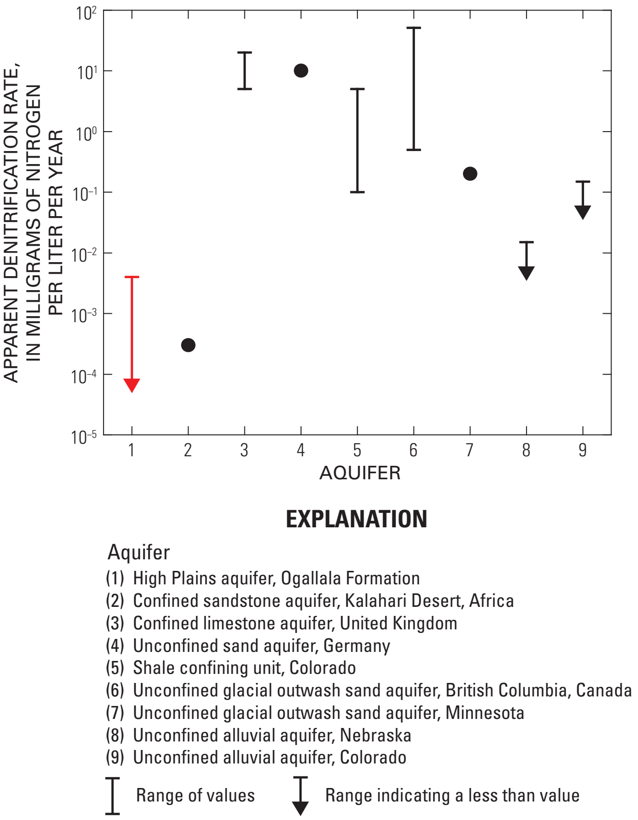


Figure 54. Apparent denitrification rates reported for selected aquifer systems. Rates for the High Plains aquifer (1) are from this study, and the other rates are from various studies as summarized by Groffman and others (2006).

Nitrate in Paleorecharge

One of the complicating factors to consider when linking the chemistry of recharge and the used resource is temporal variability in recharge chemistry. Temporal variability in recharge chemistry could occur over the course of years as a result of changes in land use/land cover (Chapter 1). Temporal variability also could occur over longer periods as a result of changes in climate, vegetation, or other natural factors. Temporal variability in recharge chemistry was not measured directly in any of the land-use study wells (Chapter 1); however, temporal variability in the concentration of nitrate in recharge was reconstructed using age-dated water samples from the transect wells (record of the past ~12,000 years) and from wells installed along flow paths in the NHP Plio-Pleistocene deposits (record of the past ~50 years) (McMahon and others, 2005; McMahon and Böhlke, 2006). Denitrification in the saturated zone could affect the concentration of nitrate in ground water and was accounted for by using the methods previously described in order to reconstruct initial nitrate concentrations and isotope values in recharge.

During the past ~12,000 years, prior to substantial anthropogenic activity in the High Plains, nitrate concentrations in recharge ranged from 0.8 to 4.2 mg/L as N in the transect study areas (fig. 55), with a median concentration of 2.2 mg/L as N. That median concentration is similar to the suggested background nitrate concentration of 2 mg/L as N in United States ground water (Mueller and Helsel, 1996), though background concentrations may be expected to vary substantially on that scale. Nitrate concentrations in paleorecharge did not vary systematically during the late Pleistocene and Holocene, indicating that warming during that period apparently did not have a substantial effect on the processes producing nitrate in recharge. In the CHP and NHP, recharge temperatures increased by about 2 to 3°C from the late Pleistocene to the present (McMahon and others, 2004a; 2007). Similar relative stability of nitrate concentrations in recharge during the Holocene was reported for parts of central New Mexico (Plummer

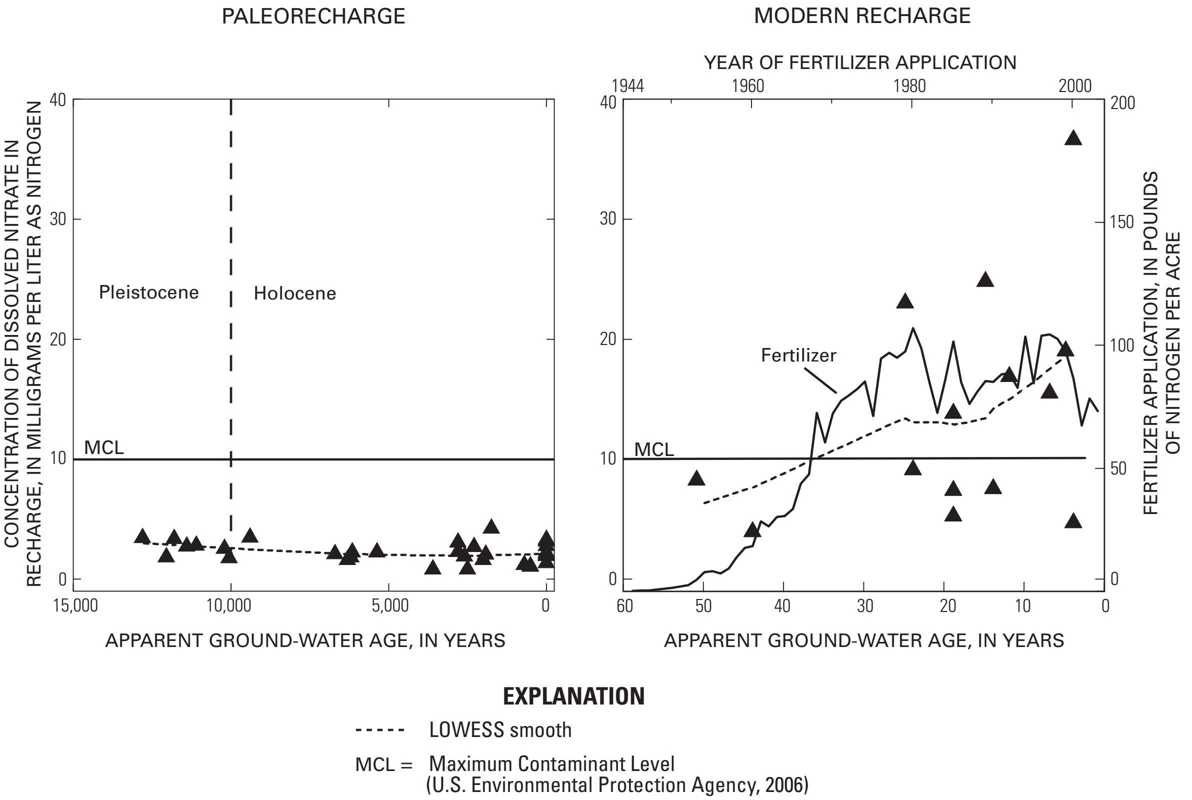


Figure 55. Concentration of nitrate in recharge as a function of apparent ground-water age for water samples from (*A*) the regional transect study wells (McMahon and Böhlke, 2006) and (*B*) shallow flow-path wells in Plio-Pleistocene deposits of the northern High Plains in eastern Nebraska (McMahon and others, 2005). Concentrations in recharge were obtained by correcting measured values for denitrification effects produced in the aquifer using neon, argon, and nitrogen gas data (McMahon and others, 2004a; McMahon and Böhlke, 2006). Fertilizer data from Ruddy and others (2006).

and others, 2006), whereas there is evidence that nitrate concentrations in recharge decreased during this time period in the Kalahari Desert in Africa (Heaton and others, 1983).

During the past 50 to 60 years, nitrate concentrations in recharge in parts of eastern Nebraska have increased substantially compared to concentrations in paleorecharge (fig. 55). Increases in concentrations of nitrate in recent recharge also are indicated by comparing data from the agricultural land-use wells in the CHP and SHP to nitrate concentrations in paleorecharge (figs. 21 and 55). As previously discussed, elevated nitrate concentrations in recharge could have important implications with respect to the quality of the used resource because of the generally small nitrate-attenuation capacity of the aquifer and because pumping or leakage could draw shallow contaminants deeper into the aquifer more quickly than would occur under undisturbed hydraulic gradients. The large increase in recharge nitrate concentrations during the past 50 years appears to be related to the increased use of agricultural fertilizer during that period (fig. 55). Contributions from other anthropogenic sources such as human and animal waste, and possibly contributions from natural sources in the subsoil that were mobilized by irrigation return flow (Chapter 1), also may be important.

The N isotope composition of nitrate in paleorecharge, which presumably was from natural sources, systematically increased from north to south in the High Plains and spans a range of values that could be interpreted as being derived from fertilizer and animal waste sources (fig. 21). N isotopic data and nitrate/chloride mole ratios for paleorecharge and for modern atmospheric deposition in the High Plains suggest that the nitrate in paleorecharge could ultimately be derived from atmospheric deposition (typically with an average N isotopic composition of 0±5 per mil) that has undergone variable amounts of isotopic fractionation in the soil zone prior to recharge (fig. 56) (McMahon and Böhlke, 2006). Similar isotopic patterns also have been observed in ground water of central New Mexico. Denitrification and ammonia volatilization in the soil zone both could be important processes for fractionating N isotopes prior to recharge. Having data on the concentration and isotopic composition of nitrate in paleorecharge across the High Plains provided a useful regional

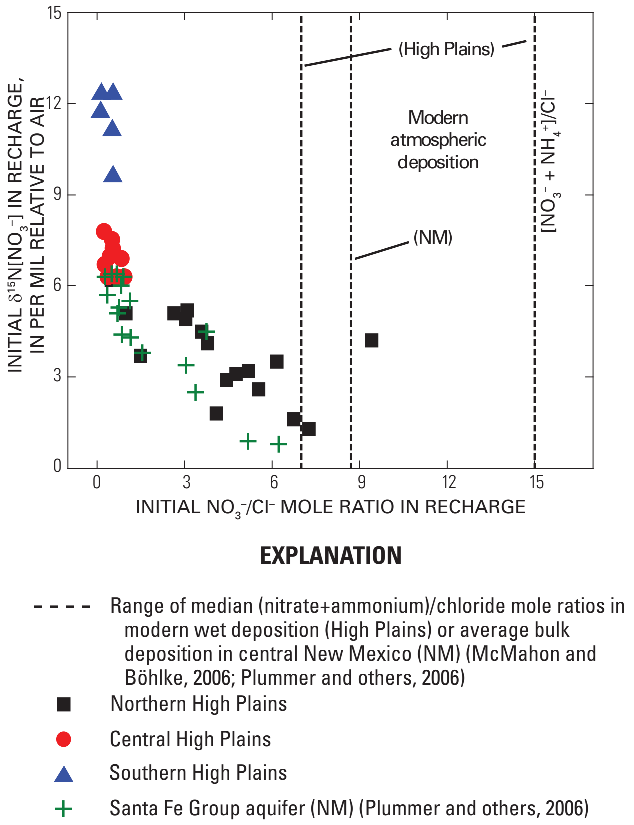


Figure 56. Initial nitrogen isotope composition of nitrate as a function of the nitrate/chloride mole ratio in paleorecharge. Initial isotope compositions were obtained by correcting measured values for denitrification effects produced in the aquifer using neon, argon, and nitrogen gas data (McMahon and others, 2004a; McMahon and Böhlke, 2006).

perspective for interpreting the origin of nitrate in water from the land-use study wells (fig. 21).

Conceptual Model Linking the Chemistry of Recharge and the Used Resource

Water/rock interactions, mixing, and redox processes occurring along flow paths are likely to influence the connection between the chemistry of recharge and the used resource in the High Plains aquifer. Superimposed on those processes are spatial and temporal variations in recharge chemistry largely related to changes in land use/land cover. A conceptual model incorporating those processes is presented in figure 57.

In each regional transect study area, mineral dissolution-precipitation reactions and cation exchange; mixing with surface water, with water from underlying formations, and (or) with water of different ages in the aquifer; and redox processes such as oxygen, nitrate, and sulfate reduction altered the chemistry of water as it moved along flow paths from recharge areas to points deeper in the aquifer. Those processes are summarized in the following generalized reactions for each of the three High Plains regions (McMahon and others, 2004a, b, 2007):

NHP:

Recharge + Calcite + Sodium Plagioclase + Pyrite + Cation Exchange + Mixing + Sedimentary Organic Carbon ⟶ Produced Water + Kaolinite + SiO_2 + Goethite

CHP:

Recharge + Dolomite + Anhydrite/Gypsum + Albite + Cation Exchange + Mixing + Sedimentary Organic Carbon ⟶ Produced Water + Calcite + Kaolinite + SiO_2

SHP:

Recharge + Calcite + Albite + Pyrite + Cation Exchange + Mixing + Sedimentary Organic Carbon ⟶ Produced Water + Kaolinite + SiO_2 + Goethite

Other processes also may have affected the chemistry of ground water as it moved along flow paths from recharge areas to points deeper in the aquifer, but those outlined here are considered to be the most important processes. Although water/rock interactions and redox processes are likely to have occurred throughout the aquifer, mixing may have been most important in areas with the greatest density of irrigation or other supply wells, and in regional discharge areas.

In the conceptual model (fig. 57), there is an important distinction to be made between ground-water flow directions in undisturbed areas beneath rangeland and flow directions in highly disturbed areas beneath irrigated cropland. Beneath rangeland, flow paths were largely horizontal because of slow recharge rates, which resulted in temporally well-stratified ground water with apparent ages of about 3,000 to 12,000 years (fig. 45). Most of that ground water was recharged prior to modern anthropogenic activity and generally is of good chemical quality. Beneath irrigated cropland, however, there was a larger component of vertical water movement caused by intense well pumping and(or) leakage through long well screens, which resulted in vertically mixed water (fig. 57). Accelerated downward movement of shallow, contaminated ground water apparently has resulted in contamination of some deep zones in the aquifer in which supply wells are screened (Chapter 3). Eventually, accelerated downward movement of shallow ground water could result in widespread contamination of the deep productive zones. Once contaminated, deep zones in the aquifer are not likely to be remediated quickly because of slow recharge rates, long water residence times in the aquifer, and slow rates of contaminant degradation (for example, slow denitrification).

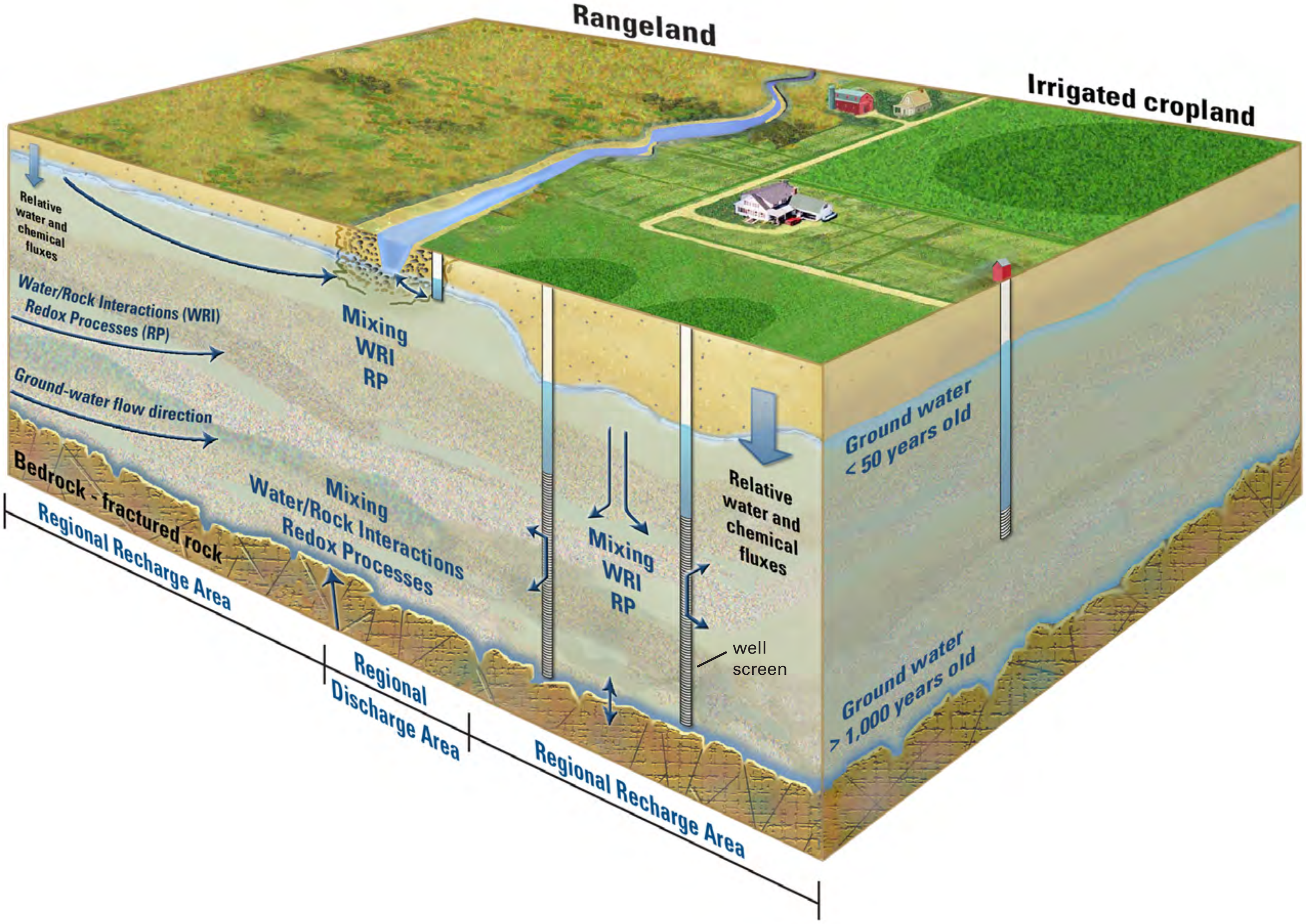


Figure 57. Conceptual model of processes affecting the chemistry of ground water along flow paths from recharge areas to points deeper in the High Plains aquifer.