Bulletin 260

Water Resources of the Dakota Aquifer in Kansas Appendix

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The first of the following two sections provides additional detail for the determination of the locations and percent Dakota yield for wells pumping water from the Dakota aquifer with water rights (the section entitled "Location and Amount of Water Use" in the bulletin). The second section is an expanded version of the section on "Groundwater Geochemistry."

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Wells with Water Rights

Water in Kansas may be appropriated for beneficial use subject to vested and existing senior water rights for a variety of uses. Water rights are not required for "domestic" uses such as household purposes, livestock as part of operating a farm (fewer than 1,000 confined head of cattle and less than 15 acre-ft [18,500 m³] of use), or irrigation over less than 2 acres (0.8 ha) (Kansas Department of Agriculture, 2011). Wells with water-right permits are mainly for largercapacity production for irrigation, industrial, municipal, large feedlots, and other purposes, although a "domestic" well may also file to have the implied domestic water right under Kansas law quantified. The Division of Water Resources (DWR) in the Kansas Department of Agriculture collects and checks data on the location and reported water use for wells with appropriation rights. The DWR stores its water-right data in an Oracle-based relational data-base management system called the Water Rights Information System (WRIS). The Kansas Geological Survey (KGS), in cooperation with the DWR, developed an online interactive website, called the Water Information Management and Analysis System, or WIMAS, to guery and analyze WRIS-based data (http:// hercules.kgs.ku.edu/geohydro/wimas/index.cfm).

The point of water access and control associated with a water right is known as a point of diversion (PD). Usually only one well is associated with a PD, although some PDs are batteries of two or more wells tied together. The WRIS includes aquifer codes for many PDs that have groundwater rights. Aquifer codes include those for the Dakota Formation, Kiowa Formation, Cheyenne Sandstone, confined or unconfined Dakota aquifer, combinations of the Dakota aquifer with alluvial or Ogallala aquifers, and the Jurassic Morrison Formation, as well as other aquifers. Up to three aquifer codes can be associated with a PD.

The first step in determining the locations of wells partially or solely in the Dakota aquifer was to search and download data for all PDs in WRIS with the aquifer codes listed in table 1. The only Dakota-related codes in table 1 that were actually found were 330-333 and 340-343. Some of the PDs with these codes also included the codes 75 (Ark River [IGUCA]), 100 (Quaternary System), 112 (Tributary alluvium), 113 (Main stem alluvium), 115 (Terrace), 144 (Meade Grand Is Fm), 130 (Illinoisan Stage), 180 (Undifferentiated Kansan/Nebraskan), 200 (Tertiary System), 210 (Ogallala aquifer), 211 (Ogallala Formation, 400 (Jurassic-Triassic systems), 420 (Dockum Group), and 500 (Permian System). The data were subdivided into PDs located within the extent of substantial saturated thickness of the High Plains aquifer (HPA) and those located outside of the extents of the High Plains and alluvial aquifers.

The next step involved using the Kansas Master Ground-water Well Inventory (http://hercules.kgs.ku.edu/ geohydro/master well/index.cfm) to determine which of the PDs have well-log records. The KGS had recently developed the system, which indexes the water rights, drillers' logs, and depth-to-water data together. This allows water usage along with water-level changes to be associated with geologic sources when the data records are available. The Kansas Department of Health and Environment (KDHE) has required well drillers to file water well completion records (WWC5 forms) for all types of constructed, reconstructed, and plugged wells since 1975. Lithologic logs are a part of the drillers' records. The KGS stores the drillers' logs and has developed an online interactive data base of the log information (http://www.kgs.ku.edu/Magellan/WaterWell/ index.html). The data extracted from WRIS were then subdivided into data sets of PDs with and without WWC5 well logs.

To facilitate examination of the data relative to other information, such as aquifer extents (for the High Plains,

Table 1. Aquifer codes used for points of diversion search	ı of
completions in the Dakota aquifer system.	

Aquifer code	Aquifer name
94	Dakota-Cheyenne
330	Dakota Aquifer System (unconfined)
331	Dakota Formation
332	Kiowa Formation
333	Cheyenne Sandstone Formation
340	Dakota Aquifer System (confined)
341	Dakota Formation
342	Kiowa Formation
343	Cheyenne Sandstone Formation
95	Cheyenne-Jurassic-Triassic
300	Cretaceous System
92	Alluvium-Dakota
93	Ogallala-Dakota
64	Bedrock
99	Rock

alluvial, and Morrison-Dockum aquifers), the data extracted from WRIS were converted into shapefiles using ArcGIS (http://www.esri.com/software/arcgis/index.html) and viewed in ArcGIS Explorer (http://www.esri.com/software/arcgis/ explorer/index.html). Additional shapefiles were created from data extracted from WRIS for PDs that are located within the extent of the Dakota aquifer but that have aquifer codes other than those in table 1 and also for PDs that have no aquifer code. As for the PDs with Dakota aquifer codes in WRIS, individual shapefiles were created for PDs with and without WWC5 records.

WWC5 records include well depth. WRIS records for some PDs include reported well depths. Well depths from both sources were used to filter data extracted from WRIS for those PDs with other aquifer codes and without codes that are located within the HPA extent and that had depths greater than 50 ft (15 m) below the depth to the bedrock surface underlying the HPA. Excel spreadsheet files were also created for the different types of data sets for examination of data from WRIS associated with the PDs. such as DWR identification number (the PD number for the same location with multiple PDs with different water rights or for replacement PDs for the same water right), water-right number, water-right identification number, legal location (township, range, section, section qualifiers), and DWR aquifer codes. The initial Excel files included the link to the online WWC5 data base for PDs with well-log records along with well depths, where available. WWC5 links and well depths were added when additional information on well depths and matches between PDs and well logs were found.

A variety of information in WWC5 records for permitted wells was examined to estimate the percentage of the recent yield (during the several years before 2012) for each well determined to be drawing water from the Dakota aquifer. This information included the completed well depth, depths of the screened intervals and of grout seal, the top depth of Dakota units below overlying strata based on the lithologic log, the static water level, water levels after a pumping test, the relative permeabilities and thicknesses of lithologic units acting as aquifer units (e.g., sand, gravel, sandstone), and any other relevant information such as whether Dakota sandstone took water during drilling. For wells located outside the HPA extent, the location relative to the extent of the Dakota aquifer confined by overlying upper Cretaceous strata and the salinity of water in the upper Dakota aquifer were also considered. For wells located within the HPA extent, the bedrock surface depth (from Macfarlane and

Wilson, 2006) at the well location was used to assist in interpretation of the lithologic log if the log description did not clearly indicate the HPA-Dakota strata contact. After determination that a well was screened in both the Dakota aquifer and overlying unconsolidated sediment, the approximate depth of the static water level expected during the winters of the several years before 2012 was compared to that for the contact between Dakota and overlying strata. For those wells that were completed before this period, the static water level was estimated based on values for nearby wells with recent WWC5 records or on measurements in the online KGS data base WIZARD (http://www.kgs.ku.edu/ Magellan/WaterLevels/index.html). This water level was used to determine the relative thickness of the saturated HPA contributing to the well yield relative to the sandstone thickness of the Dakota aquifer contributing to the yield.

The following subsections describe in more detail the types of files and the information considered for estimating the percent Dakota yield out of the total yield of a well:

1. PDs with DWR Dakota codes within the Dakota aquifer extent

A few locations of PDs with Dakota aquifer codes were found to be outside of the Dakota aquifer extent; these were deleted from the spreadsheet files. WWC5 well-log records for a few PDs indicated that the well had been plugged; these were also deleted from the files.

a. PDs with WWC5 logs

The first information examined in a WWC5 record was the completed well depth, the bottom of the deepest screened interval, and the top depth of Dakota stratigraphic units below overlying strata based on the lithologic log. The location of grout interval(s) was considered to determine whether screened intervals only in the Dakota aquifer were sealed from overlying units. Wells completed entirely in the Dakota aquifer or the Dakota aquifer and some underlying Morrison-Dockum aquifer were assigned 100% yield from the Dakota aquifer.

After determination that a well was completed in both the Dakota aquifer and overlying unconsolidated sediment, the approximate depth of the static water level expected during the winters of the several years prior to 2012 was compared to the Dakota-overlying strata contact. WWC5 forms include the static water level measured at the time of well completion. For those wells that were completed before this period, the static water level was estimated based on values for nearby wells with recent WWC5 records or on measurements in the online KGS data base WIZARD. This water level was used to determine the relative thickness of each aquifer contributing to the well yield. If the water level was at or below the contact of the Dakota aquifer and an overlying unconsolidated aquifer, then the well yield was assigned as 100% Dakota. Substantial declines in water levels in the HPA during the last few decades have caused many older wells that were originally screened in both the HPA and underlying sandstones to decrease in production and produce a substantially smaller fraction of their yield from the HPA and a larger proportion from the Dakota aquifer.

If a well could possibly have a mixture of yield from the Dakota and other aquifers, the lithologic log and other information in the WWC5 record were examined in more detail. This included determining whether the well was screened in both the other aquifer(s) and the Dakota aquifer, was screened only in the other aquifer(s) but completed into the Dakota aquifer with a gravel pack in the annular space around the casing, or screened only in the Dakota aquifer but included a gravel pack around the casing in the other aquifer(s). A greater weight to the percentage of yield from the Dakota aquifer was given for those wells screened rather than only gravel packed in Dakota strata. The depth of grout sealing the annular space of the well within the overlying unconsolidated aquifer was part of the consideration for those wells with gravel pack above the screened interval(s). In some cases where pumping test data existed for a well in a WWC5 record, the pumping rate and the water level at the end of pumping were considered. Larger pumping rates such as above 1,000 gpm and water levels that remained in the overlying aquifer suggested a larger percentage of well yield derived from the overlying aquifer than the Dakota aquifer and vice versa.

The general character of the lithologic log was examined to estimate the percentage of total yield that would probably be produced based on a recent static water level. The hydraulic conductivity of the Dakota aquifer based on 22 field hydraulic tests of supply and observation wells ranges from 3.6 to 88 ft/day (1.1–27 m/day) and has a geometric mean of 12.5 ft/day (3.8 m/day). The hydraulic conductivities of core samples of Dakota sandstone in a site in central Kansas vary greatly, from less than 1 ft/day (0.3 m/ day) to more than 100 ft/day (30 m/day); most of the values fall in the range 1–100 ft/day (0.3–30 m/day) (Macfarlane, Doveton, and Whittemore, 1998). Hydraulic conductivities

used in a regional model of the Dakota aquifer in the central Midwest ranged from less than 10 ft/day (3 m/day) in westernmost Kansas to about 50 ft/day (15 m/day) for the easternmost portion of the aquifer in Kansas (Helgeson, Leonard, and Wolf, 1993). In comparison, the hydraulic conductivities of sediments in the HPA of southwest Kansas are about 20 ft/day (6 m/day) for fine to medium sand, 100 ft/day (30 m/day) for medium to coarse sand, 200 ft/day (61 m/day) for sand and gravel, and 300 ft/day (91 m/day) for gravel based on a calibrated groundwater flow model that used lithologic descriptions from WWC5 records (Liu et al., 2010). U.S. Geological Survey (USGS) values for HPA sediments are 50-80 ft/day (15-24 m/day) for fine to medium sand, 90 ft/day (27 m/day) for coarse sand, 160 ft/ day (49 m/day) for sand and gravel, and 200-350 ft/day (61–107 m/day) for fine to coarse gravel (Guttentag et al., 1984).

Well drillers usually record sandstones of the Dakota aquifer as "sandstone," although a few instances of "brown rock" for the sandstone are also present in the lithologic logs. For a well driller to recognize a sandstone that would be productive for a well, it was assumed that the hydraulic conductivity would be approximately equivalent to fine to medium sand. Although Dakota sandstone can have chemical precipitates (mainly ferric oxide or oxyhydroxides and calcite) partially filling pore spaces, the strata can also include fractures that increase permeability. In some subsurface portions of the Dakota, the sand is uncemented and no precipitate fills pore spaces.

When examining the lithologic log in a WWC5 form, the total thickness of sandstone was estimated as the sum of the intervals designated only as sandstone, plus approximately two-thirds of an interval with sandstone and other lithologies (such as shale, soapstone, or limestone) in which sandstone was listed first, plus about one-third of those intervals in which the sandstone was listed after some other terms. On some logs, the driller included a description of the relative permeability of Dakota sandstone strata (such as poor, fair, good, very good); on others, the driller indicated the percent sandstone in an interval of multiple lithologies; and on several logs, the driller listed relative percentages for both HPA aquifer units and Dakota sandstones. A number of lithologic logs indicated one or more intervals of the Dakota aquifer that "took water" or where circulation was lost. More weight was given to these sandstone intervals than others without such indication. All of this detailed information was used, where present, to assist in the percent yield calculation.

The total thickness of productive HPA or alluvial sediments overlying Dakota units in a well completed in both of these aquifers was estimated by summing the thicknesses of fine sand through gravel units recorded on a lithologic log. A foot of fine sand was assumed to be equivalent to about a half-foot of Dakota sandstone, fine to medium sand about the same as a unit of sandstone, medium to coarse sand about twice that of sandstone, sand and gravel approximately four to five times that of sandstone depending on the description of the sand and gravel, and gravel about six times that of sandstone. Similarly to the estimates for the Dakota sandstone, the thicknesses of productive units in the overlying unconsolidated aquifer that were listed as secondary to fine-grained lithologies (clay, silt) were assumed to be about one-third of that interval. Mixtures of productive lithologies-for example, fine to medium sand and gravel-were adjusted accordingly.

The percent yield of the Dakota aquifer from the total well yield was estimated as the sum of the Dakota sandstone divided by the total equivalent of overlying productive HPA or alluvial sediment plus the Dakota sandstone sum. If the percentage was less than 5%, the contribution of the Dakota aquifer to the well yield was assumed to be insignificant and the well was not designated as producing from the Dakota. A percentage greater than 5% but less than 14% was generally rounded to 10%; several wells with between 14% and 16% were designated to have 15% Dakota sandstone yield. Percentages of about 16% and above were rounded to the nearest 10%. A percentage greater than 95% was considered to be essentially all Dakota sandstone yield with insignificant contribution from overlying unconsolidated sediment. The accuracy of the values depends on the quality of the lithologic logs, the interpretation of the logs and other data, and the assumption of relative hydraulic conductivities for the different strata. The estimated uncertainty in the percentages is $\pm 10\%$ for the 10–20% and 80–90% ranges and $\pm 20\%$ for the 30–70% range for most of the wells with well logs.

In the early stages of the percent well yield determination, the estimates were less accurate than later because the process improved with experience. Estimates improved as more time was spent in calculating the relative yield of all the permeable units in an overlying unconsolidated aquifer and in the Dakota aquifer. For wells in the HPA area, if a WWC5 record indicated that a lithologic log was attached and no such log was actually attached, an estimate of well yield was assigned based on available information. For example, if the interval between the HPA bedrock depth and the bottom of the completed well exceeded the saturated thickness of the HPA, then 70% HPA and 30% Dakota yield was assigned initially. Later, the percent yield value assigned for records without attached logs was based on additional information for wells surrounding that well

b. PDs without WWC5 well logs

For PDs located outside of the extents of the High Plains and alluvial aquifers, the location was examined relative to the confined and unconfined Dakota aquifer and to the water quality in the upper Dakota aquifer to make sure that the location was consistent with a supply well in the Dakota. These wells were assigned a percent yield of 100% for the Dakota aquifer.

For PDs located within the HPA extent that included a reported well depth in WRIS, the depth below the bedrock surface underlying the HPA was considered in the percent vield estimation, along with information for nearby wells in the Dakota that have WWC5 records. The WRIS data for a PD sometimes include well depths reported for different years that do not agree with one another. Based on comparison with well depths in WWC5 records, the earliest reported depth value appears to be more accurate; later values sometimes were substantially different as well as being obviously erroneous. A shapefile of contours for the bedrock surface with a 25-ft (7.6-m) interval was used in ArcGIS Explorer to facilitate the examination. The depth of the bedrock surface based on WWC5 lithologic logs was also considered for some wells in the same or adjacent sections to help determine actual bedrock depth because of the uncertainty in the mapped bedrock surface. More weight was given to a depth based on a lithologic log contact because the bedrock surface coverage is a regionally averaged coverage and locally can be in error by as much as 50 ft (15 m) or more.

The uncertainty in the percent Dakota for these wells is expected to be substantially greater than for the wells with well-log records. Although some of the wells to which some Dakota yield was assigned may have substantially less or even no significant Dakota yield, this is probably offset by other wells that could have some yield from the Dakota that were not identified based on the above procedure and available information. This would be the case for those wells that have reported depths less than 50 ft (15 m) below the actual bedrock surface but that are also screened in sandstone, and for wells completed to a depth of greater than 50 ft (15 m) below the actual HPA bedrock surface in areas where local contours in the bedrock surface map of Macfarlane and Wilson (2006) are deeper than actual.

If no depth information exists for a PD with a DWR Dakota code, then the percent Dakota was estimated based on an average of the values for the surrounding wells that include the Dakota aquifer.

2. PDs within the Dakota extent and with DWR aquifer codes other than the Dakota aquifer or with no aquifer code

a. PDs with WWC5 well logs outside the HPA and alluvial aquifer extents

The WWC5 record was examined to verify that the well was screened in Dakota strata and to determine whether the screened interval included any overlying consolidated material that is saturated. Nearly all of these wells were assigned 100% Dakota. If a well included overlying permeable sediment, the procedure in section 1a was followed for estimating the percent Dakota yield. Several wells with no aquifer code were found to be completed in the Dakota aquifer.

b. PDs within the HPA extent and with well depths greater than 50 ft (15 m) below the bedrock surface underlying the HPA

If a WWC5 record exists for the PD, the well depth in the well log record was used and the procedure in section 1a was followed to estimate the percent Dakota yield. For wells without WWC5 records but with a reported WRIS depth, the procedure in the second paragraph in section 1b was followed. Several wells with aquifer codes other than for Dakota system strata were found to include the Dakota aquifer. Many wells with no aquifer codes were found to be partially or solely completed in the Dakota aquifer.

The procedures in section 2 could miss characterizing wells that produce partially from the Dakota aquifer within productive parts of the HPA, that have no Dakota-related aquifer code assigned by the DWR, and that have no well log or reported depth. USGS and KGS reports on sandstone aquifers in southwest Kansas and KGS bulletins on the geohydrology of selected counties, which were published during the mid-1960s to mid-1980s (Bayne et al., 1971; Fader et al., 1964; Hodson, 1965; Kume and Sponazola, 1982, 1985; Lobmeyer and Weakly, 1979; McNellis, 1973), were examined for records of wells producing primarily or partially from the Dakota aquifer. These records were

compared to the list obtained by the above procedures and to WRIS and WWC5 records; more than a dozen wells were added based on this additional review.

Wells without Water Rights

Wells in Kansas classified as for "domestic" uses do not need a water right. Wells that pump water primarily from the Dakota aquifer for "domestic" uses tend to be distributed in areas outside the extents of alluvial aquifers and the HPA. For example, Bayne et al. (1971) listed 210 wells used for some water supply purpose in Ellsworth County in 1961. Of these, 181 were used for domestic and stock purposes and the 29 others were used for public supply, industry, and irrigation. Domestic and stock wells in the list that produced solely or primarily from the Dakota aquifer numbered 136 (75% of the total domestic and stock wells, 65% of the total wells). Most of the other sources of water were alluvium and terrace deposits of the Smoky Hill River valley that cuts diagonally across the county and thinly saturated deposits of the HPA in southwest Ellsworth County.

WWC5 records for 1975 to early March 2012 for Ellsworth County include a total of 596 wells constructed for domestic (457), lawn and garden (116), and feedlot/livestock (23) use (table 2). Stockwatering rights exist in WRIS for eight points of diversion from groundwater in Ellsworth County, of which seven are active. Three wells also have domestic rights; one of these is no longer an active point of diversion. The priority dates for all of the water rights are 1979 or after. If the eight stockwatering and three domestic wells with water rights are subtracted from the 596 total, then 585 wells were constructed during 1975-2012 for uses that would be classified as "domestic" by Kansas water law and that do not have quantified water rights. The primary water source for about 60% (351) of these wells is expected to be the Dakota aquifer based on the 65% proportion for 1961 and the general appearance of the distribution of wells with WWC5 records on a county map. If the annual rate for constructing Dakota "domestic" wells without quantified water rights between 1962 and 1975 was about the same as the average rate for 1975–2012, then approximately 133 wells would have been drilled during 1962-1975. Thus, the total number of Dakota wells constructed for "domestic" purposes would have been about 620 based on 136 for the 1961 list in Bayne et al. (1971), 133 for 1961-1974, and 351 for 1975–2012. Plugging records in the WWC5 data base for domestic, lawn and garden, and feedlot/livestock uses sum to 237 for 1975-2012. If 60% (142) of these

Table 2. Well types and ratios used in the estimation of the total number of "domestic" wells in Ellsworth, Ottawa, and Rush counties.

Well type or ratio	Ellsworth	Ottawa	Rush	Sum
	County	County	County	Sum
Domestic constructed	457	656	310	1,423
Lawn and garden constructed	116	136	22	274
Feedlot or stock constructed	23	50	31	104
Total constructed	596	842	363	1,801
Domestic plugged	225	24	77	326
Lawn and garden plugged	5	0	3	8
Feedlot or stock plugged	7	4	11	22
Total plugged	237	28	91	356
Constructed minus plugged	359	814	272	1,445
Stockwatering and domestic (WRIS PDs)	11	18	5	34
Net total (constructed minus plugged and WRIS PDs)	348	796	267	1,411
Estimated current Dakota "domestic"	478	958	129	1,565
Estimated current adjusted Dakota "domestic" (minus 5% plugged before 1975 or currently inactive)	454	910	123	1,487
Ratio adjusted Dakota "domestic"/net total	1.305	1.143	0.459	1.054

were assumed to have drawn water predominantly from the Dakota aquifer, then the number of current Dakota wells in Ellsworth County would be approximately 480. This number was further reduced by 5% to reflect wells that were either plugged before WWC5 records began in 1975 or are currently inactive, giving a total of about 450 currently active "domestic" wells drawing part or all of their water source from the Dakota aquifer.

Similar data were used to estimate the number of wells classified as for "domestic" uses with primarily a Dakota aquifer source in Ottawa and Rush counties. Mack (1962) listed 175 wells used for some supply purpose in Ottawa County during 1957–1958. Of these, 164 were for domestic and stock purposes and the 11 others were for public supply and irrigation. Domestic and stock wells producing solely or primarily from the Dakota aquifer numbered 136 (83% of the total domestic and stock wells, 78% of the total wells). McNellis (1973) listed 222 wells used for some supply purpose in Rush County during 1959–1960. Of these, 60 were domestic and stock wells and the 162 others were used for public supply, industry, and irrigation. Domestic and stock wells producing solely or primarily from the Dakota aquifer numbered 26 (43% of the total domestic and stock wells, 27% of the total wells).

WWC5 records for 1975-2012 for Ottawa County include

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842 wells constructed for domestic (656), lawn and garden (136), and feedlot/livestock (50) use (table 2). Stockwatering rights exist in WRIS for 17 points of diversion from groundwater in Ottawa County, of which 13 are active. One domestic well has a water right. The priority dates for all but one of the stockwatering rights are 1980 and after, and for the domestic well is 2001. If the 17 stockwatering wells and one domestic well with water rights are subtracted from the 842 total, then 824 wells were constructed during 1975-2012 for uses that would be classified as "domestic" by Kansas water law. The primary source for about 70% (577) of these wells is expected to be the Dakota aquifer based on the 78% for the 1957–1958 list of Mack (1962) and the map distribution of WWC5 records (many wells appear to be in alluvial aquifer areas for 1975–2012). If the annual drilling rate for Dakota "domestic" wells for 1959 to 1975 was about the same as the average rate for 1975–2012, then approximately 265 wells would have been drilled during 1959–1975. Thus, the total number of Dakota wells constructed for "domestic" purposes would have been about 980 based on 136 for the 1957-1958 list in Mack (1962), 265 for 1959-1974, and 577 for 1975–2012. Plugging records in the WWC5 data base for domestic, lawn and garden, and feedlot/livestock uses sum to 28 for 1975–2012. If 70% (20) of these were assumed to have drawn water predominantly from the Dakota aquifer, then

the number of Dakota wells would currently be about 960. Further reduction for wells plugged before 1975 or currently inactive gives a total of 910 currently active "domestic" wells producing from the Dakota aquifer.

WWC5 records for 1975-2012 for Rush County include 363 wells constructed for domestic (310), lawn and garden (22), and feedlot/livestock (31) use (table 2). Stockwatering rights exist in WRIS for six points of diversion from groundwater in Rush County, of which five are active. The priority dates for two of these water rights are 1972 and 1974 and for the others are 1975 and after. Two domestic water rights exist; the use of water is no longer active from either one. One of the domestic wells has a priority date of 1972, the other 1975. If the five stockwatering and domestic wells with priority dates of 1975 and greater are subtracted from the 363 total, then 358 wells were constructed during 1975–2012 for uses that would be classified as "domestic." The primary source for about one-fourth (90) of these wells is expected to be the Dakota aquifer based on the 27% value for the 1959–1960 list of McNellis (1973). If the annual drilling rate for Dakota "domestic" wells for 1961 to 1975 was about the same as the average rate for 1975–2012, then approximately 36 wells would have been drilled during 1961–1975. Thus, the total number of Dakota wells constructed for "domestic" purposes would have been about 150 based on 26 for the 1959–1960 list in McNellis (1973), 36 for 1961–1974, and 90 for 1975–2012. Plugging records in the WWC5 data base for domestic, lawn and garden, and feedlot/livestock uses sum to 91 for 1975-2012. If 25% (23) of these were assumed to have drawn water predominantly from the Dakota aquifer, then the number of Dakota wells would currently be approximately 129. Further reduction for wells plugged before 1975 or currently inactive gives a total of 123 active "domestic" wells in the Dakota aquifer.

The estimated number of active wells in Ellsworth, Ottawa, and Rush counties classified as for "domestic" use and producing solely or primarily from the Dakota aquifer totals more than 1,490. The number of wells for these three counties in the WWC5 data base that were constructed for "domestic" purposes during 1975–2012 is 1,801. If the total plugged wells in the WWC5 records for these counties (356) and the number of stockwatering and domestic wells with water rights with priority dates after 1974 (34) are subtracted from the constructed total, the result is a "net total" of 1,411 wells for 1975–2012. The ratio of the estimated active Dakota wells to the 1,411 "net total" is 1.05. Table 2 summarizes the data used for the above calculations.

Ellsworth, Ottawa, and Rush counties are reasonably representative of the counties in the north-central and central regions (table 3) where the Dakota aquifer is used for water supply. The usable Dakota aquifer in these regions includes both confined and unconfined strata, and unconsolidated aquifers overlying part of the Dakota are mainly alluvial systems associated with stream and river valleys. The total number of active Dakota wells used for "domestic" purposes in the north-central and central regions of Kansas was estimated by multiplying the 1.05 ratio times the "net total" wells for 1975-2012 for these regions. However, for this calculation, an adjustment must be made for the area for which "domestic" wells are summed from the WWC5 data base because not all of the counties in these two regions are underlain by Dakota strata. Thus, no wells from Clay County were considered in the north-central region to approximately balance the area of Washington County that is not underlain by the Dakota aquifer. Similarly, no wells were considered in Saline, McPherson, and Marion counties to offset the area without underlying Dakota strata in Rice County and the part of Barton County south of the Arkansas River where the HPA is essentially the only aquifer used.

The total number of domestic, lawn and garden, and feedlot/livestock wells constructed from 1975 to early 2012 in the adjusted areas of north-central and central Kansas is 9,205 (table 4). The proportion of the total "domestic" wells constructed during 1975–2012 in Ellsworth, Ottawa, and Rush counties that have post-1974 stockwatering and domestic water rights is 1.89% (34 WRIS wells divided by 1,801 wells). If this percentage is subtracted from the "domestic" well total in the adjusted north-central and central Kansas areas, the result is 9,031 wells. Subtracting the total

Kansas region	Counties in region
North-central	Clay, Cloud, Ottawa, Republic, Washington
Central	Barton, Ellis, Ellsworth, Lincoln, Marion, McPherson, Rice, Rush, Russell, Saline
South-central	Edwards, Pawnee
West-central	Lane, Ness, Scott, Trego, Wichita
Southwest	Clark, Finney, Ford, Grant, Gray, Hamilton, Haskell, Hodgeman, Kearny, Meade, Morton, Seward, Stanton, Stevens

Table 3. List of counties for different regions of the Dakota aquifer in Kansas.

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Table 4. Well types and ratios used in the estimation of the total number of "domestic" wells in north-central and central Kansas.

Well type or ratio	North-central minus Clay County	Central minus Saline, McPherson, and Marion counties	Sum
Domestic constructed	1,597	4,691	6,288
Lawn and garden constructed	297	1,871	2,168
Feedlot or stock constructed	265	484	749
Total constructed	2,159	7,046	9,205
Domestic plugged	284	864	1,148
Lawn and garden plugged	4	123	127
Feedlot or stock plugged	40	95	135
Total plugged	328	1,082	1,410
Constructed minus plugged	1,831	5,964	7,795
Estimated ratio stockwatering and domestic (WRIS)/ total constructed	0.0189	0.0189	
Estimated stockwatering and domestic (WRIS PDs)	41	133	174
Net total (constructed minus plugged and WRIS PDs)	1,790	5,831	7,621
Estimated ratio adjusted Dakota "domestic"/net total	1.05	1.05	
Estimated adjusted Dakota "domestic"	1,880	6,120	8,000

number of plugged wells for "domestic" uses (1,410) gives a "net total" of 7,621. Application of the 1.05 ratio of Dakota wells to "net total" wells for Ellsworth, Ottawa, and Rush counties gives an estimate of 8,000 "domestic" wells with a primary water source from the Dakota aquifer for these two regions (table 4).

A major portion of the south-central, west-central, and southwest regions of the Dakota aquifer (table 3) are overlain by the HPA, which is the primary source of water in these areas. Similarly to the north-central and central regions, the counties in the south-central and southwest regions were adjusted to reflect areas that are either not underlain by the Dakota aquifer or where the Dakota aquifer may not be used at all where it overlies Dakota strata. For the southcentral region, WWC5 records in Edwards County were not included; thus, only Pawnee County wells were considered. In the southwest region, WWC5 records were not included for Clark, Meade, and Seward counties to offset the areas of Morton and Stevens counties that are not underlain by the Dakota aquifer.

The total number of domestic, lawn and garden, and feedlot/livestock wells constructed from 1975 to early 2012 in west-central Kansas and the adjusted areas of south-central and southwest Kansas is 8,585 (table 5). Inspection

of WIMAS records for some of the counties in southwest Kansas indicates that the proportion of feedlot and domestic wells with water rights is greater than for north-central and central Kansas. Thus, the total number of "domestic" wells was reduced by 5% instead of 1.89% giving 8,156 wells. Subtracting the number of plugged wells for "domestic" uses gives a "net total" of 6,346 wells. The 1.05 ratio of Dakota wells to "net total" wells is expected to be too high a ratio for these areas because in most of the counties the HPA is the predominant water source. However, in much of these regions either not containing the HPA or with only thinly saturated HPA, the Dakota aquifer (along with some underlying Morrison-Dockum aquifer) is the main water source. A ratio of 0.5 was used as a rough estimate of the ratio of Dakota wells to the "net total" wells used for "domestic" purposes. This number was selected to be less than the ratio (0.65) of two fractions: the first (0.083) is the number of permitted water-right wells in the Dakota aquifer divided by the total permitted wells in all aquifers in southcentral, west-central, and southwest Kansas; the second (0.129) is the analogous value for north-central and central Kansas. This gives an estimate of 3,170 "domestic" wells with a primary water source from the Dakota aquifer for these three regions (table 5).

Well type or ratio	South-central, Pawnee County only	West-central	Southwest minus Clark, Meade, and Seward counties	Sum
Domestic constructed	657	1,379	5,067	7,103
Lawn and garden constructed	28	79	77	184
Feedlot or stock constructed	132	392	774	1,298
Total constructed	817	1,850	5,918	8,585
Domestic plugged	46	284	1,079	1,409
Lawn and garden plugged	7	3	101	111
Feedlot or stock plugged	16	79	195	290
Total plugged	69	366	1,375	1,810
Constructed minus plugged	748	1,484	4,543	6,775
Estimated ratio stockwatering and domestic (WRIS)/total constructed	0.05	0.05	0.05	
Estimated stockwatering and domestic (WRIS PDs)	41	92	296	429
Net total (constructed minus plugged and WRIS PDs)	707	1,392	4,247	6,346
Estimated ratio adjusted Dakota "domestic"/net total	0.5	0.5	0.5	
Estimated adjusted Dakota "domestic"	354	696	2,123	3,173

Table 5. Well types and ratios used in the estimation of the total number of "domestic" wells in south-central, west-central, and southwest Kansas.

The total number of "domestic" wells with a primary source from the Dakota aquifer in Kansas is estimated as 11,200 (8,000 for north-central and central and 3,170 for south-central, west-central, and southwest Kansas).

GROUNDWATER GEOCHEMISTRY

Introduction

Data about and interpretation of the geochemistry of groundwater in the Dakota aquifer is valuable for 1) determining and predicting where (including areal and vertical dimensions) water resources suitable for different uses are located, 2) understanding the origin of factors that control individual constituents of concern for various water uses, 3) differentiating between natural and contamination sources of constituents, and 4) estimating the temporal changes in chemistry related to impacts on groundwater flow caused by pumping. The initial discussion in this section describes the water chemistry data assembled for the Dakota aquifer, including new data collected during the Dakota Aquifer Program based on water sampling and interpretation of geophysical (resistivity) logs. The data interpretation begins with a section on factors that control groundwater geochemistry in the aquifer. The discussion of the relationship between groundwater conductance and dissolved constituents provides information about how well the chemical character of waters can be estimated from this easy-to-measure property. The next subsection describes characteristics of contaminated groundwater in the Dakota aquifer, including a method for distinguishing between natural and contamination sources of salinity in the aquifer. The following two subsections discuss spatial variations in the groundwater chemistry, first regional patterns and then vertical changes. The final subsection examines the geochemistry across the saline and freshwater transition in the aquifer in north-central Kansas based on numerical modeling to help in understanding the chemical development and changes in this region.

Chemical Data for Groundwaters Data for Water Samples

The basis for valid interpretation of the geochemistry of groundwater in the Dakota aquifer is chemical data for which

the quality and uncertainties are known. A substantial effort of the Dakota Aquifer Program involved assembling existing data followed by examination of quality characteristics, correction of errors, and elimination of records or values for which the uncertainty in the data was too large for use in geochemical interpretation. Another component of the program involved collection of new data from many wells distributed across the aquifer, including observation wells installed as part of the program and private and public supply wells. The data base created from the existing and new water analyses provides the most complete chemical record available for the Dakota aquifer in Kansas.

Water-Quality Data Base

Water-quality data for the Dakota aquifer were assembled from existing sources and analyses of samples collected as a part of the Dakota Aquifer Program. A data base was first developed based on INFO in ARC/INFO (ESRI programs). Tables for selected groups of data were converted to Microsoft Excel spreadsheet files and placed on the KGS website for the Dakota Aquifer Program. Well sites from which water samples were collected and analyzed were coded according to the USGS system for formations in Kansas. Chemical data were included for the Dakota Formation or older formation names equivalent to the Dakota, undifferentiated Lower Cretaceous strata, the Kiowa Formation, and the Cheyenne Sandstone.

As of late 2013, the data base contained 1,641 chemical records related to the Dakota program, of which 1,594 are for samples from wells yielding water entirely or partly from the Dakota aquifer. The 48 other records are for samples from wells obtaining water from strata above or below the Dakota aquifer. The data for samples entirely or partly from the Dakota aquifer represent 1,192 sampling locations (a unique sampling point or interval), 10 of which are in southeastern Colorado and the rest of which are in Kansas. Although most well sites consist of only one sampling interval, some wells or boreholes have been sampled at multiple depths; each of these depths represents a separate sample site identification in the data base. A total of 1,123 well sites sampled only the Dakota aquifer. Of these, 1,002 sites are coded for samples entirely from the Dakota Formation, an equivalent unit, or Lower Cretaceous Series. In addition, 81 sample locations are coded as the Kiowa Formation, 38 locations as the Chevenne Sandstone, and two locations as a combination of Dakota and Cheyenne or Kiowa and Cheyenne. Other locations are for samples from wells that obtain groundwater

from the Dakota and non-Dakota aquifer units. The data base includes records for multiple samples (collected at different dates or times) from 121 of the wells completed entirely or partly in the Dakota aquifer. A total of 433 records represent the additional samples collected after the initial sample from the 121 well locations.

There are 313 water-quality records in the data base for samples collected as a part of the Dakota Aquifer Program. The KGS collected and analyzed 170 of these samples. Kansas State University collected and analyzed 80 samples as a part of a cooperative study for the Dakota Program. The KGS arranged for Kansas companies, conducting exploration studies for groundwater supplies and for a monitoring well, to collect 63 samples and send them to the KGS for analysis and use in the Dakota Program.

Figure 1 shows the distribution of the geographic locations of the well sites in Kansas from which groundwaters were analyzed and that obtained their water solely from the Dakota aquifer. Most of the sites are located where the water in the aquifer is of good enough quality to be used for water supply. The densest distribution of points is in a band along the eastern outcrop and subcrop of the Dakota Formation, with smaller numbers of points in southwestern Kansas.

Excel spreadsheets with location and site information and chemical data for the groundwaters in the Dakota program data base are included on the online website for the Dakota Aquifer Program (http://www.kgs.ku.edu/Dakota/ vol2/qualDB/quality.htm).

Existing Data

Water-quality data were assembled from several different existing sources. Most of the existing data were obtained from a USGS electronic water-quality data base. Other data sources include the National Uranium Resource Evaluation (NURE) program (now available from the USGS website for the National Geochemical Database [Smith, 1997], http://pubs.usgs.gov/of/1997/ofr-97-0492/) and the KDHE. The electronic data sets were found to contain many problems and errors, such as duplications due to incomplete information in one of the duplicate records, mistyped numbers, incorrect locations or depths, and incorrect identification of geologic unit (for example, 15 samples from McPherson County in the NURE data base for which the water-producing formation was identified as the Kiowa Formation but which were actually sampled from the HPA or Permian strata). These errors were found during the course



Figure 1. Distribution of the locations of wells from which groundwaters were collected from the Dakota aquifer.

of the Dakota program and later as the data were examined during the preparation of this bulletin. The errors were corrected to the extent possible, including by referring to the original printed version of the data in publications (KGS and USGS) if they could be found. Some records, such as those for samples that were not actually in the Dakota aquifer, were not used. Another major source of existing data was publications of the KGS such as county bulletins. Chemical records in the bulletins were entered into the data base if not already in the USGS data set. Many missing values of major constituent concentrations for existing records in the data base were filled by referring to original data publications.

Aquifer codes were assigned if not present based on examination of the well location and depth relative to the surface elevation and contour maps of stratigraphic tops and thicknesses (Macfarlane et al., 1990). General aquifer codes in records were changed to more specific codes for many of the well sites. For example, the code 210CRCS (Cretaceous System) was changed to 210DKOT (Dakota Formation) or 217KICY (Kiowa Formation and Cheyenne Sandstone), or 211NBRR (Niobrara Formation), in order that the waterquality data could be assigned to the Dakota aquifer or other geologic units.

Selected chemical data were removed from selected records of existing data if clearly inconsistent with the body of data for the record. For example, five values of field specific conductance (NURE data) were deleted in sample records with total dissolved solids (TDS) concentrations that were more than twice the conductance. Summation of the major constituent concentrations indicated that the TDS values were correct. Four of these five values are for samples collected on November 14 and 17, 1978, suggesting that the meter used for these measurements may not have been calibrated properly. A reported TDS sum that was more than four times the measured TDS was replaced with a TDS sum computed from the reported concentrations of major constituents. Values of pH less than 4.5 units were deleted for five sample records because a substantial bicarbonate (HCO₂) concentration is in the records, an occurrence that is inconsistent because there cannot be any bicarbonate measured at that pH. Four of these five records are for samples collected on November 10, 1978, suggesting that the electrode was not properly calibrated for the field pH measurements on that day. Five additional records had pH values in the range 5-6.2 units. These values are suspected to be too low, especially the values less than 6 units. Three of these five pH measurements were made during

November 13–14, 1978, a period close to the date for which four pH values of less than 5 units were measured and which are clearly inaccurate. High pH values (greater than 9 units) were left in the data base even though most of these probably represent the effect of cement grout used to seal the annular space of the borehole and not the actual groundwater. The high pH measurements should alert the viewer to the potential impact on selected constituents such as bicarbonate, calcium (Ca), and magnesium (Mg) concentrations. One pH value of 9.6 was deleted from a record because the 25 other samples collected from the same site had a pH range of 7.0 to 7.8 units.

Although a substantial effort was made to correct obvious errors and eliminate records and values deemed to have too great an error or uncertainty for use in interpretation of water chemistry, this study does not claim to have discovered all errors in the data. The user of the data base created for the Dakota program should be aware of the possibility of undiscovered errors.

Data collected for the Dakota Aquifer Program

Sampling and analytical procedures

The KGS collected water samples from wells and analyzed them in its laboratory to provide additional data necessary for characterizing the regional water quality, determining mechanisms controlling water chemistry, assessing the supply uses of the water, and assisting in the geohydrologic evaluation of study sites of the Dakota Aquifer Program. The sampling sites included existing water-supply wells and observation wells installed in test holes drilled for the Dakota program. The KGS obtained other samples that staff of local agencies and water-resource consultants collected from test holes and observation and supply wells, and analyzed them for conservative constituents (those that do not require special sample treatment and preservation).

The KGS sampled water-supply wells after pumping for approximately one-half to one hour, wherever possible, to obtain water representative of that in the formation. The sample location was located as close to the well as practical. In a few cases, a 30-gallon pressure tank was in the system and no tap was available between the tank and the well. Where this occurred, the well had been in active use during the same day of sampling, thus, effects of the tank on the sample should be minimal. In some instances, sampled water passed through a garden house at the site during the period before and during sampling because the well owner did not want water to accumulate near the well. At one domestic well location, the pumping occurred for only about 15 minutes prior to sampling because longer pumping would draw the water level below the pump intake and damage the pump. At this site, the water came through an underground pipe from the well to an outdoor hydrant without passing through a pressure tank. Sampling at test wells was after a substantial period of pumping to provide water representative of that in the strata at the depth of the screened interval of the well.

The KGS measured temperature, specific conductance, and pH at the time of collection of water samples. Sampling during 1990–1997 included measurement of temperature and specific conductance during the pre-sampling pumping to ensure that these properties had stabilized before sampling. The pH meter was calibrated using pH 4 and 7 buffers at the beginning of each day and checked after about each half day of use with the pH 7 buffer. Buffer checks agreed to less than 0.1 pH unit.

Samples for determination of dissolved inorganic constituents were collected in polyethylene bottles. Unfiltered, unacidified samples were collected directly from the hydrant, hose, or irrigation pipe point of water exit. Samples for measurement of trace metal contents were preserved with high-quality acid. Samples sent to USGS laboratories for determination of radionuclides were collected and preserved according to the appropriate USGS protocol. For example, the USGS procedure for collecting samples for radon (Rn) determination involved extracting the water with a 10 mL glass syringe with a metal needle from a water stream that had as little agitation as possible to avoid substantial gas loss. In some cases a hose was placed in the bottom of a 1 L polyethylene bottle and the pumping rate reduced such that the water stream exited the bottle without bubbles forming. In other cases, the syringe was either placed into the stream from the sampling point or immediately into water collected in a 1 L polyethylene bottle. The water collected in the syringe was injected into mineral oil in a glass vial. Two samples were collected at each site for radon determination in order to assess the sampling error related mainly to gas loss. Samples for radon determination were sent by express mail directly to the analytical laboratory used by the USGS for this constituent.

Samples preserved with hydrochloric acid were placed into polyethylene bottles into which the acid had been previously added at the KGS. Nitric acid preservation was accomplished by adding the acid from sealed glass ampules obtained from the USGS. All samples except those for radon measurement were stored in coolers with ice after collection until being brought to Lawrence. Samples for metals determination were filtered in the field by passing the water collected in a large polycarbonate jar through a 0.45 μ m membrane filter in a polyethylene holder using pressure from a peristaltic pump with silicone tubing. Approximately 10 or more liters of water were placed in the jar, which was fitted with a polyethylene spigot and tubing attached at the bottom of the jar that allowed flow into the silicone tubing.

The KGS determined concentrations of dissolved inorganic constituents at its analytical laboratory. Alkalinity content was measured using an automated titrimeter and converted to bicarbonate. Concentrations of dissolved silica (SiO₂), boron (B), the cations calcium, magnesium, sodium (Na), potassium (K), strontium (Sr), and barium (Ba), and the metals iron (Fe), manganese (Mn), and zinc (Zn) were determined on a Jarrell-Ash inductively-coupled argon plasma spectrometer (ICP). Measurements of the trace metals cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), and silver (Ag) and the semimetals arsenic (As) and selenium (Se) were made using a graphite furnace on a Jarrell-Ash atomic absorption spectrophotometer. The trace metals iron and manganese were also determined using the graphite furnace if the concentrations were lower than the quantifiable limits of the ICP analysis, 25 and 4 µg/L, respectively. Mercury (Hg) content was determined by the cold vapor technique on the atomic absorption spectrophotometer. Concentrations of the anions chloride (Cl), sulfate (SO₄), nitrate (NO₂), ammonium ion (NH₄), phosphate (PO₄), bromide (Br), and total inorganic iodine (I) were made by segmented flow analysis on a Technicon AutoAnalyzer II system with the appropriate analytical cartridges. Fluoride (F) content was measured with a selective-ion electrode and a Hach pH/ISE meter.

The KGS laboratory carefully followed quality assurance and control procedures to ensure high accuracy of the data for research purposes. These steps included checks for charge-balance errors for major constituents. The KGS participated in the USGS Standard Reference Sample Project (http://bqs.usgs.gov/srs/) for laboratory quality assurance and always had very good agreement with the published values for the reference samples.

Supply and test well sampling

The KGS collected and analyzed groundwater samples as part of a Dakota aquifer study in central Kansas for the Kansas Corporation Commission (Macfarlane et al., 1988). The KGS collected samples from domestic, stock, and municipal wells in 1987 (and resampled one well in 1988) and from four monitoring well sites in 1987–1988. The supply wells were located in Barton, Ellis, Graham, Rooks, Rush, Russell, and Trego counties. The monitoring well sites were near Hill City in Graham County (upper Dakota and lower Dakota wells), north of Hays in Ellis County (upper Dakota, lower Dakota, Cheyenne, and Cedar Hills wells), and near Gorham in Russell County (upper Dakota, lower Dakota, Cheyenne, and Cedar Hills wells). The records for the samples from the Dakota aquifer (45 from supply wells and 11 from monitoring wells) and the underlying Cedar Hills Sandstone (two samples) listed in Macfarlane et al. (1988) were entered into the water-quality data base.

The KGS collected groundwater samples from supply wells for the developed areas of the Dakota aquifer in north-central, south-central, and southwest Kansas during 1990–1993. This included Cloud, Lincoln, Mitchell, Ottawa, Republic, and Washington counties in north-central Kansas; Barton, Ellis, Ellsworth, and Russell counties in central Kansas; and Finney, Gove, Hamilton, Hodgeman, Lane, Ness, Scott, Trego, and Wichita counties in southwest and westcentral Kansas. The wells were used for domestic, municipal, stock, and irrigation supplies. Sampling in 1992 included supply wells in southeastern Colorado as part of a traverse from Colorado to central Kansas conducted in cooperation with the Lawrence Livermore National Laboratories (LLNL). The LLNL collected samples for determination of selected trace constituents and isotopes for use in studies of the groundwater geochemistry of the Dakota aquifer.

The KGS sampled groundwaters during pumping of observation wells installed in test holes drilled as part of the Dakota Aquifer Program during 1991-1995 and 1996-1997. The sampled wells were located at the study sites in Cloud, Hodgeman, Lincoln, Stanton, Trego, and Wallace counties. The KGS also collected samples from two observation wells installed in Gray County, one in the HPA and one in the Dakota aquifer, for part of an evaluation of the hydraulic connection between the two aquifers. The KGS cooperated with consulting companies investigating the potential of the Dakota aquifer in Ellis and Russell counties to obtain water samples that the KGS then analyzed. The KGS used the data for subregional characterization of salinity and determination of the dissolved chloride source in the groundwaters. The cooperative LLNL and KGS profile of groundwater geochemistry from southeast Colorado to central Kansas also included sampling of selected observation wells at the

test-hole study sites of the Dakota program. Chemical data for these samples are in the online data base for the Dakota program.

Water Quality from Geophysical Logs

Little water sample data exist for the Dakota aquifer in northwest Kansas. However, many oil and gas boreholes pass through Dakota strata in northwest Kansas for which geophysical logs exist. Boeken (1995) estimated TDS concentrations for groundwaters in Dakota strata from geophysical logs that included self potential (SP) curves. The description of the principles on which the SP curves are based and the analysis of the curves for estimation of formation water resistivities are in Macfarlane, Doveton, and Whittemore (1998).

Boeken (1995) analyzed 977 SP logs for oil and gas boreholes in 11 counties (Cheyenne, Decatur, Gove, Graham, Logan, Norton, Rawlins, Sheridan, Sherman, Thomas, and Wallace) in northwest Kansas to estimate water resistivity values for formation waters in the Dakota aquifer. He determined water resistivities for a single sandstone unit for 890 boreholes, two sandstone units at different depths for 69 boreholes, three sandstone units for 14 boreholes, and four sandstone units for four boreholes, for a total of 1,086 values. Of that total, 1,078 values were for formation waters in sandstones in the Dakota Formation, three for sandstones in the Kiowa Formation, and five for sandstones in the Cheyenne Sandstone. Figure 2 shows the geographical distribution of the borehole locations.

The specific conductance of a water is the reciprocal of the resistance value R_w . The subsection below on factors that control groundwater chemistry shows that the TDS concentration in groundwater from the Dakota aquifer can be estimated well from the simple relationship between specific conductance and TDS concentration for the Dakota aquifer.

Boeken (1995) converted the R_w values from the 75 °F standard for the oil and gas industry to values for 25 °C (77 °F), the standard temperature used for conductance measurements in water-resources investigations. The TDS concentrations that Boeken listed in his report were based on a factor of 0.6 times the conductance of the formation water in the sandstone units for which he determined R_w from the SP curves. The TDS concentration estimates used in this bulletin were recalculated using the equation

TDS (in mg/L) = 0.64 x SpC - 20where SpC is specific conductance in μ S/cm at 25 °C. This equation, which is discussed in more detail in the following section, is based on water-sample data in the Dakota waterquality data base.



Figure 2. Distribution of the locations of the oil and gas boreholes in northwest Kansas for which the resistivities of groundwaters in the Dakota aquifer were estimated from geophysical log analysis.

Factors that Control Groundwater Chemistry

The chemistry of groundwater primarily refers to the type and concentration of dissolved substances in the water and properties such as specific conductance, pH, and hardness. The dissolved substances include gases and inorganic and organic constituents. In addition, the isotopic concentrations of selected chemical elements are sometimes used in geochemical characterization of waters. The particular concentrations of different dissolved species and isotopes and values of chemical properties in a groundwater and the spatial changes in these values within an aquifer provide information about the geochemistry of the system. An understanding of the water geochemistry coupled with information about the hydrogeologic properties of the aquifer aids in the delineation of regional and local flow systems.

Table 6 lists the chemical properties and major, minor, and trace constituents that are of value for determining the geochemical characteristics of waters in the Dakota aquifer system. The table also lists general ranges for the properties and constituent concentrations for the Dakota aquifer along with water-use criteria.

Natural rainfall contains dissolved air and a very small amount of dissolved solids. During the travel of rainfall through soil, sediment, and rock to reach an aquifer, the water dissolves additional solids. Most of the soluble solids picked up by the water are inorganic because inorganic minerals are the main component of soils, sediments, and rocks and because natural organic substances tend to be less soluble than many common minerals. Water flowing deeper into the subsurface may encounter very soluble minerals, such as gypsum (CaSO₄ \cdot 2H₂O) or anhydrite (CaSO₄) and halite (rock salt, NaCl), and produce mineralized water or saltwater after mineral dissolution. Other deep subsurface waters can be highly saline because they were originally trapped seawater that has been further altered through geologic time.

The most common substances dissolved in most groundwaters in the Dakota aquifer are the inorganic constituents calcium, magnesium, and sodium (positively charged cations) and bicarbonate, chloride, and sulfate (negatively charged anions). Bicarbonate may also be represented as alkalinity in water analyses. Inorganic constituents commonly contributing minor amounts to the dissolved solids in Dakota groundwater are silica (uncharged), potassium and strontium (cations), and nitrate and fluoride (anions). Trace to minor amounts of ammonium ion (a cation) and bromide (an anion) in groundwaters are also of value for describing the geochemistry of groundwaters.

Concentrations of major dissolved substances are commonly reported as milligrams per liter (mg/L). This concentration unit is essentially the same as a part per million (ppm) in freshwater, because the weight of a liter of dilute water at groundwater temperatures is very close to 1,000 grams (one million milligrams). In saltwater, a mg/L is a few percent different from a ppm because the density of the solution is greater than for freshwater. Concentrations of trace amounts of dissolved constituents are often listed as micrograms per liter (μ g/L), which is essentially the same as parts per billion (ppb) in freshwater.

Chemical Properties and Major Dissolved Constituents

The property pH of a water is the negative log of the hydrogen (H⁺) ion activity and is a measure of how acidic or alkaline a water is. The lowest pH measured for the Dakota aquifer that appears accurate and representative of the groundwater is 6.3 units. The main geochemical process responsible for pH values less than 7 units in Dakota aquifer waters is the oxidation of sulfide in the mineral pyrite (FeS₂) in the strata followed by the oxidation and hydrolysis of the dissolved ferrous iron released from the pyrite weathering. Varying amounts of carbonate minerals commonly occur in Dakota strata and these dissolve to buffer the pH such that it does not become very low. The highest pH values measured for the Dakota aquifer that appear accurate and representative do not exceed 9 units. Measurements of pH greater than 9 are probably related to the lingering effect of cement used to seal the borehole annulus of a well. Groundwater around the well bore that was affected by cement can continue to affect water chemistry if not completely removed by well development, such as in the case of observation wells in lower permeability sediments. Waters with pH in the 7.5–9 range are usually of sodium-bicarbonate type and occur in the confined Dakota aquifer. The elevated pHs are mainly derived from a natural softening process. Clays in confined Dakota strata that formerly contained saltwater had exchange sites dominated by sodium ions. As fresher recharge, with a higher (calcium + magnesium)/ sodium ratio than the pore saltwater, locally recharged or flowed regionally through the aquifer, the adsorption of calcium and magnesium and release of sodium on the clays decreased the calcium and magnesium contents. This

Table 6. Chemical properties, general concentration ranges, and water-quality criteria for dissolved inorganic substances and selected metals that occur naturally in Dakota aquifer waters. Natural values of the properties and concentrations can be less or greater than listed in the table but are usually within the general range.

Name	Chemical symbol or representation	General range, mg/L	Drinking water criterion, mg/L ^a	Livestock water criterion, mg/L ^b	Irrigation water criterion, mg/L ^{bc}	
Properties						
Total dissolved solids	TDS ^d	100-60,000	R 500	5,000 ^e		
Alkalinity	Represented as CaCO ₃	10–1,500	S 300			
Total hardness ⁹	Represented as CaCO ₃	10–9,000	S 400			
рН		6.3–8.8	R 6.5–8.5 units ^h			
Major constituents (usually or often greater than 5 mg/L)						
Calcium	Ca	2–2,000	S 200			
Magnesium	Mg	1–1,000	S 150			
Sodium	Na	3-22,000	S 100			
Bicarbonate ^f	HCO ₃	12-1,800	S 120 ⁱ			
Chloride	Cl	2-35,000	R 50			
Sulfate	SO4	1–6,000	R 250	1,000 ^j		
Silica	SiO	4–50	S 50			
Minor constituents (usually or often greater than 0.5 mg/L)						
Potassium	К	1–150	S 100			
Fluoride	F	0.2–8	R 2, M 4	2	1	
Nitrate	NO ₃	< 0.01–3 ^k	M 10	100		
Boron	В	0.03–3	H 0.6	5	0.75	
Iron	Fe	< 0.001-10	R 0.3		5	
Manganese	Mn	< 0.001-1	R 0.005			
Trace constituents (usually or always less than 0.5 mg/L)						
Ammonia	NH₄	< 0.01-5 ^m	S 0.1			
Antimony	Sb	< 0.0001-0.007	M 0.006			
Arsenic	As	< 0.0001-0.05	M 0.01	0.2	0.1	
Barium	Ва	0.005-0.5	M 2			
Cadmium	Cd	< 0.0001-0.002	M 0.005	0.02	0.01	
Chromium	Cr	< 0.0001-0.006	M 0.1	1	0.1	
Copper	Cu	< 0.0001-0.007	T 1.3	0.5	0.2	
Lead	Pb	< 0.0001-0.02 ⁿ	T 0.015	0.1	5	
Manganese	Mn	< 0.001-1	R 0.05		0.2	
Mercury	Hg	< 0.0001-0.004	M 0.002	0.01		
Selenium	Se	< 0.001-0.03	M 0.05	0.05	0.02	
Silver	Si	< 0.0001-0.001	R 0.1			
Zinc	7n	0.001-1	B 5	25	2	

^a Criteria from the Kansas Department of Health and Environment (KDHE). R = recommended (Federal Secondary Drinking Water Standard); S = suggested by KDHE; M = maximum contaminant level of U.S. EPA and KDHE; T = must be treated to below level for public supply; H = U.S. EPA health advisory.

^b Values recommended by the National Academy of Sciences/National Academy of Engineering or U.S. EPA except for sulfate, which is recommended by Environment Canada. Most of these values are also listed in KDHE (2004).

^c TDS and major constituent concentration limits range widely depending on salinity tolerance of plants and sensitivity of soil to sodium hazard of water. TDS concentration greater than 500 mg/L can be detrimental to sensitive crops, whereas water with up to 5,000 mg/L TDS can be used for tolerant plants on permeable soils with careful management practices.

^d TDS can either be a measured value for evaporation to dryness or a sum of constituents in which bicarbonate is multiplied by 0.4917.

^e A TDS of greater than 3,000 mg/L is not recommended for poultry. Adult cattle, sheep, swine, and horses can tolerate up to 7,000 mg/L if accustomed to elevated TDS.

^f Nearly all of the alkalinity in groundwater is bicarbonate. The bicarbonate can be calculated from the alkalinity by multiplying by 1.219.

^g Total hardness is the sum of calcium and magnesium concentrations multiplied by 2.497 and 4.116, respectively, to represent conversion to CaCO₂.

^h The unit of pH is dimensionless and represents the negative log of the activity of the hydrogen (hydronium) ion in water.

ⁱ The recommended limit for drinking water is based on conversion of the alkalinity value.

^j Very young livestock are sensitive to sulfate and may not be able to tolerate above 400 mg/L.

^k Concentration as nitrate-nitrogen. Values greater than 3 mg/L are often observed but are nearly always the result of human activities. Contaminated Dakota waters have been observed with nitrate.

¹ Ammonia is present in natural water primarily as ammonium ion (NH_{4}^{+}) .

^m Concentration as ammonia-nitrogen.

ⁿ Lead concentrations > 0.01 are occasionally observed in waters from water-supply wells. These are believed to be mainly related to lead in the piping system.

allowed calcium and magnesium carbonate minerals to dissolve, releasing carbonate ions (CO_3^{2-}) that decreased the hydrogen ion concentration by forming bicarbonate ions.

The electrical conductivity of water is a chemical property that is proportional to the dissolved ion concentration. Conductivity is measured with a cup or dip type cell with electrode surfaces that are configured such that an electric current will pass through a particular volume of water. The electrical conductivity of a substance is the reciprocal of resistance. The units of specific electrical conductance are defined as the reciprocal of the resistance of a centimeter cube of aqueous solution. The International System of Units for scientific use expresses conductance as siemens (S), which is the same quantity as the mho. The expression mho was derived as the reverse spelling of the resistance unit ohm and can be found in older publications. The units most commonly used for specific electrical conductance of water are microsiemen per centimeter (µS/ cm), which are the same in value as the units micromho/ centimeter (umho/cm). The conductivity of an aqueous solution varies proportionally with the temperature. An increase in one °C in a fresh to slightly saline water results in an increase of about 2% in the specific conductance when the temperature is near 25 °C. Specific conductance values are corrected for temperature and reported at the standard temperature of 25 °C. Measured specific conductance for the Dakota aquifer ranges from as low as 110 µS/cm for very fresh, shallow groundwater in the outcrop zone to 60,000 µS/cm for saltwater a few hundred feet deep in the confined aquifer. Several conductance values estimated from SP curve analysis for the confined aquifer in Cheyenne, Rawlins, and Sherman counties in the northwest corner of Kansas exceed 60,000 µS/cm and range up to 100,000 µS/cm (Boeken, 1995). The highest values either represent more concentrated saltwaters or could be due to estimation errors.

Freshwater is often defined as water that contains less than 1,000 mg/L TDS content. The measured TDS concentration is as low as 100 mg/L in very fresh, shallow groundwater in the Dakota aquifer and exceeds 50,000 mg/L in saltwater sampled from the confined aquifer in parts of north-central Kansas. Freshwaters in the outcrop and subcrop portions of the Dakota aquifer are usually calciumbicarbonate type waters. Most soils and near-surface rocks in Kansas, including the Dakota aquifer, contain at least small amounts of calcium carbonate present as calcite (CaCO₃), which also contains small amounts of magnesium. The mineral dolomite (CaMg[CO₃]₂) can also be present in the rocks. During infiltration of rainfall, the carbonate minerals dissolve and add calcium, magnesium, and bicarbonate to the water. When substantial rainfall recharge occurs in the drier, western areas of Kansas, it also dissolves small amounts of salts that have accumulated in soils from rainfall during periods when evapotranspiration has been sufficient to restrict recharge to underlying aquifers. Table 7 lists the typical ranges of major constituent concentrations in the most common chemical types of Dakota waters.

Fine-grained sediments in the Dakota aquifer and overlying rocks often contain pyrite. The pyrite weathers to produce dissolved ferrous iron and sulfate and the dissolved iron then oxidizes and hydrolizes to generate ferric oxyhydroxide minerals. The solution from pyrite weathering

Table 7. Typical ranges of major constituent and fluoride concentrations in the most common types of groundwater in the Dakota aquifer. The water types are listed in order of generally increasing total dissolved solids concentration.

Constituent	Typical range, mg/L			
Calcium-bicarbonate type				
Calcium	30–150			
Magnesium	10–40			
Sodium	10–60			
Bicarbonate	150–400			
Chloride	5–80			
Sulfate	10–130			
Fluoride	0.5–1.5			
Sodium-bicarbonate type				
Calcium	3–50			
Magnesium	1–20			
Sodium	100–350			
Bicarbonate	250-600			
Chloride	20–200			
Sulfate	20–200			
Fluoride	1.5–5			
Calcium-sulfate type				
Calcium	80–600			
Magnesium	15–90			
Sodium	30–400			
Bicarbonate	200–400			
Chloride	20–500			
Sulfate	200-1,800			
Fluoride	0.4–1.5			
Sodium-chloride type				
Calcium	10–800			
Magnesium	5–800			
Sodium	300-15,000			
Bicarbonate	200–1,300			
Chloride	300–20,000			
Sulfate	100-5,000			
Fluoride	0.5–4			

is acidic and dissolves additional calcite and dolomite during a natural neutralization process. This process increases the calcium, magnesium, sulfate, and bicarbonate concentrations dissolved in Dakota waters.

Rocks overlying the Dakota aquifer such as the Graneros Shale often include gypsum, a very soluble mineral. The gypsum generally occurs as a secondary mineral that was precipitated in the past as a result of pyrite weathering and carbonate mineral dissolution that increased the calcium and sulfate concentrations to above the solubility of gypsum. Water infiltrating through the Cretaceous strata overlying the Dakota aquifer can dissolve the secondary gypsum to produce relatively high concentrations of calcium and sulfate. Recharge of this water into underlying Dakota strata can then substantially increase the calcium and sulfate contents of waters in the upper aquifer. In some cases, calcium-sulfate waters may result, although this water type is not as common as the other common types of Dakota groundwaters (table 7).

Large areas of the Dakota aquifer contain saltwater (primarily dissolved sodium and chloride). Concentrations of TDS can exceed 10,000 mg/L (table 6). No known evaporite deposits occur in the Dakota aquifer in Kansas. Therefore, the saltwater has either been derived from past seawater trapped in the Dakota sediments or saltwater that has entered the aquifer from other formations. Bromide and chloride relationships in Dakota groundwaters indicate that the main source of this saltwater is dissolution of rock salt (halite, NaCl) in Permian rocks underlying Dakota strata. The source identification is described further in the subsection on characteristics of contaminated groundwater in this appendix. A short discussion of bromide concentration and sources appears later in the subsection on minor and trace constituents. Although most of the Dakota sediments probably contained seawater either during their deposition (the marine shales) or after deposition when the sea covered the Dakota system formations, bromide/chloride ratios indicate that nearly all of the seawater has been flushed out by surface recharge. However, saltwater from the underlying Permian rocks has been slowly intruding into Dakota strata for millions of years. The salt-dissolution brine replaced the seawater source of salinity long ago. During more recent geologic time, freshwater recharge has been slowly flushing saltwater from the Dakota aquifer in many areas.

Large amounts of sodium adsorbed on the clays in the shales, siltstones, and sandstones where saltwater was present in Dakota strata. As freshwater of calcium-

bicarbonate type slowly flushed saltwater from the aquifer, the process of natural softening of the water occurred as dissolved calcium and magnesium adsorbed on the clays and released sodium to solution. The decrease in calcium concentration allowed some calcite (and dolomite, if present) to dissolve where it occurred in aquifer strata, thereby supplying additional calcium, magnesium, and bicarbonate to the water. The added calcium and magnesium were then available for more cation exchange with sodium. Some additional bicarbonate may have been generated from slow oxidation of organic matter trapped in Dakota sediments. The combined effect of these processes increased dissolved bicarbonate concentration, increased sodium concentration above that which would be expected by the freshwater flushing, while decreasing dissolved calcium, magnesium, and chloride concentrations in confined parts of the Dakota aquifer where the water is now fresh to slightly saline. The water types created are, in order of increasing salinity, sodium-bicarbonate type; sodium-chloride, bicarbonate type; and sodium-chloride type with excess sodium. The bicarbonate and chloride-bicarbonate type waters are typically soft because the calcium and magnesium concentrations are relatively low. Table 7 lists the typical ranges of major dissolved constituents in sodium-bicarbonate waters in the Dakota aquifer.

Relationships among Conductance and Major Dissolved Constituents

The relationships of specific conductance with concentrations of TDS and individual dissolved constituents are valuable for estimating concentrations from conductance measurements. Relationships of TDS with individual constituents are also useful for concentration estimates, for example, if TDS values calculated from geophysical log data are available. The patterns of individual constituent concentrations versus conductance and TDS give insight into the general chemical characteristics at different salinities of groundwaters in the Dakota aquifer across Kansas and how individual samples compare with the full range for all Dakota aquifer waters. The figures for this subsection and the next on relationships for minor constituents include all Dakota samples, whether single or multiple samples collected during different years from wells. The multiple samples were included because they sometimes show chemical changes due to the influence of variations in contamination.

Conductivity is one of the easiest measurements to make in the field or laboratory. The TDS concentration is

generally very well correlated with specific conductance. Therefore, the conductivity of water is often determined and used as a measure of salinity. Plots of TDS and individual major constituent concentrations versus specific conductance can be used for estimating concentrations given a good measurement of specific conductance. The accuracy of the estimation depends on the accuracy of the conductance measurement, the error in the determinations of the constituent concentrations, and the scatter of points about the best-fit line. The scatter is greater at low conductances because the larger diversity of water types at low TDS concentrations results in different relationships between TDS and major dissolved constituent contents and conductance. At high TDS concentration, the water type is sodiumchloride and the contributions of constituents other than sodium and chloride are relatively small.

A plot of laboratory values of conductance versus TDS content (sum of measured constituents, fig. 3) based on the Dakota water-quality data base shows less scatter about a best-fit line than does a plot of field conductance versus TDS (fig. 4). This indicates the larger error in field compared to laboratory conductance measurements is due primarily to less controlled environmental conditions, especially temperature. The straight line through the data in fig. 3 is a best visual fit for a linear equation at both low and high TDS concentration ranges. The computed linear regression for all the data does not fit the data well at low conductances, whereas the best visual-fit line closely approximates the data across the whole conductance range. A third-degree polynomial computed as a best fit for the data gives a slightly better estimation of TDS content for the middle and high conductance ranges. A very simple relationship of 0.64 times the conductance fits the TDS versus field conductance data well (fig. 4). This relationship is essentially the same as for the linear equation for the laboratory conductance data and can be used for a good estimate of TDS from specific conductance values with low error. The simple 0.64 factor is also a visual best fit. As for the graph for TDS versus laboratory conductance, the computed linear regression for field conductance underestimates TDS at low conductance values.

Specific conductance measurements also correlate very well with major constituent concentrations. A plot of chloride concentration versus laboratory conductance (fig. 5) shows that the correlation is much better at high concentrations and conductances than at low values. The diversity of chemical water types for fresh to slightly saline waters results in a wide range in chloride concentrations

for a given value of low conductance. In saline waters, the contribution of chloride to the total anion content of a water is large and, along with sodium, predominantly controls the conductance value. As for the TDS and conductance relationship, a computed linear regression based on all of the data does not fit the points well in the lower conductance range. Thus, a visual best-fit based on a power equation was used in fig. 5 to better represent the range from slightly saline waters to saltwaters. It is a good estimator of chloride content at high conductances and for approximate values of maximum chloride for conductances below 4,000 µS/cm. The contribution of sulfate and bicarbonate ions to the total anionic content below 4,000 µS/cm increases substantially relative to chloride in many waters, thereby producing some waters with a higher conductance for a given chloride content than the equation predicts. The linear function on fig. 5 provides a simple relationship for estimating chloride concentration at conductance greater than 2,000 µS/cm.

The distribution of points in a plot of chloride versus TDS concentration (fig. 6) is similar to that for chloride content and specific conductance (fig. 5). The TDS values used in this graph and subsequent graphs displaying TDS data are either the sum of measured constituents or measured TDS if there was not a complete analysis allowing the sum calculation. Figure 6 includes two lines that can be used to estimate TDS concentration from a chloride value, one a power function and the other a simple linear equation. Both the linear and power equations fit the data well for TDS values greater than 4,000 mg/L and chloride concentrations greater than 1,000 mg/L. In this range, the TDS concentration is approximately twice that of chloride. Below 1,000 mg/L chloride concentration, the power function estimates the lowest TDS for a given chloride or the highest chloride for a given TDS. The power equation is a good estimator of maximum chloride content down to about 10 mg/L. Similar to the explanation for the chlorideconductance relationship, other anions besides chloride can contribute a substantial portion of the total TDS below 3,000 mg/L. This results in a generally poor correlation between chloride and TDS concentrations in fresh to slightly saline waters in the Dakota aquifer.

Figures 7 and 8 show the relationship of sulfate concentration with specific conductance and TDS content, respectively. Each of the figures displays a linear equation that approximates the general correlation of sulfate content with conductance and TDS, and another linear equation that



Figure 3. TDS concentration versus specific conductance measured in the laboratory for Dakota aquifer waters. The polynomial function is a computed best fit for which the coefficient of determination (R^2) is 0.997. The linear equation is a simple approximation visually fit to the data.



Figure 4. TDS concentration versus specific conductance measured in the field for Dakota aquifer waters. The linear function is a simple approximation visually fit to the data.



Figure 5. Dissolved chloride concentration versus laboratory specific conductance for Dakota aquifer waters. The power function curve is a visual fit to the data to best represent the relationship at high conductance values and approximate the general maximum for chloride concentration at lower conductance. The linear equation is a simple function that approximates chloride concentration well at conductance greater than 2,000 μ S/cm.



Figure 6. Dissolved chloride versus TDS concentrations for Dakota aquifer waters. The equations relating chloride and TDS concentrations are for a general maximum chloride given a TDS value below 4,000 mg/L or a minimum TDS given a chloride value below 1,000 mg/L.



Figure 7. Dissolved sulfate concentration versus laboratory specific conductance for Dakota aquifer waters. The linear functions displayed are visual fits to the general relationship between conductance and sulfate concentration and to the highest sulfate value generally found in waters with conductance in the range 300–4,500 µS/cm.



Figure 8. Dissolved sulfate versus TDS concentrations for Dakota aquifer waters. The linear functions displayed are visual fits to the general relationship between TDS and sulfate concentrations and to the highest sulfate value found in waters with TDS concentrations in the range 100–3,500 mg/L.

generally represents the highest sulfate concentration found in Dakota aquifer water for conductances in the range 300–4,500 μ S/cm and TDS in the range 100–3,500 mg/L. The points representing the maximum sulfate concentrations for given TDS values usually are for calcium-sulfate type waters that have derived most of their sulfate from gypsum dissolution or pyrite oxidation. The lowest sulfate concentration occurs in very fresh groundwaters or in parts of the confined aquifer where a chemically reducing environment has reduced most of the dissolved sulfate to sulfide.

Bicarbonate contributes a substantial percentage of the total anions in fresh groundwaters but only a small percentage in saltwaters in the Dakota aquifer. This is reflected in the generally steady increase in the maximum bicarbonate concentration with specific conductance increase up to about 1,000 μ S/cm (fig. 9) and with TDS concentration increase up to approximately 800 mg/L (fig. 10), followed by a smaller rate of increase in maximum bicarbonate for conductances greater than 1,000 μ S/cm and TDS greater than 800 mg/L. The two lines in each of figs. 9 and 10 represent equations for the approximate maximum value of bicarbonate for the two ranges of conductances and TDS contents. The correlations of sodium concentration with specific conductance and TDS content (figs. 11 and 12) are similar in pattern to those for chloride concentration. The linear equations fit the data very well for conductance greater than 5,000 μ S/cm, TDS content greater than 3,000 mg/L, and sodium concentration greater than 1,000 mg/L, where the chemical water type is always sodium-chloride. Below these values, the equations estimate the maximum sodium content for given conductance and TDS values or the minimum TDS content for a given sodium value.

The correlations of calcium and magnesium concentrations with specific conductance (figs. 13 and 14, respectively) and with TDS content (figs. 15 and 16, respectively) are not as high as for sodium when all data are considered. In general, the plots for both of these cations show a distribution of points that are clustered in two groups. The graphs for the constituent versus TDS content display this better than for specific conductance because there are more data. The first group has calcium and magnesium concentrations that contribute a major part of TDS contents less than 4,000 mg/L. These waters are generally of calcium-bicarbonate to calcium, magnesiumbicarbonate type in the low range of TDS concentration (less



Figure 9. Dissolved bicarbonate concentration versus laboratory specific conductance for Dakota aquifer waters. The two linear functions displayed are visual fits representing the approximate maximum bicarbonate concentration for the conductance ranges below and above 1,000 µS/cm.



Figure 10. Dissolved bicarbonate versus TDS concentrations for Dakota aquifer waters. The two linear functions displayed are visual fits representing the approximate maximum bicarbonate concentration for the TDS concentration ranges below and above 800 mg/L.



Figure 11. Dissolved sodium concentration versus laboratory specific conductance for Dakota aquifer waters. The linear function is a visual fit that represents the relationship well at conductance greater than 5,000 μ S/cm and approximates the maximum sodium concentration at conductance less than 5,000 μ S/cm.



Figure 12. Dissolved sodium versus TDS concentrations for Dakota aquifer waters. The linear function is a visual fit that represents the relationship well at TDS content greater than 4,000 mg/L and approximates the maximum sodium concentration at TDS less than 4,000 μ S/cm.



Figure 13. Dissolved calcium concentration versus laboratory specific conductance for Dakota aquifer waters. The linear function is a visual fit that represents the general maximum calcium concentration for conductance less than 5,000 µS/cm.



Figure 14. Dissolved magnesium concentration versus laboratory specific conductance for Dakota aquifer waters. The linear function is a visual fit that represents the general maximum magnesium concentration for conductance less than 4,000 µS/cm.

than 500 mg/L), and transition to primarily calcium-sulfate along with some mixed cation-sulfate, calcium-chloride, and mixed cation-chloride types for TDS between 500 and 4,000 mg/L. The second group of waters has calcium and magnesium concentrations that are small relative to sodium content. In the low range of TDS values, these waters range from sodium-bicarbonate up to sodium-chloride type and have experienced substantial cation exchange. At high TDS content (greater than 5,000 mg/L), the waters are of sodium-chloride type and have a narrower range of calcium and magnesium concentrations than for lower TDS values. Figures 15 and 16 each include two lines representing linear equations that bracket the high and low concentration trends with conductance and TDS.

Dissolved silica concentration comprises more than several percent of the TDS content of many freshwaters in the Dakota aquifer. No significant correlation exists between silica and specific conductance or TDS concentration. In general, the greater the TDS content, the smaller is the silica proportion of the TDS content. Most groundwaters have a silica concentration in the 5–50 mg/L range. The greatest silica concentration typically occurs in waters with a TDS content between 250 and 1,500 mg/L.

Minor and Trace Dissolved Constituents

Infiltration of rainfall through soils and shallow bedrock dissolves small amounts of minor and trace inorganic constituents from soils and near-surface rocks. These substances are present in carbonate and clay minerals, coatings on quartz and other mineral grains, minor mineral grains, salts precipitated in soils during dry periods, and decomposing organic matter, or they are adsorbed on clays and other mineral surfaces. Infiltration of contaminants derived from anthropogenic activities can increase the concentrations of natural dissolved constituents (particularly nitrate) or add synthetic chemicals such as pesticides and other dissolved organic compounds to shallow Dakota waters. Table 6 lists typical ranges of minor and trace inorganic constituent concentrations in Dakota waters, and table 7 lists fluoride content for different chemical water types.

Potassium concentration is generally correlated with specific conductance and TDS content (figs. 17 and 18, respectively). The point patterns in these graphs do not have discernable groups as for calcium and magnesium but are more similar to those for sodium, although the relative distributions of points at high conductance and TDS values


nt sigure 15. Dissolved calcium versus TDS concentrations for Dakota aquifer waters. The linear functions are visual fits that represent the general maximum and minimum calcium concentrations for low and high conductance values, respectively.



Figure 16. Dissolved magnesium versus TDS concentrations for Dakota aquifer waters. The linear functions are visual fits that represent the general maximum and minimum magnesium concentrations for low and high conductance values, respectively.



Figure 17. Dissolved potassium concentration versus laboratory specific conductance for Dakota aquifer waters. The power function displayed is a visual fit that represents the general data relationship better at both low and high conductance than a computed best-fit function.



Figure 18. Dissolved potassium versus TDS concentrations for Dakota aquifer waters. The power function displayed is a visual fit that represents the general data relationship better at both low and high TDS content than a computed best-fit function.

are not as narrow as for sodium. Simple power functions are are not as narrow as for sodium. Simple power functions are are not as narrow as for sodium. Simple power functions are and the some and the solution of the solutions are the solution of the so

Nitrate is a minor constituent in Dakota groundwaters Nitrate is a minor constituent in Dakota groundwaters free of significant anthropogenic contamination. However, Nitrate is a minor constituent on constituent in the infection of significant anthropogenic contamination. However, nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the nitrate is a minor constituent in the minor constituent in the minor constituent in the nitrate is a minor represents fresh to slightly saline waters used for domestic, stock, or irrigation purposes. These waters are generally in shallower parts of the aquifer subject to local recharge or are confined waters contaminated by water flowing from the surface or near surface through the annular space of unsealed or poorly sealed wells.

Fluoride concentration ranges between 0.1 and 10 mg/L in Dakota groundwaters (fig. 20). Although no significant correlation exists between fluoride content and specific conductance or TDS content, the maximum fluoride concentration for a given TDS value tends to increase with increasing TDS for freshwaters (less than 1,000 mg/L TDS). Low fluoride concentration (less than 1 mg/L) usually occurs in freshwaters of calcium-bicarbonate type. The greatest fluoride concentration occurs in waters with a TDS content between 600 and 4,000 mg/L. Elevated concentrations of dissolved fluoride (greater than 1 mg/L) are usually associated with sodium-bicarbonate and mixed cation-anion type waters. The high fluoride is probably derived from the dissolution of calcium minerals that contain fluoride. The relationship of dissolved fluoride and calcium in Dakota aquifer waters suggests that the mineral fluorite is the main control on fluoride concentration, although apatite minerals



nt solved nitrate-nitrogen versus TDS concentrations for Dakota aquifer waters. Nitrate contributes more than 10% of the TDS content for waters represented by points above the line on the graph.



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could be a minor control (see the discussion of fluoride in the subsection on regional groundwater geochemistry).

Recharge of waters with a (calcium + magnesium)/ sodium equivalent ratio greater than 1 to parts of the Dakota aquifer where this ratio is low on clays results in softening of the groundwater by exchange of calcium and magnesium from the water with sodium on the clay. The low (calcium + magnesium)/sodium ratio for adsorbed cations on clay is a remnant from when the water in the pores of the Dakota sediments contained saline water of sodium-chloride type. The exchange process decreases the calcium concentration,
thereby producing conditions of undersaturation with respect to calcium-containing minerals in the sediments. Common minerals such as calcite and dolomite can dissolve, as can minor calcium minerals such as apatite, fluorite, and some micas that contain fluoride, thereby increasing the dissolved fluoride concentration. This is indicated by the general increase in fluoride concentration with decreasing (calcium + magnesium)/sodium ratio for Dakota groundwaters with fluoride greater than 1 mg/L (fig. 21). The dissolution of common carbonate minerals during the exchange process causes an increase in pH. Some fluoride that is adsorbed or weakly attached to clays can be released to solution in the higher pH waters by exchange with hydroxyl ion (OH⁻),

thus further increasing the fluoride concentration of the groundwater.

Bromide is a halide with similar properties as chloride and, with chloride, is one of the most conservative (least subject to chemical reactions) dissolved constituents in water. Bromide concentration ranges from less than 0.1 mg/L in very fresh groundwaters (less than 500 mg/L TDS) up to about 5 mg/L in the most saline groundwaters that naturally occur in the Dakota aquifer (fig. 22). The point representing the highest bromide in fig. 22 and the other point with the greatest deviation above the best-fit line are for contaminated groundwaters as explained in the next section. Although the bromide concentration increases with natural salinity in the aquifer water, the bromide/chloride ratio decreases substantially with increasing chloride concentration. The mass ratio of bromide/chloride in natural saltwaters (chloride content greater than 5,000 mg/L) in the Dakota aquifer ranges between 0.00015 and 0.0005. The bromide/ chloride ratio for seawater is 0.00347, which is about an order of magnitude greater than observed in natural Dakota saltwaters. The bromide/chloride ratio of saltwater generated by the dissolution of Permian evaporite deposits containing rock salt in Kansas is within the range 0.00006-0.0003 (Whittemore, 1984, 1988, 1995). Thus, the primary source



Figure 21. Dissolved fluoride concentration versus (calcium + magnesium)/sodium equivalent ratio for Dakota aquifer waters.



Figure 22. Dissolved bromide versus TDS concentration for Dakota aquifer waters. The power function is a computed best fit for the data without the two points with the greatest deviations above the line, which represent samples of contaminated groundwater. The R² for the best-fit function is 0.717.

of bromide in saltwater in the Dakota aquifer is from the dissolution of rock salt and not from trapped seawater. Saltwater at a few locations in the Dakota aquifer has a bromide/chloride ratio exceeding 0.001. These waters have been contaminated by the past seepage of oil brine disposed at the surface into underlying Dakota groundwater or by the past injection of oil brine directly into portions of the aquifer containing natural saltwater, for example, in parts of Russell County. The use of the bromide/chloride ratio for saltwater source identification is described further in the subsection on contamination characterization later in this appendix.

Like bromide, boron generally increases in concentration with increasing to boron generally increases in concentration with increasing boron generally increases in concentration with increasing boron generally increases in concentration with increasing with increasing to boron general generated by the boron general generated by the boron general generated by the dissolution of Permian evaports of saltwater in the Dakota equiper. The boron general generated by the dissolution general generated by the dissolution of saltwater in the boron general generated by the boron general generation generated by the boron general generation generated by the boron general generation generated by the boron generated by the boron generation generated by the boron generation generated by the boron generated by the

Chemically reducing environments occur where reactions of dissolved constituents and gases with other constituents and with the sediments have essentially completely consumed dissolved oxygen (O_2) . This commonly occurs in the confined portion of the Dakota aquifer because the age of the water is old and no recent recharge of water with significant dissolved oxygen has occurred. The reducing environment allows iron, manganese, and some other heavy metals to dissolve from minerals in the sediments. These waters can sometimes have a high enough hydrogen sulfide (H₂S) content to give a "rotten egg" odor. Ammonium ion concentration can exceed 1 mg/L as ammonium-nitrogen in the reducing environment. Waters in the confined Dakota aquifer tend to have higher dissolved solids than in the unconfined, shallow portions of the aquifer. Thus, groundwater in which ammonium-nitrogen exceeds 1 mg/L tends to be slightly saline to saline (fig. 24). When ammonium ion concentration is definitely detectable (ammonium-nitrogen generally greater than 0.1 mg/L) in natural groundwaters with low oxidation-reduction potential, nitrate concentration is typically very low (nitrate-nitrogen less than 0.1). However, groundwaters with both ammoniumnitrogen concentration greater than a few tenths of a mg/L and nitrate-nitrogen greater than 1 mg/L do occasionally occur in the Dakota aquifer. These probably represent locations of



nt sigure 23. Dissolved boron versus TDS concentration for Dakota aquifer waters. The power function displayed is a visual fit that represents the general data relationship better at both low and high TDS content than a computed best-fit function.



 Figure 24. Dissolved ammonium-nitrogen versus TDS concentration for Dakota aquifer waters.

surface sources of nitrogen contamination and groundwater conditions under which the nitrogen species are in the process of transformation from one oxidation state to another.

Dissolved concentrations of iron range from less than a few μ g/L to more than 10 mg/L and of manganese range from less than a μ g/L to nearly a mg/L in the Dakota aquifer. The greater concentrations occur in two types of environments. One occurrence is the chemically reducing environment described above. The other environment is in the outcrop or subcrop area of the Dakota aquifer where recharge with dissolved oxygen reaches strata containing pyrite. Oxidation of pyrite and other sulfides, which was discussed earlier as a source of sulfate, is also a source of dissolved iron and manganese in groundwaters. Such waters in the Dakota aquifer can have a pH below 7 (slightly acidic). Usually, enough alkalinity is derived from carbonate mineral dissolution in Dakota sediments to buffer the pH and keep it from falling below 6 in the groundwater. Most of the dissolved iron and manganese released from sulfide weathering oxidizes and precipitates as oxides and oxyhydroxides (hydrated oxides) that produce the red to orange to brown coloration commonly occurring in Dakota strata. If the pyrite weathering occurs in the confined portions of the Dakota aquifer where dissolved oxygen is limited, the dissolved iron and manganese concentrations

can increase to relatively high values for these metals in groundwater.

Although trace metals are contained in a variety of natural substances, sulfide, oxide, and oxyhydroxide minerals are probably the main materials controlling the concentrations of heavy metals (e.g., cadmium, chromium, copper, lead, nickel [Ni], and zinc) and semimetals (e.g., arsenic and selenium) in Dakota groundwaters. Oxidation of sulfides and reduction of oxides and oxyhydroxides can release metals and semimetals within or adsorbed on minerals to the groundwater. Precipitation of these minerals and adsorption on their surfaces, especially on oxides and oxyhydroxides, removes trace and semimetals from solution. Adsorption on clays also can control the amount of trace ionic species in solution. Trace amounts of heavy and semimetals could also occur in small amounts of organic matter trapped in Dakota sediments where the organics were not completely oxidized after deposition with the sediments. Slow oxidation of these organics by recharge containing dissolved oxygen could release the trace constituents to solution. Surface contamination with relatively high concentrations of heavy and semimetals could also be a source of these substances in water at levels greater than usually expected. The general concentration ranges for selected heavy and semimetals in Dakota groundwaters are in table 6.

Naturally radioactive elements (e.g., uranium [U], thorium [Th], radium [Ra], and radon) are present at low levels in Dakota aquifer waters. Uranium can occur as oxide or silicate minerals and can be adsorbed on iron oxyhydroxides, organic matter, and clays in sediments (Langmuir, 1997). Oxidation of uranium-containing minerals and organic matter in sediments can release uranium to solution by oxidizing uranium from the IV to the VI oxidation state. Migration of this groundwater to a chemically reducing zone within an aquifer can then change the uranium to the reduced state, which is substantially less soluble than the oxidized state, and thereby precipitate uranium-containing minerals. Thus, the depositional, diagenetic, and hydrogeologic history of the Dakota sediments can result in zones where the uranium content of groundwater differs appreciably. Isotopes of uraniumprimarily ²³⁸U but also ²³⁵U—decay radioactively to other radioactive elements, including thorium, radium, and radon. Uranium, thorium, and radium occur as ionic species or complexes dissolved in water, whereas radon occurs as a dissolved gas.

Characteristics of Contaminated Groundwater

This subsection focuses on concentrations of inorganic constituents introduced into Dakota groundwater by human activities. The KGS did not determine concentrations of organic compounds or microorganisms in groundwaters as part of the Dakota program primarily because the focus was on natural, inorganic constituents but also because the KGS laboratory was not equipped for these analyses and the expense of obtaining outside analyses was greater than the project budgets would allow.

d The main constituent in Dakota groundwater that human d tivities have increased substituent in Dakota groundwater that n activities have increased substituent in Dakota groundwater that d activities have increased substituent in a constituent d activities have increased substituent in a constituent d substituent in undisturbed constituent and the substituent d substituent in undisturbed kansas groundwater (Townsend and Young, 1999). Another constituent elevated in some d substituent in undisturbed kansas groundwater (Townsend and Young, 1999). Another constituent elevated in some d substituent in undisturbed kansas groundwater (Townsend and Young). Another constituent elevated in some d substituent in undisturbed kansas groundwater (Townsend and young). Another constituent elevated in some d substituent in undisturbed kansas groundwater (Townsend and young). Another constituent of the large concentration of the amount of constituent of the d substituent elevated in some substituent is substituent of the d substituent elevates in some substituent elevates in some substituent elevates. Substituent elevates in some substituent elevates. Substituent elevates in some substituent elevates. Substituent elevates in some substituent elevates elevate Human sources of nitrate include fertilizer and animal and human waste. Dissolved species of nitrogen from these sources can enter groundwaters by infiltration of water through the unsaturated zone to the water table or by water flowing down the boreholes of wells, especially if the annular space between the well casing and borehole is poorly sealed or not sealed. If contaminated water reaching the water table contained a high concentration of dissolved nitrogen species in the form of ammonium ion or nitrogencontaining organic compounds and if the water contained enough dissolved oxygen or other dissolved species that could oxidize the nitrogen, oxidation to nitrate in the groundwater system could occur.

The occurrence of most high-nitrate waters (greater than several mg/L nitrate-nitrogen) at shallow depths in the unconfined portion of the Dakota aquifer (fig. 25) is consistent with a surface source of nitrate contamination. All water samples from wells with depths greater than 300 ft (91 m) in the unconfined aquifer contained nitratenitrogen less than several mg/L. Figure 25 indicates that several samples of groundwaters from the confined aquifer contained high nitrate content. It is probable, especially for wells with depths greater than 100 ft (30 m), that some water from the surface or shallow depths entered the aquifer through a poorly sealed or unsealed annular space of the wells, because the confining stratum immediately above the Dakota aquifer (Graneros Shale) should have a low enough permeability to substantially retard downward movement of contaminated water. The separation of the well locations in the water-quality data base into the unconfined (areas of Dakota outcrop and where alluvium and the HPA directly overlie the Dakota aquifer) and confined categories is based on the mapped division for these parts of the aquifer (fig. 1). If a well location for a sample fell on the confined part of the map but was approximately within one mile from the boundary, the well was included in the unconfined category because the overlying shale could have been thin and possibly fractured enough to allow some surface recharge less than a couple decades in age to reach the water table.

Animal and human waste sources of nitrate are associated with other constituents, such as in the saline water of urine. Some septic system wastes can contain saline water discharged from conventional water softeners in which rock salt is used to recharge the exchange medium. A plot of nitrate versus chloride concentration (fig. 26) indicates that nitrate tends to increase with increasing chloride content for nitrate-nitrogen values greater than 10 mg/L (the maximum



Figure 25. Depth of wells in the unconfined and confined parts of the Dakota aquifer versus nitrate-nitrogen concentration of well water. The nitrate-nitrogen concentration limit (maximum contaminant level) for public supplies of drinking.

contaminant level for public supplies of drinking water). The solid line on fig. 26 indicates that a lower limit to chloride concentration occurs in waters with greater than a few mg/L nitrate-nitrogen. Low nitrate concentration can occur at low chloride values, but once the nitrate increases above natural levels, enough chloride is associated with the nitrate that chloride concentration increases with nitrate increase. The slope of the upper limiting line in fig. 26 suggests that for every 10 mg/L increase in nitrate-nitrogen, chloride content increases about 6–7 mg/L.

 of the relationship is related to the cation content associated with chloride and other anions, including nitrate, in the contamination source water that mixes with the natural groundwater, coupled with cation exchange of sodium in the contaminated water for calcium and magnesium on clays in the aquifer sediments and overlying soils and rocks during contaminant transport.

The use of a bromide/chloride versus chloride concentration plot with conservative mixing curves is often the best approach for geochemical differentiation of anthropogenic sources of chloride contamination from natural salinity (Whittemore, 1995). Figure 29 displays the bromide/chloride mass ratio versus chloride concentration for Dakota groundwaters. All of the sample data appearing in the graph are from the Dakota program. Each of the three curves in the figure represents the conservative (without reaction) mixing of two end-member waters, one with a lower chloride and one with a higher chloride concentration. The mixing equation is

$$C_{mix} = C_1 V + C_2 (1-V)$$

where C_{mix} , C_1 , and C_2 represent concentrations of either bromide or chloride in the mixture and the two end members,



Figure 26. Nitrate-nitrogen versus chloride concentration in groundwaters in the confined and unconfined Dakota aquifer. The solid line indicates a general lower limit of chloride concentration that occurs in waters with greater than a few mg/L nitrate-nitrogen.



Figure 27. Nitrate-nitrogen concentration versus sodium/chloride mass ratio in groundwaters in the confined and unconfined being ratio versus versus



Figure 28. Nitrate-nitrogen concentration versus (calcium + magnesium)/sodium equivalent ratio in groundwaters in the confined 28. Nitrate-nitrogen concentration versus (calcium + magnesium)/sodium equivalent ratio in groundwaters in the solid line indicates the general lower limit of the (calcium + magnesium)/ sodium ratio that occurs in waters with greater than 1 mg/L nitrate-nitrogen. The dashed line is the maximum contaminant level for nitrate-nitrogen.

respectively, and V represents the volume fraction of the first respectively, and V represents the volume fraction of the sentence respectively, and V represents the volume fraction of the sentence respectively, and V represents the volume fraction of the respectively, and V represents the volume fraction of the sentence of the sentence of the terms of the terms of the respectively of the terms of the terms of the terms of the respectively of the terms of the terms of the terms of the sentence of terms of the terms of terms of the terms of terms of terms of the terms of the terms of terms of

Frye and Brazil (1943) reported that in selected early years of oil fields in Russell and Ellis counties, some waste brine produced from the oil-bearing formations was disposed of in wells drilled into lower Cretaceous sandstone as well as in deeper formations and in surface pits. The KGS sampled brines produced from oil wells in Barton, Ellis, Rush, and Russell counties during the Dakota program (Macfarlane et al., 1988); points for these samples are also plotted in fig. 29. The chemistry of the water in the Cheyenne Sandstone

at Gorham fits a mixture of oil brine with natural saltwater in the sandstone. The dashed curve in fig. 29 represents the mixing of oil brine with natural saltwater in the Dakota aquifer. The upper part of the dashed line was generated by Sandstone as one end member and a brine produced from an oil well in the Arbuckle Group located in the same quarter section as the Cheyenne observation well as the other end member. The curve was then extrapolated to a lower chloride concentration such that it ends in the middle of the zone representing the mixing of freshwater and natural saltwater in the Dakota aquifer. The chloride concentration of the uncontaminated saline water in the Dakota aquifer at this location is predicted to have been about 7,000 mg/L based on the mixing curve. The oil brine sampled at Gorham contained a chloride concentration of only 22,700 mg/L. Other brines in the Arbuckle Group in central Kansas often contain a substantially greater chloride content. If the oil brine at the Gorham location had been diluted by fresh to slightly saline water as a part of secondary recovery operations, its If the same bromide/chloride ratio as the sampled brine were



Figure 29. Bromide/chloride mass ratio versus chloride concentration in groundwaters in the confined and unconfined Dakota aquifer. The two solid lines are mixing curves that concentration concentration in groundwaters in the confined and unconfined to two solid lines are mixing curves that bound the zone of mixing of freshwaters with natural saltwaters in the Dakota aquifer. The dashed line is a curve for the mixing of with solid respective of the mixing of solid respective of the curve was extended to a lower chlorider. The dashed line is a curve for the mixing of freshwater and natural saltwater in the dashed line is a curve for the mixing of freshwater and natural saltwater in the Dakota aquifer.

used along with a chloride concentration of about 80,000 mg/L for the oil-brine end point for the dashed curve, the predicted chloride concentration for the uncontaminated saline water in the Cheyenne Sandstone (at the low bromide/ chloride end of the dashed curve) would be somewhat less than 6,000 mg/L. Thus, the original chloride content in the Cheyenne Sandstone at this location was probably in the range of 6,000 to 7,000 mg/L.

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Many more records with major constituent data exist for groundwaters from the Dakota aquifer than for samples in which the KGS measured bromide and chloride concentrations. Another ratio that is often of value for differentiating saltwater sources is sulfate/chloride. Figure 30 displays points for Dakota aquifer waters (both non-KGS and KGS analyses) on a plot of sulfate/chloride mass ratio versus chloride concentration. The figure includes two mixing curves that bound a zone in which nearly all the points for the Dakota aquifer waters fall. A few points, such as those with the lowest sulfate/chloride ratios, represent groundwaters in the confined aquifer that have naturally become chemically reducing enough to reduce some sulfate to sulfide. Oil brines in Kansas generally have relatively low sulfate/chloride ratios (nearly always less than 0.2 and usually less than 0.02). The usual range in the sulfate/chloride ratio for oil brine partially overlaps that for natural saltwaters in the Dakota aquifer. However, if a water was substantially contaminated by an oil brine with a low enough sulfate/chloride ratio, a low ratio and a higher chloride concentration than expected for the

decreases the sodium/chloride ratio a substantial amount, making the difference even larger. When a saltwater plume enters a sedimentary aquifer containing groundwater with a substantially lower salinity, the sodium/chloride ratio in the water decreases because the sodium exchanges for divalent cations (primarily calcium and magnesium) on clays in the sediments. This causes an increase in the dissolved calcium and magnesium content, thereby hardening the water.



Figure 30. Sulfate/chloride mass ratio versus chloride concentration in groundwaters in the confined and unconfined Dakota aquifer. The two solid lines are mixing curves that bound the zone of mixing of freshwaters with most natural saltwaters in the Dakota aquifer.



Figure 31. Sodium/chloride mass ratio versus chloride concentration in groundwaters in the confined and unconfined Dakota aquifer. The two solid lines are conservative mixing curves that bound the zone of mixing of freshwaters saltwaters in the Dakota aquifer.

Regional Groundwater Geochemistry Areal Geochemical Patterns

Salinity Characterization

The TDS concentration of a groundwater is the chemical parameter that is commonly used to indicate the constituents for further characterization of the salinity of a water. The regional distributions of TDS, chloride, and sulfate concentrations in groundwaters in the upper Dakota aquifer are shown in figs. 32-34. Larger sized versions of these figures are available from the KGS. The maps represent only the upper part of the Dakota aquifer in each region because the shallower portion of the aquifer at a given location generally contains the least saline water, which would be the most usable in that area. In most regions, the maps represent the quality of water in the Dakota Formation, but in the outcrop area where the Dakota Formation has been removed by erosion, the upper Dakota aquifer in the maps can be the Kiowa Formation or Chevenne Sandstone.

Data for the map of TDS concentrations in the Dakota aquifer are from chemical analyses (mainly in the area

where water is used) and geophysical log interpretation (in the area of saline water without supply wells in northwest Kansas). The procedure used in obtaining TDS estimates from geophysical logs is described in the previous subsection on water quality from geophysical logs. The chloride concentration in northwest Kansas was estimated from the TDS values obtained from the geophysical log interpretation using the equation for high dissolved solids in fig. 6. The TDS and chloride concentrations in figs. 32 and 33 in western Stafford County, the southernmost part of Barton County south of the Arkansas River, southeast Pawnee County, easternmost Edwards County, and northwest Pratt County are inferred from analyses of water samples collected from observation wells screened at the base of the HPA overlying Dakota strata and in Permian rock underlying the Dakota (Whittemore, 1993). Saltwater intrudes upwards from the Cedar Hills Sandstone and other Permian units underlying Dakota strata to affect the HPA in that area. The maps were generated using ESRI ArcGIS software.

Figure 32 shows the distribution of TDS concentration in groundwater in the upper part of the Dakota aquifer. The eight TDS intervals separate the groundwater into the following categories that are defined for the purposes of this publication:

- < 250 mg/L very fresh water
- 250–500 mg/L freshwater with less than the 500 mg/L recommended level for drinking water
- 500–1,000 mg/L freshwater with greater than the 500 mg/L recommended level for drinking water
- 1,000-2,000 mg/L slightly saline water
- 2,000-5,000 mg/L --- moderately saline water
- 5,000–10,000 mg/L saline water with less than the 10,000 mg/L limit for usability classification
- 10,000–20,000 mg/L very saline water with TDS greater than the 10,000 mg/L limit for usability classification > 20,000 mg/L — brine

The usability classification is part of the system used by the KDHE and the Kansas Corporation Commission for protection of water, such as from injection of wastewaters in the subsurface. Federal regulations for the control of underground wastewater injection also use the 10,000 mg/L TDS concentration in the definition of underground sources of drinking water (USDW) to be protected (U.S. Environmental Protection Agency, 2002).

Figure 33 displays the distribution of chloride concentration in the upper part of the Dakota aquifer. The eight divisions for chloride values have a rough correspondence to many of the divisions for TDS concentrations:

- <50 mg/L values typical for freshwater with $TDS < 500 \mbox{ mg/L}$
- 50–100 mg/L values common for freshwater with 300–1,000 mg/L TDS
- 100–250 mg/L values common in fresh to slightly saline water with TDS of 500–1,500 mg/L; less than recommended drinking water limit of 250 mg/L chloride
- 250–500 mg/L values common in slightly to moderately saline water with TDS of 1,000–2,000 mg/L
- 500–1,000 mg/L values common in slightly to moderately saline water with TDS of 1,300–2,500 mg/L
- 1,000–5,000 mg/L values common in moderately saline to saline water with TDS of 2,000–10,000 mg/L; moderately saline to saline water with less than the 5,000 mg/L chloride limit for usability classification

5,000–10,000 mg/L — values common in very saline water

with 10,000–20,000 mg/L TDS; very saline water with greater than the 5,000 mg/L chloride limit for usability classification

> 10,000 mg/L — values typically occurring in brine with > 20,000 mg/L TDS

The main reason for the overlap of the different TDS ranges for adjacent chloride intervals is that the concentrations of sulfate and bicarbonate and the cations providing the charge balance for these constituents can range widely in fresh to saline groundwaters in the Dakota aquifer.

Figure 34 shows the distribution of sulfate concentration in the upper part of the Dakota aquifer. The seven divisions for sulfate content have a rough correspondence to the following divisions for TDS:

- < 50 mg/L values typical for freshwater with TDS < 500 mg/L
- 50–100 mg/L values common for freshwater with 250–1,300 mg/L TDS
- 250–500 mg/L values common in slightly to moderately saline water with TDS of 600–6,000 mg/L
- 500–1,000 mg/L values common in slightly to moderately saline water with TDS of 1,000–10,000 mg/L
- 1,000–5,000 mg/L values common in moderately saline to saline water with TDS of 2,000–60,000 mg/L
- > 5,000 mg/L values typically occurring in saline water with > 10,000 mg/L TDS

The main reason for the overlap of the different TDS ranges for adjacent sulfate intervals is that the concentrations of chloride and bicarbonate and the cations (mainly sodium) providing the charge balance for these constituents can range widely in fresh to saline groundwaters in the Dakota aquifer. High sulfate concentration is limited by the solubility of the minerals gypsum or anhydrite; sulfate values observed in Dakota aquifer water are less than 6,300 mg/L. Water with low sodium and chloride concentrations can be saturated with respect to gypsum at sulfate concentrations less than 2,000 mg/L. Higher sulfate concentrations than 2,000 mg/L can occur in waters with substantial concentrations of dissolved constituents other than calcium and sulfate, particularly sodium and chloride. The greater the concentration of these other ions (within the TDS content range of Dakota waters), the greater the solubility of gypsum range of Dakota waters), the greater the solubility of gypsum range of Dakota waters), the greater the solubility of gypsum and anhydrite because of the greater the greater the greater than the upper range of common sulfate concentration.
Iter water the greater than the greater than the greater than the greater than the upper range of high concentration.

Groundwater in the Dakota aquifer is usually fresh (TDS content less than 1,000 mg/L) in the outcrop area and where the aquifer subcrops beneath unconsolidated deposits of alluvium in central and north-central Kansas and the HPA in south-central and southwestern Kansas (fig. 32). The freshest water (TDS content less than 250 mg/L) occurs in parts of Washington, Cloud, Clay, Ottawa, Ellsworth, and Saline counties in the central to eastern part of the outcrop belt TDS water typically contains less than 50 mg/L chloride and less than 50 mg/L sulfate concentrations. Groundwater with 250-1,000 mg/L TDS content in the outcrop and subcrop belt in central and north-central Kansas usually has a greater sulfate than chloride level as indicated by the more prevalent areas of sulfate greater than 50 mg/L in these locations in fig. 34 than of chloride greater than 50 mg/L in fig. 33.

Freshwater occurs in the subcrop area of the Dakota aquifer underlying the HPA in south-central and southwestern Kansas (fig. 32). However, Dakota strata in parts of south-central Kansas are expected to contain saline water where saltwater intrudes upwards from the Cedar Hills Sandstone and other Permian units underlying Dakota strata to affect the HPA in that area. Freshwater extends into the confined portions of the aquifer in southwest Kansas and parts of south-central and west-central Kansas. Data from the interpretation of geophysical logs suggest that fingers of fresh to nearly fresh water (near 1,000 mg/L TDS) could exist in the confined aquifer as far north as southeastern Sheridan and southwestern Graham counties. As for the case in the outcrop area, the sulfate concentration is usually greater than the chloride content for these freshwaters.

The transition of freshwater to saline water (TDS content greater than 1,000 mg/L) in the Dakota aquifer in central and north-central Kansas generally occurs near the outcrop/subcrop boundary (fig. 32). The fresh to saline water transition near this boundary is irregular due to the convolutions in the boundary caused by the erosion of major valleys into the confining zone. The salinity of the

groundwater increases substantially in a westerly direction from the outcrop/subcrop belt to a TDS level that exceeds 20,000 mg/L in most of Smith County, more than half of Osborne County, and parts of eastern Phillips, western Jewell, northwestern Mitchell, eastern Rooks, northeastern Ellis, and western Russell counties. West of this saltwater zone is a well-defined wedge of slightly to moderately saline groundwater (1,000–5,000 mg/L TDS) that points northward to the Nebraska border. The southern part of the wedge extends from Logan County on the west through Gove and Trego counties to Ellis County on the east. The center of the wedge occurs from southeastern Thomas County through Sheridan and Graham counties to western Rooks County. The top of the wedge is located in southeastern Decatur County and much of Norton County. Groundwater in the confined Dakota aquifer increases in salinity into northwest Kansas. In parts of northwest Kansas, primarily parts of Cheyenne, Rawlins, and Sheridan counties, the TDS concentration of the groundwater exceeds 20,000 mg/L.

The regional salinity pattern of Dakota groundwaters is mainly dependent on the rate at which freshwater is able to enter from above and along the long, regional flow paths in the aquifer in comparison with the rate of saltwater intrusion from the underlying Permian rocks. In some regions, the saltwater is able to more rapidly intrude into the bottom of the Dakota, such as in parts of south-central to central to north-central Kansas where the Dakota directly overlies the Cedar Hills Sandstone or other saltwater-containing Permian strata. In northwest rate of freshwater throughflow is low. The Dakota rocks contain saltwater in both of these regions. Surface recharge along the outcrop belt of the Dakota aquifer in southeast Colorado and central Kansas occurs at a much greater rate than underlying saltwater intrusion, resulting in essentially complete flushing of any previous saltwater. Fresh recharge flowing through the Dakota sandstones in southwest Kansas has also removed nearly all salinity. The freshwater flowing through sandstones in the confined aquifer between northwest and central Kansas has removed much of the saltwater but enough dissolved salt remains to make much of the water slightly to moderately saline. The western side of the wedge of Dakota groundwater with TDS less than 5,000 mg/L between northwest and north-central Kansas reflects where the flushing rate has been greater than the saltwater intrusion rate; in the eastern side, the saltwater intrusion rate is greater than that of the flushing. The rate













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Groundwater in the areas of the upper Dakota aquifer with high TDS content (greater than 5,000 mg/L) shown in fig. 32 is of sodium-chloride type. The molar ratio of sodium/chloride can approach 1 (mass ratio of 0.65) in the waters with the highest salinity. Water in the area of the confined aquifer with 500–2,000 mg/L TDS is generally soft (low calcium and magnesium content) and of sodiumbicarbonate type. The sodium/chloride molar ratio can substantially exceed 1 in this water. Groundwater with 2,000–5,000 mg/L TDS in the confined area is typically transitional between sodium-bicarbonate and sodiumchloride type. The sodium/chloride molar ratio is greater than 1 in this water. Groundwater in the outcrop and subcrop areas with less than 500 mg/L TDS content is usually of calcium-bicarbonate type and sometimes of calcium, magnesium-bicarbonate type. Concentrations

of TDS between 500 and 2,000 mg/L in water in the outcrop/subcrop areas are often due primarily to dissolved calcium and sulfate contents such that the waters can be calcium-sulfate in type. Elevated sulfate concentration with substantially lower chloride content can produce sulfate type water in less saline portions of the confined aquifer.

Fluoride and Nitrate Distributions

Groundwater in the Dakota aquifer typically contains a low fluoride concentration (less than 1 mg/L) in the outcrop and subcrop areas where calcium-bicarbonate type water is the common chemical type (fig. 35). Low fluoride water also occurs in parts of the confined aquifer near the outcrop/ subcrop boundary. Fluoride concentration is usually 1–3 mg/L in both the Dakota and High Plains aquifers in most of the region where the Dakota directly underlies the HPA in southwest Kansas. This concentration range is from less than to greater than the 2 mg/L recommended upper limit for potable use but is less than the 4 mg/L maximum contaminant level for public supplies of drinking water.



Figure 35. Distribution of fluoride concentration in groundwaters in the Dakota aquifer. The six counties in northwest Kansas are not shaded because no data for fluoride are available in that area.

Fluoride content generally increases from about 1 mg/L near the outcrop/subcrop boundary to greater than 4 mg/L in a direction toward greater thicknesses of Upper Cretaceous rocks confining the Dakota aquifer (fig. 35). Higher fluoride concentration is generally associated with confined aguifer. Water in the area of the confined aguifer with a TDS content in the range 500–2,000 mg/L that is soft (low calcium and magnesium content) often has relatively high fluoride concentration (greater than 4 mg/L). This type water occurs in the confined aquifer from west-central Kansas toward central Kansas. Whether the fluoride content of the highly saline water in northwest Kansas also exceeds 4 mg/L is unknown. However, the high calcium concentration in the saline water is generally expected to limit the fluoride content below a few to several mg/L.

Natural nitrate concentration in Dakota groundwater is usually less than 2 mg/L as nitrate-nitrogen. The low nitrate water occurs both in the unconfined and confined portions of the aquifer (fig. 36). Anthropogenic activities have contaminated groundwater to produce nitrate-nitrogen concentrations that have sometimes exceeded 100 mg/L in the Dakota aquifer (fig. 25). Contaminated groundwaters are mainly distributed in the area of the unconfined aquifer but also occur in the confined aquifer, especially near the confined-unconfined boundary in central and north-central Kansas (fig. 36). As described in the previous section on contamination characterization, nitrate contamination of the confined aquifer occurs from surface infiltration to a shallow water table or the flow of water from the surface or near surface down the unsealed or poorly sealed annulus in a well borehole. Most of the water produced from wells in the confined aquifer in western Kansas has not been contaminated by nitrate, suggesting better well construction.

Distribution of Chemical Water Types

A wide range in chemical water types occurs across the Dakota aquifer as indicated by the different distributions of major constituents. A water type is determined from calculation of the equivalent concentrations of the ionic



constituents. Table 8 lists the number of well waters for each water type based on the data set assembled and assessed for the Dakota Aquifer Program and meeting qualifications for assigning water types. The table includes all samples for which determinations of at least calcium, magnesium, sodium, bicarbonate, sulfate, and chloride concentrations exist. If potassium and nitrate determinations also exist, they were also used in the calculations. Only one sample per well was considered in the type distribution; the latest sample was included for wells from which multiple samples were collected. The well samples were divided into three different groups according to the location of the well in the Dakota aquifer: 1) the outcrop/subcrop area up to near the boundary with the confined aquifer, 2) the confined area up to near the boundary with the outcrop/subcrop area, and 3) a band along the boundary of the confined and outcrop/subcrop areas. The wells in the outcrop/subcrop area comprise the greatest number of the wells because this area generally has the best water quality and shallower depths to water. Thus, this area is preferentially drilled for water supply from the Dakota aquifer, especially domestic and small stock wells.

The following procedure was used to classify the water types: 1) if a single cation or anion comprises more than 50% of the total equivalent concentration of cations or anions, respectively, a second cation or anion is used in the type name if it exceeds 40% of the total; 2) if the cation or anion in greatest concentration is between 40% and 50% of

Chemical type of water	Outcrop/Subcrop	Confined edge	Confined	Total
Bicarbonate types				
Ca-HCO ₃	145	64	25	234
Ca–HCO ₃ , other anions	17	7		24
Mg-HCO ₃	2	1		3
Na-HCO ₃	17	37	68	122
$Na-HCO_{3}$, other anions	6	9	17	32
Mixed cation-HCO ₃	49	18	8	75
Mixed cation–HCO ₃ , other anions	6	4	2	12
Subtotal number (percent of total)	242 (28.5)	140 (16.5)	120 (14.1)	502 (59)
Sulfate types				
Ca-SO,	11	9	5	25
$Ca-SO_{a}$, other anions	14	3	5	22
Na-SO	2	1	6	9
Na–SO $_{4}$, other anions	1	3	7	11
Mixed cation-SO	8	2	2	12
Mixed cation $-SO_{4}$, other anions	7	3		10
Subtotal number (percent of total)	43 (5.1)	21 (2.5)	25 (2.9)	89 (10)
Chloride types				
Ca–Cl	10	1	1	12
Ca–Cl, other anions	7	2		9
Na-Cl	7	96	96	199
Na–Cl, other anions	4	6	17	27
Mixed cation-Cl	3		1	4
Mixed cation-Cl, other anions	2	1		3
Subtotal number (percent of total)	33 (3.9)	106 (12.5)	115 (13.5)	254 (30)
Nitrate types				
Ca-NO ₃	3			3
Mixed cation-NO ₃	1			1
Subtotal number (percent of total)	4 (0.5)			4 (0.5)
All water types (percent of total)	322 (38)	267 (31)	260 (31)	849

the total, a second cation or anion is used in the type name if it exceeds 33%; 3) if no cations or anions exceed 40% of the total, all cations or anions that have concentrations within 10% of the ion in greatest concentration are included in the type name. Multiple ion names are listed in order of decreasing percentage.

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The numbers of wells with bicarbonate and chloride as the predominant anions are about equal in the confined aquifer (not near the boundary with the outcrop/subcrop area) and are substantially greater than the number of wells with sulfate type water (table 8). Sodium-chloride and then sodium-bicarbonate are the most common of individual water types. Thus, sodium is more common than calcium as the predominant cation in the confined Dakota aquifer. Sodium is also most commonly the predominant cation for sulfate type waters in the confined aquifer.

The chemical types of waters in the Dakota aquifer near the boundary of the outcrop/subcrop and confined areas are transitional between the waters in each of the two areas (table 8). However, the percentages of different chemical types are closer to those for the confined aquifer than for the outcrop/subcrop area. Although bicarbonate is the most common of the predominant anion types, the percentage of chloride types is substantially greater than in the outcrop/ subcrop area away from the boundary with the confined aquifer. The total number of chloride water types near the boundary is only several percent less and the number of bicarbonate types only several percent more than those in the confined aquifer. Although calcium is the predominant cation for the bicarbonate type waters, sodium is the predominant cation for the chloride type waters. These distributions of water types partially reflect the flow of saline waters from

the confined aquifer in central and north-central Kansas into the edge of the outcrop/subcrop areas in that region. The percentages of sulfate water types near the boundary and for the confined aquifer away from the boundary are a few percent less than for the outcrop/subcrop area away from the boundary. Nitrate is not the predominant anion in any of the waters in the confined aquifer or near the boundary with the outcrop/subcrop area.

A Piper-Hill trilinear diagram (Piper, 1944) allows visual discernment of groups of and trends in chemical water types for systems based on the major cation and anion composition of waters. Figure 37 displays the distribution of water types for Dakota groundwaters on a Piper-Hill trilinear diagram. The same data set was used for the diagram as for table 8. Potassium was combined with sodium if a potassium determination existed, and nitrate concentration was combined with chloride content if a nitrate measurement was available. The diagram illustrates the wide range in the chemical character of Dakota aquifer waters. Most of the points for groundwaters from the outcrop/subcrop area away from the boundary with the confined aquifer fall within the triangular area defined by greater than 50% calcium in the cation triangle and within the triangular area defined by greater than 50% bicarbonate in the anion triangle. Most of the points for waters from the confined aquifer away from the boundary with the outcrop/subcrop area fall within the triangular area defined by greater than 50% sodium in the cation triangle. In the anion triangle, the confined aquifer points have a wide distribution from the chloride apex toward the bicarbonate apex, with sulfate percentages less than 40% for most waters. Points for waters in the area near the boundary between the confined and outcrop/subcrop areas are distributed mainly across the lower portions of both the cation and anion triangles and indicate the prevalent transition between calcium and sodium and between bicarbonate and chloride type waters.

The diamond area of the Piper-Hill diagram summarizes the combined cation-anion nature of the groundwaters. Most of the points representing the outcrop/subcrop aquifer fall in the area with calcium and magnesium greater than 50% and bicarbonate greater than 50%. Most of the points for waters in the confined aquifer extend along the side of the diamond with high sodium percentage from a combined chloride and sulfate percentage near 100% to a bicarbonate percentage of about 30%. However, a substantial number of points for the confined aquifer also are distributed widely across most of



Figure 37. Piper trilinear diagram for groundwaters in the Dakota aquifer. See text for description of data included.

the entire diamond. The points for the edge of the confined aquifer are also widely distributed across the cation-anion diamond.

Geochemical Profiles Across an Aquifer Flow Path

A cross section of the chemical characteristics in the Dakota aquifer from southeast Colorado to central Kansas illustrates the spatial variation in constituent concentrations and water types along a major regional path of groundwater flow in the aquifer. Inclusion of groundwater data for selected overlying and underlying aquifers illustrates the similarities and differences in water chemistry between the Dakota aquifer and these units. The following geochemical profiles are based on data collected during the Dakota Aquifer Program, including sampling by the KGS during cooperative investigations with the Texas Bureau of Economic Geology (TBEG) (Dutton, 1995) and Lawrence Livermore National Laboratory (LLNL) (Clark et al., 1998; Macfarlane et al., 2000).

by the KGS are listed in table 11. Minor constituent concentrations for samples collected and analyzed by the KGS and LLNL are in table 12. Trace metal data for samples collected and analyzed by the KGS and LLNL are in table 13. Uranium and radiochemical concentrations for the samples collected by the KGS and submitted to a USGS regional laboratory for analysis are in table 14. Stable isotope results for samples collected and analyzed by the TBEG and the LLNL and collected by the KGS and submitted to a USGS regional laboratory for analysis are in table 15. Additional radiochemical and isotopic data of the TBEG and LLNL are in Dutton (1995), Clark et al. (1998), and Macfarlane et al. (2000). The tables include data for the waters sampled from the HPA during the cooperative

studies as well as for a sample collected from the Morrison Formation during a pumping test at a test-well site of the Dakota program.

Figure 39 is a cross section depicting the elevations of the land surface and the middle of the screened interval of the wells sampled. A decrease in the general slope of the land surface is apparent near the boundary between Colorado and Kansas. The groundwater flow in the Colorado subregion of the cross section is primarily within a local flow system. The cross section in Kansas is confined until the farthest eastern well, although the confining strata are thin enough at the next to most eastern well that vertical recharge through the confining unit is sufficient to appreciably change the water chemistry. The eastern-most well is in the local recharge and discharge flow system of the outcropping Dakota aquifer. The cross section graphically illustrates that the wells in the Dakota aquifer are generally shallower in the western and eastern local flow areas and deeper in the confined portion of the aquifer in western Kansas. Points for the three water-supply wells in the HPA and the observation well in the Morrison Formation in southwestern Kansas near the Colorado studies are included in fig. 39.



Figure 38. Map location of wells illustrating regional changes in groundwater geochemistry along flow paths in the Dakota aquifer from Southeast Colorado to central regional changes in groundwater geochemistry along flow paths in the Dakota aquifer in the indicate the samples listed in tables 9–15. Open circles indicate wells in the HPA, filled circles wells in the Morrison Formation. Blue lines represent the elevation (ft above sea level) of the predevelopment potenticity of the gene shaded area is the extent of the Dakota aquifer within the figure boundaries.



Figure 39. Elevation of the land surface and the middle of the screened interval for wells sampled along a regional flow path of the Lands and the middle of the screened interval.

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Site sample number	Site description	Geologic unit	Type or use of well	Legal location	Sample date
Southeastern Colorad	o sites				
57	Commanche National Grasslands windmill	Dakota	Stock	32S-49W-08BAAA	5/20/92
56	Town of Pritchett	Dakota, Cheyenne	Municipal	30S-49W-36ADDA	5/20/92
55	Colorado State University Experiment Station	Dakota	Stock	31S-48W-13ACCD	5/20/92
54	Town of Springfield, well 9	Dakota	Municipal	30S-46W-31AAAA	5/20/92
53	Town of Springfield, well 11	HPA, Dakota, Cheyenne	Municipal	31S-46W-04BCCB	5/19/92
62	Town of Vilas	Kiowa, Cheyenne, Morrison	Municipal	31S-45W-02CABC	5/22/92
58	Town of Walsh, well 3	Cheyenne	Municipal	30S-43W-32DBCD	5/21/92
59	Town of Walsh, well 2	Cheyenne	Municipal	30S-43W-32CCDC	5/21/92
61	Irrigation well, Double J hog farm	Dakota	Irrigation	25S-44W-16ACAC	5/21/92
60	Rangeland windmill in Prowers County	Dakota	Stock	25S-42W-11BBBB	5/21/92
Kansas sites in gener	al location of northern flow path				
52	Morrison observation well in Stanton County	Morrison	Monitoring	29S-43W-21DCDD	5/19/92
78	Cheyenne pumping test well in Stanton County	Cheyenne	Monitoring	29S-43W-21DCDD	9/6/92
46	Town of Coolidge, south well	Dakota	Municipal	23S-43W-14CDCA	11/5/91
63	Town of Coolidge, north well	Dakota	Municipal	23S-43W-14CDCA	5/22/92
68	Terry Boy residence	Dakota, Cheyenne	Domestic	21S-41W-02BBBB	7/14/92
47	Town of Leoti, Dakota well	Dakota	Municipal	18S-37W-24BACC	11/6/91
20	Town of Leoti, Dakota well	Dakota	Municipal	18S-37W-24BACC	7/14/92
49	Poky Feeders feedlot	Dakota	Stock	20S-32W-18DBDC	11/7/91
72	Carlos Roberts stock well	Dakota	Stock	15S-28W-21BCCC	7/15/92
50	Ranger Feeders feedlot, well 4	Dakota	Stock	18S-28W-22DBDC	11/8/91
71	Ranger Feeders feedlot, well 5	Dakota	Stock	18S-28W-22DACD	7/15/92
73	William Montgomery residence	Dakota	Domestic	15S-24W-15CCCB	7/15/92
74	Cedar Bluffs Christian Camp	Dakota	Camp supply	14S-22W-33AACC	7/16/92
75	Randy Marintzer residence	Dakota	Domestic	12S-18W-34CDDA	7/16/92
76	Jacob Klein residence	Dakota	Domestic	11S-11W-13DCBB	7/16/92
77	Melvin Obermuller residence	Dakota	Domestic	11S-08W-36AAAB	7/17/92
Kansas site between r	north and south flow path				
51	KPL Sunflower power plant, Dakota well	Dakota	Industrial	24S-33W-20CCCA	11/9/91
Kansas sites, HPA wel	S				
48	Town of Leoti, HPA well	HPA	Municipal	18S-37W-24BACC	11/6/91
69	Town of Leoti, HPA well	HPA	Municipal	18S-37W-24BACC	7/14/92
KS05	Town of Scott City, well 4	HPA	Municipal	18S-33W-24ACDD	11/8/91
KS08	KPL Sunflower power plant, HPA well	НРА	Industrial	24S-33W-31CAC	11/9/91

estimates. Lon Site sample	ngitude values are us	ed for plotting	Land surface	Total well	Bottom of well		Middle of screened	Middle of screened
number	Site name	Longitude	elevation, ft	depth, ft bls	elevation, ft	Screened interval, ft	interval, depth, ft bls i	nterval, elevation, ft
Southeaster	n Colorado sites.							
57	Grasslands	102.95	4,951	261	4,690		e230	e4,721
56	Pritchett	102.85	4,775	e370	e1,343		e340	e4,435
55	CSU Exp. Station	102.77	4,666	270	4,396	200–270	235	4,431
54	Springfield 9	102.62	4,348	134	4,214		e120	e4,228
53	Springfield 11	102.61	4,410	360	4,050	90-130, 290-360	247	4,163
62	Vilas	102.46	4,160	305	3,855	243.5-305	274	3,886
58	Walsh 3	102.29	3,964	220	3,744		e200	e3,764
59	Walsh 2	102.28	3,956	155	3,801		e140	e3,816
61	Hog farm	102.37	3,885	580	3,305		e500	e3,385
60	Prowers windmill	102.16	3,621	537	3,084	236–537	387	3,234
Kansas site	s in general locatior	ι of northern	flow path					
52	Stanton Morrison	102.02	3,568	422	3,146	395-415	405	3,163
78	Stanton Cheyenne	102.02	3,568	280	3,288	240-280	260	3,308
46	Coolidge south	102.01	3,375	360	3,015	e270-340	e305	e3,070
63	Coolidge north	102.01	3,383	360	3,023	270–340	305	3,078
68	Terry Boy	101.95	3,624	1,025	2,599	900-1,000	950	2,674
47	Leoti Dakota	101.36	3,303	1,050	2,253	820-860, 930-970, 1,010-1,050	940	2,363
70	Leoti Dakota	101.36	3,303	1,050	2,253	820-860, 930-970, 1,010-1,050	940	2,363
49	Poky Feeders	100.89	2,920	1,000	1,920		e950	e1,970
72	Roberts	100.44	2,502	700	1,802	600-620, 640-700	655	1,847
50	Ranger Feeders 4	100.40	2,678	942	1,736		e860	e1,818
71	Ranger Feeders 5	100.40	2,678	925	1,753	775–925	850	1,828
73	Montgomery	99.96	2,375	617	1,758	365–375, 395–415, 520–560, 580–617	521	1,854
74	Christian Camp	99.76	2,185	470	1,715	450-470	460	1,725
75	Marintzer	99.31	2,110	505	1,605	485-505	495	1,615
76	Klein	98.49	1,660	232	1,428	192–232	112	1,548
77	Obermuller	98.15	1,440	80	1,360	60–80	20	1,370
Kansas site	between north and	south flow p	ath					
51	KPL Dakota	100.97	2,950	669	2,251	479–699	589	2,361
Kansas site	s, HPA wells							
48	Leoti HPA	101.36	3,303	170	3,133	132–142, 153–158	143	3,160
69	Leoti HPA	101.36	3,303	170	3,133	132–142, 153–158	143	3,160
KS05	Scott City 4	100.91	2,964	214	2,750		e204	e2,760
KS08	KPL HPA	100.99	2,916	437	2,479	257–457	357	2,559

Jor A UN analyse	es except for the tast th	o sampres, wur	if are no	UT DUIN	.(C 6 6 1) n								
Site sample	Site name	Sp.C., field, μS/cm	Hq	TDS mg/L	si0 ₂ mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HC0 ₃ mg/L	SO₄ mg/L	CI mg/L	Water type
Southeastern	Colorado sites)))))))))	
57	Grasslands	388	7.45	235	21.8	57.2	10.3	6.9	2.6	198	17.0	7.7	Ca-HCO ₃
56	Pritchett	330	7.05	193	11.6	35.0	12.6	14.7	3.0	167	29.0	2.6	Ca-HCO ₃
55	CSU Exp. Station	916	7.45	577	8.5	48.4	30.5	104.0	10.3	269	217	23.6	Na,Mg,Ca-SO ₄ ,HCO ₃
54	Springfield 9	759	7.30	502	16.0	84.4	17.9	45.8	3.7	170	214	20.4	Ca-SO4
53	Springfield 11	594	7.65	377	19.3	80.5	16.1	13.9	3.3	136	136	25.0	Ca-SO ₄ ,HCO ₃
62	Vilas	484	7.60	290	10.9	37.3	18.4	41.1	4.3	234	55.3	5.4	Ca,Na,Mg-HCO ₃
58	Walsh 3	1,230	7.60	824	16.2	88.3	56.3	105.0	3.3	247	358	49.1	Mg,Na,Ca-SO₄
59	Walsh 2	824	7.60	536	17.8	62.7	36.3	66.7	3.7	240	198	22.2	Ca,Mg,Na-SO ₄ ,HCO ₃
61	Hog farm	620	7.10	377	13.6	62.5	21.7	33.6	3.8	224	121	9.2	Ca-HCO ₃
60	Prowers windmill	522	7.40	329	15.3	58.8	16.7	23.8	4.0	184	100	7.5	Ca-HCO ₃
Kansas sites i	n general location of I	northern flow	path										
52	Stanton Morrison	786	8.15	501	15.0	43.8	26.8	83.1	8.7	236	184	20.3	Na,Mg,Ca-HCO ₃ ,SO ₄
78	Stanton Cheyenne	840	7.55	515	11.1	47.7	32.5	76.3	6.6	234	207	15.9	Na,Mg,Ca-SO ₄ ,HCO ₃
46	Coolidge south	673	7.01	422	10.0	62.8	21.3	44.7	5.7	196	167	11.7	Ca,Na,Mg-SO,,HCO3
63	Coolidge north	670	7.25	422	10.4	64.3	21.6	45.7	6.3	197	163	11.9	Ca,Na,Mg-SO ₄ ,HCO ₃
68	Terry Boy	753	8.40	466	11.4	2.9	1.5	172.0	3.5	280	118	16.6	Na-HCO ₃
47	Leoti Dakota	1,650	8.45	1,033	10.2	5.5	2.0	369	4.6	345	407	61.6	Na-SO ₄
70	Leoti Dakota	1,675	8.50	1,049	11.6	5.4	2.5	367	4.8	345	421	63.6	Na-SO ₄
49	Poky Feeders	1,503	7.32	985	61.9	84.8	60.6	149.0	8.5	371	289	124.0	Na,Mg,Ca-HCO ₃ ,SO ₄
72	Roberts	1,590	8.20	937	11.0	3.9	2.0	344	4.3	384	211	168.0	Na-HCO ₃ ,CI,SO ₄
50	Ranger Feeders 4	1,870	7.86	1,025	11.7	6.3	2.7	376	6.7	268	113	374	Na-CI
71	Ranger Feeders 5	1,800	7.65	966	14.2	18.2	8.2	351	7.0	340	126	300	Na-CI
73	Montgomery	1,950	7.85	1,053	10.8	7.2	3.4	382	4.0	356	188	278	Na-CI,HCO ₃
74	Christian Camp	2,280	8.25	1,288	10.3	5.3	3.0	480	5.8	442	196	365	Na-CI,HCO ₃
75	Marintzer	5,640	7.90	3,233	11.5	15.5	20.5	1,160	11.1	387	457	1,363	Na-CI
76	Klein	1,450	8.05	892	8.8	21.0	4.3	324	3.4	547	159	100.0	Na-HCO ₃
77	Obermuller	1,150	7.05	753	22.6	173.0	12.3	62.3	5.9	379	128	58.5	Ca-HCO ₃
Kansas site be	stween north and sou	th flow path											
51	KPL Dakota	458	7.45	279	13.8	40.6	12.0	37.4	3.5	183	74.0	5.6	Na,Ca-HCO ₃
Kansas sites,	HPA wells												
48	Leoti HPA	550	7.52	353	53.0	53.5	22.7	19.8	4.5	195	46.0	38.7	Ca-HCO ₃
69	Leoti HPA	550	7.65	348	54.6	53.1	22.6	19.2	4.6	216	40.1	30.8	Ca-HCO ₃
KS05	Scott City 4		7.85	371	58.2	51.0	22.6	30.0	6.3	209	54.1	27.9	Ca,Mg-HCO ₃
KS08	KPL HPA		7.78	254	20.0	50.0	9.8	21.2	3.0	175	48.9	6.5	Ca-HCO ₃

Table 11. Chemical properties, dissolved major constituent concentrations, and water types for samples in the regional cross section of a Dakota aquifer flow path. Data are

the samples wer	vea minor consuluent concen 2 analyzed. Data are for KGS	analyses	except wh	un une reg ere noted f	or LLNL and	ites and	for the la	quijer juw _l st two sampl	les, which a	ana LLINL are from Di	rejer 10 ine utton (1995,	iaboraior).	и миси
Site sample	Site name	F mg/L	NO ₃ -N mg/L	NH₄-N mg/L	PO₄-P mg/L	KGS Sr mg/L	LLNL Sr mg/L	LLNL Bb mg/L	KGS Ba mg/L	LLNL Ba mg/L	B mg/L	Br mg/L	l mg/L
Southeastern (Colorado sites												
57	Grasslands	0.75	2.96	< 0.08	0.003	0.62	0.58	0.0012	0.180	0.231	0.048	0.079	0.015
56	Pritchett	1.28	< 0.02	< 0.08	0.007	0.69	0.64	0.0047	0.019	0.024	0.119	0.043	0.022
55	CSU Exp. Station	1.56	< 0.02	0.23	0.007	1.12	1.04	0.0188	0.014	0.018	0.317	0.40	0.051
54	Springfield 9	0.69	3.25	< 0.08	0.007	0.91	0.86	0.0039	0.037	0.049	0.162	0.199	0.020
53	Springfield 11	0.42	3.25	< 0.08	0.003	1.06	1.01	0.0018	0.042	0.056	0.064	0.32	0.017
62	Vilas	1.64	< 0.02	< 0.08	< 0.003	0.79	0.71	0.0059		0.042	0.200	0.070	0.012
58	Walsh 3	1.53	4.99	< 0.08	0.003	2.38	2.18	0.0047	0.053	0.070	0.446	0.39	0.088
59	Walsh 2	1.72	1.58	< 0.08	0.007	1.77	1.58	0.0040	0.038	0.052	0.335	0.137	0.049
61	Hog farm	0.77	< 0.02	< 0.08	< 0.003	0.96	0.90	0.0033	0.024	0.031	0.108	0.154	0.017
60	Prowers windmill	0.61	2.48	< 0.08	0.003	1.02	0.96	0.0029	0.019	0.026	0.103	0.085	0.014
Kansas sites ir	n general location of northe	rn flow p	ath										
52	Stanton Morrison	1.36	0.20	0.08	0.010	1.08	1.03	0.0092	0.031	0.038	1.42	0.191	0.031
78	Stanton Cheyenne	1.89	< 0.02	< 0.08	< 0.010	1.29			0.018		0.301	0.20	0.034
46	Coolidge south	0.81	< 0.02	< 0.08	< 0.010	1.35			0.018		0.094	0.165	0.024
63	Coolidge north	0.84	< 0.02	< 0.08	< 0.003	1.39	1.32	0.0061		0.025	0.167	0.158	0.022
68	Terry Boy	2.11	< 0.02	0.47	0.013	0.06	0.06	0.0037	0.012	0.017	0.296	0.131	0.030
47	Leoti Dakota	3.37	< 0.02	1.01	0.060	0.14			0.014		006.0	0.50	0.086
70	Leoti Dakota	3.10	< 0.02	1.09	0.029	0.14	0.13	0.0051	0.015	0.020	0.751	0.46	0.087
49	Poky Feeders	2.64	4.29	< 0.08	0.010	3.27			0.022		0.500	0.59	0.107
72	Roberts	3.99	< 0.02	0.70	0.029	0.08	0.07	0.0032	0.018	0.025	0.630	0.36	0.066
50	Ranger Feeders 4	2.85	< 0.02	0.47	0.040	0.09			0.007		0.410	0.21	0.040
71	Ranger Feeders 5	3.47	< 0.02	0.54	0.020	0.29	0.27	0.0066	0.022	0.029	0.469	0.30	0.083
73	Montgomery	4.08	< 0.02	1.01	0.023	0.17	0.23	0.0049	0.015	0.024	0.654	0.30	0.055
74	Christian Camp	5.16	< 0.02	1.17	0.026	0.10	0.10	0.0046	0.019	0.027	0.938	0.33	0.061
75	Marintzer	3.35	< 0.02	1.79	0.033	0.46	0.46	0.0083	0.021	0:030	0.830	0.55	0.065
76	Klein	2.16	< 0.02	0.31	0.039	0.33	0.30	0.0024	0.007	0.009	0.740	0.100	0600.0
77	Obermuller	0.29	23.3	< 0.08	0.062	0.63	0.58	0.0021	0.337	0.407	0.082	0.137	0.0036
Kansas site be	tween north and south flow	r path											
51	KPL Dakota	1.09	0.11	< 0.08	< 0.010	0.63			0.035		0.106	0.061	0.020
Kansas sites, I	HPA wells												
48	Leoti HPA	1.47	3.70	< 0.08	0.010	1.21			0.110		0.100	0.26	0.049
69	Leoti HPA	1.47	3.12	< 0.08	0.010	1.21	1.14	0.0020	0.115	0.145	0.086	0.183	0.034
KS05	Scott City 4	2.10	3.34			1.03			0.080		0.150		
KS08	KPL HPA	0.56	1.72			0.62			0.050		< 0.04		

in which the san	nples were analyzed.													
:		KGS	KGS		KGS	LLNL	KGS	LLNL LLNL	KGS	LLNL	KGS	- LLNL	KGS	
Sample site	Site name	Fe µg/L	Mn µg/L	Mn µg/L	אן µg/L	ug/L	Ni Mg/L	Ni Mg/L	cu µg/L	ug/L	Zn µg/L	Zn ⊮g/L	ug/L	cd µg/L
Southeastern	Colorado sites													
57	Grasslands	22	CI	2.1	19	0.04	< 0.1	0.2	7.5	4.3	130	197		0.36
56	Pritchett	824	17	18	18		0.1		< 0.1		28	6	< 0.1	
55	CSU Exp. Station	768	43	44	26	0.02	0.9	0.4	< 0.1	2.8	793			0.05
54	Springfield 9	29	0 V	1.0	33		0.3		0.1		4		< 0.1	
53	Springfield 11	< 10	0 V	0.1	43		1.0		0.4		36	58	< 0.1	
62	Vilas			34		0.04		0.9		1.4		19		0.03
58	Walsh 3	< 10	0 V	< 0.2	32	0.11	0.2	0.3	< 0.1	5.2	< 2	20		0.01
59	Walsh 2	< 10	0 V	0.2	16	0.29	0.3	0.9	0.4	1.1	< 2	12		0.03
61	Hog farm	1,660	81	85	10	0.05	0.7	0.3	0.4	2.5	100	291		0.03
60	Prowers windmill	15	9	6.2	0	0.05	0.2	0.2	< 0.1	0.5	<	ω		0.02
Kansas sites	in general location of nor	thern flow p	ath											
52	Stanton Morrison	< 10	19	17	45	0.04	9.1	2.4	1.1	2.5	25	70		0.04
78	Stanton Cheyenne	44	54		35		2.4		0.5		64			
46	Coolidge south	797	70		က				0.5		31		< 0.1	
63	Coolidge north			71		0.04		0.7		1.2		40		0.04
68	Terry Boy	108	7	7.4	45	0.07	2.0	0.3	0.2	0.3	0	19		< 0.1
47	Leoti Dakota	< 20	15		က				0.5		< 4		0.1	
20	Leoti Dakota	105	12	13	0	0.01	1.1	0.3	0.5	5.2	< 2	20		0.01
49	Poky Feeders	< 20	44		9				0.9		115		0.1	
72	Roberts	37	4	5.4	-	< 0.01	0.2	0.3	0.6	2.5	0	14		0.07
50	Ranger Feeders 4	330	4		7				0.3		< 4		< 0.1	
71	Ranger Feeders 5	675	36	37	4	< 0.01	1.8	0.9	0.8	2.9	7	29		< 0.01
73	Montgomery	48	က	4.2	က	< 0.01	0.2	0.2	0.2	1.0	112			0.08
74	Christian Camp	28	4	4.6	N	< 0.01	0.2	0.4	0.1	1.1	< 2	12		0.06
75	Marintzer	166	12	14	က	0.01	1.1	0.3	3.9	2.5	12	24		0.06
76	Klein	< 10	10	11	-	0.04	1.6	1.6	2.2	4.0	22	39		0.05
77	Obermuller	12	0 V	0.3	10	0.09	0.1	0.9	6.7	3.8	46	60		0.03
Kansas site b	etween north and south f	low path												
51	KPL Dakota	123	43		00				0.3		7		0.1	
Kansas sites,	HPA wells													
48	Leoti HPA	< 20	< 4		9				0.8		<u>-</u>		< 0.1	
69	Leoti HPA	< 10	< 2	< 0.2	2	0.05	0.7	0.4	0.7	0.8	9	37		0.04

Table 13. Dissolved trace metal and semimetal concentrations for samples in the regional cross section of a Dakota aquifer flow path. KGS and LLNL refer to the laboratory

a aquifer flow path (continued). KGS and LLNL refer to the	
ons for samples in the regional cross section of a Dakota	
Table 13. Dissolved trace metal and semimetal concentratio	laboratory in which the samples were analyzed.

,											
Sample	Site name	KGS Be	KGS Ac	TLNL As	KGS	CLNL	KGS S 2	KGS An		KGS	DP C
site		hg/L	μg/L	hg/L	μg/L	μg/L	μg/L	hg/L	hg/L	μ g/L	hg/L
Southeastern Co	lorado sites										
57	Grasslands	0.22	0.3	0.2	5.8	< 0.1	1.2	< 0.1	< 0.01	- V	0.13
56	Pritchett	0.25	< 0.1	< 0.1	4.3	< 0.1	1.9	< 0.1		- V	
55	CSU Exp. Station	0.20	< 0.1	0.4	5.3	< 0.1	0.6	< 0.1	0.16	- V	1.2
54	Springfield 9	0.08	< 0.1	0.3	4.9	0.1	1.7	< 0.1		- V	
53	Springfield 11	0.08	0.1	0.9	2.2	0.5	3.7	< 0.1		- V	
62	Vilas			0.7		< 0.1			0.07		0.12
58	Walsh 3	0.19	< 0.1	0.8	7.4	0.9	2.8	< 0.1	< 0.01	က	0.02
59	Walsh 2	0.18	1.2	0.9	9.3	0.3	1.5	0.2	< 0.01	-	0.37
61	Hog farm	0.16	1.2	0.2	9.4	< 0.1	3.3	0.2	< 0.01	- V	0.16
60	Prowers windmill	0.19	1.1	0.1	9.2	< 0.1	2.3	< 0.1	0.11	-	0.29
Kansas sites in g	eneral location of northern flow path										
52	Stanton Morrison	0.31	3.0	3.6	5.6	0.5	5.4	< 0.1	< 0.01	5	0.25
78	Stanton Cheyenne		4.8		0.4			0.5			
46	Coolidge south		0.8		1.7			< 0.1			
63	Coolidge north			0.2		< 0.1			< 0.01		< 0.01
68	Terry Boy	0.01	0.5	1.2	< 0.1	0.3	1.3	0.4	0.02	, V	0.51
47	Leoti Dakota		1.2		0.8			< 0.1			
70	Leoti Dakota	0.14	1.1	0.8	1.1	0.1	7.5	0.2	< 0.01	- V	0.04
49	Poky Feeders		5.4		12			< 0.1			
72	Roberts	0.10	0.9	1.1	< 0.1	0.4	6.4	< 0.1	0.05	, V	0.66
50	Ranger Feeders 4		1.2		0.3			0.2			
71	Ranger Feeders 5	0.23	1.1	3.2	< 0.1	1.3	4.3	< 0.1	< 0.01	-	2.0
73	Montgomery	0.10	1.1	3.4	0.1	1.6	3.2	< 0.1	0.04	, V	0.68
74	Christian Camp	0.11	1.3	2.5	< 0.1	1.2	3.5	< 0.1	0.19	0	1.0
75	Marintzer	< 0.01	< 0.1	13.2	0.3	7.5	5.5	< 0.1	0.16	0	1.9
76	Klein	0.10	0.1	1.3	< 0.1	0.3	3.9	< 0.1	< 0.01	, V	1.1
77	Obermuller	< 0.01	0.5	0.8	1.3	0.2	4.3	< 0.1	0.06	, V	0.34
Kansas site betw	een north and south flow path										
51	KPL Dakota		< 0.1		1.3			< 0.1			
Kansas sites, HP.	A wells										
48	Leoti HPA		3.6		3.7			< 0.1			
69	Leoti HPA	0.08	8.6	4.6	1.1	0.5	3.3	0.2	< 0.01	, V	0.19

Table 14. Tritium, uranium1995) refer to the laboratevalues were determined by	n, and other radioc ory in which the san o the USGS.	hemical concen nples were ana	ttrations for sc lyzed. Uraniu	umples in the re n values are fr	egional cros om LLNL e	ss section of a D xcept for sample	akota aquifer) s 49, 50, and 7	low path. LLN 8, which are fi	L, USGS, an om the USG.	l BEG (Dutton, S. All other
Site sample	Site name	LLNL Tritium TU	USGS Tritium TU	BEG Tritium TU	U µg/L	Gross alpha, μ g/L as U-natural	Gross alpha minus U pCi/L	Gross beta, pCi/L as Sr/Yt-90	Ra-226 pCi/L	Ra-228 pCi/L
Southeastern Colorado s	ites									

values were detern	nined by the USGS.									
Site sample	Site name	LLNL Tritium TU	USGS Tritium TU	DEG Tritium TU	U µg/L	Gross alpha, μ g/L as U-natural	Gross alpha minus U pCi/L	Gross beta, pCi/L as Sr/Yt-90	Ra-226 pCi/L	Ra-228 pCi/L
Southeastern Col	orado sites									
57	Grasslands	0.9			6.53	11.0	3.1	5.9	0.08	< 1.0
56	Pritchett	0.1				13.0	< 9.1	6.1	2.20	4.1
55	CSU Exp. Station	0.7			0.06	12.0	8.4	15.0	1.80	2.5
54	Springfield 9	5.8				14.0	< 9.8	9.8	0.12	< 1.0
53	Springfield 11	5.0				14.0	< 9.8	13.0	0.34	1.2
62	Vilas	12.8			1.95					
58	Walsh 3	1.1			23.2	43.0	13.9	21.0	1.80	3.2
59	Walsh 2	4.0			15.5	23.0	5.3	14.0	0.56	2.0
61	Hog farm	0.1			0.59	84.0	58.4	24.0	31.00	2.4
60	Prowers windmill	0.4			4.14	10.0	4.1	7.7	1.40	< 1.0
Kansas sites in ge	eneral location of northern	flow path								
52	Stanton Morrison	2.0			6.58	6.9	0.2	6.9	0.03	< 1.0
78	Stanton Cheyenne		0		0.53	5.1	3.2	8.2	0.45	< 1.0
46	Coolidge south			0.0						
63	Coolidge north	0.0			1.33					
68	Terry Boy	1.4			< 0.01	3.0	2.1	4.3	0.37	< 1.0
47	Leoti Dakota			0.0						
20	Leoti Dakota	0.6			0.03	< 0.6	< 0.4	4.6	0.37	< 1.0
49	Poky Feeders		4.6	5.6	36.1	47.2	7.8	29.9	1.19	
72	Roberts	0.9			0.02	4.4	3.1	11.0	0.45	< 1.0
50	Ranger Feeders 4		0.2	0.0	0.01	2.0	1.4	7.5	0.28	
71	Ranger Feeders 5	1.1			0.25	1.6	0.9	8.2	0.56	< 1.0
73	Montgomery	0.0			0.04	2.0	1.4	6.8	0.63	< 1.0
74	Christian Camp	0.9			0.03	9.9	6.9	7.2	0.51	< 1.0
75	Marintzer	0.3			0.03	3.9	2.7	9.6	1.60	1.8
76	Klein	5.7			0.68	3.9	2.3	4.6	0.28	< 1.0
77	Obermuller	3.7			10.9	39.0	19.7	23.0	4.60	6.2
Kansas site betwo	een north and south flow p	ath								
51	KPL Dakota		0.1	0.0						
Kansas sites, HP/	A wells									
48	Leoti HPA			6.4						
69	Leoti HPA	4.1			12.4	14.0	1.1	9.1	0.20	< 1.0
KS05	Scott City 4			0.9						
KS08	KPL HPA			0.0						

Table 15. Stable isotope concentrations for samples in the regional cross section of a Dakota aquifer flow path. LLNL, USGS,
and BEG (Dutton, 1995) refer to the laboratory in which the samples were analyzed. The data listed in the "plot" columns
were selected as "best" values for use in figures.

Site	Site name	δ 0-18 %	ბ 0-18 %	δ 0-18 %	δ 0-18 %	δ D %	δ D %	δ D %	δ D %
sample		LLÑL	USĜS	BĔĞ	plot	LLÑL	USĜS	BĔĞ	plot
Southeastern Colorado sites									
57	Grasslands	-9.84	-9.85		-9.84	-66.5	-66.0		-66.3
56	Pritchett	-11.49	-11.55		-11.52	-80.0	-81.5		-80.7
55	CSU Exp. Station	-14.12	-14.20		-14.16	-103.5	-106.0		-104.7
54	Springfield 9	-10.67	-10.70		-10.68	-75.0	-74.5		-74.8
53	Springfield 11	-11.43	-11.05		-11.24	-85.0	-79.5		-83.3
62	Vilas	-12.20			-12.20	-88.0			-88.0
58	Walsh 3	-9.43	-9.35		-9.39	-68.0	-65.0		-66.5
59	Walsh 2	-9.70	-9.60		-9.65	-66.0	-66.5		-66.2
61	Hog farm	-10.04	-10.05		-10.04	-69.0	-69.0		-69.0
60	Prowers windmill	-9.17	-9.20		-9.18	-60.0	-63.0		-61.5
Kansas sites in general location of northern flow path									
52	Stanton Morrison	-10.94	-12.00		-11.47	-79.0	-85.5		-82.2
78	Stanton Cheyenne		-11.27		-11.27		-81.0		-81.0
46	Coolidge south			-12.80	-12.80			-88.0	-88.0
63	Coolidge north	-13.02			-13.02	-93.0			-93.0
68	Terry Boy	-13.24	-13.30		-13.27	-99.0	-97.5		-98.3
47	Leoti Dakota			-12.05	-12.05			-88.5	-88.5
70	Leoti Dakota	-12.07	-12.10		-12.08	-90.0	-88.5		-89.3
49	Poky Feeders		-8.50	-7.93			-59.0	-52.0	
72	Roberts	-11.75	-11.80		-11.77	-97.0	-85.5		-86.3
50	Ranger Feeders 4			-12.95	-12.95			-93.0	-93.0
71	Ranger Feeders 5	-12.52	-12.60		-12.56	-95.0	-92.5		-93.8
73	Montgomery	-11.95	-11.90		-11.92	-88.0	-87.5		-87.8
74	Christian Camp	-11.85	-12.00		-11.92	-87.0	-86.5		-86.8
75	Marintzer	-11.71	-11.85		-11.78	-88.0	-86.5		-87.3
76	Klein	-9.27	-9.35		-9.31	-64.0	-61.5		-62.8
77	Obermuller	-8.52	-8.55		-8.53	-61.0	-57.5		-59.3
Kansas site between north and south flow path									
51	KPL Dakota			-11.55				-84.0	
Kansas sites, HPA wells									
48	Leoti HPA			-9.24	-9.24			-62.0	-62.0
69	Leoti HPA	-8.93	-9.00		-8.97	-61.0	-61.5		-61.2
KS05	Scott City 4			-9.40	-9.40			-60.5	-60.5
KS08	KPL HPA			-10.11	-10.11			-74.5	-74.5

Profiles of Salinity and Major Constituents

Figures 40-45 illustrate changes in TDS and major constituent concentrations and properties along the flow path from southeastern Colorado to central Kansas shown in figs. 38 and 39. One of the Dakota well samples (Poky Feeders well in southern Scott County) is represented as a different symbol (open triangle) because the chemical and isotopic composition indicate that enough water from bedrock overlying the Dakota aquifer and/or the HPA mixed with the Dakota water to cause appreciable changes in some of the chemical characteristics. This may be due to a gravel pack that extends up into the HPA sediments or a leaky seal in the well above the Dakota aquifer. The Dakota groundwater collected from Finney County (KPL power plant) near a flow path in the aquifer to the south of that in fig. 38 is plotted as a different symbol (open diamond) in the figures to show the chemical contrast with groundwaters in the northern flow path. The Finney County well lies near the boundary where Dakota strata become confined by overlying Upper Cretaceous shale. South of the boundary, the Dakota aquifer is directly overlain by the HPA. Points for the waters sampled from the overlying HPA (open circles)

and underlying Morrison Formation (open square) are also plotted for comparison to the Dakota groundwaters in the flow cross section.

Groundwater in the Dakota aquifer is fresh in the recharge and local flow area of southeast Colorado. The TDS concentration increases to about 1,000 mg/L in water in the confined aquifer in western Kansas and then increases substantially in the zone of Permian saltwater intrusion in the confined aquifer in central Kansas (fig. 40). The TDS content then decreases farther to the east in the discharge and local flow system of the outcrop/subcrop belt where freshwater recharge flushes and dilutes saline water in the Dakota aquifer. The TDS concentrations in groundwaters in the HPA overlying the confined aquifer in west-central Kansas, the underlying Morrison Formation near the Colorado border, and Dakota aquifer in the southern flow path are all in the same range as for the Dakota groundwaters in southeastern Colorado.

The chloride concentration is low (mainly less than 30 mg/L) in the Dakota aquifer in the southeast Colorado and westernmost Kansas part of the profile (fig. 41). The chloride content increases in a general logarithmic trend



n Witter from wells along regional flow paths of the Dakota aquifer.



n Kigure 41. Change in chloride concentration in water from wells along regional flow paths of the Dakota aquifer.

along the flow path through the confined aquifer. The highest chloride concentration is located in central Kansas where the Dakota aquifer overlies the area of greatest intrusion of Permian saltwater. The chloride concentration in the HPA overlying the Dakota aquifer and in the Dakota aquifer along the southern flow path is generally similar to that in southeastern Colorado. Although chloride is the predominant anion contributing to the large increase in TDS concentration in the Dakota aquifer in central Kansas, other anions are more important for the TDS content increase in the confined aquifer near and west of 101° longitude. Dissolved sulfate (fig. 42) generally contributes a greater proportion of the anionic composition in groundwaters in southeast Colorado and in Kansas near and west of 101° longitude than chloride. The sulfate concentration is sometimes higher than the bicarbonate concentration in these areas (fig. 43), resulting in sulfate-type waters. Farther to the east along the flow path, the sulfate content varies substantially, whereas the bicarbonate concentration shows an increasing trend. Sulfate and bicarbonate contents of groundwaters in the HPA along the southern flow path and in the Dakota aquifer to the south near and within the unconfined areas tend to be substantially lower than in Dakota aquifer waters in the northern flow

path at the same longitude. The range in bicarbonate concentration at a location along the flow path is generally much smaller than that for sulfate.

Sodium concentration in Dakota waters along the flow path (fig. 44) follows a similar pattern as for the TDS content (fig. 40). The sodium profile is also similar to that of chloride except that the sodium concentration increases at a greater rate than chloride concentration with distance through southeast Colorado into the confined area of westcentral Kansas. The sodium content then remains relatively constant until reaching the main saltwater intrusion area in central Kansas, where it increases substantially. Sodium concentration in the HPA and the unconfined Dakota aquifer to the south is substantially smaller than in the confined area of west-central Kansas and is in the lower part of the range for Dakota waters in southeast Colorado.

 The profile of calcium concentration across the flow path The profile of calcium concentration across the flow path end to be the profile of calcium concentration across the flow profile is similar to that for calcium and the terminant of the terminant end terminant of the terminant of the terminant of the terminant end terminant of terminant of terminant of terminant of terminant end terminant of terminant of terminant of terminant of terminant end terminant of terminan



n Kigure 42. Change in sulfate concentration in water from wells along regional flow paths of the Dakota aquifer.



n Kigure 43. Change in bicarbonate concentration in water from wells along regional flow paths of the Dakota aquifer.


Figure 44. Change in sodium concentration in water from wells along regional flow paths of the Dakota aquifer.



Figure 45. Change in calcium concentration in water from wells along regional flow paths of the Dakota aquifer.

Kansas line. Calcium and magnesium concentrations are appreciably smaller in the confined Dakota aquifer in western and central Kansas than in the local flow area of the Dakota aquifer in southeast Colorado. The change to low calcium and magnesium levels along the flow path is especially great as the water enters the confined area in western Kansas. Calcium and magnesium concentrations then generally increase along the flow path within the confined aquifer from west to central Kansas.

The nearly three orders-of-magnitude change in the (calcium + magnesium)/sodium equivalent ratio across the flow path in the Dakota aquifer from southeastern Colorado through Kansas (fig. 46) is related to carbonate equilibria and cation exchange. Groundwaters in southeast Colorado initially derive calcium and magnesium from leaching of carbonate minerals concentrated in soils in an environment of greater evapotranspiration than precipitation. The aquifer is well flushed in this area; thus, any previous saline water in the aquifer has been essentially all removed and sodium and chloride concentrations in the groundwater are low. The flushing in the Dakota aquifer in southeast Colorado has been extensive enough to also remove high sodium contents adsorbed on clays deposited in brackish or marine

environments or subjected to later saltwater intrusion from underlying Permian strata. Thus, any former capacity of high adsorbed sodium content to soften recharge waters has been largely removed, and recharge, usually of calciumbicarbonate type, retains its higher calcium-plus-magnesium than sodium content. Additional calcium in the Dakota aquifer in the recharge area is probably obtained from calcite dissolution in the bedrock as well as dissolution of secondary gypsum. As described earlier, secondary gypsum in the strata can be precipitated from locally high concentrations of sulfate derived from pyrite oxidation coupled with high calcium from increased dissolution of calcite by the acidic solutions produced during the pyrite weathering.

When the calcium-bicarbonate to calcium-sulfate type waters flowing deep enough in the system reach the confined portion of the Dakota aquifer in western Kansas, exchange of calcium and magnesium in the groundwater for sodium on clay surfaces becomes important. This causes softening (decrease in calcium and magnesium concentrations) of the groundwater. The aquifer in the confined area has not been as well flushed as in the local flow areas, leaving high sodium concentrations on marine clays or on clays subjected to saline waters derived from Permian saltwater intrusion



Figure 46. Change in the (calcium + magnesium)/sodium ratio in water from wells along regional flow paths of the Dakota aquifer.

in earlier geologic time. The removal of saline groundwater from the confined aquifer is more rapid than the removal of the high adsorbed sodium because the saline water is preferentially diluted and replaced by flow through the larger pore spaces whereas clays are present in higher amounts in the lower permeability sediments. The high exchange capacity of most aquifer clays acts as a reservoir that must be depleted through interactions with large volumes of inflowing water before the adsorbed cation concentrations approach ratios that are in near equilibrium with the inflows and, thus, no longer appreciably change the inflow chemistry (see later section on geochemical modeling of groundwater evolution for further explanation of this phenomenon).

Calcium and magnesium concentrations can become as low as a few mg/L each in the confined Dakota aquifer along the cross section in western Kansas (table 11, fig. 45) as a result of the water-softening process. In contrast, the calcium concentrations in overlying HPA waters and in the Dakota water along the southern flow path are within the range of the Dakota aquifer waters in southeast Colorado. The calcium and magnesium contents and the (calcium + magnesium)/ sodium ratio in the Poky Feeders well water are higher than expected for the location in the aquifer. These observations and other evidence discussed later in this subsection indicate that the well probably allowed downward flow of water from the overlying HPA and possibly some groundwater of calcium-sulfate type from the Upper Cretaceous shales and chalks overlying the Dakota aquifer at this location. The downward flow was probably in the gravel pack of the annular space of the well, which is a common construction practice for stock and irrigation wells in Kansas. The TDS content in the HPA in the area of the Poky Feeders well is higher than in other parts of the aquifer due to the effect of evapotranspiration concentration of dissolved solids in the closed Whitewoman Basin.

After the abrupt decrease in the (calcium + magnesium)/ sodium ratio from the local to the confined flow system near the Colorado-Kansas state line, the ratio remains low along the flow path until the confining layer thins in central Kansas (fig. 46). Flushing of the saline water that intrudes from the underlying Cedar Hills Sandstone and removal of the high adsorbed sodium content on clays by recharge in the local flow area in central Kansas allows the return of the water type to calcium-bicarbonate type. The (calcium + magnesium)/sodium ratio in the HPA and Dakota waters near the southern flow path in western Kansas is within the same range as for the Dakota groundwaters in southeast Colorado and in the local recharge-discharge area in central Kansas. Calcium-sulfate type water also occurs in the local flow area in central Kansas as in southeast Colorado. The origin of the water types is probably similar in the different areas.

When the dissolved calcium and magnesium concentrations decrease in the Dakota aquifer from cation exchange, the groundwater can become undersaturated with respect to the common carbonate minerals calcite and dolomite. Dissolution of the carbonate minerals can then occur to reestablish saturation conditions. This commonly results in an increase in pH and can also increase the bicarbonate concentration. The profile of pH along the flow path in the Dakota aquifer (fig. 47) indicates that where the (calcium + magnesium)/sodium ratio is low, the pH is generally greater than 7.6. The highest pH values (up to 8.5) occur in the early part of the confined flow path where the cation exchange becomes substantial. Where the (calcium + magnesium)/sodium ratio is relatively high, the pH ranges from near to less than 7.6. The bicarbonate content of the Dakota aquifer water (fig. 43) is also generally greater in the areas of the Dakota aquifer in which the (calcium + magnesium)/sodium ratio is low than where the ratio is relatively high.

The increase in sodium concentration in Dakota waters along the flow path (fig. 44) is derived from both the water-softening process and increased intrusion of saltwater from the underlying Permian strata as the waters approach central Kansas. Although the sodium concentration is low in the recharge area of southeast Colorado, the sodium/ chloride equivalent (or molar) ratio is generally much greater than 1 (fig. 48). The excess sodium could either be adsorbed sodium released by exchange from Dakota sediments previously containing saline water or weathering of minerals that contain sodium. The sodium/chloride ratio reaches a maximum in the confined aquifer in westernmost Kansas where the cation exchange process starts to occur in the confined aquifer and then decreases along the flow path within Kansas as the salinity of the waters increases. The intrusion of saltwater derived from dissolution of halite becomes a much stronger control on the sodium/chloride ratio than the effect of the cation exchange. The sodium/ chloride ratio is closest to the theoretical molar ratio of one for halite dissolution at the location with the highest chloride concentration. However, the sodium/chloride ratio is greater than 1 for this water, indicating that cation exchange maintains an excess equivalent concentration of sodium concentration relative to chloride.



Figure 47. Change in pH in water from wells along regional flow paths of the Dakota aquifer.



Figure 48. Change in the sodium/chloride ratio in water from wells along regional flow paths of the Dakota aquifer.

Profiles of Minor Constituents and Isotopes

As described earlier in this chapter, the bromide/ chloride ratio is useful for determining the source of high chloride concentration in water. The bromide/chloride profile along the flow path in the Dakota aquifer from southeastern Colorado to central Kansas (fig. 49) shows a progressive decrease in the ratio until the last two locations in the path. The pattern in the bromide/chloride profile is approximately the inverse of that for chloride concentration (fig. 41). This is caused by the decrease in the bromide/chloride ratio with increasing chloride concentration for the mixing of freshwater with saltwater derived from the dissolution of halite (fig. 29). Once the chloride concentration exceeds about 150 mg/L along the flow path, the bromide/chloride mass ratio drops below 0.003. The lowest ratio (0.0004) occurs in the sample with the highest chloride concentration (1,363 mg/L) obtained from the confined aquifer in central Kansas where the intrusion of Permian saltwater has a substantial impact on the water quality. The profile illustrates well that the source of increasing chloride in the flow path across the confined Dakota aquifer in Kansas is from the intrusion of saltwater with a halite-dissolution origin. It also indicates

that most of the chloride in the Poky Feeders sample fits a similar origin.

Changes in dissolved fluoride concentration in the Dakota aquifer water along the flow path from southeastern Colorado to central Kansas (fig. 50) are generally inversely related to the calcium concentration (fig. 45) due to the dissolution of fluoride-containing calcium minerals as described in the earlier section in this chapter on geochemical factors. The profile shows that the fluoride content is greatest in the main part of the confined flow path in Kansas where the water has low calcium concentration from cation exchange. A simple function, the square of the fluoride concentration equal to a constant divided by calcium concentration (the solid line shown in fig. 51) generally fits the fluoride-calcium relationship for Dakota groundwaters along the flow path, as expected if the simplest calcium-fluoride mineral, fluorite (CaF₂) primarily controlled the dissolved fluoride concentration. That is because the solubility product (a constant at a particular temperature and pressure) for fluoride equals the product of the activities (effective concentrations in solution) of calcium and of the square of fluoride. Other minerals that could control dissolved fluoride concentration are apatites, which are



Figure 49. Change in the bromide/chloride ratio in water from wells along regional flow paths of the Dakota aquifer.



Figure 50. Change in fluoride concentration in water from wells along regional flow paths of the Dakota aquifer.



Figure 51. Relationship between fluoride and calcium concentrations in water from wells along regional flow paths of the Dakota aquifer. The fluoride and calcium values in the functions for the lines are fluoride and calcium concentrations.

calcium fluorophosphates, such as *fluorapatite* ($Ca_{s}(PO_{4})_{2}F$). The relationship of fluoride to calcium concentration for fluorapatite would be expected to be related to a function in which the fluoride concentration was inversely proportional to calcium concentration raised to the 5th power. This function plots as the dashed line on fig. 51 and does not fit the sample data as well as that based on $(F)^2$. The character of the actual minerals controlling dissolved fluoride and the effect of ionic strength of the aquifer waters on the activity coefficients in the solubility products of the minerals would determine the actual shape of the function best fitting the data. However, the functions displayed as lines in fig. 51 suggest that fluorite could play the major role in controlling dissolved fluoride concentration in Dakota groundwater. Adsorption of fluoride on clays could be a minor factor controlling the dissolved fluoride content.

The profiles for nitrate and ammonium ion concentrations in Dakota groundwaters (fig. 52) are, in general, inversely related. Freshwater samples from the Dakota aquifer in southeast Colorado had a nitrate-nitrogen concentration that was either in the few to several mg/L range or was undetectable. One of the samples from southeast Colorado with undetectable nitrate contained a small concentration of ammonium ion. Except for the Poky Feeders well water, the samples from the confined Dakota aquifer in Kansas did not contain detectable nitrate content but ranged from a few tenths to more than one mg/L of ammonium ion. The sample from the Poky Feeders well contained 4.3 mg/L dissolved nitrate-nitrogen but no detectable ammonium ion, in contrast with what would be expected for the confined aquifer at that location. This indicates that a surface or near-surface source of water had entered the well water before collection of the sample. Groundwaters in the Dakota aquifer along the southern flow path and in the HPA overlying the confined Dakota aquifer contain measurable nitrate content but undetectable ammonium ion. The water in the unconfined Dakota aquifer at the eastern end of the flow path had a substantial concentration of nitrate but no detectable ammonium ion.

The major geochemical control on whether nitrate or ammonium ion is present at detectable limits common to analyses for these constituents is the oxidation potential of the groundwater. The data illustrate the change in the chemical environment from usually oxidizing or intermediate in oxidation potential in the local flow system of southeast Colorado, in which nitrogen in the form of nitrate is stable,



Figure 52. Change in ammonium ion and nitrate concentrations in water from wells along regional flow paths of the Dakota aquifer. Points representing determinations below the detection limit are shown as values of half the detection limit.

to a reducing environment along the regional flow path through the confined aquifer, in which the reduced form of nitrogen as ammonium ion is stable, then back to a more oxidizing environment in the local flow system of central Kansas. Dissolved iron and manganese concentrations (defined as the amounts determined in the samples filtered through 0.45 μ m membrane filter paper in the field, table 13) also illustrate changes in the oxidation-reduction potential of the groundwaters (fig. 53). Dissolved iron and manganese contents in the local flow system of southeast Colorado range substantially from less than 10 and less than 1 μ g/L, respectively, up to about 1,000 and 100 µg/L, respectively. In the confined Dakota aquifer along the northern flow path, iron and manganese concentrations are typically greater than 30 and 3 μ g/L, respectively. The iron and manganese contents can then again be low in the local flow system of central Kansas (fig. 53), which usually has measurable nitrate and undetectable ammonium ion concentrations, because the groundwater generally is in an oxidizing environment. The groundwater sampled in the unconfined Dakota along the southern regional flow path is generally not reducing enough to contain detectable ammonium ion but can have a low enough oxidation potential to contain measurable

dissolved iron and manganese concentrations. In general, the HPA waters are oxidizing enough that they do not contain detectable amounts of dissolved iron and manganese. Tables 12 and 13 indicate that when a groundwater in the Dakota aquifer contains both dissolved iron and manganese concentrations greater than 40 and greater than 4 μ g/L, respectively, the nitrate-nitrogen content is usually less than 1 mg/L and commonly less than 0.1 mg/L. Based on these same tables, when the ammonium ion concentration in Dakota groundwater is greater than 0.2 mg/L, the dissolved iron and manganese contents are usually greater than 40 and greater than 40 and greater than 40 and greater than 40 and greater than 40 manganese contents are usually greater than 40 and greater than 40 manganese contents are usually greater than 40

For other trace metal or semimetal concentrations in table 13, no clear patterns emerge related to dissolved nitrate, ammonium ion, iron, and manganese concentrations and oxidizing to reducing conditions in the Dakota aquifer along the flow paths. A general pattern exists for the concentration of uranium and uranium series radionuclides, radium, and ionizing radiation (alpha and beta) (table 14) and oxidationreduction environments along the flow paths of the Dakota aquifer. Some of the waters in the local flow systems in southeast Colorado and central Kansas that are expected to exist in an oxidizing environment (no detectable ammonium



Figure 53. Change in dissolved iron and manganese concentrations in water from wells along regional flow paths of the Dakota aquifer. Points representing determinations below the detection limit are shown as values on the x-axis.

ion, nitrate-nitrogen greater than 1 mg/L) contain greater than 10 µg/L dissolved uranium. The groundwaters occurring in a reducing environment (ammonium-nitrogen greater than 0.2 mg/L) have very low uranium concentrations (usually less than 0.3 mg/L). This fits the relatively high solubility of the oxidized state of uranium, U(VI), present as the dissolved uranyl ion UO₂²⁺ and its complexes, especially carbonate complexes, in water. In a reducing environment, minerals that contain the reduced state of uranium, U(IV), such as uraninite (UO_2) and coffinite $(USiO_4)$, which have low solubility, occur (Langmuir, 1997). Thus, groundwater in the confined portion of the Dakota flow path tends to have low uranium concentration. Groundwater with a reducing environment in the confined part of the flow path also commonly has low concentrations of radium and alpha and beta radiation (table 14). In the local flow portions of the system, groundwater can sometimes contain a gross alpha value (as uranium-natural) of about 40 pCi/L or greater, in which case the gross alpha minus uranium can be near 10 pCi/L or above, the gross beta greater than 20 pCi/L (reported as Sr/Yt-90), the Ra-226 greater than 1 pCi/L, and the Ra-228 greater than 2 pCi/L.

The radioactive isotope of hydrogen, tritium (³H), has a half-life of 12.35 yrs. Natural levels of tritium measured in the atmosphere before the first atmospheric test of a thermonuclear explosion were about 4 to 25 TU (tritium units) (Fontes, 1980). Recharge from precipitation entering a groundwater system before explosion of thermonuclear devices would start with this level of tritium. If the groundwater became isolated from meteoric precipitation, even the highest level of pre-bomb tritium would decay to less than 1 TU in about 60 years and to less than 0.1 TU (about the detection limit for tritium by modern methods) after approximately 100 years. Atmospheric tests of thermonuclear bombs extended from 1952 to 1963 and produced levels of tritium in the northern hemisphere that exceeded 100 TU during most of that period and reached more than 2,000 TU (Fontes, 1980). Thus, post-1952 recharge to groundwater in Colorado and Kansas introduced a measurable signal of tritium that can be used to indicate whether a groundwater sample contains relatively recent atmospheric precipitation.

The tritium profile of groundwater along the flow path for the Dakota aquifer (fig. 54) illustrates that some of the water sampled in southeastern Colorado contained a significant amount of relatively recent recharge, as indicated by a tritium concentration of greater than 3 TU. Some



Figure 54. Change in tritium concentration in water from wells along regional flow paths of the Dakota aquifer.

Dakota groundwaters in southeastern Colorado and all the waters along the regional flow path in the confined aquifer contained less than 2 TU. The age of meteoric recharge in the confined Dakota aquifer along the regional flow path greatly exceeds 100 years (Clark et al., 1998). Thus, the low levels of tritium content between the detection limit and 2 TU probably represent very small amounts of surface or near-surface water that leaked down into the sampled wells. The relatively substantial concentration of tritium in the groundwater from the Poky Feeders well indicates an appreciable amount of recent meteoric water was in the sample. This substantiates the explanation for the differences in water chemistry for this sample described earlier in this chapter as leakage of surface or shallow groundwater. The two samples of Dakota water at the easternmost part of the flow path contained substantial tritium concentration, also indicating the presence of relatively recent recharge. Even though the second to most eastern well is in the confined aquifer, the well is relatively shallow, the confining unit is thin, and the topography indicates that the flow system is local, which is consistent with the tritium level observed. Groundwater samples from the Dakota aquifer along the southern flow path, as well as one of the samples from the

HPA, did not contain detectable tritium content, indicating that the recharge was more than 100 years old. Other HPA waters contained from low to moderate levels of tritium, indicating either recent recharge that naturally entered the groundwater or leakage along the annular space of the wells.

The stable isotope geochemistry of oxygen and hydrogen in water is useful for assessing changes in the environment of precipitation that recharged groundwater. Various factors—such as the distance from the ocean, the altitude, the temperature of precipitation formation, and the amount of precipitation-affect the stable isotopic composition of oxygen and hydrogen (Mazor, 1991). The isotopic composition of water is expressed as the amount of O-18 and deuterium in the units δ^{18} O ‰ and δ D ‰, respectively. The profiles of δ^{18} O ‰ and δ D ‰ along flow paths in the Dakota aquifer (fig. 55, based on data in table 15) indicate that the ranges in δ^{18} O ‰ and δ D ‰ for the confined part of the Dakota flow path from the Colorado-Kansas line to longitude 99 degrees are appreciably narrower than those for the local flow system in southeast Colorado. The water from the CSU Experiment Station contained the lowest $\delta^{18}O$ ‰ and δD ‰ values. This water sample is the only one in southeast Colorado with a detectable ammonium



Figure 55. Change in the stable isotopic composition of water from wells along regional flow paths of the Dakota aquifer.

ion concentration. Thus, the reducing environment present in the Dakota aquifer interval in which this well is screened suggests that the Dakota strata may be more confined than at the other sites. The Dakota groundwaters with the highest $\delta^{18}O \%$ and $\delta D \%$ values are in the local flow system of southeast Colorado near Kansas and in the local flow system at the end of the flow path in central Kansas. The $\delta^{18}O \%$ and $\delta D \%$ values for the sample from the Poky Feeders well and for some of the samples from the HPA are also high. The stable isotope values for the groundwater in the Morrison Formation are in the range of the main confined zone of the Dakota flow path in Kansas.

The distance from the ocean and the altitude of the well locations have been essentially constant during the last 100,000 years. However, the temperature of rainfall formation and the rain intensity pattern during seasons is expected to have been different in the past. Lower temperatures and greater rates of rainfall result in a lighter (more negative) isotopic composition of $\delta^{18}O$ ‰ and δD ‰. The older, more confined groundwaters in the system are interpreted to be those with lower $\delta^{18}O$ ‰ and δD ‰ values that reflect cooler and wetter conditions in the past that provided the source of recharge to the Dakota aquifer. The groundwater in the Morrison Formation also fits in this category. The highest (least negative) $\delta^{18}O$ ‰ and δD ‰ represent more recent rainfall recharge. For example, the chemical constituent data described earlier in this section for the sample from the Poky Feeders well indicate a mixture of surface or shallow groundwater with the Dakota groundwater. The high δ^{18} O ‰ and δ D ‰ data also reflect this interpretation.

Other geochemical aspects of the Dakota flow paths in southeast Colorado and Kansas that are related to the age dating of the water are discussed in Clark et al. (1998) and Macfarlane et al. (2000).

Vertical Geochemical Changes

Saltwater occurs in the Permian rocks underlying the Dakota aquifer in much of Kansas. The saltwater intruded into Dakota aquifer strata in the geologic past and continues to intrude at varying rates into the overlying aquifer. Freshwater recharge from the surface and lateral flow of that recharge have been diluting and flushing the saline water from the aquifer at a faster rate than upward intrusion of the saltwater. Thus, the salinity in the Dakota aquifer generally increases with depth. The rate of salinity change with depth is seldom uniform; the TDS concentration is usually substantially greater below lowpermeability layers that impede either the upward transport of saline water or the downward movement of fresh groundwater recharge, depending on the local hydraulic gradient. Salinity can also increase with depth within a thick sandstone if saltwater occurs in underlying units.

The substantially greater permeability of the sandstone units within the Dakota aquifer in comparison with the shales can allow a faster rate of flushing of salinity by fresher regional flow. The general inverse correlation of the particle size of the Dakota sediments with TDS concentrations in areas where some salinity exists, primarily in the confined aquifer, means that there can be substantial local differences in both the vertical and areal distribution of water quality depending on the particular sandstone-to-shale ratio. Often, the better the water-yielding characteristics of the aquifer, the better the water quality within a given area. In some locations where a substantial sandstone receiving regional flow lies below low-permeability rocks in the Dakota aquifer, the water can be fresher in the sandstone than in the overlying, less permeable units.

Regional Changes

Although a general increase in salinity with depth occurs within subregions of the Dakota aquifer, differences in the geohydrology among subregions result in a wide-range of TDS concentration with depth across the aquifer in Kansas (fig. 56). This is also true for concentrations of the major constituents, such as chloride and sulfate (figs. 57 and 58). A more recognizable relationship exists between depth and (calcium + magnesium)/sodium ratio for the Dakota aquifer (fig. 59). In general, the greater the depth, the lower the ratio. This reflects higher values of the ratio for shallow groundwaters, which are often of calcium, magnesiumbicarbonate type, in comparison with deeper waters that have undergone cation exchange of calcium and magnesium for sodium on clays during recharge and saltwater flushing by the fresher waters. The chemical signature of water affected by the exchange process tends to occur more commonly in the confined aquifer (fig. 59). Recharge by freshwater occurs more easily in the unconfined aquifer and has largely flushed out waters with a low (calcium + magnesium)/sodium ratio as the clays have lost their water-softening capacity with time after substantial throughflow by recharge water.

Fluoride concentration in the Dakota aquifer generally increases with depth (fig. 60) and tends to be higher in the confined aquifer than the unconfined aquifer for similar depths. These trends are associated with the inverse change



Figure 56. Well depth versus TDS concentration in groundwaters in the Dakota aquifer.



Figure 57. Well depth versus chloride concentration in groundwater in the Dakota aquifer.



Figure 58. Well depth versus sulfate concentration in groundwater in the Dakota aquifer.



Figure 59. Well depth versus (calcium + magnesium)/sodium ratio based on equivalent concentrations in groundwater in the Dakota aquifer.



Figure 60. Well depth versus fluoride concentration in groundwater in the Dakota aquifer.

in the calcium concentration and (calcium + magnesium)/ sodium ratio with depth and the lower ratios in the confined than the unconfined aquifer. Lower calcium and magnesium concentrations in the aquifer water allow greater dissolution of minerals that contain calcium and fluoride. The higher salinity of water associated with greater sodium content has a small added effect of increased mineral dissolution associated with the higher ionic strength of the water. Thus, greater fluoride concentration is often associated with sodium-bicarbonate or mixed cation-anion type waters. In the confined region, fluoride usually increases and calcium decreases with depth from the top of the Dakota, then fluoride decreases and calcium increases with depth at the bottom of the Dakota system where saltwater occurs. Dispersion and diffusion of sodium-chloride water from underlying Permian rocks into the lower part of the Dakota aquifer largely saturates clay surfaces with sodium. Where calcium-bicarbonate or calcium-sulfate waters with low fluoride from upper Cretaceous rocks enter the upper part of the underlying Dakota aquifer, exchange of calcium for sodium on clays substantially lowers the calcium concentration within the aquifer to levels at which fluorite and/or fluoride-containing apatite phases can dissolve.

Nitrate concentration tends to be the highest (greater than 10 mg/L as nitrate-nitrogen) in the unconfined aquifer at depths less than 200 ft (fig. 25), indicating a surface source of contamination, as previously described in the section in this chapter on characteristics of contaminated groundwater. Many unconfined aquifer and most confined aquifer waters contain less than 2 mg/L nitrate-nitrogen. As described earlier, the confined aquifer waters with greater than 2 mg/L nitrate-nitrogen probably represent wells in which contaminated water from the surface or near surface can flow down a poorly sealed or unsealed annular space and enter the confined aquifer.

Site-Specific Changes

The greatest salinity changes with depth occur across substantial shale units with appreciable lateral extent that confine or separate aquifer units. Where the Graneros Shale is laterally continuous over miles (not isolated strata separated by multiple valleys), it can separate fresh or slightly saline water in the Greenhorn Limestone from very saline water (greater than 10,000 mg/L TDS) in the Dakota aquifer. Shales with a continuous lateral extent within the Dakota can also produce confined conditions in which saline waters are protected from significant flushing by fresh recharge. In addition, shallow Dakota groundwater located in river valleys can be affected by local upward discharge of saltwater from deeper in the aquifer as a result of local groundwater flow and discharge to rivers. For example, the depth from land surface to the top of the Dakota Formation is 108 ft (33 m) at the location of an observation well in upland northwest of Beloit in north-central Mitchell County (NW NE NE sec. 36, T. 6 S., R. 8 W.). The surface elevation of the location at the well site north of the Solomon River is about 100 ft (30 m) higher than that of the floodplain. The TDS, chloride, and sulfate concentrations were 19,000, 7,940, and 3,060 mg/L, respectively, in groundwater from the screened interval depth of 110–160 ft (34–49 m). Fresh groundwater occurs in the Dakota Formation along the outcrop/subcrop boundary several miles to the southeast of this observation well.

Where the Kiowa Formation is mainly shale, it can separate saltwater in the Cheyenne Sandstone from substantially less saline water in the overlying Dakota Formation. An example is saline water in the Dakota Formation at Gorham in Russell County (NW SW NE sec. 32, T. 13 S., R. 15 W.) with TDS, chloride, and sulfate concentrations of 3,570, 1,700, and 345 mg/L, respectively, at a screened interval depth of 200–210 ft (61–64 m). Groundwater in the Cheyenne Sandstone at a depth interval of 470–480 ft (143–146 m) contained TDS, chloride, and sulfate concentrations of 44,000, 22,100, and 4,650 mg/L, respectively.

The importance of a low-permeability zone on vertical salinity changes within the Dakota Formation is illustrated by data from water samples and geophysical logs for the Jones site (NE NE NE sec. 2, T. 10 S., R. 8 W.) in northcentral Lincoln County along the border with Mitchell County. Two observation wells and a pumping well were drilled as a part of the Dakota Aquifer Program along the side of a hill above Rattlesnake Creek. Although the Graneros Shale overlies the Dakota Formation at the well location, the shale only extends along the upland between Salt Creek to the north and Rattlesnake Creek to the south. The limited shale cover and the avenue for discharge of groundwater from the upper Dakota Formation along the lower hillsides allowed freshwater recharge to flush saltwater out of the upper Dakota sands. The groundwater in the upper Dakota sandstone at a depth interval of 76-96 ft (23-29 m) contained TDS, chloride, and sulfate concentrations of 416, 31, and 63 mg/L, respectively. Nearly 60 ft (18 m) of siltstone and shale with thin sandstones separates the

upper aquifer sandstones from a 100-ft (30-m) thickness of sandstone at a depth interval of 170–225 ft (52–69 m) in the lower Dakota Formation. Water from an observation well screened at a depth of 135-145 ft (41-44 m) within the siltstone and shale interval contained chloride and sulfate concentrations of 3,250 and 907 mg/L, respectively. The salinity of the Dakota Formation increased through the lowpermeability zone to the 100-ft (30-m) sandstone interval. The TDS content of the groundwater in the lower part of the 100-ft (30-m) sandstone is assumed to be similar to the salinity of the low flow in Rattlesnake Creek below the well site because the saline water in the creek is expected to have been derived primarily from discharge of groundwater from the 100-ft (30-m) sandstone interval. Water collected from the creek during the same period as the sampling of the 135-145 ft (41-44 m) well had chloride and sulfate concentrations of 10,800 and 3,760 mg/L, respectively.

In the confined aquifer, recharge passing through the overlying upper Cretaceous limestones and shales can have appreciably higher calcium, magnesium, and sulfate concentrations than in fresh to slightly saline portions of the upper Dakota aquifer. An example of the changes with depth in these and other dissolved constituents and TDS in the Dakota Formation is illustrated by the water chemistry for a test hole drilled in 1992 during exploration for water resources in the Dakota aquifer by the City of Hays (figs. 61–64). The test hole was located in southwest Ellis County above the western edge of where the Cedar Hills Sandstone directly underlies the Dakota aquifer and allows a greater rate of saltwater intrusion from the Permian to the Dakota aquifer base than where shales separate the strata. The depth interval for the Dakota Formation is 295-548 ft (90-167 m) in the test hole; the hole then penetrated the Kiowa Formation starting at 548 ft (167 m) before drilling was stopped at 595 ft (181 m). The lithology of the Dakota interval at the location is mainly siltstone and sandstone and of the Kiowa Formation is siltstone and shale.

The TDS concentration of groundwater at the test-hole location generally increases by a relatively small amount in the upper to middle part of the siltstone and sandstone interval of the Dakota Formation, then increases markedly in the lower portion from just above the Kiowa Formation and into the Kiowa (fig. 61). The sulfate content decreases in the uppermost part of the interval and then does not change substantially, whereas both the sodium and chloride concentrations increase appreciably across the interval (fig. 62). The calcium concentration decreases greatly



Figure 61. Depth profile of TDS concentration in the Dakota aquifer for samples collected during drilling of a test hole in southwest Ellis County.



Figure 62. Depth profile of sodium, chloride, and sulfate concentrations in the Dakota aquifer based on data for a test hole in southwest Ellis County.

and the magnesium content declines more moderately in the uppermost part of the Dakota Formation, followed by relatively small changes in the rest of the interval (fig. 63). The decrease in calcium and magnesium and the increase in sodium content caused by the cation exchange (softening process) is marked in the upper part of the Dakota aquifer, as indicated by the large decrease in the (calcium + magnesium)/sodium ratio (fig. 64). A small increase in the sodium/chloride ratio occurs in the uppermost Dakota Formation, followed by a more substantial decline in the lower part of the Dakota and Kiowa interval caused by the intrusion of saltwater from the underlying strata (fig. 64). The fluoride concentration follows a pattern with depth opposite to that of the calcium because the low calcium concentration within the aquifer waters allows fluoridecontaining calcium minerals to dissolve (fig. 63). Dissolved fluoride then decreases with depth at the bottom of the Dakota aquifer and into Permian strata (below the interval shown in fig. 63) where calcium concentration is much greater in the saline water. The TDS and constituent concentration and ratio changes with depth in figs. 61–64 parallel the changes along the regional flow-path in the Dakota aquifer (figs. 40-42, 44–46, 48, and 50) from the recharge area near the southeast Coloradosouthwest Kansas border to the saline water in the confined aquifer in central Kansas.

Changes in Russell County

Russell County is an area where some of the greatest spatial variations in salinity in Dakota aquifer waters occur (fig. 32). The groundwater in the Dakota aquifer is most saline in western Russell County where the base of the Dakota aquifer directly overlies the saltwater-containing Cedar Hills Sandstone. Regional

flow in the confined aquifer in the western part of the county discharges saline water to river valleys. Where the upper Cretaceous confining units are thin or absent, local recharge and discharge systems have flushed much of the saltwater in the upper aquifer. The freshest water occurs in the uppermost part of the confined and outcropping Dakota Formation in eastern Russell County. Water-quality data for test wells drilled during an exploration for water supply for the City of Russell by Ground Water Associates (GWA) illustrate the vertical increase in the salinity of water in the Dakota aquifer and the importance of low permeability units in separating low- from highsalinity zones. The KGS chemically analyzed many of the samples to determine whether there was any oil brine contamination contributing to the chloride content of the water; no detectable evidence of an oil-brine source was found in the test-hole waters. Most of the test wells drilled for GWA were in southeast Russell County. These included 12 test wells in nine different sections in an area 7 by 7 mi (11 by 11 km) (table 16). The wells were located in the upland between the valleys of the Smoky Hill and Saline rivers. Most of the wells penetrated a small thickness of upper Cretaceous strata above the Dakota Formation, although a few wells were at the edge of the outcrop/subcrop boundary of the Dakota strata (fig. 1). The chemical data for water samples from the test wells are in table 17.

The salinity of the waters in the Russell County test holes generally increases with depth. Figure 65 illustrates the change in TDS concentration for the test-hole waters with depth from land surface to the middle of the sample interval, elevation of the sample interval, and the sample interval depth below the top of the Dakota Formation (or extrapolation of the top where eroded). The lines in the figures connect the letter symbols (listed in tables 16 and 17) that represent groundwaters from different depths in the same test hole. An individual letter symbol without



Figure 63. Depth profile of calcium, magnesium, and fluoride concentrations in the Dakota aquifer based on data for a test hole in southwest Ellis County.



Figure 64. Depth profile of equivalent ratios of sodium/chloride, sulfate/chloride, and (calcium + magnesium)/sodium in the Dakota aquifer based on data for a test hole in southwest Ellis County.

a connecting line indicates that a water sample was collected from only one depth in a test well. Plots B and C in fig. 65 are relatively similar because the top elevation of the Dakota Formation does not change substantially across the area. The relative spread in the vertical dimension for the points in the figures is smaller for graphs B and C than for graph A in fig. 65. This indicates that the vertical location within the Dakota strata can be a better predictor of the salinity than the depth below land surface within an area with substantial differences in topographic surface elevation. However, below a depth of 130 ft (40 m) from the top of the Dakota Formation, a large

Test-hole number	Graph symbol	Legal location	Sample depth interval, ft	Depth to middle of sample	Elevation of land surface, ft	Middle of sam- ple interval,	Depth to top of first Dakota	Elevation to top of first Da-	Depth of sample interval below
				interval, ft		elevation, ft	sand, ft	kota sand, ft	top sand, ft
TH 4-92	0	13S-12W-31DDDD	261–282	271.5	1,853	1,581.5	137	1,716	134.5
TH 4-92	0	13S-12W-31DDDD	310-331	320.5	1,853	1,532.5	137	1,716	183.5
TH 5-92	Ω	13S-12W-25CCCB	261–282	271.5	1,813	1,541.5	200	1,613	141.5
TH 5-92		13S-12W-25CCCB	282-303	292.5	1,813	1,520.5	200	1,613	162.5
TH 6-92	Ш	13S-12W-36AAAB	219–240	229.5	1,792	1,562.5	193	1,599	112.5
TH 6-92	Ш	13S-12W-36AAAB	240-261	250.5	1,792	1,541.5	193	1,599	133.5
TH 2-93	ш	13S-11W-30CBBB	264–284	274	1,809	1,535	175	1,634	143
TH 3-93	IJ	14S-12W-11BBBB	209–230	219.5	1,807	1,587.5	130	1,677	114.5
TH 3-93	IJ	14S-12W-11BBBB	272–293	282.5	1,807	1,524.5	130	1,677	177.5
TH 3-93	IJ	14S-12W-11BBBB	293–314	303.5	1,807	1,503.5	130	1,677	198.5
TH 4-93	Т	14S-12W-12CBCC	65–75	20	1,735	1,665	47	1,688	27
TH 4-93	Т	14S-12W-12CBCC	135-145	140	1,735	1,595	47	1,688	97
TH 4-93	Т	14S-12W-12CBCC	220-230	225	1,735	1,510	47	1,688	182
TH 5-93	J	14S-12W-12CBCC	55-75	65	1,735	1,670	47	1,688	26
TH 6-93	\mathbf{x}	14S-12W-09AABB	221–242	231.5	1,822	1,590.5	126	1,696	113.5
TH 7-93	_	14S-11W-30BAAB	41-62	51.5	1,671	1,619.5	47	1,624	85.5
TH 7-93	_	14S-11W-30BAAB	105-126	115.5	1,671	1,555.5	47	1,624	149.5
TH 7-93		14S-11W-30BAAB	126–147	136.5	1,671	1,534.5	47	1,624	170.5
TH 8-93	Σ	14S-12W-23DDDA	152-173	162.5	1,695	1,532.5	62	1,633	172.5
TH 10-93	Z	14S-12W-23CCCC	113–124	118.5	1,710	1,591.5	45	1,665	113.5
TH 11-93	0	14S-11W-30ADDD	96–117	106.5	1,636	1,529.5	21	1,615	175.5
TH 11-93	0	14S-11W-30ADDD	117-138	127.5	1,636	1,508.5	21	1,615	196.5

Table 16. Sample interval information for test holes drilled into the Dakota Formation by Ground Water Associates in Russell County.

Table 17. Chemical data for samples collected from test holes drilled into the Dakota Formation by Ground Water Associates in Russell County. The analytical data are from KGS analyses except where noted as analyzed by Servi-Tech for GWA.

Test-hole number	Graph symbol	Legal location	Sample date	TDS sum mg/Lª	Ca mg/L	Mg mg/L	Na mg/L	HCO ³ mg/L	SO₄ mg/L	CI mg/L	F mg/L	NO ₃ -N mg/L
TH 4-92	Ο	13S-12W-31DDDD	9/17/92	3,640	80	52	1,230	(254)	405	1,736	1.21	2.6ª
TH 4-92	0	13S-12W-31DDDD	9/16/92	3,696	79	52	1,260	(381)	405	1,712	1.16	< 0.1 ^a
TH 5-92	Ω	13S-12W-25CCCB	9/28/92	1,274	5.2	2.4	477	(427)	214	326	4.58	7.8ª
TH 5-92	Ω	13S-12W-25CCCB	9/28/92	1,551	40	20	525	(400)	233	535	1.22	< 0.1 ^a
TH 6-92	ш	13S-12W-36AAAB	9/30/92	815	24	9.8	261	(223)	184	187	2.52	8.4 ^ª
TH 6-92	ш	13S-12W-36AAAB	9/30/92	1,099	7.2	က	405	(295)	221	307	2.54	1.8 ^a
TH 2-93	ш	13S-11W-30CBBB	6/4/93	1,511	36	19	513	398	338	400	1.60	< 0.02
TH 3-93	IJ	14S-12W-11BBBB	6/10/93	926	47	15	266	335	267	154	1.74	0.36
TH 3-93	IJ	14S-12W-11BBBB	6/6/93	5,745	77	58	2,080	484	481	2,790	2.14	0.07
TH 3-93	IJ	14S-12W-11BBBB	6/6/93	7,137	100	81	2,570	528	603	3,500	2.25	0.09
TH 4-93	Т	14S-12W-12CBCC	6/16/93	926	231	17	46.3	225	416	67.8	0.26	7.41
TH 4-93	т	14S-12W-12CBCC	6/16/93	587	43	11	161	256	111	126	1.06	0.41
TH 4-93	т	14S-12W-12CBCC	6/16/93	12,307	146	131	4,410	492	861	6,490	1.77	0.14
TH 5-93	J	14S-12W-12CBCC	6/17/93		281 ^b	18 ^b	45 ^b			77 ^b	0.24 ^b	
TH 6-93	\mathbf{x}	14S-12W-09AABB	6/21/93	1,164	122	29	235	299	489	133	0.76	0.09
TH 7-93		14S-11W-30BAAB	9/29/93	1,628	81	21	503	361	213	620	1.27	0.75
TH 7-93		14S-11W-30BAAB	9/29/93	2,090	93	24	663	383	237	874	1.33	0.11
TH 7-93		14S-11W-30BAAB	9/28/93	3,388	105	35	1,130	419	280	1,617	1.83	0.09
TH 8-93	Σ	14S-12W-23DDDA	9/30/93	1,259	106	18	340	393	182	412	0.86	0.05
TH 10-93	z	14S-12W-23CCCC	10/5/93	2,062	24	13	772	454	139	879	3.26	0.02
TH 11-93	0	14S-11W-30ADDD	10/10/93	2,271	137	30	672	327	289	970	1.22	0.14
TH 11-93	0	14S-11W-30ADDD	10/10/93	2,884	103	29	943	398	286	1,313	1.54	0.05
^a Analysis by Servi ^b Sum of constituen ^c Values in parenth	i-Tech nts in table pi esis were cal	lus an estimated 15 mg/L SiO_2 culated from the charge balance	difference.									



Figure 65. TDS concentration versus depth below land surface (A), elevation (B), and depth below the top of the Dakota Formation (C) of the middle of the sample interval for test wells in Russell County. See tables 16 and 17 for identification of letter symbols.

spread in the salinity exists at the same depth or elevation. The data also show that water in sandstone bodies near the outcrop boundary can be more saline than water at the same depth below land surface but at a higher elevation in the Dakota where overlain by Upper Cretaceous rocks. In general, water at the same depth below the top of the Dakota Formation is fresher on the northern than on the southern flank of the upland between the Saline and Smoky Hill River valleys because the gentle north-northeast dip of the strata and lower elevation of the Saline River valley appear to have resulted in deeper flushing of the aquifer by fresh recharge.

Figures 66 and 67 illustrate changes in selected, individual constituent concentrations with depth for the same test-hole samples in Russell County as for fig. 65. The letter symbols and connecting lines in all three figures represent the same samples and test holes as listed in tables 16 and 17. The main dissolved constituents that control the range in salinities of the Russell County waters are sodium and chloride (table 17). Sulfate concentration in the groundwaters is substantial (111–861 mg/L) but has an



Figure 66. Sulfate (A) and chloride (B) concentrations versus elevation of the middle of the sample interval for test wells in Russell County. See tables 16 and 17 for identification of letter symbols.

appreciably smaller range than chloride content (67.8–6,490 mg/L). Sulfate concentration increases moderately with depth in some of the test wells (fig. 66A) in comparison with chloride content, which increases substantially with depth (fig. 66B). The sulfate concentration in the Dakota aquifer waters has both external and internal sources: the saltwater that intrudes from Permian strata into the overlying Dakota, oxidation of pyrite within the aquifer sediments, and sulfate in groundwater flowing from the overlying upper Cretaceous strata, where present, which is derived from pyrite oxidation or dissolution of gypsum. The chloride source is mainly the external, upward intrusion of saltwater from the underlying Permian strata.

Nitrate concentration (less than 0.1–8.4 mg/L) generally decreases with depth in the test holes in the Dakota aquifer in Russell County (fig. 67A), pointing to a surface source of nitrate. Half of the detection limit was used as the value for plotting nitrate content in the figure to include all samples for which nitrate was determined. Nitrate-nitrogen levels are less than a mg/L in the Dakota aquifer in this area where not impacted by surface sources.

The range in fluoride concentration (0.24–4.58 mg/L) is substantial for the relatively small area in which the test holes are located (fig. 67B). Although the correlation of fluoride content with depth is not as apparent as for nitrate, fluoride values do increase with depth in some of the test



Figure 67. Nitrate (A) and fluoride (B) concentrations versus elevation of the middle of the sample interval for test wells drilled in Russell County. See tables 16 and 17 for identification of letter symbols.

holes. The areal and vertical changes in fluoride concentration in the Dakota Formation in Russell reflect the influence of mineral equilibria conditions in the aquifer as indicated by the inverse relationship of fluoride versus calcium concentrations (fig. 68), which is similar to the relationship shown for the regional flow paths in fig. 51. An even better correlation exists between the fluoride concentration and the equivalent ratio of (calcium + magnesium)/sodium (fig. 69). The correlation is high enough that the (calcium + magnesium)/sodium ratio could be used as a predictor of fluoride content in the Dakota groundwater in this area of Russell County. Figure 69 includes a simple function that fits the data and that could be used to estimate fluoride content from calcium, magnesium, and sodium concentrations. The reason that the correlation between fluoride content and the cation ratio is better than between fluoride and calcium concentrations could be related to the ionic strength effect on the cation ratios. The values in a solubility product equation such as for the mineral fluorite

are activities of dissolved ions and not concentrations. The activities of dissolved constituents in solution are a product of activity coefficients and the concentration; the activity coefficient depends on the ionic charge of a dissolved species (-1 for fluoride and +2 for calcium) as well as the ionic strength.

Geochemical Modeling of Groundwater Evolution

Chemical data for groundwater samples indicate that distinct chemical water types occur in different regions of the Dakota aquifer system. These water types have been generated by a combination of mixing of groundwaters of different chemical types and chemical reactions that occur in response to rock-water interactions. Cation exchange and concomitant mineral dissolution and precipitation are the main reactions that affect water chemistry. Mixing of fresh groundwater (derived from the interaction of surface recharge with Dakota sediments) and saline groundwater (affected by the intrusion



Figure 68. Fluoride versus calcium concentrations for test well waters in Russell County. The function for the line is the same as in Figure 51 that is based on the calcium and fluoride relationship in fluorite.

Figure 69. Fluoride concentration versus (calcium + magnesium)/sodium ratio based on equivalent concentrations for test well waters in Russell County. The function is a visual fit to the data and is nearly the same as a more complicated function based on a computed best fit to the data, for which the R^2 is 0.905.

of saltwater from underlying Permian strata) in the Dakota aquifer is the main factor setting up conditions for substantial chemical changes in the aquifer. These geochemical and mixing processes were simulated by numerical modeling to better understand the evolution of groundwater in the Dakota aquifer in central and north-central Kansas. The modeling was conducted by T.-M. Chu for his doctoral dissertation (Chu, 1995). A model of one-dimensional flow coupled with chemical reactions (1-D model) was developed to simulate the hydrogeochemical processes involving cation exchange and calcite precipitation/dissolution along a hypothetical flow path in the aquifer. A model of two-dimensional flow coupled with chemical reactions (2-D model) was designed to simulate a chemical transition zone along a subregional lateral profile that incorporated geohydrologic complexities of the Dakota aquifer. The following sections on the 1-D and 2-D models are summaries of the modeling results in Chu's (1995) dissertation.

Chemical Water Types and Mixing

The profiles of water chemistry described in the section on regional groundwater geochemistry in this chapter indicate the general changes in chemical water types in the Dakota aquifer along the regional flow path from the recharge area in southeast Colorado, through the confined aquifer in southwestern and west-central Kansas, and to the discharge area in central Kansas (figs. 41–46). The water type changes from predominantly calcium-bicarbonate in the unconfined aquifer in the recharge zone to sodium-bicarbonate that typically occurs in the confined aquifer in west-central Kansas. As the regional flow in the confined Dakota aquifer approaches the western edge of the subcrop of the Cedar Hills Sandstone, the salinity of the confined Dakota groundwater increases substantially from the intruding saltwater and the water changes to sodium-chloride type. The groundwaters are then diluted by local recharge to the east of the Cedar Hill subcrop and revert primarily to calciumbicarbonate in the outcrop zone of the unconfined aquifer in central and north-central Kansas.

The vertical profile of water chemistry in the confined Dakota aquifer in central Kansas just west of the Cedar Hills subcrop is somewhat similar to that along parts of the regional profile from southeast Colorado to central Kansas. A small amount of recharge enters the top of the confined Dakota aquifer from the overlying confining beds of the upper Cretaceous strata. This groundwater typically ranges in composition from calcium-bicarbonate to calcium-sulfate type. For example, fresh groundwater in the upper Cretaceous Greenhorn Limestone is commonly of calcium-bicarbonate type and has a composition that is relatively similar to that of groundwater with similar TDS concentration in the unconfined Dakota aquifer. Groundwater in the Greenhorn Limestone also ranges to calcium-sulfate in type. The vertical profile of groundwater in the confined Dakota aquifer at a borehole in southwest Ellis County (figs. 61-64) represents a change from fresh, calcium-sulfate water derived from upper Cretaceous recharge at the top of the profile, to sodium-bicarbonate type water in the middle of the profile, to saline, sodium-chloride type water in the lower part of the profile.

The origin of the saline water now present in the Dakota aquifer is predominantly from halite dissolution, as indicated by bromide-chloride relationships (see discussion of bromide in the subsection on minor and trace dissolved constituents in this appendix). The substantial decrease in the bromide/chloride ratio that results from the mixing of fresh groundwater with saltwater in the Dakota aquifer is illustrated by the points within the two mixing-curve boundaries, which represent Dakota water uncontaminated by oil field brine, in fig. 29. This decrease reflects the low bromide/chloride ratio in saltwater from halite dissolution that is derived from underlying Permian formations such as the Cedar Hills Sandstone. Although the bromide/chloride ratio in saltwater in the Dakota aquifer ranges up to about twice that of natural saltwater with the same chloride concentration in Permian strata in Kansas, the ratio places a maximum limit of only a couple percent of remnant seawater in the Dakota aquifer. This seawater could potentially come from slow diffusion from the thickest shale units in the Dakota strata. Alternatively, the additional bromide could come from the diagenesis of organics enriched in bromide in thick shales followed by diffusion from these shales. Overall, the bromide-chloride relationships indicate that salinity in the Dakota aquifer evolved from a seawater origin after deposition in marine to brackish environments to a halitedissolution source over time as caused by saltwater intrusion from underlying Permian strata.

The high sodium content in seawater that was in the pores of Dakota sediments, such as in estuarine, beach, and deltaic environments, would have adsorbed on clays in the sediments to give very low (calcium + magnesium)/sodium ratios for the exchangeable ions on the clays. The later intrusion of saltwater from underlying Permian strata would also have produced very low (calcium + magnesium)/sodium ratios for the exchangeable ions on the Dakota sediments. Fresh groundwaters of calcium-bicarbonate or calciumsulfate type have a high (calcium + magnesium)/sodium ratio. Recharge of this freshwater into the Dakota aquifer containing saline water would not only dilute the salinity but cause cation exchange of calcium (and other divalent alkaline earth elements, primarily magnesium and strontium) for sodium on clay surfaces. The change in the calcium and magnesium concentrations and the ionic strength of the water caused by the mixing and cation exchange alters the ion activity products relative to minerals that are prevalent in the aquifer sediments, especially the carbonate minerals calcite and dolomite. Dissolution or precipitation of these carbonates result from the chemical changes.

The coupled flow and reaction models for the Dakota aquifer were designed to simulate the primary chemical changes in the system resulting from the mixing of groundwaters with differing salinities along a flow path and the accompanying cation exchange and major mineral dissolution-precipitation reactions, as described in the preceding paragraphs.

1-D Coupled Flow and Reaction Model

The purpose of the 1-D coupled flow and chemical reaction model was to improve the understanding of the fundamental

concepts of coupled hydrogeochemical processes occurring in the Dakota aquifer. Although the general characteristics and factors that cause major chemical changes in the chemistry of Dakota groundwater are known, it is unclear how the concomitant reactions interact with each other during mixing of waters along flow paths in the aquifer. A 1-D model helped to explain these interactions and the evolution of the groundwater chemistry with time along a hypothetic flow path (Chu, 1995).

The numerical modeling program HYDROGEOCHEM (Yeh and Tripathi, 1990, 1991; Yeh, 1992a) was used for the simulation of the 1-D model. HYDROGEOCHEM is a 2-D finite-element coupled transport and chemical reaction model that computes solutions by sequentially iterating between transport and geochemical equilibrium equations. The first step in the solute transport simulation was the determination of a flow field for the model using HYDROFLOW (Yeh, 1992b). Then, the chemical reactions were computed by EQMOD (Yeh, 1992c) based on an ion association and equilibrium constant approach under the assumption of local equilibrium.

The 1-D model simulated the chemical interactions occurring as a result of the mixing of fresh to saline water, having a calcium-bicarbonate composition in equilibrium with calcite, with saltwater of sodium-chloride type, along with the reactions of ion exchange, ion complexing, and calcite dissolution/precipitation. The model grid was designed so that the chemical retardation and conservative mixing front of the incoming freshwater and initial saltwater can all be represented at a particular simulation time with a substantial number of nodes for each stage. A lateral flow path 7 km (4.3 mi) in length and 1 m (3 ft) in depth was used with 200 elements and 402 nodes. The conditions along the top and bottom of the 1-m (3-ft) depth were the same to represent one-dimensional flow. Thus, the model effectively has only 201 unique node results. The grid size varied from 10 to 50 m (33-164 ft) in horizontal distance.

An effective porosity of 0.2, a bulk density of 2.0 g/cm³, and a longitudinal dispersivity of 25 m (82 ft) were assigned to the model based on hydrogeologic characteristics of the Dakota aquifer. A constant Darcy flow velocity of 5 x 10^{-3} m/ day (0.0164 ft/day) from west to east was used based on the regional hydraulic gradient in the Dakota aquifer in central Kansas and hydraulic conductivity values from available pumping-test data.

A cation-exchange capacity (CEC) of 25 meg/kg of sediment was selected for the model after consideration of CEC determinations made on 22 samples of sandstone, siltstone, and mudstone from the Jones #1 core (see Macfarlane, Doveton, and Whittemore [1998] for lithologic characterization of the strata through which the borehole was drilled). Seven basic chemical components (H⁺, Ca²⁺, Mg^{2+} , Na^+ , CO_2^{2-} , SO_4^{2-} , Cl^-), six aqueous complex species (OH⁻, H_2CO_3 , HCO_3^- , $CaSO_4^{\circ}$, $MgSO_4^{\circ}$, $NaSO_4^{\circ}$), and one mineral (low magnesian calcite, Ca_{0.95}Mg_{0.05}CO₃) were included in the model. The equilibrium constants for the complex species and calcite were from the geochemical model SOLMINEQ.88 (Kharaka et al., 1988). The selectivity coefficients for the cation exchange reactions were based on Bruggenwert and Kamphorst (1979) and additional literature review.

The base run for the 1-D model involved freshwater entering the western boundary of the flow path, all of which initially contained saltwater (table 18). The compositions of the incoming freshwater and initial saltwater were based on waters sampled from the Dakota aquifer and the Cedar Hills Sandstone, respectively. These conditions represented the end-member, extreme salinity contrast between the incoming water and initial saltwater. Higher salinities for the incoming water and lower salinities for the initial saltwater were used to examine the sensitivity of the model to ranges in water chemistry. These additional incoming water and initial saltwater compositions were based on chemical analyses of groundwaters sampled from wells in

Table 18. Concentrations of dissolved constituents in the incoming freshwater at the western boundary and initial saltwater used in the base run of the 1-D model.

	TDS mg/L	pH units	Ca meq/L (mg/L)	Mg meq/L (mg/L)	Na meq/L (mg/L)	HCO ₃ meq/L (mg/L)	SO₄ meq/L (mg/L)	Cl meq/L (mg/L)
Incoming water	450	7.1	4.87 (98)	0.884 (10.7)	1.63 (37.5)	5.13 (313)	1.33 (64)	1.16 (41)
Initial saltwater	76,080	7.2	37.0 (741)	159 (1,930)	1,108 (25,470)	3.56 (217)	178 (8,550)	1,108 (39,280)

the Dakota aquifer. Adjustments were made to the dissolved constituent concentrations of the analyzed samples before input to the model using geochemical equilibria calculations to satisfy assumptions such as selected sodium/chloride ratios. Additional sensitivity runs were made using different values of CEC and selectivity coefficients (adsorption of magnesium relative to calcium and of calcium relative to sodium) for the aquifer material.

Conservative mixing and transport in the 1-D base run showed that the center (concentration midpoint) of the breakthrough curve or front of freshwater for the conservative constituent chloride dissolved in the water is at 5.17 km (3.21 mi) along the flow path after 2.07×10^5 days (567 years) of

travel time (fig. 70). The figure indicates that the saltwater in the aquifer has been flushed by the incoming freshwater up to 3.1 km (1.9 mi) along the flow path. Dispersion caused the curved shape in the flushing front that extends from about 3.1 km (1.9 mi) to slightly downstream of the eastern end of the model.

The base model results for the dissolved cations calcium, magnesium, and sodium in the water along the flow path are much different from those for the conservative constituent chloride due to the effect of the cation exchange reactions on the aquifer sediments and calcite dissolution/ precipitation (fig. 71). The curves for the dissolved concentrations of calcium and magnesium along the flow path have troughs that represent the removal of these cations by adsorption on the aquifer clay that initially was largely saturated with sodium as a result of equilibrium with a predominantly sodium-chloride solution (fig. 71a and b). The curve for dissolved sodium content has two fronts (fig. 71c), a sharp front near the west end of the flow path and the conservative mixing front in the east half. The shapes of the curves are largely affected by the ion chromatographic process of cation exchange along the flow path.

Zone I on the right-hand side of fig. 71 represents the largely unaltered



Figure 70. Dissolved chloride concentration in the groundwater along the 1-D model profile at 567 years resulting from conservative transport.



Figure 71. Dissolved calcium, magnesium, and sodium concentrations in the groundwater along the 1-D model profile at 567 years with cation exchange and calcite dissolution/precipitation.

initial saltwater and the conservative mixing front. Zone III is a composite zone that includes the condition near the west edge of the flow path where the aquifer solid (formation sediment) is in equilibrium with the incoming freshwater and a complex transition condition of active cation exchange and calcite dissolution. The shapes of the curves for the different cations in zone III are different due to the different velocities of the retardation fronts of calcium and magnesium that are affected by differences in the incoming concentration, the selectivity coefficients for these cations, and the relative amounts of calcium and magnesium released by calcite dissolution. Zone II is a result of the cation exchange of calcium and magnesium for sodium on clays that occurred in zone III reaching cation ratios similar to those of the cations on the aquifer solids. The much larger cation concentrations adsorbed on the solid than in solution control the cation ratios. The amount of cation exchange from the much lower concentrations of dissolved cations has not yet substantially changed the large buffering capacity of the adsorbed cations in zone II; thus, the (calcium + magnesium)/sodium ratio in the solution is similar in zone II to that in zone I.

Calcite dissolution occurs primarily in zone III and at the western part of zone II (fig. 72). The incoming water is slightly undersaturated with respect to calcite. The amount of calcite that dissolves increases along the flow path in the first part of zone

III as the concentration of calcium decreases from adsorption on the aquifer clays in exchange for sodium. The dissolution of calcite releases CO_3^{2-} ion to solution, much of which converts to dissolved HCO_3^{-} by combining with H⁺ ion from the dissociation of water. The decrease in the H⁺ ion activity raises the pH (fig. 73), which in turn allows a greater amount of CO_3^{2-} ion to be in solution based on dissolved carbonate equilibria. Thus, as the water flows along the flow path,



Figure 72. Dissolution and precipitation of calcite along the 1-D model profile at 567 years.



Figure 73. Distribution of pH in the groundwater along the 1-D model profile at 567 years.

the amount of calcite that can dissolve decreases due to the increase in CO_3^{2} ion activity.

The amounts of calcium and magnesium released to solution through the dissolution of calcite are much greater than the calcium and magnesium concentrations in the incoming water. However, the exchange capacity of the aquifer clay is so great for divalent cations that the extra calcium and magnesium are largely removed from solution by adsorption. If calcite dissolution did not occur, the dissolved calcium and magnesium concentrations would be even lower in zone II than they are with calcite dissolution. The dissolved sodium concentration is greater in zone II with calcite dissolution than without because the extra calcium and magnesium provided by the dissolution increases the amount of sodium exchanged from the aquifer clay. The combined effect of the increased sodium and bicarbonate concentrations in solution raises the TDS content of the water in zone II (fig. 74) above what would be expected from conservative mixing (compare with the curve shape in fig. 70). The dissolved calcium and magnesium concentrations in zone II are relatively small in comparison with the dissolved sodium content (fig. 71). Thus, sodium-bicarbonate type water is generated in zone II.

As the dissolved CO_3^{2-} ion activity increases into the western part of zone II, the solution approaches saturation with respect to calcite. A very small amount of calcite precipitation is indicated in the eastern part of zone II and the westernmost part of zone I in fig. 72, which occurs as a result of the chemical reactions during mixing of water along the flow path. The initial saltwater is saturated with respect to calcite as shown in zone III in fig. 72. The pH exceeds 9.5 units in nearly all of zone II for the base 1-D model (fig. 73). The pH then decreases and the dissolved calcium, magnesium, and sodium concentrations increase in zone I as the water from zone II mixes with the initial saltwater.

The differences between the dissolved cation concentrations with chemical reactions and without the reactions (conservative mixing only) are shown in fig. 75. The magnitudes of the differences are small in zone III because the dissolved concentrations are relatively



Figure 74. TDS concentration in the groundwater along the 1-D model profile at 567 years.



Figure 75. Dissolved concentration differences for exchangeable cations between the simulation with reactions and one with only conservative transport (with the same initial and boundary water compositions) along the model flow path at 567 years.

small. The increase in the amount of sodium with reactions relative to conservative mixing is much larger than that for calcium and magnesium in zone II due to the supply of the divalent cations by calcite dissolution that increases the amount of cation exchange that releases sodium. The sodium peak and the calcium and magnesium troughs in zone I result from the mixing of the high dissolved sodium and low dissolved calcium and magnesium concentrations from cation exchange in zone II with the initial saltwater. The effect of these changes along the flow path not only gives low (calcium + magnesium)/sodium and high sodium/ chloride ratios in zone II but also changes these ratios in the western part of zone I from what would be expected from conservative mixing.

Changes in water chemistry in aquifer systems can be illustrated on a Piper-Hill trilinear diagram (fig. 76). Chemical changes along straight lines on a trilinear diagram are sometimes used to indicate the change from one water type to another during mixing of waters. However, the patterns of chemical changes during evolution of the water chemistry with cation exchange and calcite dissolution as simulated for the Dakota aquifer are not linear in portions of fig. 76. The initial saltwater of sodium-chloride type in the aquifer (at the start of zone I as represented in fig. 76)

changes to sodium-bicarbonate type (at the end of zone I) during and after the freshwater mixing front passes a point in the aquifer. The water type (sodiumbicarbonate) remains nearly constant in zone II as indicated by the short evolution paths for this zone in fig. 76. In zone III, the chemistry first evolves to a mixed cation-bicarbonate type before changing to the calcium-bicarbonate type of the incoming water. The changes displayed in fig. 76 indicate that a conservative mixing model is not able to describe the chemical evolution occurring as a result of the chromatographic and dissolution reactions simulated by the coupled geochemical model. The path for a conservative mixing model would be represented by a straight line from the start of zone I to the end of zone II. Although the simulated evolution path is not greatly different from a straight line for the anion triangle, the simulated paths

for the cation triangle and the composite diamond parts of the diagram greatly diverge from a straight line connecting the starting and ending compositions.

Comparison of fig. 76 with the Piper-Hill diagram displaying water sample data for the Dakota aquifer (fig. 37) indicates that the evolution paths fit parts of the distribution of the observed groundwater chemistry. For example, the distribution of points for the confined aquifer near the axis of the diamond that represents 100% sodium and 0-100% bicarbonate (the lower right-hand axis) fits the evolution path in zone I. The curved evolution path in the cation triangle fits well the maximum extent of the points for observed water composition. Comparison of the path in the cation triangle with the data distribution suggests that the magnesium concentration used for the starting saltwater may have been too high for the actual typical composition of saltwater in the Dakota aquifer derived from intrusion from the Cedar Hills Sandstone. A lower starting magnesium content would have produced a curved evolution path that did not reach as high a magnesium percentage as simulated. Another factor that would cause a lower curve trajectory in the cation triangle would be if the starting freshwater in the simulation had a higher calcium content, such as from gypsum dissolution or combined pyrite weathering and calcite dissolution.



Figure 76. Evolution of water chemistry along the flow path in the 1-D model with coupled flow and chemical reactions at 567 years. The bicarbonate concentration was assumed to be equal to the total dissolved carbonate concentration. The arrows indicate the evolution direction.

A greater sulfate concentration in the incoming freshwater would have produced an evolution path for zone III that would be rotated in a clockwise direction to end at a higher sulfate percentage in the anion triangle of fig. 76 and shifted towards a higher sulfate and chloride percentage in the diamond part of the diagram. These paths would fit the distribution of many points for water analyses in fig. 37 that have a greater sulfate percentage.

2-D Coupled Flow and Reaction Model

The 1-D numerical model demonstrates the effect of mixing and cation exchange on groundwater chemistry. Chemical data for groundwater samples from the Dakota aquifer show that the mixing process in the aquifer system is more complicated than simulated by the 1-D model (Chu, 1995). The chemical data imply that the past distribution of salinity in the Dakota aquifer was not uniform. In addition, the unevenly distributed intrusion of saltwater is continuing, as indicated by the saltwater zone above the subcrop of the Cedar Hills Sandstone. The area of zone II sodium-bicarbonate type water currently extends over a large area of the confined aquifer from southwest to central Kansas before entering the saltwater zone in central to north-central Kansas.

A 2-D profile model was designed to simulate complexities of the hydrogeological system of the Dakota

aquifer in the chemical transition zone along the regional groundwater flow path that extends across Ellis and western Russell counties. The 2-D numerical model simulated the mixing of slightly saline groundwater in the confined Dakota aquifer flowing from the west, intruded saltwater from the Cedar Hills Sandstone, and fresh to slightly saline leakage from the overlying confining layer of Upper Cretaceous strata. The west end of the model started east of the middle of R. 19 W. along the line separating T. 13 and 14 S. in westcentral Ellis County, and extended in an easterly direction across the Cedar Hills subcrop zone, curving in the last fourth of the flow path to the northeast to end at the Saline River valley along the line separating T. 12 and 13 S. west of the middle of R. 14 W. in northwestern Russell County (fig. 77). The conceptual geologic framework of the model (fig. 78) was constructed based on the hydrostratigraphy of the study area. The cross-section length is 48 km (30 mi).

The model included six hydrogeological units: an alluvial aquifer (representing the Saline River valley), the upper Dakota aquifer (Dakota Formation), a lower Dakota aquifer (representing the Longford Member of the Kiowa Formation), a combined unit of Kiowa marine shale and Cheyenne Sandstone, a Permian aquitard, and the Cedar Hills Sandstone (fig. 78). The Saline River is at the edge of the alluvial aquifer at the east end of the model. The marine shale of the Kiowa Formation was lumped with



Figure 77. Location of the flow path for the 2-D model on a map of major hydrogeologic zones of the Dakota aquifer in part of central and north-central Kansas.



Figure 78. Hydrogeologic units and dimensions for the profile in the 2-D coupled flow and chemical reaction model.

the underlying Cheyenne Sandstone to reduce the model complexity. The dip, thickness, and subcrop zone of the Cedar Hills Sandstone was based on previous studies and test-hole logs. The model thickness ranged from 227 m (745 ft) at the west boundary to 102 m (335 ft) at the east boundary (fig. 78).

The finite element grid used in the 2-D simulation in the program HYDROGEOCHEM had 1,848 nodes and 1,700 quadrangular elements (fig. 79). The ranges in the horizontal and vertical distances between the nodes were 100–500 m

(328-1,640 ft) and 2-15 m (6.6-49 ft), respectively. Constant heads were assigned to two sections of the west model boundary to represent the head difference between the confined Dakota aquifer and the underlying Permian strata (fig. 80). The model top was made a constant flux boundary with sections of different recharge rates, which represent the variation in the top leakage due to the thinning of the Upper Cretaceous confining layer from west to east. A constant flux was used for the model bottom boundary to indicate constant diffusion of underlying saltwater. The east boundary was located

at the hydraulic divide under the Saline River. A constant head was assigned to the river-bottom nodes, which were the discharge location for the model. The boundary flow conditions are illustrated in fig. 80.

One set of hydrological parameters was associated with each of the hydrogeologic units in the model. The assumption of homogenous units was necessary to simplify the model to allow computation of the coupled flow and chemical reactions in a practicable manner. The homogenous hydrologic properties are effective averages for the actual



Figure 79. Finite element grid used in the 2-D coupled profile model.



Figure 80. Hydrogeologic units and flow boundary conditions for the 2-D coupled profile model. Constant heads (H) were assigned to the west side boundary and river bottom nodes at the upper-right corner of the model. Constant fluxes were given to the top and bottom boundaries.

heterogeneous strata of shales, siltstones, sandstones, and limestones in the system. Initial hydrologic parameters were assigned to each hydrogeologic unit based on values for previous numerical simulations (Macfarlane, 1995) and general characteristics of the strata, such as anisotropy in the hydraulic conductivity. Some of these parameters were then adjusted after analyses of the sensitivity of the model by steady-state conservative transport of chloride concentration in the groundwater. The sensitivity analyses included tests for the horizontal and vertical hydraulic conductivities, vertical dispersivity, the hydraulic head difference between the Dakota and Cedar Hills aguifers at the west boundary, and vertical recharge rates from the top and bottom boundaries. The final parameters were selected based on the aquifer properties and matching of the steady-state distribution of chloride concentration in the hydrogeologic units with that based on well water samples in the general area of the model profile (table 19).

The chemistry of the pore water at the boundaries and in the different hydrogeologic units of the model was based on water samples (table 20). The top recharge was represented by calcium-sulfate, bicarbonate type water in the Greenhorn Limestone. It was assumed that the water chemistry would not change substantially after passing through the Graneros Shale. The water entering the west boundary of the confined Upper Dakota aquifer in the model was represented by a groundwater sample from eastern Trego County. The chemistry of saline water along the west boundary of the combined Kiowa shale and Cheyenne Sandstone was based on a sample from the Cheyenne Sandstone in central Ellis County. Saltwater along the west boundary of the Permian aquitard and the Cedar Hills Sandstone and along the bottom boundary of the Cedar Hills Sandstone was represented by a water sample from that Sandstone in southwest Russell County. The basic chemical components and the chemical reactions in the 2-D model were the same as in the 1-D model except that dissolution/precipitation of minerals included magnesite (MgCO₃) as well as calcite.

Steady-state flow for the 2-D model shows a nearly linear regional flow through the Dakota aquifer units and the Cedar Hills Sandstone in most of the model and upward, local flow to the discharge location of the Saline River valley (fig. 81). The flow lines from the Cedar Hills Sandstone enter the Lower Dakota aquifer in the subcrop zone. The flow lines also cross from the Lower to the Upper Dakota aquifer above the Cedar Hills Sandstone subcrop. The upward flow and dispersion of the saltwater transported from the Cedar Hills Sandstone generates saline water in the Lower and Upper Dakota east of the subcrop zone as indicated in the steady-state distribution of chloride concentration (fig. 82). However, dispersion also causes some of the slightly saline Dakota aquifer to slightly dilute the saltwater in the uppermost part of the Cedar Hills Sandstone. Leakage from the Upper Cretaceous strata in the eastern two-thirds of the model profile produces a relatively thin zone of slightly saline water along the top of the Upper Dakota aquifer above

Table 19.	Geohydrological	parameters for	the hydr	ogeological	units used in	the 2-D profile model
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Unit	Hydraulic conductivity (m/day) K K	Dispersivity (m)	Diffusion co- efficient (m²/	Bulk densi- ty (g/cm³)	CEC	Porosity
	K _x K _z	$\alpha_{\rm l} \alpha_{\rm v}$	uay		(meg/100g)	
Alluvial aquifer	30 5	20 0.3	0	1.8	2.5	0.30
Upper Dakota	3 0.001	20 0.3	0	2.0	2.5	0.20
Lower Dakota	1 0.0005	15 0.2	0	2.1	5.4	0.18
Kiowa shale & Cheyenne Sandstone	1 1 x 10 ⁻⁵	10 3 x 10-3	5 x 10-7	2.2	20	0.15
Upper Permian aquitard	1 x 10-5 1 x 10-6	1 1 x 10-3	3 x 10-7	2.4	10	0.05
Cedar Hills Sandstone	1 0.05	15 0.2	0	2.2	3.0	0.15

K_x and K_z are the horizontal and vertical hydraulic conductivities, respectively.

 α_i and α_j are the longitudinal and vertical dispersivities, respectively.

Table 20. The groundwater chemistry used as the initial and boundary conditions in the 2-D profile model.

Location	7S-10W-08BBB	14S-22W-21BCB	12S-18W-30AA	14S-14W-25BB
Geology	Greenhorn Limestone	Dakota Formation	Cheyenne Sandstone	Cedar Hills Sandstone
рН	7.02	8.45	7.45	6.56
Ca meq/L (mg/L)	9.88 (198)	0.210 (4.2)	3.19 (64)	39.4 (790)
Mg meq/L (mg/L)	1.49 (18)	0.182 (2.2)	58.9 (716)	94.3 (1,146)
Na meq/L (mg/L)	5.00 (115)	19.4 (446)	448 (10,300)	976 (22,440)
HCO ₃ meq/L (mg/L)	4.88 (298)	7.93 (484)	17.5 (1,068)	11.4 (696)
SO ₄ meq/L (mg/L)	7.72 (371)	4.00 (192)	85.6 (4,110)	128 (6,150)
CI meq/L (mg/L)	3.53 (125)	5.70 (202)	412 (14,600)	970 (34,400)
TDS mg/L	1,002	1,122	30,410	65,610

the Cedar Hills subcrop. The discharge of groundwater at the Saline River valley results in highly saline water at a relatively shallow depth.

The time step used in the transient simulation increased from 1 to 100 years. The simulation required about 3,000 years for the flow entering the west boundary of the Upper Dakota aquifer to travel far enough to the east to produce the transition zone from relatively low to high chloride concentration above the start of the Cedar Hills Sandstone subcrop similar to that in the steady-state model. The water in the Upper Dakota aquifer entering the west boundary of the model was already affected by cation exchange. Thus, no substantial change occurs in the water chemistry due to cation exchange reactions as in the transition from zone II to zone III in the 1-D model. Figure 83 displays the dissolved calcium concentration in the 2-D coupled flow and reaction model for the 3,000-year simulation. Although no leakage exists from the top of the western third of the model, the constant chemistry conditions along the top boundary and the slow lateral movement of the regional flow result in a zone of calcium content greater than in the incoming Upper Dakota aquifer water in the uppermost part of the Upper Dakota to the west of the Cedar Hills subcrop. East of the subcrop, the calcium concentration within most of the Upper Dakota aquifer remains within a relatively small range from about 200 mg/L to less than 400 mg/L.

The mixing and cation exchange that occur within the 2-D model produce conditions in which a small amount of calcite can be dissolved throughout most of the Upper and Lower Dakota aquifers east of the Cedar Hills Sandstone subcrop (fig. 84). The starting calcite content in the model was 30,000 mg per volume containing 1 L of pore water. For a porosity of



Figure 81. Flow field for the steadystate simulation by the 2-D coupled profile model.

Figure 82. Distribution of dissolved chloride concentration for the steadystate simulation by the 2-D coupled profile model.

Figure 83. Distribution of dissolved calcium concentration for a 3,000year simulation by the 2-D coupled

profile model.



Figure 84. Calcite dissolution for a 3,000-year simulation by the 2-D coupled profile model. The initial calcite concentration was 30,000 mg per volume containing 1 L of pore water in the hydrogeologic units (equivalent to about 0.3% by weight of dry rock). Values less than 30,000 represent calcite dissolution.

about 0.2, the calcite content is approximately equivalent to 0.3% by weight of dry aquifer mass. A zone of greater calcite dissolution occurs along the top of the Upper Dakota aquifer east of the Cedar Hills subcrop. These results could explain why parts of the Dakota aquifer are commonly not cemented by carbonate minerals. Calcite dissolution could have increased the permeability of parts of the Dakota aquifer.

The sensitivity of the water chemistry to vertical leakage from above and the distribution of the zone of most calcite dissolution near the top of the Upper Dakota aquifer in the 2-D model indicate the importance of a small amount of recharge through the strata overlying the confined Dakota aquifer. Thus, the increase in the amount of vertical recharge along the transition from thick confining strata in the regional flow system of the aquifer to a thinner confining layer approaching the Dakota outcrop zone helps explain the substantial chemical changes observed along the transition from the regional to local flow system.

Summary and Conclusions

During the Dakota Aquifer Program, the KGS assembled existing water chemistry data for the Dakota aquifer from several different sources and reviewed the data for errors and uncertainties. The KGS also added substantial amounts of new data by sampling and analysis of groundwaters from observation and supply wells across the aquifer. The data are for chemical properties and concentrations of inorganic constituents and are in online Excel spreadsheets on the KGS website. The data base includes 1,594 chemical records for wells yielding water entirely or partly from the Dakota aquifer. The records represent 1,192 sampling locations, of which 1,123 well locations are for only the Dakota aquifer. TDS concentration was estimated from 977 geophysical logs in northwest Kansas to supplement the chemical analyses in the region where essentially no water-supply wells exist due to the high salinity of the groundwater in the Dakota aquifer. TDS values of Dakota groundwaters, as well as concentrations of sodium, chloride, and sulfate for waters with more than a few thousand mg/L TDS, can be estimated well from a specific conductance measurement of a water sample.

The TDS content and chemical character of groundwater in the Dakota aquifer range substantially in both spatial and vertical dimensions across Kansas. The TDS concentration is as low as 100 mg/L in shallow groundwater in the Dakota aquifer and exceeds 50,000 mg/L in saltwater sampled from the confined aquifer in parts of north-central Kansas. Freshwaters in the outcrop and subcrop areas of the Dakota aquifer in Kansas, in parts of the confined aquifer in Kansas where the confining beds are thin, and in portions of the recharge area of southeast Colorado are usually of calciumbicarbonate type. Sodium-bicarbonate type water is common in the confined aquifer and along the transition zone from the confined to unconfined aquifer. Calcium-sulfate type water occurs in some locations in both the unconfined and confined aquifer. Waters of a composition transitional among these types are also common, such as mixed cation-bicarbonate type (usually in the unconfined aquifer) and sodiummixed anion type (typically in the confined aquifer). The transitional water types have a greater TDS concentration than that of calcium-bicarbonate type water. Large areas of the Dakota aquifer contain saltwater (sodium-chloride type). The saltwater occurs within the entire thickness of the confined Dakota aquifer in parts of central and northcentral Kansas overlying the Cedar Hills Sandstone and in

the confined aquifer in northwest Kansas. Elsewhere in most of the confined and parts of the unconfined aquifer, fresh to slightly saline water exists in the upper part of the aquifer and the salinity increases substantially with depth, especially below major shale units.

The flushing of saltwater from the Dakota aquifer by vertical and lateral recharge is the main process leading to the diversity in chemical character of groundwaters. Data for the chemical nature of the water, mineralogy of the sediments, and hydrogeologic properties of the aquifer, together with numerical modeling of coupled hydrologic and geochemical processes, provide an understanding of the evolution of water quality in the aquifer. The origin of the saltwater in the aquifer is interpreted as the intrusion of saltwater from underlying Permian strata in which evaporite deposits (mainly rock salt) have been dissolved. Bromide/ chloride ratios indicate that little seawater remains in the Dakota aquifer even though most of the Dakota sediments probably contained seawater either during their deposition or after deposition when the sea covered Dakota formations. The seawater has apparently been flushed and replaced by fresh recharge, intruding Permian saltwater, or a mixture of these two.

The rate of vertical and lateral freshwater recharge relative to the rate of Permian saltwater intrusion controls the overall salinity of groundwater in the Dakota aquifer. The inflow of fresh recharge is too small to flush the saltwater in the region of thick confining beds in northwest Kansas, in the area where the rate of saltwater intrusion from the Cedar Hills Sandstone is large, and elsewhere within the aquifer where it contains saltwater below thick confining beds. The varying rates of local and regional flow of freshwater recharge cause a range in groundwater salinities in lateral and vertical directions by mixing with and diluting the saltwater. The dilution mixing affects the water chemistry faster than cation exchange because the clays in the sediment contain a large cation exchange capacity.

Large amounts of sodium adsorbed on clays in Dakota strata while the pore waters in the sediments contained saltwater (sodium-chloride type water). During the inflow of freshwater recharge of calcium-bicarbonate type, which usually also contains a relatively significant magnesium concentration, the dissolved calcium and magnesium exchange for sodium on the clays. This increases the dissolved sodium content above that resulting from the conservative mixing of the freshwater and saltwater, while decreasing the calcium and magnesium concentrations in the pore water, often to the point where the water becomes undersaturated with respect to calcite and dolomite. Where these carbonate minerals are present in the aquifer, they can dissolve, leading to increases in dissolved calcium and magnesium that can then drive further cation exchange. The carbonate mineral dissolution increases the bicarbonate concentration and the pH of the water. This process generates sodium-bicarbonate type groundwater. The composition of the recharge water and the different adsorption affinities of calcium and magnesium relative to sodium result in bicarbonate waters with differing ratios of dissolved cations and anions. The large exchange capacity of the clays means that it takes much longer for the cation and bicarbonate chemistry of the water in the aquifer to become similar to that of the inflowing recharge than the flushing of the salinity.

The low dissolved calcium concentration that results from the cation exchange process not only results in dissolution of calcite but also of calcium-containing minerals that include fluoride, such as fluorite and fluorapatite. This can increase the dissolved fluoride concentration in the Dakota aquifer to more than 2 mg/L. Most of the highfluoride water is present in the confined aquifer where the water type is sodium-bicarbonate.

Iron sulfide minerals (primarily pyrite) occur in shales in the Dakota aquifer and overlying upper Cretaceous shales. Recharge water containing dissolved oxygen can oxidize the sulfide minerals and increase the sulfate concentration of pore waters. The oxidation of sulfide minerals also increases the dissolved iron content of the pore water. Oxidation and hydrolysis of the dissolved iron to ferric oxyhydroxides decreases the pore water pH and produces the orange to red coloring often present in Dakota sands and silts. The lower pH can dissolve carbonate minerals. Recharge water containing a substantial calcium content from the dissolution of calcite or dolomite can combine with the high sulfate from pyrite oxidation to precipitate secondary gypsum in upper Cretaceous shale, such as has occurred in the Graneros Shale overlying the Dakota Formation. The dissolution of this gypsum by later recharge and the entrance of this recharge into underlying Dakota strata can increase the sulfate content of the aquifer groundwater. Pyrite weathering and dissolution of calcium carbonate minerals in Dakota strata or the entrance of recharge water that had dissolved gypsum in overlying shale can produce calcium-sulfate type water in either the unconfined or confined Dakota aquifer. This groundwater usually contains a TDS concentration that is greater than that for calcium-bicarbonate type water.
Contaminants in recharge from or near the land surface or introduced through poorly constructed wells can further change the chemical characteristics of Dakota groundwater by introducing additional substances or increasing the concentration of existing constituents. The main inorganic constituent affected by this type of contamination is nitrate. Past injection of oil brine into saltwater-containing strata of the Dakota aquifer has altered the composition of the saltwater in only limited areas.

The processes of conservative mixing, reactive cation exchange, and mineral dissolution and precipitation

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produce a complex range of chemical characteristics for the groundwater in the Dakota aquifer due to the differing rates of flow and dispersion of the end-member freshwaters and saltwaters and of diffusion of dissolved constituents, coupled with the differing freshwater and saltwater composition and sediment mineralogy. The multidisciplinary approach of the Dakota Aquifer Program provided the information for understanding how these processes affected the origin and evolution of the current water quality of the aquifer. These processes also control the concentrations of other constituents such as heavy metals.

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