

Prepared in cooperation with the Papio-Missouri River Natural Resources District

Altitude, Age, and Quality of Groundwater, Papio-Missouri River Natural Resources District, Eastern Nebraska, 1992 to 2009



Scientific Investigations Report 2012–5036

Cover. Figure 1 from the report with modifications.

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By Virginia L. McGuire, Derek W. Ryter, and Amanda S. Flynn

Prepared in cooperation with the Papio-Missouri River Natural Resources District

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Conversion Factors and Datums

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
inch (in.)	25,400	micrometer (μm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.004047	square kilometer (km^2)
section (640 acres or 1 square mile)	259.0	square hectometer (hm^2)
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.00378	milliliter (mL)
gallon (gal)	0.003785	cubic meter (m^3)
million gallons (Mgal)	3,785	cubic meter (m^3)
cubic inch (in^3)	0.01639	liter (L)
Flow rate		
foot per day (ft/d)	0.3048	meter per day (m/d)
gallons per minute (gal/min)	0.06309	liter per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
inch per year (in/yr)	2.54	centimeters per year (cm/yr)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)
millirem (mrem)	10,000	microsievert (μSv)
Hydraulic conductivity		
foot per day (ft/d)	0.3048	meter per day (m/d)
Hydraulic gradient		
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
Application rate		
pounds per acre per year [(lb/acre)/yr]	1.121	kilograms per hectare per year [(kg/ha)/yr]

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

Altitude or vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29). Altitude refers to distance above or below NGVD 29. NGVD 29 can be converted to the North American Vertical Datum of 1988 by using the National Geodetic Survey conversion utility available at <http://www.ngs.noaa.gov/TOOLS/Vertcon/vertcon.html>.

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L), micrograms per liter ($\mu\text{g}/\text{L}$), or micromoles per liter ($\mu\text{M}/\text{L}$).

Water year is the 12-month period from October 1 through September 30. The water year is designated by the calendar year in which the water year ends and that includes 9 of the 12 months. Thus, the water year ending September 30, 2009, is called the “2009 water year.”

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Altitude, Age, and Quality of Groundwater, Papio-Missouri River Natural Resources District, Eastern Nebraska, 1992 to 2009

By Virginia L. McGuire, Derek W. Ryter, and Amanda S. Flynn

Abstract

The U.S. Geological Survey, in cooperation with the Papio-Missouri River Natural Resources District (PMRNRD), conducted this study to map the water-level altitude of 2009 within the Elkhorn River Valley, Missouri River Valley, and Platte River Valley alluvial aquifers; to present the predevelopment potentiometric-surface altitude within the Dakota aquifer; and to describe the age and quality of groundwater in the five principal aquifers of the PMRNRD in eastern Nebraska using data collected from 1992 to 2009. In addition, implications of alternatives to the current PMRNRD groundwater-quality monitoring approach are discussed.

In the PMRNRD, groundwater altitude, relative to National Geodetic Vertical Datum of 1929, ranged from about 1,080 feet (ft) to 1,180 ft in the Elkhorn River Valley alluvial aquifer and from about 960 ft to 1,080 ft in the Missouri River Valley and Platte River Valley alluvial aquifers. In the PMRNRD, the estimated altitude of the potentiometric surface of the Dakota aquifer, predevelopment, ranged from about 1,100 ft to 1,200 ft.

To assess groundwater age and quality, groundwater samples were collected from a total of 217 wells from 1992 to 2009 for analysis of various analytes. Groundwater samples collected in the PMRNRD from 1992 to 2009 and interpreted in this report were analyzed for age-dating analytes (chlorofluorocarbons), dissolved gases, major ions, trace elements, nutrients, stable isotope ratios, pesticides and pesticide degradates, volatile organic compounds, explosives, and ²²²radon.

Apparent groundwater age was estimated from concentrations of chlorofluorocarbons measured in samples collected in 2000. Apparent groundwater-recharge dates ranged from older than 1940 in samples from wells screened in the Missouri River Valley alluvial aquifer to the early 1980s in samples from wells screened in the Dakota aquifer.

Concentrations of major ions in the most recent sample per well collected from 1992 to 2009 indicate that the predominant water type was calcium bicarbonate. Samples from 4 wells exceeded the U.S. Environmental Protection Agency (USEPA) Secondary Drinking Water Regulation (SDWR) for sulfate [250 milligrams per liter (mg/L)], and samples from

4 wells exceeded the USEPA Drinking Water Advisory Table for sodium (30–60 mg/L).

Eighteen of the 21 trace elements analyzed in samples from PMRNRD wells have USEPA drinking-water standards. Sixteen of the trace elements with USEPA standards were detected in the selected samples. In the samples selected for trace-element analysis, the only trace-element concentration that exceeded an enforceable USEPA drinking-water standard, the Maximum Contaminant Level (MCL), was for arsenic; arsenic concentration exceeded the USEPA MCL of 10 micrograms per liter ($\mu\text{g/L}$) in 4 percent of the samples. Trace-element concentrations that exceeded the USEPA SDWR or Lifetime Health Advisory level were iron (46 percent of the samples were greater than USEPA SDWR of 300 $\mu\text{g/L}$), manganese (70 percent of the samples were greater than USEPA SDWR of 50 $\mu\text{g/L}$), and strontium (4 percent of the samples were greater than USEPA Lifetime Health Advisory level of 4,000 $\mu\text{g/L}$).

The concentration of nitrate plus nitrite as nitrogen (nitrate-N) in the most recent nutrient samples collected from the network wells and from one randomly selected well in the well nests from 1992 to 2009 for most wells (80 percent) ranged from less than 0.06 to 8.55 mg/L, with a median value of 0.12 mg/L. Concentrations of nitrate-N in 13 (7 percent) nutrient samples, 1992 to 2009, were greater than or equal to the USEPA MCL and Nebraska Title-118 standard of 10 mg/L, and concentrations of nitrate-N in 35 (18 percent) nutrient samples, 1992 to 2009, were greater than or equal to 5 mg/L, which is the PMRNRD action level for possible management implementation to reduce nitrate concentrations in groundwater.

Of the 61 pesticides or pesticide degradates analyzed from 2007 to 2009, 21 were detected. Three of the 21 pesticides detected (alachlor, atrazine, and metolachlor) have established health-based criteria; all detections of these compounds were at concentrations less than their USEPA standards. From 2007 to 2009, 1 or more pesticide compounds were detected in 16 of the 82 network wells and in 18 of the 26 wells in well nests. From 2007 to 2009, the individual pesticide compounds that were detected most frequently were alachlor ethane sulfonic acid, a degradate of alachlor; deethylcyanazine acid, a degradate of cyanazine; and atrazine.

Analytes with concentrations that exceeded 30 percent of the applicable Nebraska Title-118 standard were identified so that the PMRNRD can plan to monitor groundwater in the area and consider possible actions should the analyte concentrations continue to rise. The analytical results from the most recent samples collected in the network wells and all the wells in well nests from 1992 to 2009 indicate that, in at least 1 sample, there was a concentration that exceeded 30 percent of the Nebraska Title-118 standard for at least 1 of 3 major ions (chloride, fluoride, and sulfate), 1 nutrient (nitrate-N), 1 pesticide (atrazine), or 3 trace elements (arsenic, iron, and manganese). In addition, 30 percent of the USEPA MCL or Nebraska Title-118 standard for gross alpha activity likely was exceeded in samples from three wells screened in the Dakota aquifer. Study findings indicate that some alternatives to the current PMRNRD groundwater-sampling approach that could be considered are to collect fewer samples for nutrient analysis and to collect samples periodically for determining concentrations of additional analytes, particularly the analytes with concentrations that were at least 30 percent or more than the Nebraska Title-118 standard.

Introduction

The groundwater resources of the Papio-Missouri River Natural Resources District (PMRNRD) comprise five principal aquifers—the Dakota aquifer and Elkhorn River Valley, Missouri River Valley, Platte River Valley, and upland area alluvial aquifers. In December 1989, PMRNRD management submitted a groundwater-management plan for the district to the Nebraska Department of Environmental Quality (Papio-Missouri River Natural Resources District, 1989) as required by the Nebraska Groundwater Management and Protection Act (State of Nebraska, variously dated). In 1991, Nebraska passed legislation (LB51) requiring each Natural Resources District (NRD) to amend the water-quality section of its groundwater-management plan by July 1, 1993, to “...identify...levels and sources of ground water contamination within the district... and practices recommended to stabilize, reduce, and prevent the occurrence, increase, or spread of ground water contamination” (State of Nebraska, variously dated). The PMRNRD submitted a revised groundwater-management plan in 1994 (Papio-Missouri River Natural Resources District, 1994). The PMRNRD revised groundwater-management plan states that if an analyte concentration exceeds 50 percent of its Nebraska Title-118 standard, “a management, control, or special protection area will be strongly pursued” (Papio-Missouri River Natural Resources District, 1994).

In 1991, knowledge of the quality of groundwater in the PMRNRD was limited to information on major-ion chemistry, dissolved nitrate plus nitrite as nitrogen (hereinafter referred to as nitrate-N), pesticides, and uranium (Exner, 1980; U.S. Department of Energy, 1981; Engberg, 1984; Spaulding, 1990). After a reconnaissance study in 1992, Verstraeten and Ellis (1995)

concluded that groundwater quality in the PMRNRD principal aquifers was generally suitable for most uses; however, detections of pesticides and a limited number of constituent concentrations that exceeded the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL), USEPA Secondary Drinking Water Regulations (SDWR), or Nebraska Title-118 were of concern (Nebraska Department of Environmental Quality, 2006; U.S. Environmental Protection Agency, 2009a). From 1994 to 2009, the U.S. Geological Survey (USGS), in cooperation with the PMRNRD, monitored groundwater quality in the PMRNRD, and in 2007, the USGS began this study to interpret and report the groundwater or potentiometric-surface altitude in 4 of the 5 PMRNRD principal aquifers, age-dating results for the 5 principal aquifers of the PMRNRD for 2000, and water-quality results for the 5 principal aquifers of the PMRNRD from 1992 to 2009. The objective of this study was to provide a current (2011), robust analysis of the groundwater-quality results from 1992 to 2009 sampling to aid PMRNRD management in making decisions and plans regarding groundwater quality in the district.

The purposes of this report are to present the water-level altitudes within the Elkhorn River Valley, Missouri River Valley, and Platte River Valley alluvial aquifers; to present the predevelopment potentiometric-surface altitude within the Dakota aquifer; and to describe the age and quality of groundwater in the five principal aquifers of the PMRNRD in eastern Nebraska using data collected from 1992 to 2009. In addition, implications of alternatives to the current PMRNRD groundwater-quality monitoring approach are discussed.

The scope of this report is to (1) define the water-level altitudes within the alluvial aquifers generally using groundwater-level measurements from spring 2009 and estimated surface-water altitudes, (2) present predevelopment potentiometric-surface altitudes and the altitude of available groundwater-level measurements from spring 2009 in the Dakota aquifer, (3) describe the groundwater-quality monitoring approach and the analytical methods used in the PMRNRD sampling program from 1992 to 2009, (4) present the analytical results for the regular and quality-control (QC) samples for the PMRNRD sampling program from 1992 to 2009, and (5) discuss results of statistical comparisons among selected constituents of groundwater quality. Results of groundwater-quality analyses were statistically compared for the periods 1992 to 2009, 1992 to 1994, 1999 to 2009, and 2007 to 2009. Gross alpha and beta activities, ²²⁶radium activities, and the ²³⁴uranium:²³⁸uranium ratios from samples collected in 1992 were not interpreted in this report because samples have not been collected for analysis of these radionuclides since 1992, and Verstraeten and Ellis (1995) interpreted the 1992 results.

Description of Study Area

The PMRNRD encompasses approximately 1,790 square miles (mi²) [4,640 square kilometers (km²)] in eastern Nebraska (fig. 1); the PMRNRD includes all or parts of seven

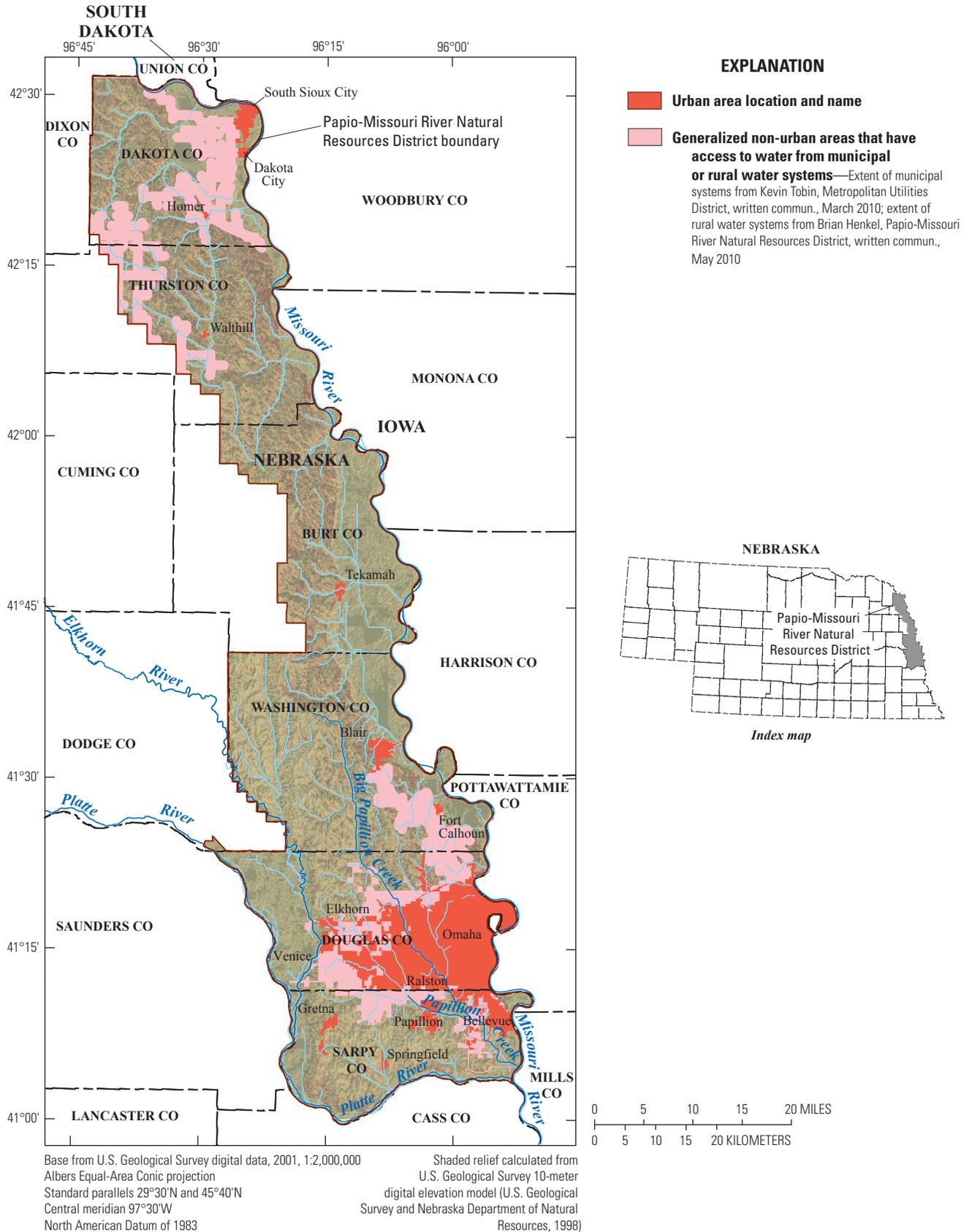


Figure 1. Location of urban areas and generalized non-urban areas that have access to water from municipal or rural water systems, Papio-Missouri River Natural Resources District, eastern Nebraska.

counties in eastern Nebraska—Burt (58 percent), Dakota (98 percent), Dodge (less than 1 percent), Douglas (100 percent), Sarpy (100 percent), Thurston (65 percent), and Washington (100 percent). In this report, the small area of the PMRNRD in Dodge County is not discussed in county summaries because it was not considered to be relevant. Major cities in the PMRNRD are, in order of decreasing population, Omaha, Bellevue, Papillion, South Sioux City, Blair, Ralston, Elkhorn, Gretna, Tekamah, and Dakota City (U.S. Census Bureau, 2001).

The PMRNRD is bounded on the east by the Missouri River and to the south and southwest by the Platte and Elkhorn Rivers. In the northwest, the PMRNRD is bounded by the Dakota and Washington County boundaries and, in Thurston and Burt County, by the western edge of the Missouri River watershed boundary (Watermolen, 2005). Other major streams in the PMRNRD include Papillion Creek and its tributaries (fig. 1). The Elkhorn River is a tributary to the Platte River; the Platte River and Papillion Creek are tributaries to the Missouri River.

The PMRNRD is located in the Dissected Till Plains section of the Central Lowland physiographic province (Fenneman, 1938). The land-surface altitude of the PMRNRD, relative to the National Geodetic Vertical Datum of 1929 (NGVD 29), ranges from about 1,520 feet (ft) [460 meters (m)] in the uplands on the western side of the study area to about 950 ft (290 m) in the Missouri River Valley at the Platte River confluence. The principal physiographic features are nearly level river valleys bordered by steep bluffs and escarpments with irregular slopes or uplands. The glaciated uplands consist of gently rolling ridges and valleys formed by erosion and deposition. The deposits in the uplands primarily consist of relatively impermeable glacial till overlain by thin to thick layers of eolian loess (University of Nebraska–Lincoln, Conservation and Survey Division, 1986).

The climate in the PMRNRD is continental and temperate with large seasonal variations in temperature and precipitation. The climate (from 1948 to 2009 monthly climatic summaries for Omaha and for the vicinity of South Sioux City, Nebr.) is characterized by moderate precipitation [30.4 inches per year (in./yr) or 77.2 centimeters per year (cm/yr) in Omaha and 26.5 in./yr or 67.3 cm/yr near South Sioux City] and a wide range of daily average temperatures [12.0 to 87.7 degrees Fahrenheit (°F) or -11.1 to 30.9 degrees Celsius (°C) in Omaha and 8.4 to 86.2°F or -13.1 to 30.1°C near South Sioux City] (High Plains Regional Climate Center, 2010a and 2010b). About 73 percent of the precipitation is received as rainfall during April through September.

Hydrogeology

Verstraeten and Ellis (1995) describe the hydrogeology in the PMRNRD area on the basis of geologic and hydrogeologic information in published reports and unpublished data available at the University of Nebraska–Lincoln, Conservation and Survey Division (UNL–CSD) and the USGS office in Lincoln, Nebr. For this report, six aquifers are distinguished

as groundwater resources of the PMRNRD (table 1). Four of these are composed of surficial deposits, and two are bedrock aquifers. The surficial and bedrock hydrogeologic characteristics are described briefly in separate subsections that follow this subsection.

The geology and hydrogeologic characteristics of the PMRNRD area in Dakota County are described by Condra (1908) and Todd (1908). The geology of the Omaha area is described by Condra and others (1931) and Miller (1964). Geologic characteristics of the Missouri River Valley alluvium and bedrock are reported by Burchett (1965); the hydrogeology of the Dakota aquifer is discussed by O'Connor (1987). Lithologic logs with the altitudes of geologic formations from test holes drilled by UNL–CSD and USGS in the PMRNRD area are presented by Burchett and Smith (1989a, 1989b, 1989c, 1991a, 1991b, 1992) and the University of Nebraska–Lincoln, Conservation and Survey Division (2010c). Other relevant publications on the geology and hydrogeology of Nebraska include Condra and Reed (1959), Reed and Dreeszen (1965), Dreeszen (1970), Burchett and others (1975 and 1988), Nebraska Department of Environmental Quality and UNL–CSD (1980a, 1980b, 1980c, and 1980d), Ellis (1984 and 1986), Helgesen and others (1993), Jorgensen and others (1993 and 1996), University of Nebraska–Lincoln, Conservation and Survey Division (1996, 2010a, 2010b), Soller and Packard (1998), and Shroba and others (2002). In addition, Gutentag and others (1984) discussed the characteristics of the High Plains aquifer, which includes most of the Elkhorn River Valley alluvial aquifer.

Hydrogeologic Units in Surficial Deposits

The surficial deposits in the PMRNRD are predominantly Quaternary-age deposits of alluvial, eolian, and glacial origin. The Quaternary-age deposits are unconsolidated and vary from relatively permeable sand-and-gravel units to relatively impermeable silts and clays. Only the sand-and-gravel units were considered aquifers for this study. In this report, the Quaternary-aged sand-and-gravel deposits in the PMRNRD area are divided into four aquifers (Verstraeten and Ellis, 1995)—the Elkhorn River Valley, Missouri River Valley, Platte River Valley, and upland area alluvial aquifers (fig. 2). Additional discussion of the composition and characteristics of surficial deposits in the PMRNRD can be found in Verstraeten and Ellis (1995).

Bedrock Hydrogeologic Units

The PMRNRD is underlain by bedrock formations ranging in age from Precambrian through Cretaceous; bedrock formations of Permian, Triassic, and Jurassic age are not present in the PMRNRD. The surficial (uppermost) bedrock formations in the PMRNRD range in age from Pennsylvanian to Cretaceous (fig. 3). The bedrock underlying the PMRNRD is divided into five hydrogeologic units—the Great Plains

Table 1. Description of hydrogeologic units, Papio-Missouri River Natural Resources District, eastern Nebraska.

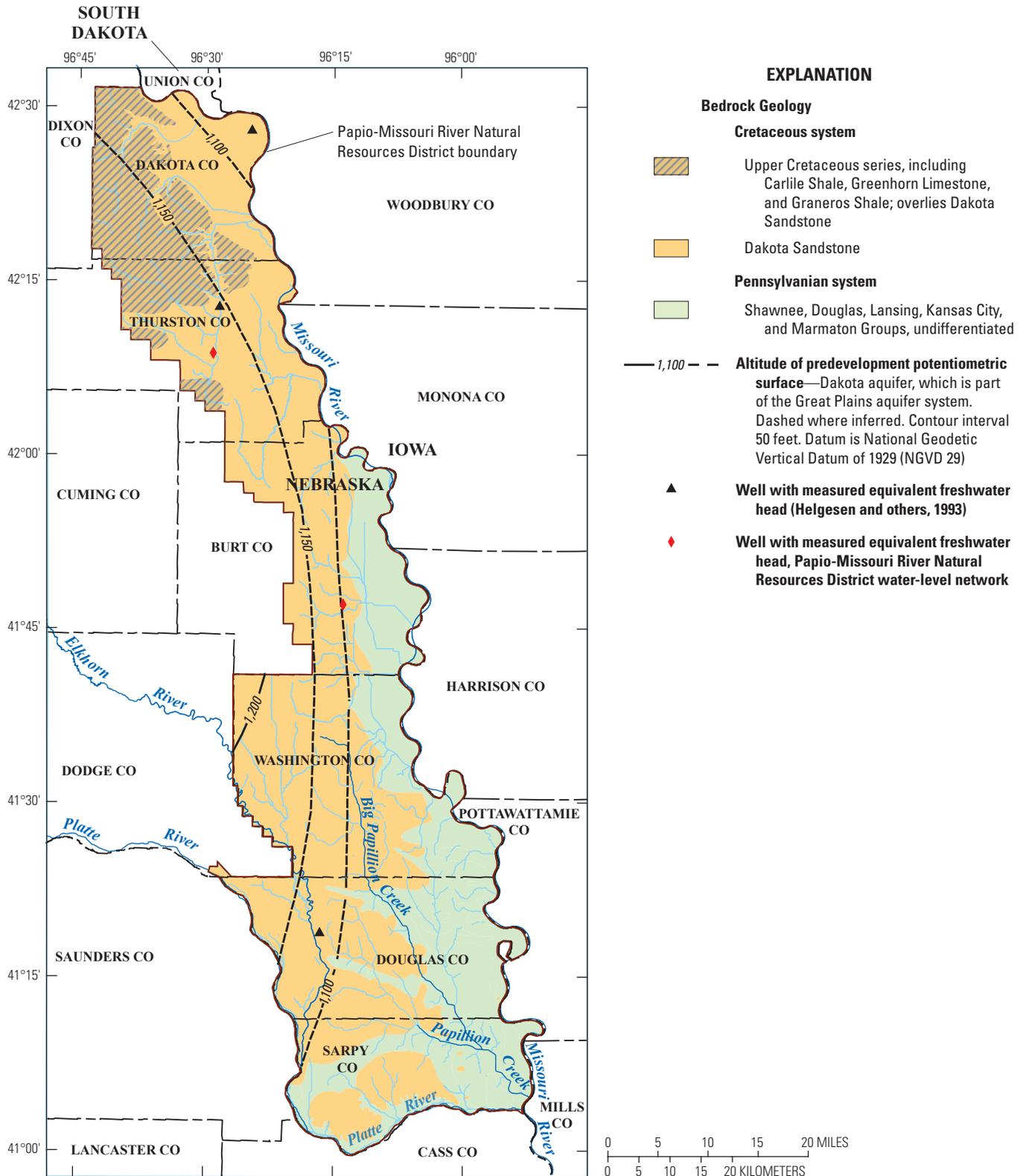
[Descriptions modified from Verstraeten and Ellis (1995) and Jorgensen and others (1993). PMRNRD, Papio-Missouri River Natural Resources District; ft, feet; gal/min, gallons per minute; depths are in feet below land surface]

Era	System	Geologic unit	Geologic characterization, description, and distribution	Hydrogeologic unit	Hydrogeologic characteristics
Cenozoic	Quaternary	Undifferentiated deposits of Holocene and Pleistocene age	Clay, silt, sand, and gravel. Includes eolian, glacial, and alluvial deposits found over almost all of the PMRNRD area, except in small areas where bedrock crops out. The total thickness of the deposits in river valleys in the PMRNRD are usually less than 100 ft. In the upland part of the PMRNRD, the total thickness of the deposits usually ranges from 50 to 250 ft; maximum thickness of the deposits in the upland area is about 300 ft and is in the northern part of the PMRNRD. Eolian deposits are loess, consisting of silt- and clay-sized grains, and usually are the surficial deposits in upland areas of the PMRNRD. Loess thickness usually ranges from 10 to 50 ft. Glacial deposits are clay tills that contain silt, sand, and gravel and underlie the eolian deposits in most of the upland areas of the PMRNRD. Glacial deposits occur in the form of multiple till beds, and total thickness usually is 25 to 125 ft but may be as much as 175 ft or be absent due to erosion. Alluvial deposits include clay, silt, sand, and gravel. Clay and silt deposits usually are intermixed or interbedded with the sand and gravel deposits. Sand and gravel deposits are most common in the river valleys.	Elkhorn River Valley alluvial aquifer	Unconfined aquifer with wells yielding 700 to 1,200 gal/min. Depth to water ranges from about 5 to 30 ft. Saturated thickness ranges from 50 to 90 ft.
				Missouri River Valley alluvial aquifer	Aquifer usually unconfined but locally may be partially confined. Most wells yield 600 to 1,200 gal/min. Depth to water ranges from about 5 to 40 ft. Saturated thickness ranges from 70 to 100 ft.
				Platte River Valley alluvial aquifer	Unconfined aquifer with wells yielding 900 to 2,000 gal/min. Depth to water ranges from about 5 to 15 ft. The saturated thickness ranges from 60 to 100 ft.
				Upland area alluvial aquifers	Confined or partially confined discontinuous beds of saturated sand and gravel. Well yields range from 10 to 300 gal/min. Depth to water ranges from about 10 to 170 ft. The saturated thickness of the sand and gravel deposits usually is less than 20 ft.
Mesozoic	Cretaceous	Undifferentiated Carlile Shale, Greenhorn Limestone, and Graneros Shale	Shale, marl, and limestone. Shale is calcareous. Limestone is thin-bedded, argillaceous, and interbedded with marl and shale beds. Present in parts of Dakota and Thurston Counties. Maximum thickness is about 125 ft in Dakota County.	Great Plains confining system	Forms a regional confining unit that, where present, separates the Dakota aquifer from the overlying alluvial aquifers.
		Dakota Sandstone Formation	Sandstone and claystone. Sandstone is very fine to coarse-grained, lenticular, friable, and locally is cemented with iron oxide. About 70 percent of the formation is sandstone. Claystone is massive and often silty. Maximum thickness, about 500 ft, is in Dakota and Thurston Counties where the unit is primarily sandstone and overlain by Graneros Shale. In the rest of the PMRNRD, the formation thins toward the south and east due to erosion. Erosional remnants that are less than 20 ft thick occur in Sarpy County.	Dakota aquifer (part of the Great Plains aquifer system)	Confined or partially confined aquifer with wells yielding 10 to 600 gal/min depending on the thickness of the saturated sandstone. Depth to water ranges from about 5 to 200 ft. The sandstone thickness ranges from less than 1 to about 300 ft.

Table 1. Description of hydrogeologic units, Papio-Missouri River Natural Resources District, eastern Nebraska.—Continued

[Descriptions modified from Verstraeten and Ellis (1995) and Jorgensen and others (1993). PMRNRD, Papio-Missouri River Natural Resources District; ft, feet; gal/min, gallons per minute; depths are in feet below land surface]

Era	System	Geologic unit	Geologic characterization, description, and distribution	Hydrogeologic unit	Hydrogeologic characteristics
Paleozoic	Pennsylvanian	Undifferentiated limestone, shale, and sandstone beds	Limestone and shale. Limestone is thin-bedded to massive and usually dense. Shale is calcareous and fissile. Maximum thickness, about 500 ft, is in southwestern part of the PMRNRD. These sediments are absent in the northern part of Dakota County.	Western Interior Plains confining system	Forms a regional confining bed that, where present in the PMRNRD, separates the Western Interior Plains aquifer system from the Dakota aquifer and from the alluvial aquifers. In the PMRNRD, wells completed in local fracture zones near the top of the unit may yield 5 to 50 gal/min.
	Mississippian-Cambrian, undifferentiated	Undifferentiated limestone, dolomite, sandstone, and shale beds	Predominantly massive dolomite bedding with some limestone beds in upper part, thin dolomitic shale in the middle, and sandstone beds in the lower parts. Thickness increases from about 900 ft in Dakota County to 1,600 ft in Washington County. Thickness decreases to the south and east.	Western Interior Plains aquifer system	Confined aquifers. Available information indicates that, in the PMRNRD, well yields range from 200 to 1,300 gal/min, water levels range from 150 to 300 ft below land surface, and well depths range from 1,100 to 2,400 ft.
Precambrian	Undifferentiated	Undifferentiated	Undifferentiated igneous, metamorphic, and sedimentary rocks.	Basement confining unit	Regional base of the Western Interior Plains aquifer system.



Base from U.S. Geological Survey digital data, 2001, 1:2,000,000 Modified from Helgesen and others, 1993; Albers Equal-Area Conic projection University of Nebraska-Lincoln, Standard parallels 29°30'N and 45°40'N Conservation and Survey Division, 2010b Central meridian 97°30'W North American Datum of 1983

Figure 3. Generalized bedrock geology, location of wells screened in the Dakota aquifer with water-level data, and altitude of the predevelopment potentiometric surface of the Dakota aquifer, Papio-Missouri River Natural Resources District, eastern Nebraska.

confining system, the Dakota aquifer (part of the Great Plains aquifer system), the late Paleozoic-age Western Interior Plains confining system, the Western Interior Plains aquifer system, and the basement confining unit (Jorgensen and others, 1993; Verstraeten and Ellis, 1995). For this report, because withdrawals from the Dakota aquifer are substantial and withdrawals from the Western Interior Plains aquifer system are minimal (Verstraeten and Ellis, 1995), only the Dakota aquifer is considered as 1 of the 5 principal aquifers in the PMRNRD. Additional discussion on the composition and characteristics of bedrock units in the PMRNRD can be found in Verstraeten and Ellis (1995).

Soils

The soils in the PMRNRD area are silty, clayey to silty, or sandy (Verstraeten and Ellis, 1995). The estimated water-infiltration rates range from high in some small areas of bottomland in the Elkhorn, Missouri, and Platte River Valleys to low or very low in the large areas of bottomland along the Missouri River Valley in eastern Burt and Washington Counties (fig. 4; U.S. Department of Agriculture, 2009). These water-infiltration rate estimates assume the soil is not protected by vegetation, is thoroughly wet, and receives precipitation from a storm of long duration.

Land and Water Use

Agriculture dominates the land use in the PMRNRD area (fig. 5). In 2005, the principal land-use types in the PMRNRD were dry cropland, rangeland, irrigated cropland, and urban land (Center for Advanced Land Management Information Technologies, 2007). From 1991 to 2008, the predominant crops in the PMRNRD were corn, soybeans, and alfalfa (fig. 6) (U.S. Department of Agriculture, 2010). In Burt, Dakota, Thurston, and Washington Counties the number of harvested acres did not change greatly from 1992 to 2008; however, mostly as a result of urbanization, the number of harvested acres in Douglas and Sarpy Counties decreased by about 40 percent and 20 percent, respectively (fig. 6).

Both groundwater and surface water are substantial water sources in the PMRNRD (U.S. Geological Survey, 2010c). In 2005, total water use for purposes other than those related to generation of power was about 270 million gallons per day. Groundwater was the source for 60 percent of this total, and surface water was the source for the remainder (fig. 7A). Because this report focuses on groundwater, no further discussion of surface-water use is presented here. Domestic self-suppliers, some public supply for municipal and rural water systems, irrigation, and other uses, such as industrial water users, depend on groundwater sources in and near the PMRNRD area (fig. 7B). The water for the rural water system in the western part of the PMRNRD in Thurston and Washington

Counties is imported into the PMRNRD from a well field that is west of the PMRNRD boundary.

Groundwater withdrawals increased from 1990 to 2005 in all the counties of the PMRNRD, except for Sarpy County (fig. 7B). The increases in groundwater withdrawals in Burt, Dakota, Dodge, Thurston, and Washington Counties were primarily for irrigation use. The increases in groundwater withdrawals in Douglas County were primarily for domestic, self-supplied, and public-supply use. The decreases in groundwater withdrawals in Sarpy County reflect decreases in withdrawals for public supply, domestic self-supply, and other uses, including for livestock and industrial use (U.S. Geological Survey, 2010c). Groundwater withdrawals in Douglas County during 2010 will likely be greater than withdrawals in 2005 because a new municipal well field with wells screened in the Elkhorn River Valley or Platte River Valley alluvial aquifer was completed and placed into production in July 2008 (<http://www.mudomaha.com/plattewest/timeline.html>).

Agricultural Chemical Use

In the PMRNRD, agricultural chemicals, typically fertilizers and pesticides, commonly are applied to the land surface in agricultural and urban settings to increase crop yield, promote plant and lawn growth, or control competing vegetation, insects, and fungi. Many of these chemicals can move beneath the plant root zones and into groundwater. This report refers to chemicals in groundwater that are derived at least partly from commercial fertilizer or manure as nutrients—ammonia, nitrate, nitrite, and orthophosphate. In the PMRNRD, the estimated commercial fertilizer inputs for nitrogen in 2001, normalized by total county area, ranged from 46 pounds per acre per year [(lb/acre)/yr] in Sarpy and Washington Counties to 72 (lb/acre)/yr in Douglas County. The estimated commercial fertilizer input for phosphorus in 2001, normalized by total county area, ranged from 6 (lb/acre)/yr in Sarpy and Washington Counties to 10 (lb/acre)/yr in Douglas County (table 2; Ruddy and others, 2006).

In 2005, the 10 most commonly applied pesticides in the PMRNRD, in decreasing order of estimated use, were atrazine, glyphosate, acetochlor, S-metolachlor, chlorpyrifos, 2,4-D, alachlor, pendimethalin, dimethenamid, and dicamba (table 3). Nine of these pesticides are herbicides; the remaining pesticide, chlorpyrifos, is an insecticide. In 2005, the total number of acres treated with atrazine or glyphosate in the PMRNRD was estimated to be 595,000; about 80 percent of these acres are in Burt, Dakota, Thurston, and Washington Counties (table 3).

Because pesticide use has changed since 2005, county extension agents were contacted to ascertain current (2010) pesticide use in the PMRNRD. County extension agents reported that glyphosate currently (2010) is the most widely used pesticide, but atrazine still is used on agricultural lands. Acetochlor still is used but usually in a mixture of several pesticides; dicamba and 2,4-D also continue to be used. Use

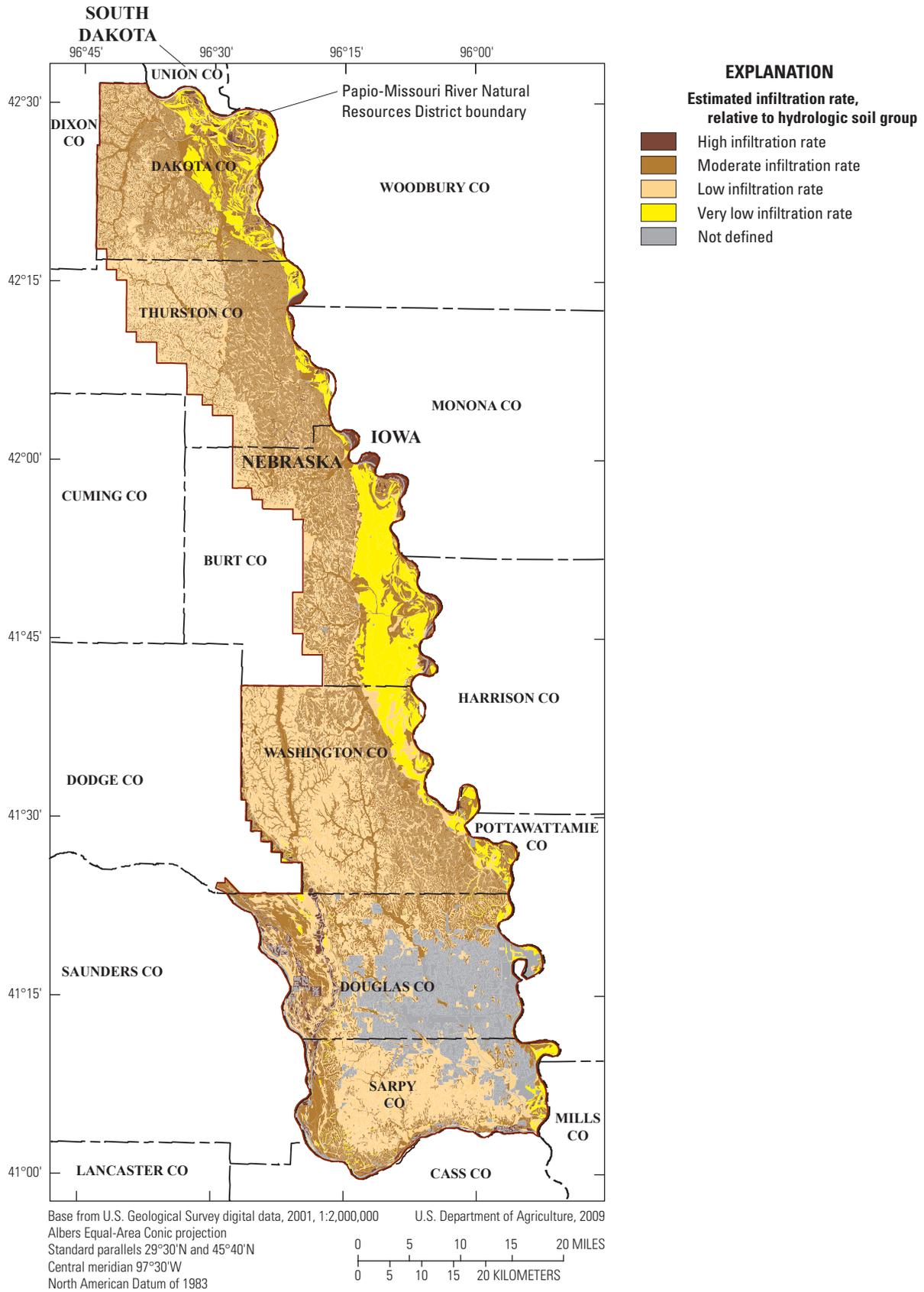


Figure 4. Distribution of estimated infiltration rates, by hydrologic soil group, Papio-Missouri River Natural Resources District, eastern Nebraska.

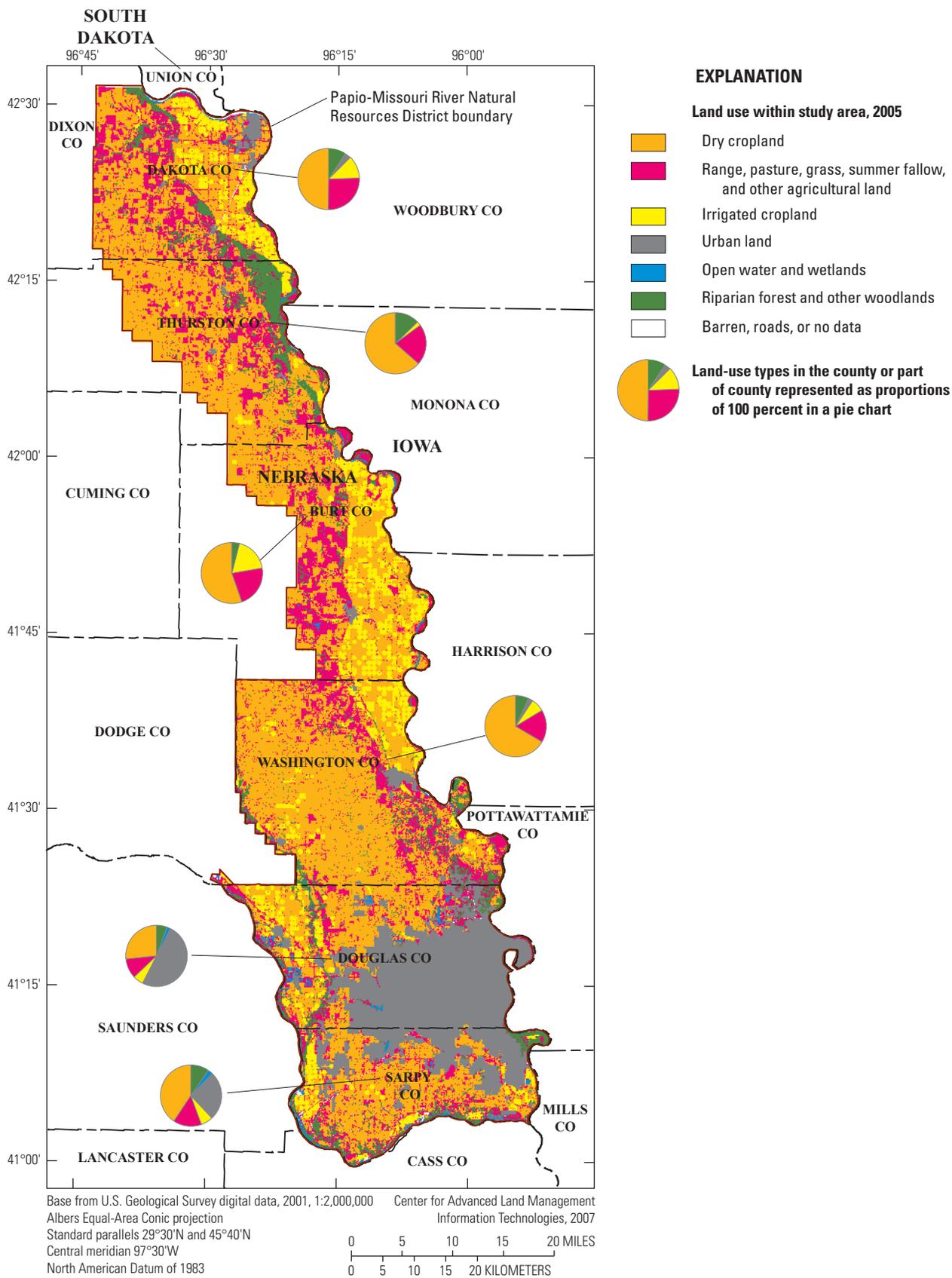
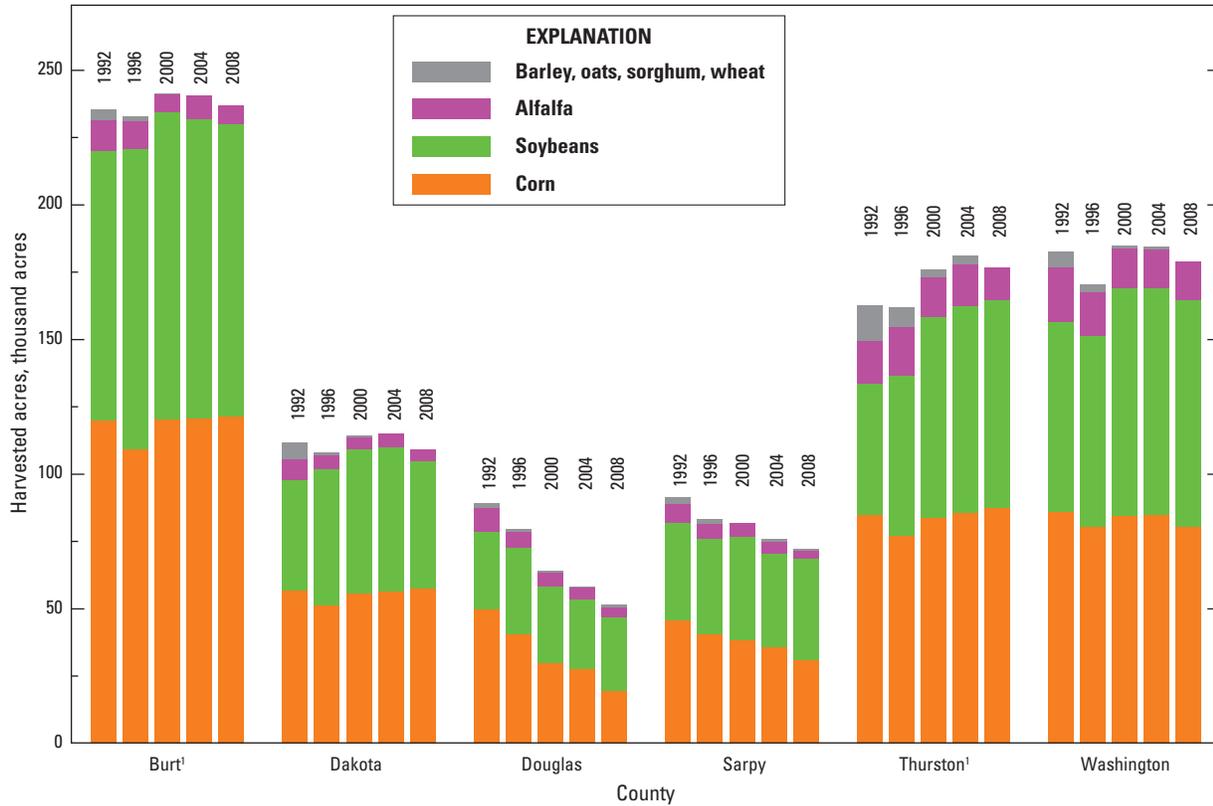


Figure 5. Distribution of primary land-use types and graphs showing proportion of land-use types, by county or part of county, Papio-Missouri River Natural Resources District, eastern Nebraska, 2005.



¹Harvested acres for Burt and Thurston Counties reflect acres harvested for the entire county, not just the area in the Papio-Missouri River Natural Resources District.

Figure 6. Harvested acres, by crop and county, for all counties except Dodge County, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992, 1996, 2000, 2004, and 2008 (Modified from U.S. Department of Agriculture, 2010).

of organophosphate insecticides, such as chlorpyrifos, has decreased, although chlorpyrifos still is used, for example, to control aphids in wet years. Use of pyrethroid-based insecticides (typical active ingredient: bifenthrin; typical trade names: Ambush and Pounce) has increased since 2002 (John A. Wilson, Burt County extension agent, written commun., July 2010; Dennis Ferraro, Douglas and Sarpy County extension agent, oral commun., July 2010; Keith Jarvi, Dakota, Thurston, and Dixon County extension agent, oral commun., July 2010; Steve Tonn, Washington County extension agent, oral commun., July 2010).

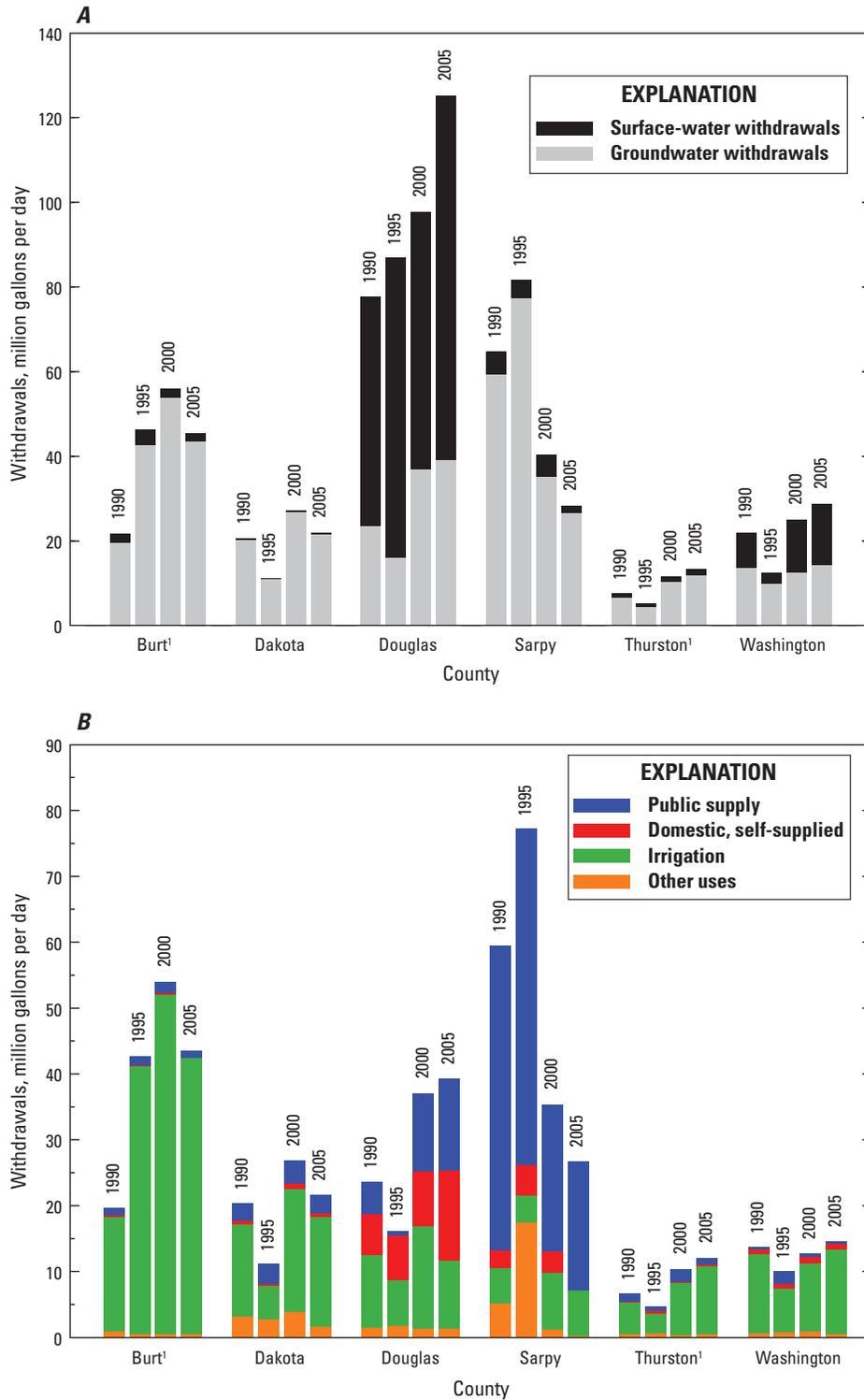
Methods of Investigation

This section describes the installation in 1999 of wells in well nests used in this study; processes used by USGS to select the network wells (from 1992 to 2009) and wells in well nests (from 1999 to 2009) used for groundwater sampling; and methods used by USGS for groundwater-sample collection and documentation, chemical analysis, and quality assurance and quality control for the PMRNRD study from 1992 to 2009. This section also describes data treatment and analysis used in this report. Analytical results from 1992 to 2009,

presented in this report, were evaluated by comparing the results to Federal drinking-water standards that are applied to treated drinking water and to State regulations for groundwater (U.S. Environmental Protection Agency, 2009a; Nebraska Department of Environmental Quality, 2006). The data presented in this report characterize the quality of untreated groundwater resources within the study unit, not the treated drinking water delivered to consumers by municipal or rural water systems.

Well Nest Installation, 1999

In 1999, the USGS oversaw the installation of 26 wells in 9 well nests in the PMRNRD. Each well nest was constructed with 2 to 3 short-screened (5 to 10 ft) monitoring wells installed in individual boreholes. A test hole drilled to the base of the aquifer was used to obtain lithologic cuttings to determine the number and depth of the wells in the nest. If sufficient aquifer thickness existed, three wells were installed in the well nest—a shallow well with a 10-ft screen located near the water table, a medium-depth well with a 5-ft screen located approximately in the middle of the aquifer, and a deep well with a 5-ft screen located near the base of the aquifer. If aquifer thickness did not allow for 3 wells, only 2



¹Withdrawal data for Burt and Thurston Counties reflect withdrawal amounts for the entire county, not just the area in the Papio-Missouri River Natural Resources District

Figure 7. A, total groundwater and surface-water withdrawals for all uses except those related to generation of power and B, groundwater withdrawals by type of use except those related to generation of power, by county, for all counties except Dodge County, Papio-Missouri River Natural Resources District, eastern Nebraska, 1990, 1995, 2000, and 2005 (Modified from U.S. Geological Survey, 2010c).

Table 2. Estimated nonpoint-source inputs of nitrogen and phosphorus, by county, Papio-Missouri River Natural Resources District, eastern Nebraska, 2001.

[Input estimates from Ruddy and others (2006)]

Nitrogen or phosphorous source	Total nitrogen and phosphorus inputs divided by total county area, in pounds per acre per year					
	Burt County ¹	Dakota County ¹	Douglas County	Sarpy County	Thurston County ¹	Washington County
Nitrogen from commercial fertilizer						
Farm use	65	60	24	33	57	45
Non-farm use	0	1	48	13	0	1
Total	65	61	72	46	57	46
Nitrogen from manure	5	2	3	4	5	6
Nitrogen from atmospheric deposition	4	4	4	4	4	4
Phosphorus from commercial fertilizer	9	8	10	6	8	6

¹About 58 percent of Burt County, 98 percent of Dakota County, and 65 percent of Thurston County are within the boundary of the Papio-Missouri River Natural Resources District.

Table 3. Ten most commonly applied pesticides, estimated treated area, and average pesticide application rate, by county, Papio-Missouri River Natural Resources District, eastern Nebraska, 2005.

[Pesticide application rates in 2002 by crop (CropLife Foundation, 2010) applied to 2005 crop acreage (Center for Advanced Land Management Information Technologies, 2007)]

Pesticide	Pesticide type	Estimated treated area, in thousand acres, in decreasing order by total estimated treated acres						Total	Average pesticide application rate (pounds of active ingredient applied per treated acre)
		Burt County ¹	Dakota County ¹	Douglas County	Sarpy County	Thurston County ¹	Washington County		
Atrazine	Herbicide	60.9	48.9	34.3	30.1	50.0	83.1	307.3	0.9
Glyphosate	Herbicide	59.9	44.9	27.7	34.6	41.2	79.0	287.3	1.0
Acetochlor	Herbicide	16.3	13.0	9.2	8.0	13.3	22.2	82.0	1.6
S-Metolachlor	Herbicide	16.5	13.2	9.1	8.4	13.2	22.5	82.9	.9
Chlorpyrifos	Insecticide	9.4	7.1	4.6	5.2	6.7	12.5	45.5	.6
2,4-D	Herbicide	6.3	5.9	3.7	3.4	5.4	7.5	32.2	.8
Alachlor	Herbicide	3.2	2.5	1.6	1.8	2.4	4.3	15.8	1.5
Pendimethalin	Herbicide	5.3	4.0	2.4	3.1	3.6	7.0	25.4	.9
Dimethenamid	Herbicide	4.2	3.4	2.4	2.1	3.5	5.8	21.4	.8
Dicamba	Herbicide	8.7	7.4	4.9	4.4	7.2	11.4	44.0	.3

¹Estimated treated acres are for the area of the county in the Papio-Missouri River Natural Resources District and not for the entire county.

wells were installed in the nest—a shallow well with a 10-ft screen located near the water table and a deep well with a 5-ft screen located near the base of the aquifer. Three wells were installed in the well nests in or near Venice, Blair, Tekamah, Homer, Walthill, Springfield, Fort Calhoun, and Ashland, Nebr. [Ashland, Nebr., which is not shown in fig. 1, is located about 11 miles (mi) southwest of Gretna, Nebr.]; 2 wells were installed in the well nest near Elkhorn, Nebr.

Well Selection

In 1992, Verstraeten and Ellis (1995) sampled 58 existing wells in the PMRNRD; from 1994 to 2009 an additional 133 existing wells were sampled. For this report, these 191 wells are termed “network” wells; the word “network” is used to distinguish these wells from the dedicated monitoring well clusters that were installed in 1999 and are hereafter referred to as “wells in well nests.”

Well Selection, 1992 to 1994

In 1992, Verstraeten and Ellis (1995) selected the network wells using a random, spatially stratified approach by aquifer from a set of available wells with specific well-construction information (such as depth and screened interval). Each selected well was screened in only 1 of the 5 principal aquifers of the PMRNRD. Verstraeten and Ellis (1995) also sampled three additional wells (D-007, M-005, and M-007) that are not discussed in this report because of current uncertainty regarding the location of the wells or construction information for the wells (refer to fig. 11 in Verstraeten and Ellis, 1995, for the approximate location of these excluded wells). In addition, the field identifiers for two of the wells sampled in 1992 have been renamed in this report; the renamed wells are D-005D, which was called D-005 by Verstraeten and Ellis (1995), and M-009A, which was called M-009 by Verstraeten and Ellis (1995).

In 1994, the USGS selected a total of 36 wells for sampling. Six of these 36 wells (D-009, P-005, U-002, U-005, U-009, and U-011) were sampled during the Verstraeten and Ellis (1995) study. The remaining 30 wells that had not been previously sampled were added to the PMRNRD set of network wells.

Well Selection, 1995 to 2009

From 1995 to 2009, a subset of the network wells was selected manually from the set of existing network wells with preference given to wells with the greatest number of previous determinations of nitrate and to wells that would produce a well-distributed spatial coverage of the aquifer areas in the PMRNRD. Additional registered wells, primarily production (irrigation or public supply) and domestic wells (Nebraska Department of Natural Resources, 2010), were added to the set of network wells if an existing network well was no longer

available for sampling or there were areas where the designated aquifer(s) lacked an existing network well. Securing the land owner’s permission to sample also was a requirement for continued inclusion in the set of network wells selected for sampling.

From 1995 to 1998, the USGS sampled between 17 and 67 wells each year; 47 of these wells had not been previously sampled and were added to the PMRNRD set of network wells. In 1995 to 1997, wells from all aquifers were sampled; in 1998, only wells screened in the Missouri River Valley alluvial aquifer were sampled.

From 1999 to 2009, the USGS continued or began collecting samples in the network wells and wells in well nests. The network wells generally were sampled, by aquifer, using a rotating 3-year schedule; the number of network wells sampled each year ranged from 17 to 40. Fifty-six of these wells had not been previously sampled and were added to the PMRNRD set of network wells. The 26 wells in 9 well nests were sampled on varying schedules from 1999 to 2009—every 2 months to annually.

Well Identification

Network wells were assigned a unique USGS station identifier and a field identifier when they were (1) first sampled or (2) installed (that is, for the wells in well nests). The field identifier format for network wells is alphabetic aquifer code, dash, number, and (optional) letter; the field identifier format for wells in nests is alphabetic aquifer code, dash, nest identifier, and number. The aquifer codes used in the field identifiers are D (Dakota aquifer), E (Elkhorn River Valley alluvial aquifer), M (Missouri River Valley alluvial aquifer), P (Platte River Valley alluvial aquifer), and U (upland area alluvial aquifers). The nest identifiers used in the field identifiers are A (Ashland), B (Blair Airport), BC (Boyers Chute), EC (Elkhorn Crossing), H (Homer), S (Springfield), T (Tekamah), V (Venice), and W (Walthill). The locations of the network wells and wells in well nests sampled from 1992 to 2009 are shown in figure 8 with the field identifiers. Available construction information for network wells and well nests is listed in appendix 1.

Sample Collection, 1992 to 2009

From 1992 to 2009, samples were collected generally in accordance with the protocols established by the USGS National Field Manual (U.S. Geological Survey, variously dated). These sampling protocols ensure that a representative sample of groundwater is collected at each site and that the samples are collected and handled in a way that minimizes contamination.

Many network wells in the PMRNRD are irrigation wells that typically operate periodically during summer to fall. Consequently, samples from network wells used for irrigation, which typically were collected only when the pumps

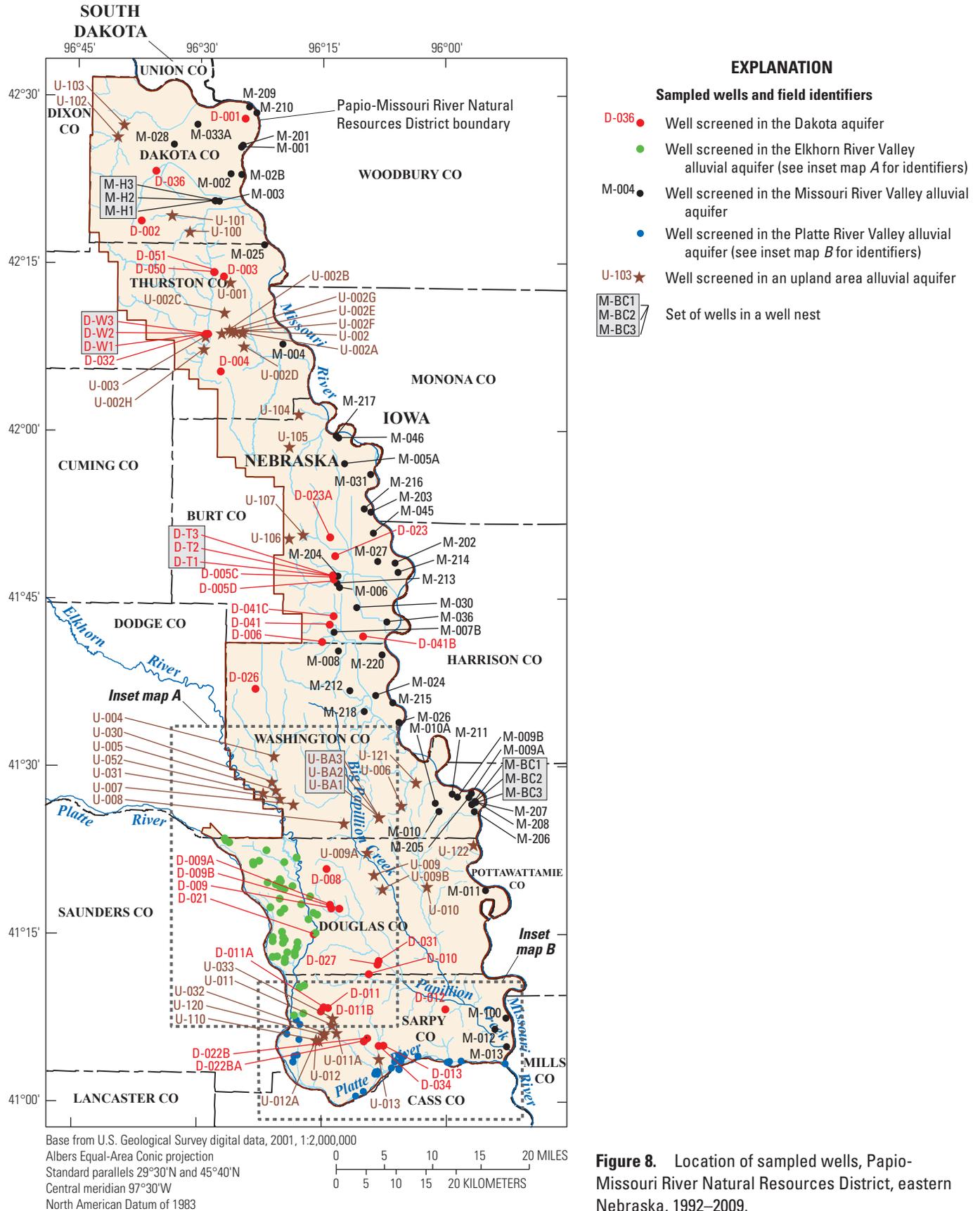
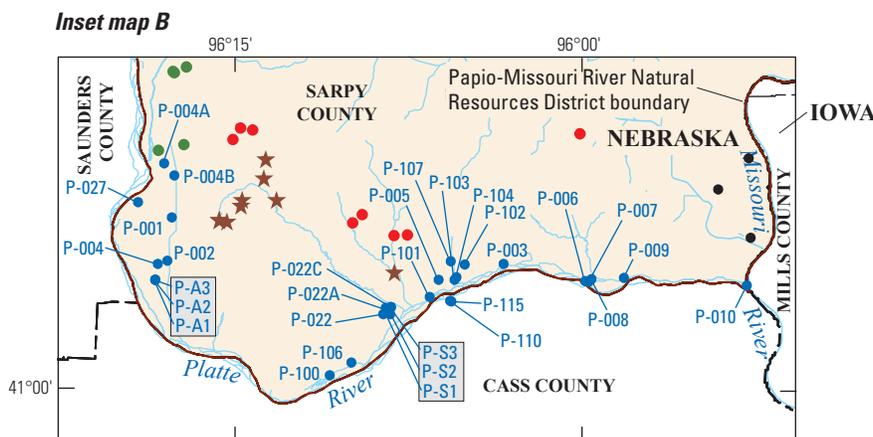
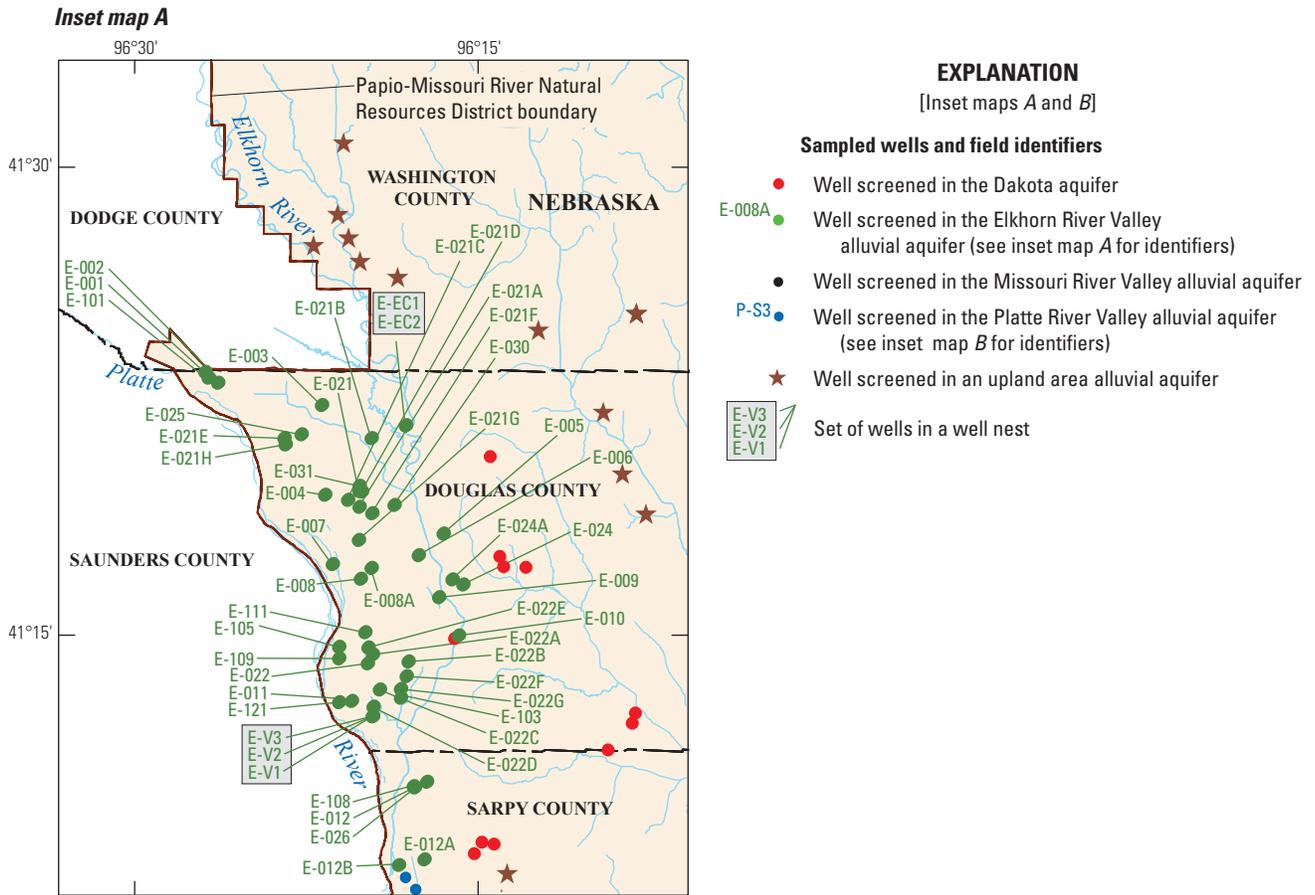


Figure 8. Location of sampled wells, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.



Base from U.S. Geological Survey digital data, 2001, 1:2,000,000
 Albers Equal-Area Conic projection
 Standard parallels 29°30'N and 45°40'N
 Central meridian 97°30'W
 North American Datum of 1983

0 5 10 MILES 0 5 10 MILES

Figure 8. Location of sampled wells, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.—Continued

were in operation for irrigation, were collected in summer to fall. With respect to wells in well nests, sampling occurred at regular intervals throughout the year because each well could be sampled easily at any time. Generally, wells in well nests were sampled more than twice per year. If wells in well nests were sampled twice a year, sampling generally occurred in the late winter or spring and during summer to fall. If sampling occurred once a year, samples generally were collected in either late winter or spring, or during summer to fall.

Dedicated pumps, which were installed in the network wells and in the wells in well nests, were used to obtain all water samples. Water was collected from each well as close to the pump as possible and prior to any treatment of the water. Observations about the well's integrity, the sampling location, and any point sources of contamination were made for all wells. Sampling protocol differed slightly for network wells and the wells in well nests.

Prior to sampling wells in well nests, the water level and well depth were measured to the nearest 0.01 ft using a graduated steel tape; in addition, the pumping rate was measured manually using a 5-gallon bucket. When sampling network wells, water level, well depth, and pumping rate were not measured prior to sampling. In the network wells, water level and well depth were not measured because the network wells generally were in operation prior to sampling, and pumping rate was not measured because the discharge amount generally is greater than the amount that can be manually measured using a bucket. When sampling network wells and wells in well nests, measurements of specific conductance, pH, water temperature, and dissolved oxygen generally were made using a flow-through chamber until measurements stabilized as per protocol and at least three well-casing volumes of water had been withdrawn. For network wells that are domestic wells with a supply tank located between the pump and the sampling point, the well was pumped until the supply tank likely had been flushed (U.S. Geological Survey, variously dated).

For all wells, collection, processing, and preservation of all environmental and QC samples (excluding equipment blanks and reference samples) were completed on site (table 4). Often, when a well, network or nested, was sampled only for nitrate or nutrients and pesticides, samples were collected in a Teflon® container at the faucet, carried to the sampling vehicle (usually a mobile laboratory), and processed. Sample processing in these situations involved using a peristaltic pump to transfer the water from the Teflon® container through the filter, if necessary, into the sample bottle. The samples to be analyzed for trace elements, volatile organic compounds (VOCs), and explosives and the remaining samples to be analyzed for nutrients and pesticides were collected using Teflon® tubing to convey the well's discharge into the mobile laboratory for sample processing (U.S. Geological Survey, variously dated).

For analyses that required filtered water, samples underwent filtration during sample collection using a 0.45-micrometer (μm) filter or a nominal 0.7- μm glass fiber filter. Water

samples for ^{222}Rn analysis were collected using a syringe method. The samples for chlorofluorocarbons (CFCs) and dissolved gases analyses required specialized sampling equipment or procedures to ensure the groundwater samples did not come in contact with the atmosphere (Busenberg and Plummer, 1992; U.S. Geological Survey, 2006a, 2009a, variously dated).

Field equipment was decontaminated and cleaned immediately following sample collection. Samples generally were sent to the appropriate analytical laboratory within 2 days of sample collection. Pesticide samples that were screened for triazines (a group of related chemicals that includes atrazine) or metolachlor using enzyme-linked immunosorbent assay (ELISA) screening kits generally were held in the cooler at the USGS office in Lincoln, Nebr., for 2 to 6 days to allow time to split and analyze the sample; when detections were identified, a subset of the sample was sent to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., or the USGS Organic Research Laboratory (OGRL), Lawrence, Kans., for pesticide analysis. Samples needing to be chilled were maintained on ice in coolers with the intended maximum temperature of 4°C from sample collection until arrival at the analytical laboratory.

Sample Analysis and Reporting

Water samples were analyzed at USGS and other laboratories using analytical methods approved by USEPA or USGS (table 4). For the reader's convenience, results from water samples collected from 1992 to 2009 are available in appendix 2, on the USGS National Water Information System (NWIS) web site (U.S. Geological Survey, 2010a), and in the USGS annual reports (Boohar and others, 1993, 1995, and 1996; Boohar and Walczyk, 1997 and 1998; Boohar, 1999 and 2000; Engel, 2001; Hitch and others, 2002, 2003, 2004, 2005; U.S. Geological Survey, 2006b, 2007, 2008, 2009b, and 2010b). In the USGS annual reports, the results from water samples are reported by water year. A water year is defined as the 12-month period October 1, for any given year through September 30, of the following year. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. That is, the 12-month period ending September 30, 2009 is called the "2009" water year.

For this report, the samples selected for analysis were the latest available results in the designated time period for the network wells and for one randomly selected well in each of the well nests. The randomly selected wells in the well nests were E-EC1, E-V1, D-W3, D-T2, M-BC1, M-H1, P-A1, P-S1, and U-BA2.

Delta (δ) notation is used in this report to present the results of isotopic analysis of $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in nitrate and $^{15}\text{N}/^{14}\text{N}$ ratio in atmospheric nitrogen gas (N_2). Values of $\delta^{15}\text{N}$ in nitrate and in dissolved N_2 are reported in per mil relative to N_2 in the atmospheric air standard (AIR); values of $\delta^{18}\text{O}$ in nitrate are reported in per mil relative to the

Table 4. Laboratory analytical methods and field preservation procedures for water-quality constituents, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[μm , micrometer; CFCs, chlorofluorocarbons; USGS, U.S. Geological Survey; RCFC, Reston Chlorofluorocarbon Laboratory, Reston, Va.; GC, gas chromatography; mL, milliliter; TestAmerica, TestAmerica Laboratory, Denver, Colo.; USEPA, U.S. Environmental Protection Agency; °C, degrees Celsius; NWQL, National Water Quality Laboratory, Denver, Colo.; RSIL, Reston Stable Isotope Laboratory, Reston, Va.; GC/IRMS, gas chromatography/isotope-ratio mass spectrometer; OGRL, Organic Geochemistry Research Laboratory, Lawrence, Kans.; GC/MS, gas chromatography/mass spectrometry; HPLC/MS, high-performance liquid chromatography/mass spectrometry; NEWSC, Nebraska Water Science Center, Lincoln, Nebr.; <, less than]

Constituent or constituent group	Analyzing laboratory	Analytical method(s)	Reference(s), listed in publication order	Field preservation procedure(s)	Years samples collected
Physical properties	Analyzed onsite	Various methods	U.S. Geological Survey, variously dated	None.	1992–2009
Carbonate alkalinity	Analyzed onsite	Inflection point titration	U.S. Geological Survey, variously dated	Filter through 0.45- μm filter.	1992–2009
CFCs	USGS RCFC	Purge-and-trap GC with an electron capture detector	Busenberg and Plummer, 1992; U.S. Geological Survey, 2009a	Fill 62-mL borosilicate ampule; fuse ampule closed with a gas torch.	2000
Dissolved gases	USGS RCFC	GC with flame ionization or thermal conductivity detection	U.S. Geological Survey, 2006a	Fill 150-mL septum bottle with sample; in 2004 only, add two potassium hydroxide pellets; chill and maintain at temperature of groundwater.	2000, 2004
Explosives	TestAmerica	USEPA methods 8330 (also known as 8330a) and 8321a (modified from 8321b)	U.S. Environmental Protection Agency, 1986	Chill and maintain at 4°C.	2007–2009
Nutrients (nitrogen and phosphorus compounds)	USGS NWQL	Various methods	Fishman, 1993	Filter through 0.45- μm filter, chill, and maintain at 4°C.	1992–2009
Nitrogen and oxygen isotopes in nitrate	USGS RSIL	GC/IRMS	Sigman and others, 2001; Casciotti and others, 2002	Filter, chill, and maintain at 4°C.	2004
Nitrogen isotopes in dissolved nitrogen gas	USGS RSIL	GC/IRMS	Casciotti and others, 2002; Böhlke and others, 2003; Révész and Casciotti, 2007	Same as dissolved gases procedure (above).	2004
Pesticides and pesticide degradates	USGS NWQL and USGS OGRL	C-18 solid-phase extraction and capillary-column GC/MS; graphitized carbon-based solid-phase extraction and HPLC/MS	Sandstrom and others, 1994; Lee and others, 2002; Lee and Strahan, 2003	Filter through baked glass fiber filter, 0.7- μm nominal pore size, chill sample, and maintain at 4°C.	1992, 1995, 1999–2009
Pesticide screening	USGS NEWSC	Enzyme-linked immunosorbent assay	Abraxis Corporation, 2010a and 2010b	Filter through baked glass fiber filter, 0.7- μm nominal pore size, chill sample, and maintain at 4°C.	1992, 1995, 1999–2009
Major ions	USGS NWQL	Inductively coupled plasma	Fishman and Friedman, 1989; Fishman, 1993	Anions: filter through 0.45- μm filter, Cations: filter through 0.45- μm filter, acidify sample to pH <2 with nitric acid (HNO_3).	1992, 1999–2009
Trace elements, including natural uranium	USGS NWQL	Inductively coupled plasma, atomic absorption spectrometry	Fishman and Friedman, 1989; Fishman, 1993; Garbarino, 1999; Struzeski and others, 1996; Garbarino and Damrau, 2001; Garbarino and others, 2006	Filter through 0.45- μm filter, acidify sample to pH <2 with nitric acid (HNO_3).	1992, 2008 (for most constituents) and 1992, 1999–2009 (iron, manganese)
Radon	USGS NWQL	Liquid scintillation	Whittaker and others, 1989; American Society for Testing and Materials, 1998	20-mL glass vial filled with 10-mL mineral oil liquid scintillation cocktail and 10 mL of sample. Sample must be received at laboratory within 48 hours of collection.	1992, 2008
Volatile organic compounds	USGS NWQL	Purge and trap capillary column GC/MS	Connor and others, 1998	Completely fill vial with sample to exclude air bubbles, acidify sample to a pH <2, protect sample from sunlight, chill, and maintain at 4°C.	2007–2009

Vienna Standard Mean Ocean Water (VSMOW) standard. The general expression for the δ value uses the following equation (Kendall and Caldwell, 1998):

$$\delta_{std} = \left[\frac{R_{sample} - R_{standard}}{R_{standard}} \right] \times 1000, \quad (1)$$

where

- δ_{std} is the δ value relative to the standard (AIR or VSMOW),
- R_{sample} is the ratio of the rare (usually heavy) isotope to the abundant isotope (for example, $^{15}\text{N}/^{14}\text{N}$ or $^{18}\text{O}/^{16}\text{O}$) in the sample, and
- $R_{standard}$ is the ratio of the rare isotope to the abundant isotope in the standard.

A negative δ value indicates that the sample is depleted of the rare isotope relative to the standard; that is, the sample is isotopically “light.” A positive δ value indicates that the sample is enriched in the rare isotope relative to the standard; that is, the sample is isotopically “heavy.” Additional information on isotopes and their presence in the environment can be found in references such as Kendall and McDonnell (1998) and Clark and Fritz (1997).

Data-Analysis Procedures

Construction of Water-Table and Potentiometric-Surface Maps

Contour maps of the water-table altitude were constructed for the Elkhorn, Missouri, and Platte River Valley alluvial aquifers (fig. 2) using water levels typically measured in spring 2009, estimated river altitude, and a published map of the water table in the PMRNRD area for 1995 (University of Nebraska–Lincoln, Conservation and Survey Division, 2010b). If spring 2009 water levels were not available for a well measured by the PMRNRD or USGS, historical water levels for that well were used. The river altitude was estimated using a 10-m digital-elevation model along the river centerline; use of the 10-m digital-elevation model for estimated groundwater altitude (fig. 2) was considered appropriate because of the map scale and because of the relatively shallow river depth (U.S. Geological Survey and Nebraska Department of Natural Resources, 1998). Water-table-altitude contours were not constructed for the upland area alluvial aquifers because few water-level measurements in wells screened in the upland area alluvial aquifers were available, and there was inadequate information about the connection or lack of connection between the saturated parts of the upland area alluvial aquifers.

The Dakota aquifer is semiconfined or unconfined in most of the PMRNRD, except in the areas in Dakota and Thurston Counties where the Dakota aquifer is overlain by Late Cretaceous-age confining units (fig. 3). Because there are few recent measurements of water levels (where the aquifer is

unconfined) or hydraulic heads (where the aquifer is confined or semiconfined), a current potentiometric-surface map of the Dakota aquifer in the PMRNRD was not constructed for this report. Instead, a published map of the predevelopment potentiometric surface is shown in figure 3 along with the location of wells with recent (2009) depth-to-water measurements (Helgesen and others, 1993; U.S. Geological Survey, 2010a). These recent (2009) depth-to-water measurements do not indicate any changes to the Dakota aquifer’s potentiometric surface since predevelopment.

Depth to Water Estimates

For this report, depth to water for 2009 was estimated for sampled wells if water levels were not measured by USGS during sample collection or by PMRNRD personnel prior to or after the 2008 irrigation season and if there was information on the depth to top and bottom of the well’s screen(s) (appendix 1). The water levels for 2009 were estimated using either (1) the water level reported by the driller at the time the well was constructed on well registration forms (Nebraska Department of Natural Resources, 2010) or (2), if the driller did not report a water level at the time the well was constructed, water level was derived by subtracting the land-surface altitude from the water-level altitude interpolated from figures 2 and 3. Water levels measured by the driller at the time of well construction were the preferred estimate of water level in 2009 because that water level was measured, not estimated, and no large-scale water-level declines currently (2011) have been reported in the PMRNRD area (University of Nebraska–Lincoln, Conservation and Survey Division, 2009).

Conventions for Reporting Analytical Results

From 1992 to 1998, the NWQL used the Minimum Reporting Limit (MRL) convention for reporting most analytical results. In 1998, the NWQL began implementing a new convention for reporting analytical results, called the long-term method detection limit (LT-MDL) (Childress and others, 1999). With respect to the samples collected for this study, by 2008 NWQL was using (1) the LT-MDL convention for major ions, all nutrients except nitrite, trace elements, and volatile organic compounds, and (2) the MRL convention for nitrite and pesticides. NWQL uses a convention similar to MRL for ^{222}Rn activity.

Using the MRL-type convention, measured concentrations greater than the MRL generally are reported as an unqualified value. Concentrations less than the MRL are considered “censored” and are reported as “less than” the MRL value.

Using the LT-MDL convention, two concentration levels are used for reporting analytical results—the current method detection level (MDL) and the laboratory reporting level (LRL), which generally is a value equal to two times the MDL. The MDLs and LRLs differ among analytes and analytical methods. MDLs and LRLs are annually reevaluated by

the NWQL on the basis of laboratory spike-sample measurements and, therefore, can increase or decrease over time. The objective of the LT-MDL convention is to minimize both false positive and false negative errors in the analytical results. The MDL is determined from the standard deviation of long-term laboratory spiked-sample measurements and is set to the level at which false positive errors are minimized to no more than 1-percent probability. The LRL is set to the level at which false negative errors are minimized to no more than 1-percent probability and, as stated previously, is generally equal to twice the MDL.

Under the LT-MDL conventions, concentrations greater than the LRL and the smallest laboratory calibration standard are reported in USGS NWIS (U.S. Geological Survey, 2010a) as the measured value, not qualified with remark codes. A concentration smaller than the MDL is generally termed “censored” and reported in USGS NWIS (U.S. Geological Survey, 2010a) as “less than” the value of the LRL unless information-rich laboratory methods are used for the analysis. In this study, information-rich laboratory methods were used only for analysis of VOCs. Under the LT-MDL conventions, measured concentrations smaller than either the LRL or the smallest laboratory calibration standard but greater than the MDL are reported in USGS NWIS (U.S. Geological Survey, 2010a) as the measured value and qualified by the respective laboratory with a remark code of “E” for estimated. The measured concentration of nutrients, pesticides, and trace elements also will be qualified by the respective laboratory in USGS NWIS (U.S. Geological Survey, 2010a) with an “E” if the analysis did not meet the laboratory’s method-specific performance criteria for the method (Childress and others, 1999). For information-rich laboratory methods, the laboratory instruments can provide additional qualitative information about the concentration of the compound and concentrations less than the MDL can be reported in USGS NWIS (U.S. Geological Survey, 2010a) as the measured value, qualified with a remark code of “E” for estimated.

For samples requiring dilution because of interference or low sample volume, which for this study included four analyses for nitrite and three analyses for orthophosphate, the MRL (for nitrite) or LRL and MDL (for orthophosphate) values were multiplied by the dilution factor. For nitrite, concentrations less than the elevated MRL are reported as “less than” the elevated MRL value. For orthophosphate, concentrations of diluted sample analytes less than the elevated MDL are reported as “less than” the elevated LRL value, and concentrations less than the elevated LRL but greater than the elevated MDL are reported as the measured value with an “E” remark code.

Reporting conventions used by USGS laboratories other than NWQL differed but codes used to qualify the analytical results, such as the remark code, have the same meaning and value as those used by NWQL. The OGRL pesticide results are reported in USGS NWIS (U.S. Geological Survey, 2010a) using the MRL reporting convention. The USGS Reston Chlorofluorocarbon Laboratory (RCFC), Reston, Va., results for dissolved gases and CFCs are reported in USGS NWIS

(U.S. Geological Survey, 2010a) (1) without qualification, if the analytical results met RCFC’s method reporting criteria and (2) as null with an “U” remark code, if the analyte was analyzed for but not detected. The USGS Reston Stable Isotope Laboratory (RSIL), Reston, Va., reported stable isotope results in USGS NWIS (U.S. Geological Survey, 2010a) without qualification and consistent with precision and accuracy of the standards used in the analysis (Révész and Casciotti, 2007).

TestAmerica Laboratory in Denver, Colo., used a convention for reporting results of analyses for explosives that is similar to the LT-MDL convention. The TestAmerica analytical results in this study were all non-detect; these results were recoded to “less than” the LRL for the respective analyte and loaded into USGS NWIS (U.S. Geological Survey, 2010a).

Other remark codes used in this report to qualify analytical results are M, presence of analyte was verified but could not be quantified; S, most probable value; and V, results likely affected by contamination. The remark code M was most often used for dissolved oxygen results measured on site; the value was assigned when the dissolved oxygen concentration was less than the concentration that can be reliably detected by the dissolved oxygen meter. The remark code S was used to qualify specific conductance results that are measured on site; this remark code was used when there were operational problems with the respective meter. The remark code V was used when the analyte was detected in the QC samples at a similar concentration to the concentration detected in the environmental samples; remark code V was used to qualify results for two trace elements—copper and mercury.

Data Treatment

For this report, the analytical results from 1992 to 2009 were “treated” to standardize the quantification of analytical results and qualifiers prior to calculating statistical results and preparing the tables and figures in this report for the study period; however, the analytical results and qualifiers in appendix 2 are not “treated” but are listed as stored in USGS NWIS (U.S. Geological Survey, 2010a). Treatment was necessary, with the statistical analysis procedures used in this study, prior to analysis because the results for most analytes from 1992 to 2009 incorporated different reporting conventions (MRL, LT-MDL, or other) and different MRL or MDL and LRL values. Without treatment, many of these results, as stored in USGS NWIS (U.S. Geological Survey, 2010a), are not statistically comparable using the selected statistical methods (Helsel, 2005a). The treatment approach was to redefine the stored value and the associated remark code for the 1992 to 2009 and 2007 to 2009 periods in USGS NWIS (U.S. Geological Survey, 2010a) by first determining maximum MRL or LRL in each time period. This determination disregarded the analytical method and did not include elevated MRLs or LRLs resulting from dilutions of the original sample. The treated results for the 1992 to 2009 and 2007 to 2009 periods for a given analyte were derived as follows:

- If the original analytical result was qualified with a “less than” remark code, the treated analytical result was encoded as less than the corresponding maximum MRL or LRL;
- If either (1) the original analytical result was not qualified and was less than the maximum MRL or LRL or (2) the original analytical result was qualified with a remark code of E or V and was less than or equal to the maximum MRL or LRL, the treated analytical result was encoded as less than the corresponding maximum MRL or LRL;
- If the original result has censored quantification (for example, the remark code was M), the treated analytical result was encoded as less than the corresponding maximum MRL or LRL or the minimum unqualified concentrations for this analyte;
- If the original result was determined after diluting the sample and was qualified as “less than” an elevated MRL or LRL, the treated analytical result was encoded as less than the corresponding maximum MRL or LRL for undiluted results; and
- If either (1) the original remark code was blank and the original result was greater than or equal to the maximum MRL or LRL or (2) the remark code was E or V and the original result was greater than the maximum LRL, the treated analytical result was encoded as the original result with no qualification.

The authors assumed that no errors were introduced in applying the treatment described above.

Statistical Methods

Statistical measures calculated for this report include summary statistics (median and percentile concentrations or values) and correlation analysis using the following methods.

- The regression-on-order statistics method (Helsel and Cohn, 1988; David Lorenz, U.S. Geological Survey, written commun., March 2010) was used to calculate summary statistics for sets of treated analytical results with censored values. For example, the regression-on-order statistics method was used to determine the median concentration of nitrate-N during 1992–2009.
- The generalized Wilcoxon test (David Lorenz, U.S. Geological Survey, written commun., March 2010) was performed on flipped data (Helsel, 2005b, p. 17, 145–150) to compare groups of treated analytical results with censored values to each other. For example, the generalized Wilcoxon test was used to compare iron results from the Dakota aquifer samples to iron results from the Elkhorn River Valley alluvial aquifer samples.

- The Kendall *tau* test with the Akritas-Theil-Sen slope estimate (Akritas and others, 1995; David Lorenz, U.S. Geological Survey, written commun., March 2010) was used to test correlations for sets with censored values (Helsel, 2005b, p. 189–192 and 212–215). For example, the Kendall *tau* test was used to determine whether there was a significant trend in summer-to-fall nitrate-N concentrations for each year from 1999 to 2009 in a given well in the well nests. The value of *tau* will be approximately zero if the correlates are independent. *Tau* will be greater than zero for a positive correlation and *tau* will be less than zero for a negative correlation.
- Nonparametric methods were used to calculate summary statistics for data sets without censored values and to test whether there was a significant relation between groups of analytical results. The tests used to determine a relation between groups of results were (1) Spearman’s correlation to compare two paired groups or (2) the Kruskal-Wallis rank-sum test of differences to compare more than two groups (Helsel and Hirsch, 1992).

In this report, statistical-test results were evaluated using a significance level of 95 percent ($\alpha = 0.05$). A significance level is the probability that the test conclusion is accurate for the populations under consideration. The *p*-value associated with a particular test-statistic result is the probability of obtaining a test statistic equal to or more unlikely than the computed value from repeated sampling when the null hypothesis is true. A typical null hypothesis is that the difference in the medians of the two populations is zero. A *p*-value of 0.05 or less was used in this report to assert, with 95 percent confidence, that there is a statistically significant difference between populations or that two groups are significantly correlated.

Water-Quality Standards

Analyte concentrations in groundwater may be of concern when they approach levels that may be harmful to human health. Several types of standards were used to identify analyte concentrations of potential concern. In this report, the analyte results for groundwater in the PMRNRD are grouped into the following categories: groundwater-age dating, dissolved gases, explosives, major ions, nutrients, pesticides, ²²²radon, stable isotopes, trace elements, and VOCs. The analytes included in each category are listed in appendixes 3 through 7, along with the standard(s) currently (2011) associated with each analyte. The number of samples per well is listed in appendix 8.

The following types of groundwater-quality standards are compared to PMRNRD water-quality results in this report:

Abbreviation	Description	Comments
MCL	Maximum Contaminant Level	U.S. Environmental Protection Agency (USEPA) determines MCLs for selected analytes. MCLs are legally enforceable standards for the maximum permissible level of an analyte in drinking water that is delivered by a public water system (U.S. Environmental Protection Agency, 2009a).
Title 118	Nebraska Title-118 standard	Nebraska Department of Environmental Quality sets standards for selected analytes. Nebraska Title-118 standards, which generally are the same as the USEPA MCLs, are the groundwater-quality standards used by the Nebraska Department of Environmental Quality, when applicable, in administration of regulatory programs related to groundwater other than groundwater delivered by public water systems as drinking water (Nebraska Department of Environmental Quality, 2006).
AMCL	Alternative MCL	AMCLs are legally enforceable standards set by USEPA for the maximum permissible level of analytes in drinking water that is delivered by a public water system; the AMCL is applicable only in specific circumstances. The only AMCL relevant to this report is the proposed AMCL for ²²² radon, which is 4,000 picocuries per liter (pCi/L) for public water supplies that have a program to limit radon exposure (U.S. Environmental Protection Agency, 2009a and 2010b).
SDWR	Secondary Drinking Water Regulation	SDWRs are nonenforceable Federal guidelines for drinking water set by the USEPA and relate to the maximum concentration of an analyte to avoid adverse cosmetic or aesthetic effects. Possible cosmetic effects are tooth or skin discoloration; possible aesthetic effects are water with undesirable taste, odor, or color (U.S. Environmental Protection Agency, 2009a).
DWAT	Drinking Water Advisory Table	DWATs are nonregulatory upper concentration limits for analytes in drinking water. These limits are set by the USEPA at a level that is unlikely to cause adverse effects on health or aesthetic properties. A DWAT-Low sodium diet suggests maximum concentrations for individuals on a restricted sodium diet (U.S. Environmental Protection Agency, 2009a).
TT Action Level	Treatment Technique Action Level	TT Action Levels are legally enforceable standards for copper and lead concentration in drinking water delivered to the consumer and are applicable to public water systems only. If more than 10 percent of the sampled tap water exceeds the TT Action Level, the public water system must take corrective steps (U.S. Environmental Protection Agency, 2009b).
LTHA	Lifetime Health Advisory level	Nonenforceable USEPA guideline for the maximum concentration of a constituent in drinking water that is not expected to cause any adverse noncarcinogenic effects after a lifetime of exposure. LTHAs are calculated assuming consumption of 2 liters of water per day over a 70-year lifetime by a 154-pound (70-kilogram) adult and that 20 percent of a person's exposure to this constituent comes from drinking water (U.S. Environmental Protection Agency, 2009a).
10 ⁻⁴ CR	10 ⁻⁴ Cancer Risk	Nonenforceable USEPA guideline for the concentration of a constituent in drinking water that corresponds to an excess estimated lifetime-cancer risk of 1 in 10,000 (U.S. Environmental Protection Agency, 2009a).
DWEL	Drinking Water Equivalent Level	Nonenforceable USEPA guideline for lifetime-exposure concentration that will not result in adverse, non-cancer health effects. DWEL assumes all exposure to the constituent is from drinking water (U.S. Environmental Protection Agency, 2009a).

Age Dating of Groundwater Using Chlorofluorocarbons

CFCs were used to estimate the apparent recharge age of groundwater in the PMRNRD. The apparent recharge age, called groundwater age in this report, refers to the time elapsed since recharge and isolation of the newly recharged water from the soil atmosphere. CFC age-dating techniques estimate groundwater age on the basis of increasing concentrations of three CFC gases [dichlorodifluoromethane (CFC-12), trichlorofluoromethane (CFC-11), and trichlorotrifluoroethane (CFC-113)] introduced into the North American air from the 1930s to the 1990s. During that period, CFCs were used as refrigerants, aerosol propellants, cleaning agents, solvents, and blowing agents in the production of foam, rubber, and plastics. CFCs used in these processes eventually leaked into the atmosphere at a nearly linear rate (fig. 9) and subsequently were transported into the hydrosphere where they could be used as environmental tracers in age-dating groundwater (Plummer and Busenberg, 2000). The concentrations of these three compounds in groundwater samples provide three independent estimates of apparent recharge or modeled groundwater age. Results of the CFC analyses were examined using two flow or mixing scenarios—piston flow (water moving as a slug) and binary mixing (old water mixed with young water). Additional information on the use of CFCs to date groundwater can be found in text books such as Clark and Fritz (1997).

Dissolution of gases (nitrogen, argon, methane, carbon dioxide, and oxygen) produces measureable gas concentrations in groundwater, which, in turn, allows for calculation of estimated excess air concentrations, recharge temperature, and recharge elevation. In addition, concentrations of dissolved oxygen, excess dissolved nitrogen, or dissolved methane can be indicators of reducing and denitrifying conditions in the

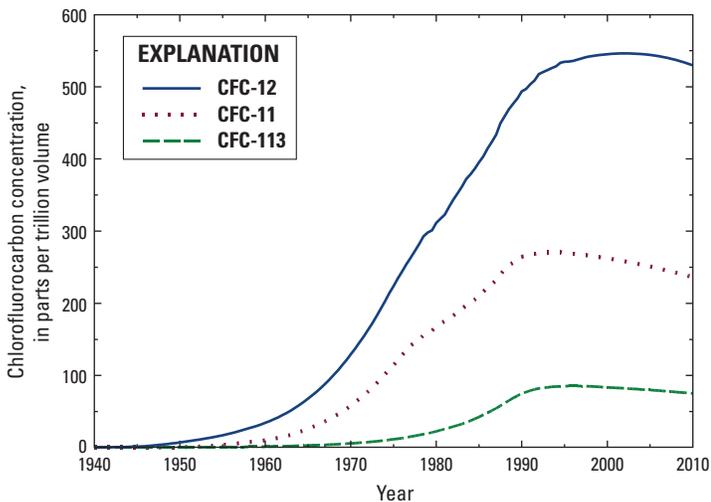


Figure 9. Atmospheric concentrations of chlorofluorocarbons (CFCs) in North American air, 1940–2010. (Modified from U.S. Geological Survey, 2011).

aquifer. Analyses of samples for dissolved gases were completed at the RCFC Laboratory (Peggy Widman, U.S. Geological Survey, written commun., 2001). Dissolved gases were used to help determine groundwater age from CFC concentrations by constraining the conditions of water temperature and elevation at the time of recharge.

Reduction-Oxidation Reactions

To analyze the types of reduction-oxidation (redox) reactions occurring in groundwater in the PMRNRD over time, the samples collected from 1999 to 2009 in each of the wells in well nests that had results for dissolved oxygen, nitrate, manganese, iron, and sulfate were selected. For each well in the well nests, there were 4 to 12 samples for each water year from 1999 to 2009 that satisfied these criteria. The concentrations of these constituents from each sample were input to a worksheet used to predict the prevalent redox processes for each sample as described by Jurgens and others (2009).

Denitrification

Estimated excess nitrogen, which is calculated from estimated recharge temperature and concentrations of dissolved gases, can be used to estimate the initial nitrate value, prior to denitrification, using the following equation (McMahon and others, 2007):

$$[NO_3^-]_{initial} = [NO_3^-]_{measured} + 2 \times [excess N_2], \quad (2)$$

where

$$[NO_3^-] \text{ and } [excess N_2] \text{ are expressed in micromoles per liter } \left(\frac{\mu M}{L} \right).$$

The process of denitrification was quantified by calculating the fraction (f) of the initial NO_3^- in recharge that has been removed by denitrification using the following equation (McMahon and others, 2007):

$$f = 1 - \frac{[NO_3^-]_{measured}}{[NO_3^-]_{initial}}. \quad (3)$$

Quality Assurance and Quality Control

QC samples collected for the PMRNRD study include source-solution blanks, field blanks, equipment blanks, field replicates, laboratory matrix spikes, and reference samples. QC samples were collected to evaluate evidence of contamination of the samples and bias and variability of the water-chemistry data that may have originated during collecting, processing, storing, or analyzing the samples.

Field-Blank, Equipment-Blank, and Source-Solution Blank Samples

Field-blank samples were collected to determine the occurrence and magnitude of sample contamination during sample collection, processing, and analysis. Blank samples were collected using water that was specially prepared and certified to be free of relevant categories of constituents (for example, inorganic-free or organic-free blank water). Blank samples were analyzed for nutrients, pesticides, major ions, trace elements, VOCs, and explosives. Because it is not presently (2012) possible to prepare blank water that is certifiably free of CFCs, dissolved gases, nitrogen isotopes, or radon, no field- or equipment-blanks samples were collected for analysis for these constituents.

Field-blank sample results for constituents with detections are summarized in table 5. Median concentrations in blank samples indicated that sample contamination generally was minimal for all constituents. Maximum concentrations in blank samples for some major ions—silica, sodium, and sulfate—and some trace elements—cadmium, iron, lead, manganese, mercury, and silver—were within an order of magnitude or exceeded the lowest environmental-sample concentrations. These results indicate concentrations in environmental samples collected in the same time period as these blanks should be used with caution. Maximum concentrations in blank samples for some trace elements—cadmium, lead, and silver—were within an order of magnitude or exceeded the highest environmental-sample concentrations. Results for these blanks were further investigated using equipment-blank samples to determine the likely source of contamination in the sample-collection or -processing procedures. This investigation indicated that, in 2008, a possible source of the contamination was the sample tubing used to deliver water from the pump to the sample preservation chamber.

Replicate Samples

Replicate samples are two (or more) environmental samples collected sequentially for duplicate analysis of approximately the same sample water. Replicate samples were collected to determine the variability of the data resulting from sampling and analytical procedures. The relative percent difference (RPD) between concentrations of paired replicate samples was calculated (table 6) using the formula

$$RPD = \frac{\left| \frac{\text{sample 1} - \text{sample 2}}{\frac{\text{sample 1} + \text{sample 2}}{2}} \right|}{2} \times 100. \quad (4)$$

When there is no variability between the paired analyses, the RPD is zero percent. The RPD was not calculated if one or both of the paired replicate concentrations were less than the maximum LRL or quantified as an estimated value by the laboratory.

There were 48 individual constituents with paired environmental and replicate samples (table 6). The median RPD by constituent group for environmental samples ranged from 0 to 16 percent. The constituent groups that had the largest median RPDs were stable isotopes (16 percent) and pesticides (8 percent). Stable isotope replicates were collected only in 2004. A possible reason for the large variation in the stable isotopes replicability in 2004 could be inadequate pumping of the wells in well nests prior to sampling (J.K. Böhlke, U.S. Geological Survey, written commun., 2005). Pesticide analysis generally resulted in very small [less than 1 microgram per liter ($\mu\text{g/L}$)] concentrations. For very small concentrations, small differences in replicates can cause large calculated variability. For the constituent groups other than stable isotopes and pesticides, the individual analytes with the largest average RPDs were silver (40 percent), nitrite (38 percent), methane (27 percent), dissolved oxygen (16 percent), and orthophosphate (12 percent). The average RPDs for individual analytes indicated an acceptable amount of variability between paired environmental and replicate samples.

Laboratory Matrix Spikes

Laboratory matrix-spike (LMS) results are used to quantify the imprecision or bias (apparent gain or loss of analytes) resulting from groundwater properties (that is, matrix effects) or laboratory procedures. LMSs are not intended to quantify the apparent gain or loss of analytes during sample holding time or from field procedures. A spike recovery of about 100 percent indicates minimal matrix interference or errors in laboratory procedures. A spike recovery of less than or greater than 100 percent indicates matrix interference or errors in laboratory procedures. In this study, LMS samples were used for QC of analyses of explosive and pesticide compounds. When a second LMS sample was collected, it was referred to as a laboratory matrix-spike duplicate (LMSD).

The LMS and LMSD samples were shipped to the laboratory concurrently with the environmental samples. Prior to analysis, the laboratory added a specified amount of the target analytes to the designated LMS and LMSD sample bottles and generally analyzed these QC sample(s) and the associated environmental samples in the same “batch” (run cycle of the analytical instrument). In 2008, samples for LMS and LMSD were submitted for one site (E-V1) for explosive analysis, and samples for LMS were submitted for one site (E-V3) for pesticide analysis. In 2009, samples for LMS and LMSD were submitted for one site (P-A3) for pesticide analysis. The RPDs and percent recoveries for these laboratory matrix spikes are summarized in table 6.

In 2008, percent recovery for explosives in the LMS ranged from 56 to 160 percent; the RPD between results in the LMS and LMSD samples were 0 to 30 percent (table 6). The results for 1,3,5-trinitrohexahydro-1,3,5-triazine, also called royal demolition explosive (RDX), which is the explosive analyte that is most widespread at the former Nebraska Ordnance Plant (NOP) about 6 mi west of Gretna, Nebr. (U.S. Army

Table 5. Constituents detected in field-blank samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[LRL, laboratory reporting level; MDL, method detection level; µg/L, micrograms per liter; --, no data or not calculated; E, estimated; mg/L, milligrams per liter; Nitrate-N, nitrate plus nitrite as nitrogen; <, less than]

Constituent	Parameter code	Number of field-blank samples	Maximum LRL, 1992–2009	Number of detections above the maximum LRL, 1992–2009	Number of detections at or above the LRL or MDL at the time the sample was analyzed	Median concentration ¹ of detected analytes in field-blank samples	Maximum concentration ¹ in field-blank samples	Range of dates for blank samples	Range of concentrations in environmental samples ¹	Range of dates for environmental samples
Pesticide compounds (concentrations in µg/L)										
Atrazine	39632	11	0.05	1	1	--	0.05	1992, 1995, 2001–2009	E0.01–1.8	1992, 1995, 1999–2009
Nutrients (concentrations in mg/L)										
Ammonia	00608	60	0.04	0	5	E0.007	E0.012	1995, 1999–2009	E0.005–1.81	1995, 1999–2009
Nitrate-N	00631	150	.06	0	3	E.03	E.04	1992–1995, 1998–2009	E0.02–74.6	1992–2009
Ortho-phosphate	00671	60	.02	0	3	E.005	E.005	1995, 1999–2009	0.007–1.0	1995, 1999–2009
Major ions (concentrations in mg/L)										
Calcium	00915	35	0.04	5	19	E0.02	0	1992, 1999–2009	42.3–210	1992, 1999–2009
Magnesium	00925	35	.02	2	5	E.008	0	1992, 1999–2009	6.34–57.3	1992, 1999–2009
Potassium	00935	25	.16	0	1	--	E0.01	1992, 1999–2009	1.8–28.5	1992, 1999–2009
Silica	00955	35	.5	1	1	--	0	1992, 1999–2009	9.1–38	1992, 1999–2009
Sodium	00930	35	.2	1	3	E.09	0	1992, 1999–2009	7.6–140	1992, 1999–2009
Sulfate	00945	35	.31	0	2	--	0	1992, 1999–2009	0.8–590	1992, 1999–2009
Trace elements (concentrations in µg/L)										
Boron	01020	4	10	0	3	1.2	1.2	1992, 2008	30–730	1992, 2008
Cadmium	01025	4	1	1	1	--	0	1992, 2008	E0.02–3	1992, 2008
Iron	01046	35	10	1	1	--	0	1992, 1999–2009	E2–17,000	1992, 1999–2009
Lead	01049	4	10	0	1	--	5.47	1992, 2008	E0.04–1.16	1992, 2008
Manganese	01056	35	3.2	1	8	1.1	0	1992, 1999–2009	<0.2–2,300	1992, 1999–2009
Mercury	71890	3	.01	2	2	.014	.03	2008	E0.007–0.077	2008
Silver	01075	4	1	1	1	--	0	1992, 2008	<0.1–3	1992, 2008
Strontium	01080	4	.8	1	1	--	0	1992, 2008	220–4,500	1992, 2008

¹Summarized concentrations were those at or above the laboratory reporting or method detection level at the time the sample was analyzed.

Table 6. Summary of relative percent differences for replicate samples and percent recoveries for laboratory matrix-spike and reference samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[RPD, relative percent difference; --, not calculated; LMS, laboratory matrix spike; LMSD, laboratory matrix-spike duplicate]

Compound class (number of analytes with data ¹)	Range of dates, by water year ² , with replicate samples	Number of replicated or spiked values ¹	Minimum	Value of indicated percentile ¹						Maximum
				10	25	50	75	90	95	
Comparison of environmental and replicate sample results (RPD, in percent)										
Dissolved gases (5 analytes)	2000, 2004	67	0	0	0	1	2	24	62	130
Explosives (0 analytes)	2008–2009	--	--	--	--	--	--	--	--	--
Major ions (10 analytes)	1992, 1999–2009	346	0	0	0	1	3	6	9	120
Nutrients (4 analytes)	1992–1994, 1997–2009	151	0	0	0	1	5	22	40	130
Pesticides (14 analytes)	2002–2009	25	0	0	1	8	22	57	67	71
²²² Radon (1 analyte)	2008	4	0	0	0	0	6	11	11	11
Stable isotopes (3 analytes)	2004	6	4	4	8	16	30	47	47	47
Trace elements (11 analytes)	1992, 1999–2009	91	0	0	0	1	4	7	10	56
Volatile organic compounds (VOCs) (0 analytes)	2008–2009	--	--	--	--	--	--	--	--	--
Comparison of LMS and LMSD sample results (RPD, in percent)										
Pesticides and pesticide degradates (22 analytes)	2008–2009	22	4	7	30	48	61	71	80	89
Explosives (16 analytes)	2008	16	0	7	21	23	25	29	30	30
Recovery of measured spike amount in LMS samples (in percent)										
Pesticides and pesticide degradates (54 analytes)	2008–2009	53	39	64	83	92	110	120	140	220
Explosives (16 analytes)	2008	16	56	76	100	120	120	140	160	160
Comparison of reference-sample results from method 8330 and method 8321a analysis (RPD, in percent)										
Explosives (13 analytes)	2008	13	6	6	12	18	25	32	39	39
Recovery of measured reference amount from method 8330 and method 8321a analysis (in percent)										
Explosives, method 8330 (13 analytes)	2008	13	86	89	100	110	120	130	150	150
Explosives, method 8321a (13 analytes)	2008	13	72	78	94	97	100	110	110	110

¹Percent difference was not calculated, and the replicate was not included in the table if the laboratory results of either the environmental or replicate sample were qualified with remark code “E” or “<.”

²Water year is the 12-month period beginning October 1 and ending September 30. It is designated by the year in which it ends.

Corp of Engineers, 2008), were percent recoveries of 113 and 89 for the LMS and LMSD, respectively, and RPD of 24. These LMS and LMSD results for RDX were considered acceptable, and qualifying comments were not recommended for RDX (Carl Schlosslin, Analytical Quality Associates, Inc., Albuquerque, N. Mex., written commun., 2008). The LMS and LMSD results for explosives were used to annotate the analytical results with comments to indicate the precision and accuracy of the results, but they were not used to disqualify or modify analytical results included in this study because all environmental results for the explosive compounds were non-detects and, therefore, were not subject to statistical analysis.

In 2008 and 2009, the percent recoveries for the pesticide analytes in the LMS samples ranged from 39 to 220 percent.

In 2009, the RPD for the pesticide analytes in the LMS and LMSD samples ranged from 4 to 89 percent (table 6). The LMS and LMSD results for pesticides were used to indicate the precision and accuracy of the results, but they were not used to disqualify or modify analytical results included in this study.

Reference Samples

A reference sample and associated replicate were used in 2008 to indicate the precision and accuracy of laboratory analytical procedures for analysis of explosive analytes. The concentration of each analyte in the reference sample and

associated replicate was certified by the supplier to range from 0.30 µg/L for RDX to 1.87 µg/L for 2-nitrotoluene (Heidi M. Senft, Environmental Resource Associates, Denver, Colo., written commun., 2008). The reference sample and associated replicate were submitted with the environmental samples for one site in 2008. The reference sample was analyzed using USEPA method 8330, the standard USEPA method for explosives, and the replicate sample was analyzed using USEPA method 8321a. All environmental samples were analyzed using USEPA method 8330, and one environmental sample was also analyzed using method 8321a. A reference sample recovery result of about 100 percent indicates that (1) there was minimal compound degradation from the time the sample was certified until the sample was analyzed and (2) the laboratory's analysis procedures were accurate and precise.

The replication differences in the results for the reference sample and associated replicate, and the percent recoveries for the reference sample and associated replicate, are summarized in table 6. The median percent recovery values for all explosive compounds in the reference sample were 110 percent (method 8330) and 97 percent (method 8321a). The percent recovery of each explosive compound ranged from 86 to 150 percent with method 8330, and 72 to 110 percent with method 8321a. The maximum RPD between the two methods was 39 percent (table 6) for analysis of RDX. The analytical results for RDX were 0.46 µg/L using method 8330 and 0.31 µg/L using method 8321a.

Groundwater Altitude

A map of the water-table-altitude contours was created for the Elkhorn, Missouri, and Platte River Valley alluvial aquifers using water levels measured in spring 2009, estimated river altitude, and a published map of the water table in the PMRNRD area for 1995 (fig. 2). Because of insufficient data, water-table-altitude contours were not created for the upland area alluvial aquifers, and a current potentiometric-surface map was not created for the Dakota aquifer (fig. 3). In the PMRNRD, groundwater altitude, relative to the NGVD 29 datum, ranged from about 1,080 ft to 1,180 ft in the Elkhorn River Valley alluvial aquifer and from about 960 ft to 1,080 ft in the Missouri River Valley and Platte River Valley alluvial aquifers. Groundwater flow generally is toward or parallel to the rivers. In the PMRNRD, the estimated altitude of the potentiometric surface of the Dakota aquifer, predevelopment, ranged from about 1,100 ft to 1,200 ft. Groundwater flow in the Dakota aquifer is generally toward the east.

Groundwater velocity can be estimated using groundwater gradient, horizontal hydraulic conductivity, and effective porosity (Freeze and Cherry, 1979). Groundwater gradient was estimated for each aquifer using figures 2 and 3, except because of lack of data, the upland area alluvial aquifers.

Groundwater gradients were about 5.0 feet per mile (ft/mi) for the Dakota aquifer, 5.3 ft/mi for the Elkhorn River Valley

alluvial aquifer, 3.1 ft/mi for the Missouri River Valley alluvial aquifer, and 5.7 ft/mi for the Platte River Valley alluvial aquifer. Horizontal hydraulic conductivity and effective porosity were estimated to be 25 feet per day (ft/d) and 0.15 (dimensionless), respectively, for the Dakota aquifer (Helgesen and others, 1993); 150 ft/d and 0.15 (dimensionless), respectively, for the Elkhorn River Valley alluvial aquifer (Gutentag and others, 1984); and 700 ft/d and 0.17 (dimensionless), respectively, for a section of the Missouri River Valley alluvial aquifer downgradient from the PMRNRD (Emmett and Jeffery, 1969; Smith and Richards, 2008). Because the lithologic descriptions of the Missouri and Platte River Valleys alluvial aquifers in the PMRNRD are similar to that of the Elkhorn River Valley alluvial aquifer (table 1), for the purpose of this study, horizontal hydraulic conductivity and effective porosity for the Missouri and Platte River Valleys alluvial aquifers were assumed to be the same as those for the Elkhorn River Valley alluvial aquifer. Groundwater velocity was estimated as 0.2 ft/d for the Dakota aquifer, 1.0 ft/d for the Elkhorn and Platte River Valleys alluvial aquifers, and 0.6 ft/d for the Missouri River Valley alluvial aquifer.

Groundwater Age

Samples analyzed for both CFCs and dissolved gases (appendix 7) were collected from 15 wells in well nests in June 2000 (appendix 8). Results for dissolved gases, including dissolved oxygen concentrations less than 0.5 milligrams per liter (mg/L); the presence of methane; or the presence of excess nitrogen gas indicate that anoxic or reducing conditions were present in all samples, except the sample from well P-S1 (table 7). Reducing conditions could result in the degradation of CFC-11 and CFC-113, but reducing conditions typically do not greatly affect the concentration of CFC-12 (Plummer and Busenberg, 2000); therefore, where appropriate, CFC-12 concentrations are given more weight in the age-dating analysis.

Groundwater ages (as of 2000) ranged from early 1960s to early 1980s in 3 samples from the Dakota aquifer, early 1960s to 1970s in 3 samples from the Elkhorn River Valley alluvial aquifer, older than 1940 and late 1960s to early 1970s in 3 samples from the Missouri River Valley alluvial aquifer, mid-to-late 1950s and early-to-mid 1970s in 5 samples from the Platte River Valley alluvial aquifer, and early 1970s in 1 sample from one of the upland area alluvial aquifers (table 7). As expected, groundwater age in the shallow well of a given well nest was approximately the same or younger than water from the deepest well from the same well nest. These results for the Elkhorn and Platte River Valleys alluvial aquifers are consistent with age-dating result from tritium analysis of samples collected from 2002 to 2004 in the eastern part of what is termed the Platte River Valley hydrogeologic unit of the High Plains aquifer (Stanton and Qi, 2007). If all of these wells were resampled for CFCs currently (2011), the

Table 7. Analytical results for dissolved gases and chlorofluorocarbons in samples collected in 2000 and calculated results associated with determining the apparent age of groundwater using chlorofluorocarbons, Papio-Missouri River Natural Resources District, eastern Nebraska.

[All dates calculated from month and year of sample collection. mg/L, milligram per liter; °C, degrees Celcius; N₂, nitrogen gas; CFC, chlorofluorocarbon; pptv, part per trillion by volume; U, material specifically analyzed for but not detected; PD, concentration of one CFC tracer less than expected by other data, indicating sample probably degraded for the purposes of age dating]

Field identifier (fig. 8)	Sample date (month/ day/ year)	Dissolved gases		Calculated from dissolved gases		Calculated atmospheric mixing ratio corrected for excess air and recharge temperature			Apparent age from CFC results
		Oxygen, field, mg/L	Methane, mg/L	Recharge temperature (°C)	Excess N ₂ (mg/L)	CFC-11 (pptv)	CFC-12 (pptv)	CFC-113 (pptv)	
Dakota aquifer									
D-T1	6/14/2000	0.1	U	6	2	17	81	4	Mid-1960s
D-T3	6/14/2000	8.5	U	9	1	PD	309	33	Early 1980s
D-W3	6/13/2000	.6	U	7	2	12	50	3	Early to mid-1960s
Elkhorn River Valley alluvial aquifer									
E-EC2	6/15/2000	0.5	U	14	10	PD	108	4	Late 1960s to 1970s
E-V1	6/15/2000	.1	U	10	3	PD	81	2	Early to mid-1960s
E-V3	6/15/2000	.5	U	18	13	PD	49	0	Early to mid-1960s
Missouri River Valley alluvial aquifer									
M-BC3	6/15/2000	1.1	U	8	3	PD	97	PD	Late 1960s
M-H1	6/13/2000	.1	U	5	3	0	0	0	Older than 1940
M-H3	6/13/2000	2.4	U	11	2	PD	148	0	Early 1970s
Platte River Valley alluvial aquifer									
P-A1	5/31/2000	0.7	0.039	12	0	7	18	0	Mid-1950s
P-A2	6/12/2000	.8	.030	14	0	2	21	0	Mid-1950s; possible mixture
P-A3	6/12/2000	.6	.016	12	2	7	34	0	Mid-to-late 1950s; possible mixture
P-S1	6/12/2000	6.5	U	12	0	147	190	9	Early 1970s
P-S3	6/12/2000	3.5	U	14	5	104	136	10	Early to mid-1970s
Upland area alluvial aquifers									
U-BA1	6/14/2000	4.2	U	8	1	34	169	25	Early 1970s or possible mixture

groundwater ages might be slightly younger than measured in 2000 because at least a portion of the current samples would be from water that formerly was upgradient and, therefore, includes more recently recharged water than did the water samples collected in 2000.

Groundwater Quality

From 1992 to 2009, groundwater samples were collected from 217 wells (191 network wells and 26 wells in well nests) in the PMRNRD for analysis of 36 analytes classified as major ions, nutrients, radionuclides, and trace elements (appendix 3), 71 analytes classified as pesticides and pesticide degradates (appendix 4), 85 analytes classified as VOCs (appendix 5), 16 analytes classified as explosives compounds (appendix 6), and 3 stable isotopes ratios (appendix 7). All environmental sample results are provided in appendix 2.

Depth to Water and Well Characteristics

The median depth to water in 2009 for all sampled network wells and for one randomly selected well in each of the well nests was 15 ft (table 8). The median depth to water was greater in the upland area alluvial aquifers than in the other aquifers (fig. 10A). Well characteristics including depth to the top of the uppermost screened interval, screen length, and well depth were compiled, if available, for the sampled wells generally prior to the first time the well was sampled (appendix 1). For all sampled network wells and for one randomly selected well in each of the well nests, the median depth to the top of the uppermost screen was 61 ft (table 8); the median depth to the top of the uppermost screen was greater for wells in the Dakota aquifer than for the other aquifers (fig. 10B). For all sampled network wells and for one randomly selected well in each of the well nests, the median well depth was 95 ft (table 8); the median well depth was greater in the Dakota aquifer than in the other aquifers (fig. 10D).

Table 8. Summary statistics for well characteristics and depth to water in selected wells and field measurements from the most recent summer-to-fall samples from selected wells, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[All depths in feet below land surface. ft, feet; mg/L, milligrams per liter; <, less than; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; $^{\circ}\text{C}$, degrees Celsius; Well construction information from Nebraska Department of Natural Resources (2010)]

Characteristic or property	Number of wells or samples with information	Minimum	Value at percentile indicated					Maximum
			10th	25th	50th	75th	90th	
Well characteristics and depth to water for all sampled network wells and for one randomly selected well in each well nest								
Depth to water, ft, 2009	167	2	6	9	15	38	128	250
Depth to top of uppermost screened interval, ft	149	9	19	36	61	104	198	535
Screen length, ft	149	5	8	10	28	40	55	91
Well depth, ft	182	26	46	62	95	149	247	565
Field measurements from the most recent summer-to-fall samples from the network wells and from one randomly selected well in each well nest								
pH, standard units	195	6.6	6.9	7.0	7.1	7.3	7.6	8.0
Dissolved oxygen, mg/L	191	<.1	<.1	.1	.9	4.8	7.2	15.3
Specific conductance, $\mu\text{S}/\text{cm}$ at 25°C	193	342	484	541	658	860	1,200	1,800
Water temperature, $^{\circ}\text{C}$	196	9.0	11.6	12.0	12.5	13.5	15.0	24.0

Field Measurements

Measurements of pH, dissolved oxygen, specific conductance, and water temperature were made onsite prior to sampling. The field measurement results for pH, dissolved oxygen, specific conductance, and water temperature in the most recent summer-to-fall samples in the network wells and in one randomly selected well in each of the well nests from 1992 to 2009 when nitrates were also measured (hereafter referred to as the field-measurements samples, 1992 to 2009) are discussed below.

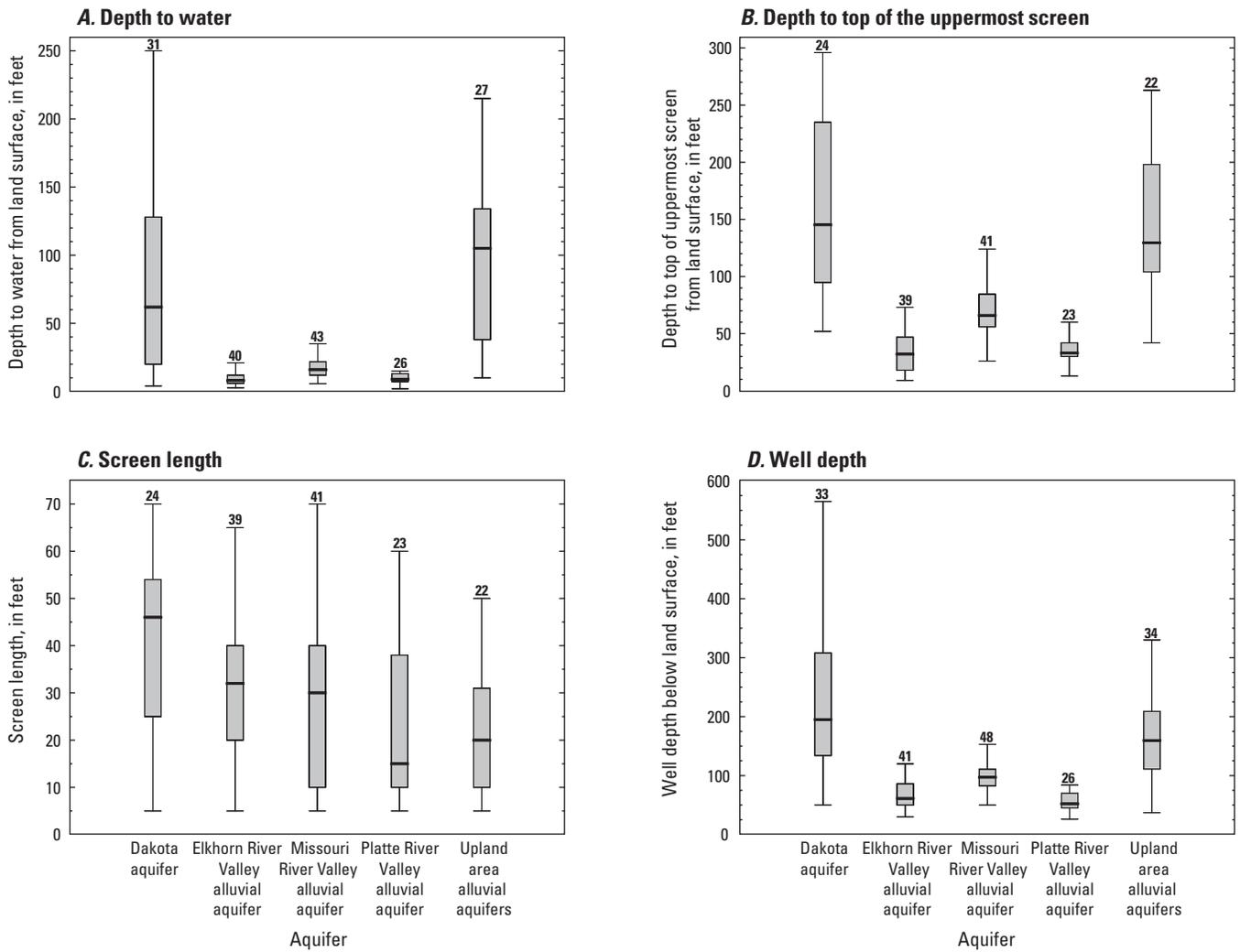
The hydrogen ion concentration in water, indicated by pH, directly affects the solubility of metals. Highly acidic water (low pH) and highly basic water (high pH) can corrode pipes and may result in an unpleasant taste and appearance (World Health Organization, 2008). The USEPA SDWR recommends a pH of drinking water between 6.5 and 8.5 standard units (U.S. Environmental Protection Agency, 2009a). None of the field-measurements samples, 1992 to 2009, had pH values outside this recommended range. The field measurements of pH for most (80 percent) field-measurements samples, 1992 to 2009, ranged from 6.9 to 7.6, with a median value of 7.1 (table 8). Median pH was greater in the Platte River Valley alluvial aquifer than in the other aquifers (fig. 11).

The field measurements of dissolved oxygen in most (80 percent) of the field-measurements samples, 1992 to 2009, ranged from less than 0.1 to 7.2 mg/L; the dissolved oxygen concentration in all these samples ranged from less than 0.1 to

15.3 mg/L (table 8). Dissolved oxygen was less than 0.5 mg/L in 43 percent of the samples, indicating anoxic conditions were frequently observed. The distribution of anoxic samples by aquifer varied—Dakota aquifer, 23 percent; Elkhorn River Valley alluvial aquifer, 48 percent; Missouri River Valley alluvial aquifer, 61 percent; Platte River Valley alluvial aquifer, 44 percent; upland area alluvial aquifers, 33 percent. Overall median dissolved oxygen concentration was 0.9 mg/L. The median dissolved oxygen concentrations in samples from the Dakota and upland area alluvial aquifers were greater than the median concentrations in the samples from the Elkhorn, Missouri, and Platte River Valley alluvial aquifers (fig. 11B).

Dissolved oxygen concentrations in groundwater can help to predict the type of reduction-oxidation (redox) reactions that occur in groundwater. Microorganisms in groundwater utilize redox processes for energy. Typically, the most common electron donor available in aquifer systems is organic carbon in its dissolved and particulate forms. Under oxic conditions (dissolved oxygen concentrations of 0.5 mg/L or more), the most common electron acceptor is dissolved oxygen. Under anoxic conditions, the favored electron acceptors, in the order preferred by microorganisms and in descending order of energy yield, are nitrate, manganese (IV), ferric iron, sulfate, and carbon dioxide (McMahon and others, 2009).

Redox reactions can positively or negatively affect the quality of groundwater. Redox processes can alternately mobilize or immobilize potentially toxic metals, such as arsenic, which are associated with naturally occurring aquifer



EXPLANATION

Depth to water and well characteristics of selected wells, 1992–2009—The selected wells are network wells and one randomly selected well in each well nest with samples collected in summer or fall for analysis of nitrate plus nitrite as nitrogen

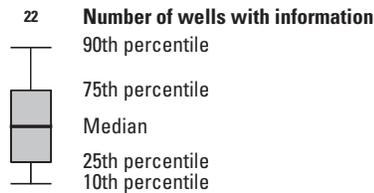
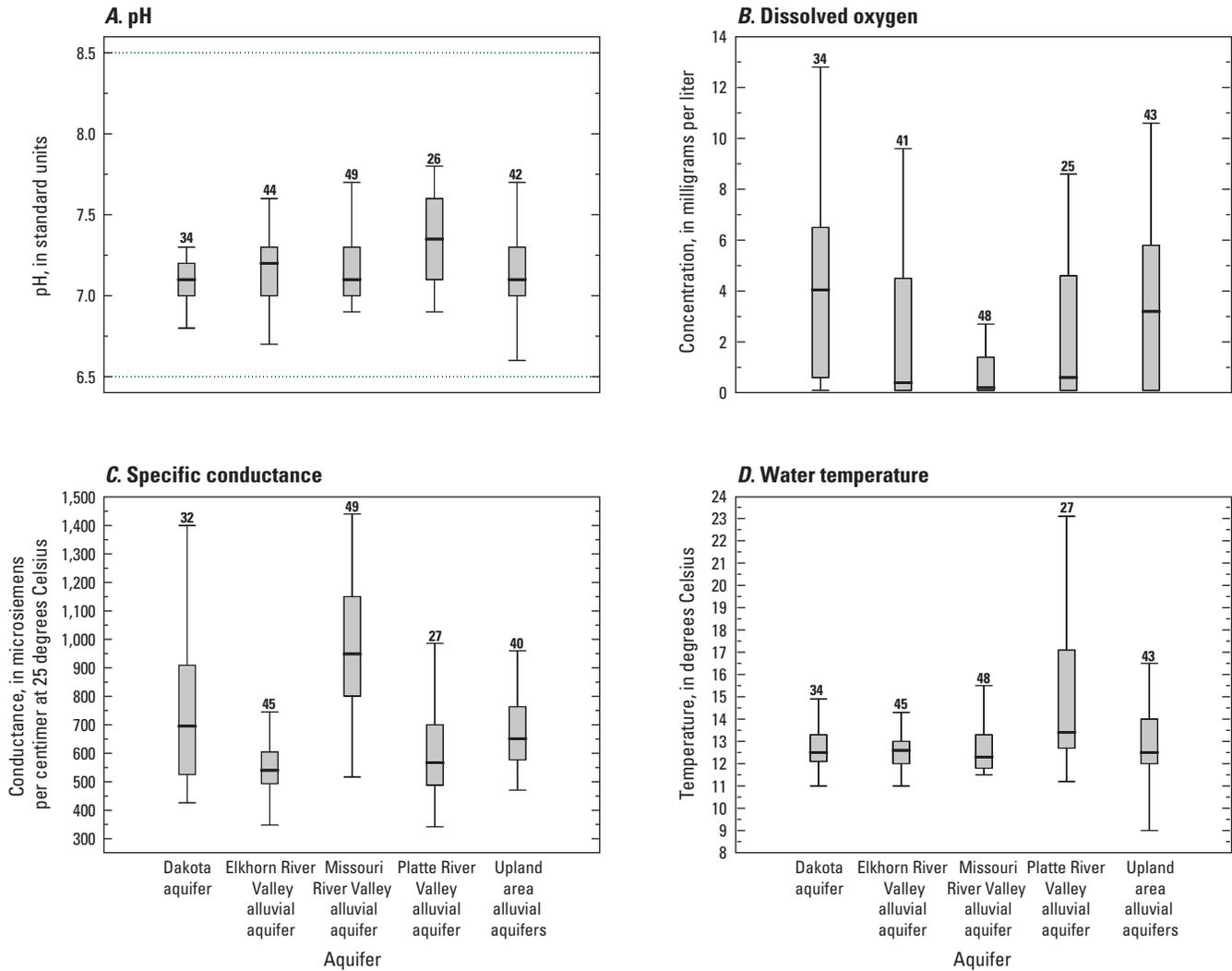


Figure 10. Distribution of *A*, depth to water, *B*, depth to the top of the uppermost screen, *C*, screen length, and *D*, well depth of selected wells, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.



EXPLANATION

Frequency distribution of results from selected samples, 1992–2009—The selected samples are the most recent samples collected in summer-to-fall for analysis of nitrate plus nitrite as nitrogen from the network wells and one randomly selected well in each of the nine well nests

Drinking-water non-health guideline (U.S. Environmental Protection Agency, 2009a)

..... Secondary Drinking Water Regulation

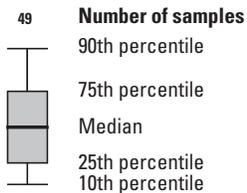


Figure 11. Distribution of A, pH, B, dissolved oxygen, C, specific conductance, and D, water temperature in selected samples, Pappo-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

materials; contribute to the degradation or preservation of man-made contaminants, such as VOCs and pesticides; and generate or mobilize undesirable chemicals, such as dissolved manganese, ferrous iron, hydrogen sulfide, and methane. Other byproducts of the redox processes are nitrogen and hydrogen gases (Chapelle and others, 1995; McMahon and others, 2009).

Oxygen reduction has consistently been the predominant redox process in only three of the wells in two of the well nests (D-T3, P-S2, and P-S1). In five wells in the well nests (D-T1, D-T2, E-V1, E-V2, and E-V3) nitrate reduction is indicated in addition to other redox processes. In the remaining wells, the dominant redox processes are manganese, iron, or sulfate reduction under anoxic conditions or oxygen and manganese, iron, or sulfate reduction under mixed oxic-anoxic conditions (table 9).

Specific conductance is a measure of the water's ability to conduct electric current, which results from the presence of dissolved ions in the water (Hem, 1985). Because the electrical conductance varies with temperature, specific conductance measurements are reported relative to a standard temperature (25°C). Specific conductance for most (80 percent) of the field-measurements samples, 1992 to 2009, ranged from 484 to 1,200 microsiemens per centimeter at 25°C (table 8). The median specific conductance was greater in the Missouri River Valley alluvial aquifer than in the other four aquifers (fig. 11C).

Groundwater temperature, which is approximately equal to mean annual air temperature, can affect chemical reactions (Hem, 1985). The water temperature for most (80 percent) of the field-measurements samples, 1992 to 2009, ranged from 11.6 to 15.0°C; median water temperature was 12.5°C (table 8). The median water temperature in the Platte River Valley alluvial aquifer (13.4°C) was greater than in the other aquifers (fig. 11D) and had the greatest range of 11.2°C to 24.0°C.

Major Ions

Major ions analyzed in groundwater samples from the PMRNRD (appendix 3) included the positively charged ions (cations) calcium, magnesium, sodium, and potassium, and the negatively charged ions (anions) bicarbonate (generally referred to in this report as acid-neutralizing capacity), chloride, fluoride, nitrate, and sulfate. Silica, an uncharged species, also was included in major-ion analysis. Figure 12 presents, by aquifer, major-ion compositions for the most recent samples collected in the PMRNRD from 1992 to 2009, including all samples from wells in well nests. In the samples analyzed for this study, the predominant water type was calcium bicarbonate (fig. 12A–E). In three samples from network wells in the Dakota aquifer (D-001, D-002, D-003), the water type was predominantly a calcium sulfate. The wells in each well nest generally had similar ionic compositions; the exception was well M-H1 (the deep well in the well nest near Homer, Nebr.) that had a substantially higher sulfate concentration and lower carbonate plus bicarbonate concentration than wells M-H2 and

M-H3 (the medium-depth and shallow wells in the well nest, respectively).

The selected samples discussed in the remainder of this section are the most recent samples with a major ions determination collected from network wells and one randomly selected well from each well nest. The major ion results from these samples indicate that concentrations of sulfate in four samples exceeded the USEPA SDWR and Nebraska Title-118 standards, and concentrations of sodium in four samples exceeded USEPA nonenforceable Drinking Water Advisory Table (DWAT) standards (table 10; appendix 2). In addition, the chloride concentration in one sample exceeded 50 percent of the USEPA SDWR, and the fluoride concentration in one sample exceeded 30 percent of the USEPA MCL and Nebraska Title-118 standard. The concentrations of major ions, calcium and magnesium, were used to calculate “hardness;” water from all samples is considered “hard” [121 to 180 mg/L as calcium carbonate (CaCO₃)] to “very hard” (greater than 180 mg/L as CaCO₃) (Durfor and Becker, 1964).

Sulfate

Concentrations of sulfate in most (80 percent) of the samples from selected samples ranged from 17 to 200 mg/L (table 10), which is less than the USEPA SDWR and Nebraska Title-118 standard of 250 mg/L (appendix 3). Overall, sulfate concentrations ranged from 0.80 to 590 mg/L. The concentration of sulfate was greater than the USEPA SDWR in samples from four wells (D-001, D-002, D-003, and M-H1). Water with high sulfate concentrations tends toward scale deposition when heated, can have an unpleasant taste, and may cause gastrointestinal effects (World Health Organization, 2008). In the Dakota, Platte River Valley alluvial, and upland area alluvial aquifers, concentrations of sulfate correlated positively with specific conductance ($\tau = 0.618$ to 0.667 ; $p < 0.05$).

Sodium

Sodium concentration was greater than the lower range of USEPA DWAT range of 30 to 60 mg/L in 39 percent of the samples. Sodium concentration was greater than the USEPA DWAT of 20 mg/L for people on low sodium diets in 69 percent of the samples.

Chloride

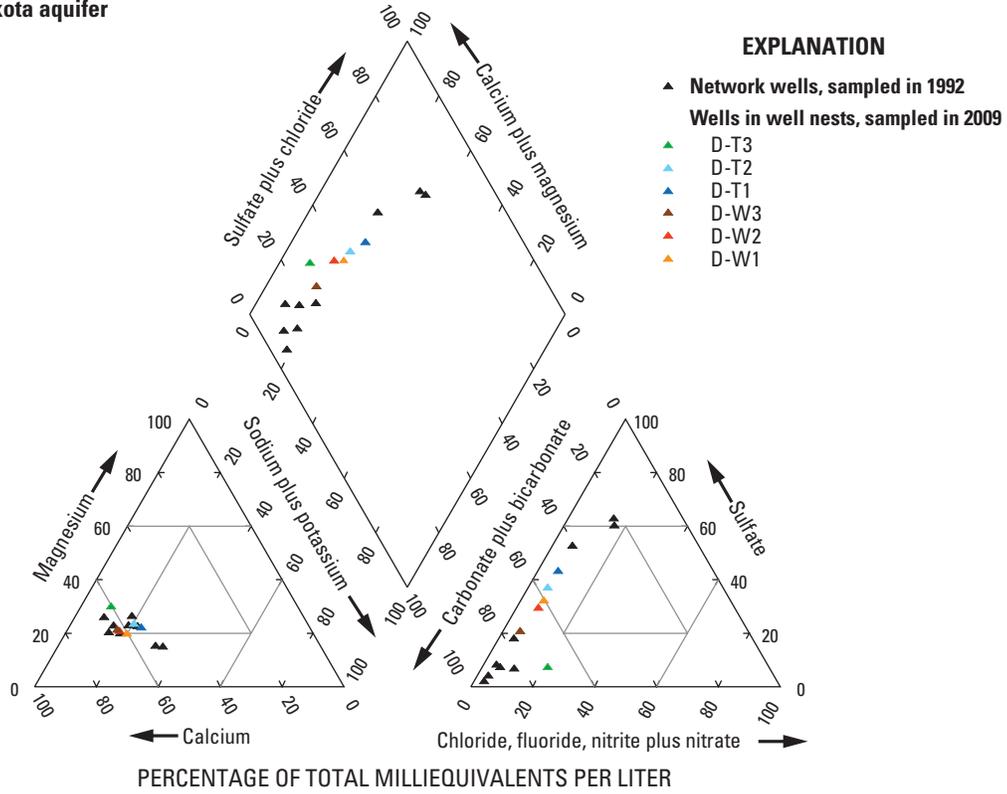
Chloride concentrations in water from most samples (80 percent) ranged from 2.0 to 43.0 mg/L. The maximum chloride concentration was 210 mg/L, which is less than the USEPA SDWR of 250 mg/L (table 10). Water with high chloride can have an unpleasant taste (World Health Organization, 2008). Chloride concentrations were positively correlated with specific conductance for samples from the Dakota aquifer ($\tau = 0.909$, $p = 0.0001$); correlations for the other aquifers were not significant ($p > 0.05$).

Table 9. Range of oxidation-reduction classifications, by well, for samples from selected wells in well nests, Papio-Missouri River Natural Resources District, eastern Nebraska, 1999–2009.[O₂, dissolved oxygen; NO₃⁻, dissolved nitrate; Mn(IV), oxidized manganese; Fe(III), ferric iron; SO₄²⁻, dissolved sulfate; Med-depth, medium-depth; --, not applicable]

Well identifier (fig. 8)	Well screen depth in aquifer	Number of samples	Percentage of samples								
			Oxic conditions	Suboxic conditions ¹	Anoxic conditions				Mixed oxic-anoxic		
			O ₂ reduction		NO ₃ ⁻ reduction	Mn(IV) reduction	Fe(III)/SO ₄ ²⁻ reduction	NO ₃ and Mn(IV) reduction	O ₂ and Mn(IV) reduction	O ₂ and Fe(III)/SO ₄ ²⁻ reduction	
Dakota aquifer											
D-T3	Shallow	11	100	--	--	--	--	--	--	--	--
D-T2	Med-depth	11	--	--	--	18	9	18	55	--	--
D-T1	Deep	11	--	--	--	36	--	9	55	--	--
D-W3	Shallow	11	--	--	--	--	64	--	--	--	36
D-W2	Med-depth	11	--	--	--	--	45	--	--	--	55
D-W1	Deep	11	--	--	--	--	100	--	--	--	--
Elkhorn River Valley alluvial aquifer											
E-EC2	Shallow	11	--	--	--	--	9	--	--	--	91
E-EC1	Deep	11	--	--	--	--	45	--	--	--	55
E-V3	Shallow	11	--	--	--	9	--	36	55	--	--
E-V2	Med-depth	11	--	9	--	45	--	36	9	--	--
E-V1	Deep	11	27	36	36	--	--	--	--	--	--
Missouri River Valley alluvial aquifer											
M-BC3	Shallow	11	--	--	--	--	18	--	--	--	82
M-BC2	Med-depth	11	--	--	--	--	82	--	--	--	18
M-BC1	Deep	12	--	--	--	--	92	--	--	--	8
M-H3	Shallow	10	--	--	--	--	20	--	--	--	80
M-H2	Med-depth	10	--	--	--	--	30	--	--	--	70
M-H1	Deep	10	--	--	--	--	80	--	--	--	20
Platte River Valley alluvial aquifer											
P-A3	Shallow	11	--	--	--	--	64	--	--	--	36
P-A2	Med-depth	11	--	--	--	--	36	--	--	--	64
P-A1	Deep	11	--	--	--	--	82	--	--	--	18
P-S3	Shallow	12	--	--	--	--	--	--	8	--	92
P-S2	Med-depth	12	100	--	--	--	--	--	--	--	--
P-S1	Deep	12	100	--	--	--	--	--	--	--	--
Upland area alluvial aquifers											
U-BA3	Shallow	4	--	--	--	--	--	--	75	--	25
U-BA2	Med-depth	9	--	--	--	--	--	--	--	--	100
U-BA1	Deep	11	--	--	--	--	--	--	--	--	100

¹Further definition of the oxidation-reduction processes not feasible.

A. Dakota aquifer



B. Elkhorn River Valley alluvial aquifer

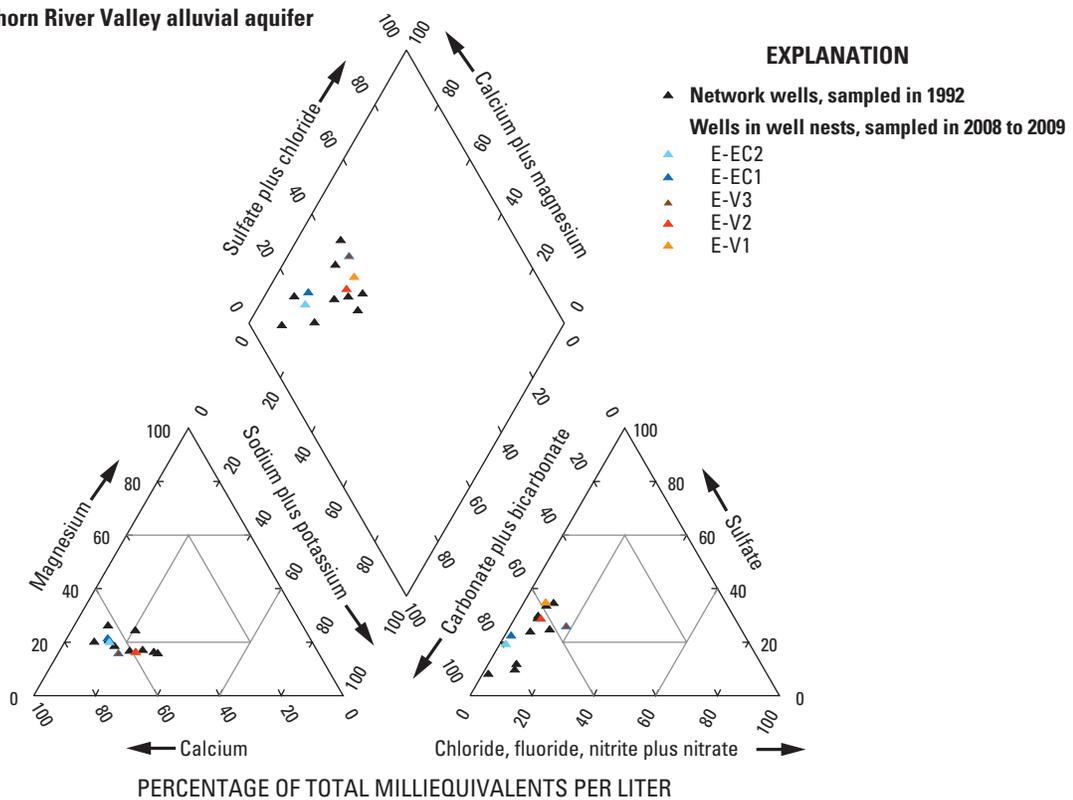
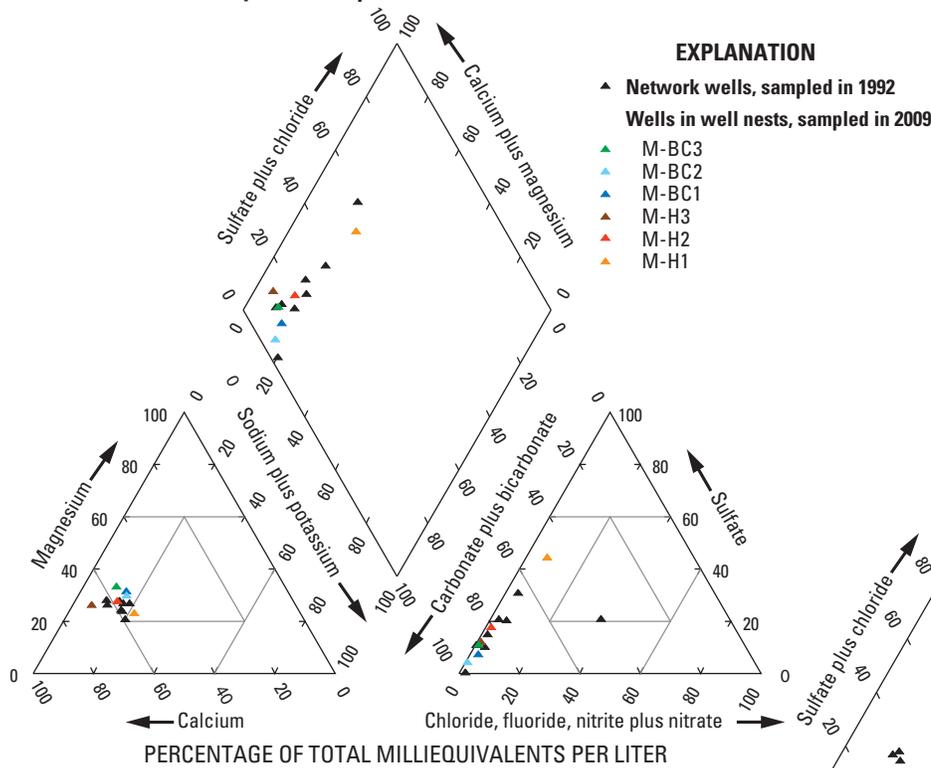
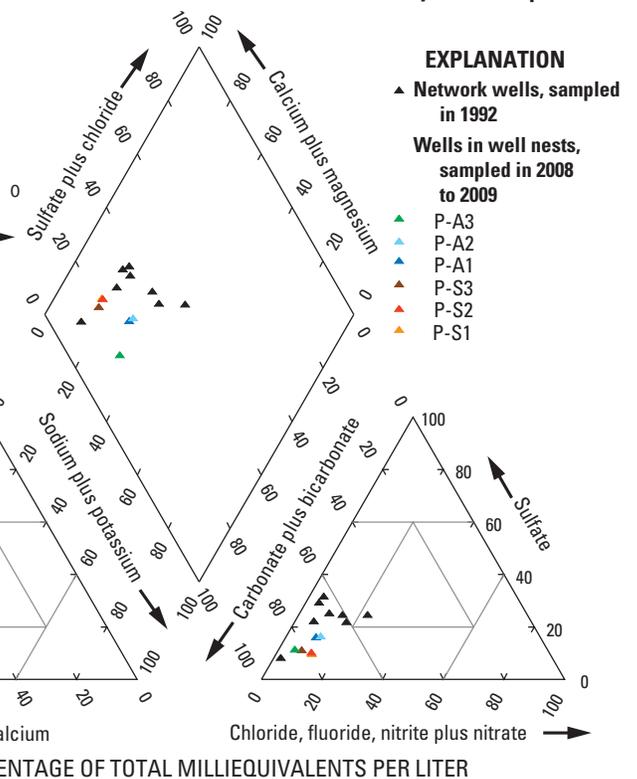


Figure 12. Ionic composition of groundwater in the A, Dakota aquifer, B, Elkhorn River Valley alluvial aquifer, C, Missouri River Valley alluvial aquifer, D, Platte River Valley alluvial aquifer, and E, upland area alluvial aquifers, in the most recent samples in network wells and all wells in the well nests, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

C. Missouri River Valley alluvial aquifer



D. Platte River Valley alluvial aquifer



E. Upland area alluvial aquifers

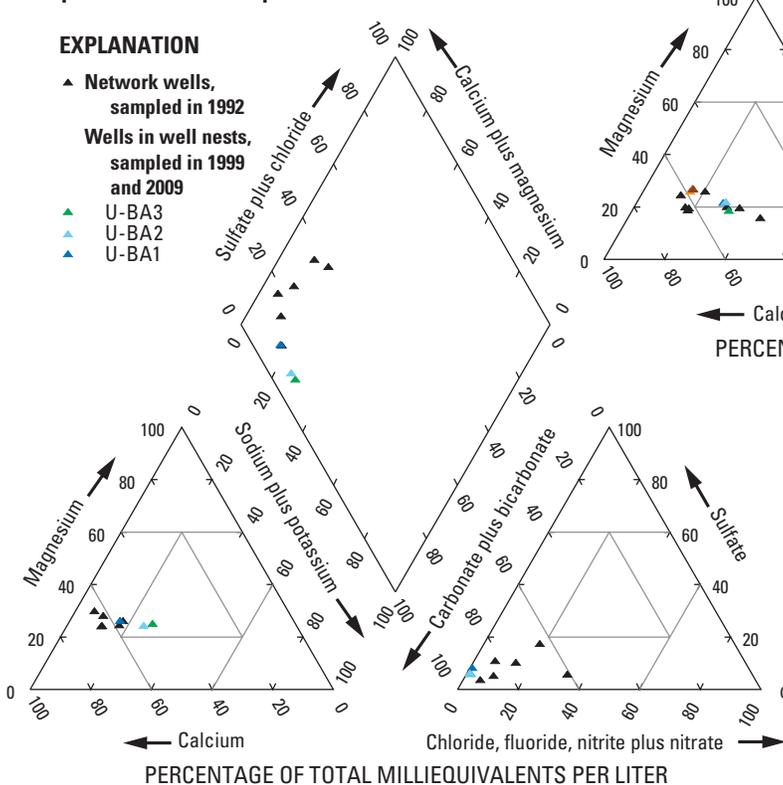


Figure 12. Ionic composition of groundwater in the A, Dakota aquifer, B, Elkhorn River Valley alluvial aquifer, C, Missouri River Valley alluvial aquifer, D, Platte River Valley alluvial aquifer, and E, upland area alluvial aquifers, in the most recent samples in network wells and all wells in the well nests, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.—Continued

Table 10. Summary statistics for major ions, hardness, silica, and nutrients in the most recent selected groundwater samples collected in the network wells and in one randomly selected well in each well nest, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[USGS, U.S. Geological Survey; LRL, laboratory reporting limit; mg/L, milligrams per liter; USEPA, U.S. Environmental Protection Agency; CaCO₃, calcium carbonate; --, no data or not defined; SDWR, Secondary Drinking Water Regulation; MCL, Maximum Contaminant Level; DWAT, Drinking Water Advisory Table; DWAT-Low sodium diet, Drinking Water Advisory Table maximum concentration for individuals on a restricted sodium diet; Reserved, a standard will be promulgated for this analyte; N, nitrogen; P, phosphorus; <, less than]

Name of major ion or nutrient	USGS parameter code	Highest LRL, 1992 to 2009 ¹ , mg/L	Number of samples	Number of detections	Concentration, in mg/L							USEPA drinking-water standard(s)/type of standard ² , mg/L	Nebraska Title-118 standard ³ , mg/L
					Minimum	10th percentile	25th percentile	Median	75th percentile	90th percentile	Maximum		
Major ions results for anions in the most recent selected samples													
Acid neutralizing capacity, laboratory, as CaCO ₃	90410	8	49	49	120	173	213	275	328	438	677	--	--
Chloride	00940	.33	49	49	.80	2.0	6.3	15.0	19.0	43.0	210	250/SDWR	250
Fluoride	00950	.17	49	49	.2	.2	.3	.3	.4	.8	1.8	4/MCL and 2/SDWR	4
Sulfate	00945	.31	49	49	.80	17.0	27.5	68.2	95.0	200	590	250/SDWR	250
Major ions results for cations in the most recent selected samples													
Calcium	00915	0.04	50	50	47.0	55.0	68.0	93.0	118	171	210	--	--
Magnesium	00925	.02	50	50	9.80	12.0	16.0	19.5	29.0	44.0	56.0	--	--
Potassium	00935	.16	49	49	1.80	2.40	4.10	7.50	8.90	12.0	22.0	--	--
Sodium	00930	.2	50	50	7.60	17.0	20.0	26.0	37.0	61.7	140	30–60/DWAT; 20/DWAT-Low sodium diet	Reserved
Results for hardness, calculated from the most recent selected samples													
Hardness, as CaCO ₃	00900	--	51	51	167	196	237	317	412	637	741	--	--
Results for silica in the most recent selected samples													
Silica	00955	0.5	50	50	9.10	19.5	24.0	28.9	32.0	35.0	37.0	--	--
Nutrients results in the most recent selected summer-to-fall samples													
Ammonia as N	00608	0.04	113	57	<0.04	<0.04	<0.04	0.08	0.41	1.04	1.81	30/DWAT	--
Nitrate plus nitrite as N	00631	.06	200	113	<.06	<.06	<.06	.12	2.89	8.55	74.6	10/MCL	10
Nitrite as N	00613	.008	113	14	<.008	<.008	<.008	<.008	<.008	.022	.088	1/MCL	1
Orthophosphate as P	00671	.02	113	102	<.02	.03	.06	.11	.18	.25	.89	--	--

¹Source: U.S. Geological Survey National Water Quality Laboratory, Denver, Colo.

²Source: U.S. Environmental Protection Agency, 2009a.

³Source: Nebraska Department of Environmental Quality, 2006.

Fluoride

Fluoride concentrations ranged from 0.2 to 1.8 mg/L in the selected samples (table 10). Fluoride in low concentrations (0.7 to 1.2 mg/L) can prevent tooth decay (Centers for Disease Control and Prevention, 2010), but concentrations in drinking water of about 4 mg/L or greater can lead to staining of teeth and cause bone damage (U.S. Environmental Protection Agency, 1985 and 2011). The USEPA MCL for fluoride in drinking water is 4 mg/L; the USEPA SDWR for fluoride is 2 mg/L. None of the selected samples had fluoride concentrations greater than USEPA drinking-water standards. For samples from the Dakota aquifer, concentrations of fluoride were positively correlated with specific conductance ($\tau = 0.618$, $p = 0.008$), which is consistent with the fact that fluoride in groundwater usually originates from the dissolution of minerals (Freeze and Cherry, 1979; Hem, 1985), and negatively correlated with dissolved oxygen ($\tau = -0.709$, $p = 0.002$), possibly because groundwater is older in the Dakota aquifer than in the alluvial aquifers. Older waters are more likely to have high solute concentrations (Bartos and others, 2004) and less dissolved oxygen (DeSimone, 2009) than younger waters.

Calcium, Magnesium, and Hardness

Calcium concentration in water from most samples (80 percent) ranged from 55.0 to 171 mg/L; the maximum calcium concentration was 210 mg/L. Magnesium concentration in water from most samples (80 percent) ranged from 12.0 to 44.0 mg/L; the maximum magnesium concentration was 56.0 mg/L. Calcium and magnesium are the principal contributors to hardness. Hardness is a qualitative indicator of how readily water forms insoluble residues with soap and scale deposits when heated; water used for domestic purposes is generally considered “hard” when hardness is greater than 120 mg/L of CaCO_3 (Hem, 1985). Hardness results for samples from all wells were greater than 120 mg/L of CaCO_3 (table 10).

Trace Elements

Trace elements, which occur naturally in rocks, include metals and semimetallic elements that typically are found in groundwater at concentrations less than 1 mg/L. A given trace element’s concentration, oxidation state, species, and complexes in groundwater are determined by (1) the abundance of the element in aquifer materials, (2) geochemical conditions, such as redox conditions and pH, (3) concentrations of other dissolved constituents, such as chloride, sulfate, and bicarbonate, and (4) attenuation processes, such as adsorption (Freeze and Cherry, 1979; Hem, 1985). The mobility, bioavailability, and toxicity of a given trace element can differ among the trace element’s species (Hem, 1985).

Eighteen of the 21 trace elements analyzed in samples from PMRNRD wells (appendix 3) have USEPA

drinking-water standards (U.S. Environmental Protection Agency, 2009a). Sixteen of the trace elements with USEPA standards were detected in the most recent samples collected from network wells and from one randomly selected well from each well nest (hereafter referred to as the selected trace-element samples; table 11). In the selected trace-element samples, the only trace-element concentration that exceeded an enforceable USEPA drinking-water standard (MCL) was for arsenic; this occurred in 4 percent of the samples. In the selected trace-element samples, trace elements detected at concentrations that exceeded a nonenforceable USEPA drinking-water standard (SDWR or LTHA) were iron (46 percent of samples), manganese (70 percent), and strontium (4 percent). Trace elements that were detected in the selected trace-element samples but did not have a USEPA drinking-water standard were cobalt, lithium, and vanadium. Mercury was detected in the selected samples, but it was also detected in the associated equipment- and field-blank samples at a similar concentration; therefore, the mercury detections likely were caused by contamination during sampling or processing. The only trace elements that were not detected in any of the selected samples were lead and nickel (table 11).

Arsenic

Arsenic in drinking water can contribute to skin, bladder, and lung cancers and has been associated with cardiovascular and neurological effects (National Research Council, 2001; World Health Organization, 2008). The USEPA MCL and the Nebraska Title-118 standard for arsenic are each 10 $\mu\text{g/L}$ (Nebraska Department of Environmental Quality, 2006; U.S. Environmental Protection Agency, 2009a, 2009b). Samples were analyzed for arsenic in 40 network wells (collected in 1992) and 21 wells in well nests (collected in 2008). The areal distribution of arsenic concentrations from the most recent results for all the 61 sampled wells is shown in figure 13; arsenic concentration was greater than the USEPA MCL and Nebraska Title-118 standard in samples from two of the wells.

In the selected trace-element samples, arsenic was detected in 37 of these samples—31 samples from 1992 and 6 samples from 2008. Among the selected samples, those from the Missouri River Valley alluvial aquifer had the highest median arsenic concentration (5.4 $\mu\text{g/L}$) and included the two samples with concentrations greater than 10 $\mu\text{g/L}$ (fig. 14). Arsenic concentrations were significantly greater in the Missouri River Valley alluvial aquifer than in the Dakota ($p = 0.001$) and upland area alluvial ($p = 0.012$) aquifers but were not significantly greater than those from the Elkhorn River Valley ($p = 0.095$) or Platte River Valley alluvial aquifers ($p = 0.325$).

Previous studies found that the alluvial and glacial aquifers in the upper Midwest, which includes the PMRNRD, can contain high concentrations of aqueous arsenic (Ziegler and others, 1993; Welch and others, 2000). In a national study, the median concentration of arsenic in groundwater in Nebraska was estimated to be 4 $\mu\text{g/L}$ (Focazio and others, 1999).

Table 11. Summary statistics for trace elements in the most recent samples collected in network wells and in one randomly selected well in each well nest, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[USGS, U.S. Geological Survey; LRL, laboratory reporting level; µg/L, micrograms per liter; USEPA, U.S. Environmental Protection Agency; <, less than; MCL, Maximum Contaminant Level; LTHA, Lifetime Health Advisory level; --, no data or not defined; <number>/TT Action level, Treatment Technique required by public water systems if more than 10 percent of tap water samples exceed <number> concentration; SDWR, Secondary Drinking Water Regulation; V, value may be affected by contamination; Reserved, a standard will be promulgated for this analyte]

Trace element	USGS parameter code	Number of samples	Number of detections, using maximum LRL, 1992 to 2009	Concentration, in µg/L							USEPA drinking-water standard(s)/type of standard ¹ , µg/L	Nebraska Title-118 standard ² , µg/L
				Minimum	10th percentile	25th percentile	Median	75th percentile	90th percentile	Maximum		
Arsenic	01000	49	37	<1	<1	1	2	4	8	14	10/MCL	10
Barium	01005	50	50	14	52	130	185	250	350	530	2,000/MCL	2,000
Beryllium	01010	50	10	<.5	<.5	<.5	<.5	<.5	.8	.9	4/MCL	4
Boron	01020	49	49	30	50	56	70	170	370	730	1,000/LTHA	1,000
Cadmium	01025	50	8	<1	<1	<1	<1	<1	2	3	5/MCL	5
Chromium	01030	50	1	<5	<5	<5	<5	<5	<5	7	100/MCL	100
Cobalt	01035	50	5	<3	<3	<3	<3	<3	3	12	--	--
Copper	01040	50	5	<10	<10	<10	<10	<10	10	210	1,300/TT Action level and 1,000 SDWR	1,300
Iron	01046	50	34	<10	<10	<10	170	2,200	7,200	17,000	300/SDWR	--
Lead	01049	50	0	<10	<10	<10	<10	<10	<10	<10	15/TT Action level	15
Lithium	01130	50	50	8	13	17	21	52	79	190	--	--
Manganese	01056	50	42	<1.0	<1.0	11	329	740	1,250	2,300	300/LTHA and 50/SDWR	50
Mercury	71890	10	7	<.01	<.01	<.01	V.02	V.03	V.06	V.06	2/MCL	2
Molybdenum	01060	50	1	<10	<10	<10	<10	<10	<10	10	40/LTHA	Reserved
Nickel	01065	50	0	<10	<10	<10	<10	<10	<10	<10	100/LTHA	Reserved
Selenium	01145	49	17	<1	<1	<1	<1	2	5	12	50/MCL	50
Silver	01075	50	10	<1	<1	<1	<1	<1	2	3	100/LTHA and 100/SDWR	100
Strontium	01080	50	50	220	300	340	420	840	1,800	4,500	4,000/LTHA	--
Uranium	22703	48	44	<.1	.1	.6	1.8	3.8	6.7	7.7	30/MCL	30
Vanadium	01085	50	1	<6	<6	<6	<6	<6	<6	9	--	Reserved
Zinc	01090	50	38	<3	<3	3	6	12	42	460	2,000/LTHA and 5,000/SDWR	5,000

¹Source: U.S. Environmental Protection Agency, 2009a.

²Source: Nebraska Department of Environmental Quality, 2006.

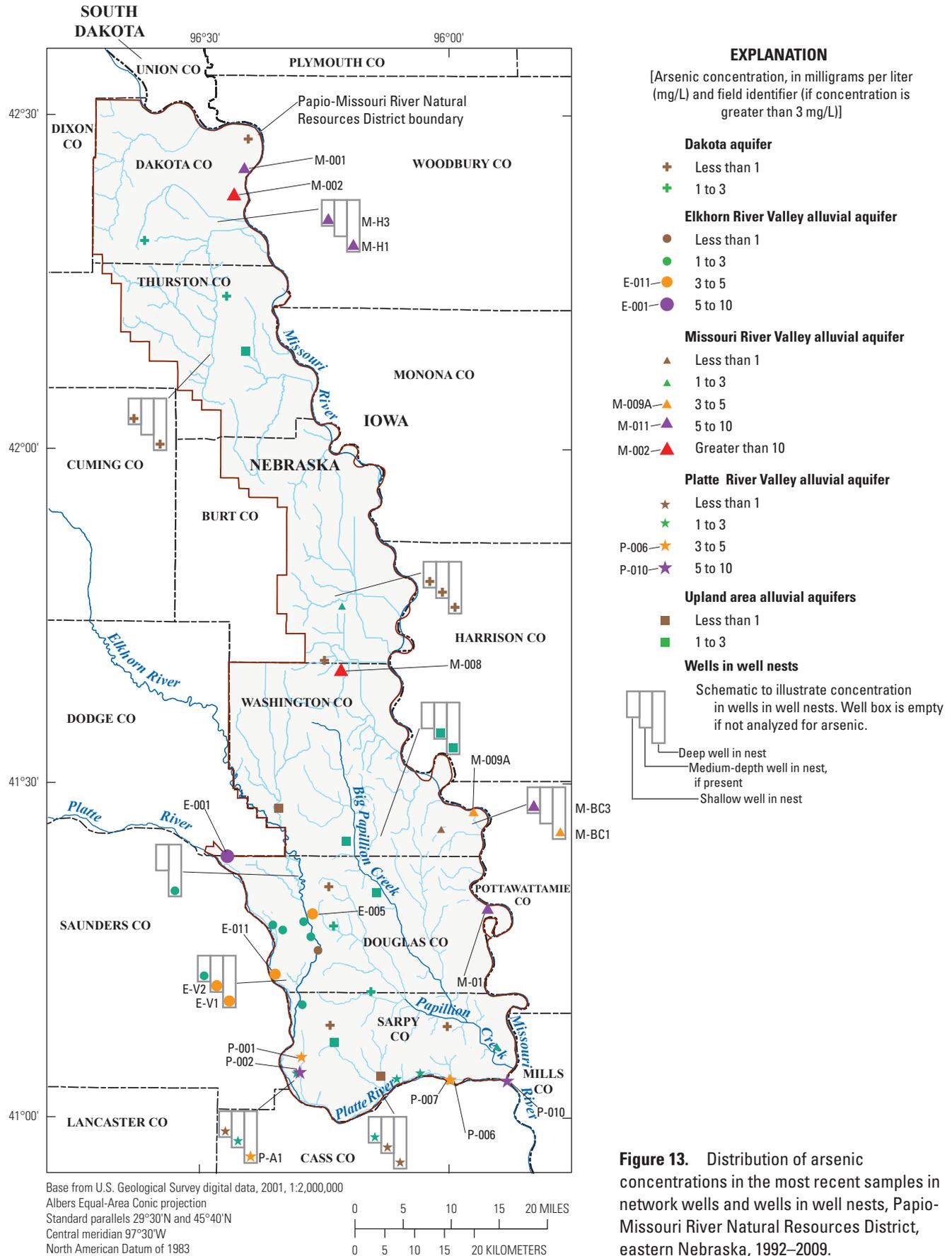


Figure 13. Distribution of arsenic concentrations in the most recent samples in network wells and wells in well nests, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

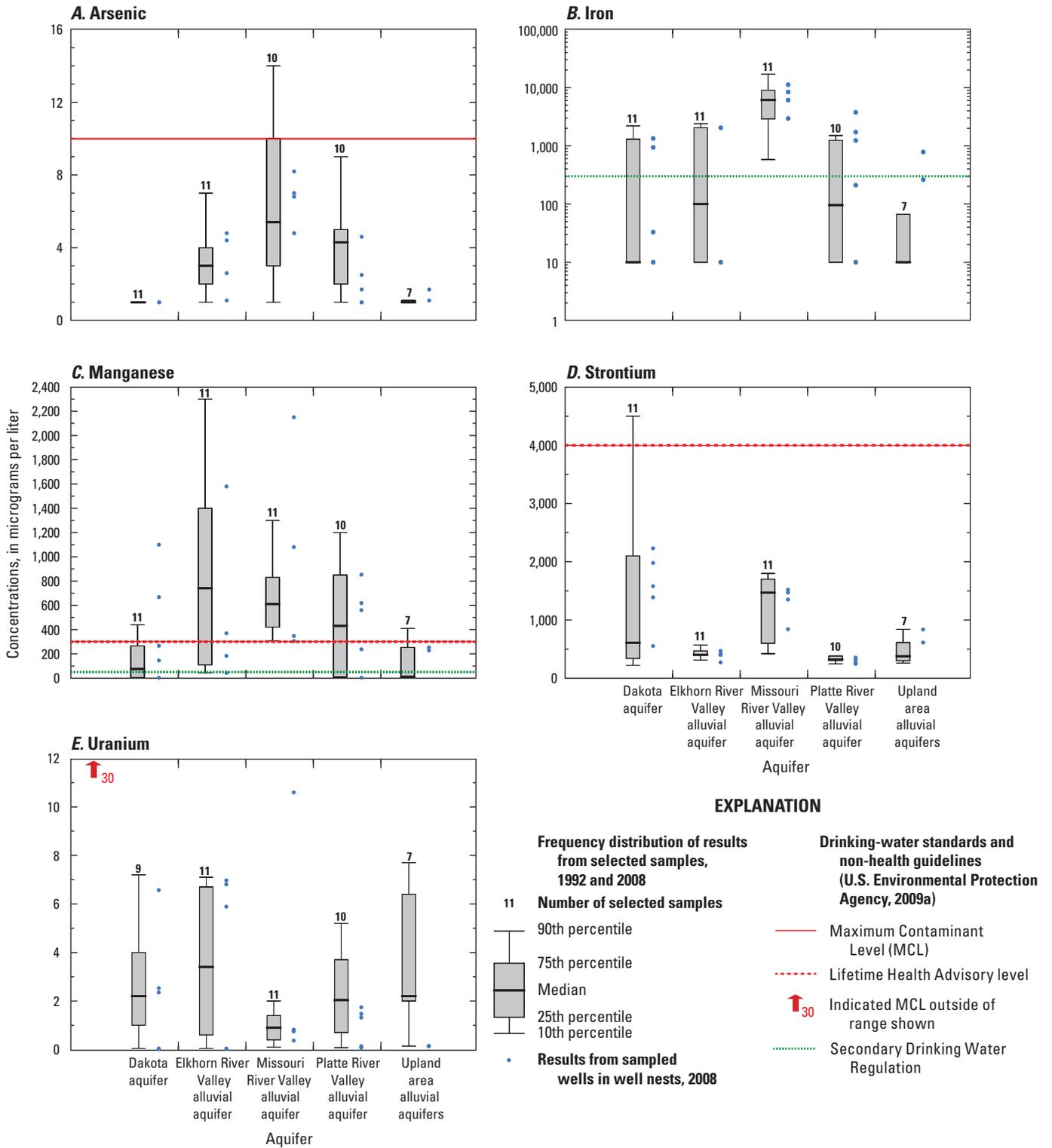


Figure 14. Concentrations, by aquifer, of *A*, arsenic, *B*, iron, *C*, manganese, *D*, strontium, and *E*, uranium as a frequency distribution using box plots in the most recent samples in network wells in 1992 and in one randomly selected well in each well nest in 2008, and as results using dot plots for all sampled wells in well nests in 2008, Papio-Missouri River Natural Resources District, eastern Nebraska.

Geologic sources of arsenic to groundwater include arsenic sulfides, iron oxides, and other common minerals containing arsenic. Compounds containing arsenic also have been used as pesticides and wood preservatives, and in glass production. Geochemical conditions and the distribution of arsenic sources in the aquifer affect arsenic concentrations in groundwater. For example, processes that result in elevated arsenic in groundwater include arsenic release from iron oxides, which is favored by high pH and low dissolved oxygen concentrations. In this study, arsenic concentrations were positively correlated with pH only in samples from wells in the Platte River Valley alluvial aquifer ($\tau = 0.588$, $p = 0.028$). In general, arsenic concentration did not correlate with dissolved oxygen concentration for this study's samples, but for wells screened in the Missouri River Valley alluvial aquifer, dissolved oxygen concentration was low (less than 0.5 mg/L) in 70 percent of the samples that had arsenic concentrations greater than 3.33 $\mu\text{g/L}$. Arsenic concentrations differed over short distances and by more than 2 mg/L among samples from wells in one well nest (fig. 13), which is consistent with findings in other studies (Focazio and others, 1999; Kelly and others, 2005).

Iron and Manganese

Iron- and manganese-bearing minerals, which are common constituents of aquifer material, are more soluble in water with low dissolved oxygen concentration (anoxic conditions) and low pH. Both iron and manganese are essential for human health. Manganese may have adverse neurological effects at high doses, but food, rather than drinking water, is the primary source of manganese for people (Agency for Toxic Substances and Disease Registry, 2008). Although neither iron nor manganese have an enforceable USEPA drinking-water standard (MCL), both have a nonenforceable USEPA drinking-water standard (SDWR)—300 $\mu\text{g/L}$ for iron and 50 $\mu\text{g/L}$ for manganese (U.S. Environmental Protection Agency, 2009a).

Iron was detected in 68 percent of the selected trace-element samples. Iron concentrations were greater than the USEPA SDWR of 300 $\mu\text{g/L}$ in about 46 percent of samples. In general, wells with sample results where iron concentrations are greater than the USEPA SDWR were screened in the Dakota aquifer or the Elkhorn, Missouri, and Platte River Valleys alluvial aquifers, but not the upland area alluvial aquifers (fig. 14).

Manganese was detected in 84 percent of the selected trace-element samples. Manganese concentrations were greater than the USEPA SDWR of 50 $\mu\text{g/L}$ in about 70 percent of the samples; exceedances of the standard were particularly frequent for samples from wells screened in the Elkhorn, Missouri, and Platte River Valleys alluvial aquifers (fig. 14).

Manganese concentrations did not correlate with dissolved oxygen concentration or pH in the selected samples, but dissolved oxygen concentrations were less than 0.5 mg/L in 48 percent of the samples with manganese concentrations greater than 300 $\mu\text{g/L}$. Manganese concentrations were positively correlated with iron concentrations in samples from the

Elkhorn ($\tau = 0.6482$, $p = 0.008$) and Platte River Valleys alluvial aquifers ($\tau = 0.562$, $p = 0.038$), likely because in groundwater, the chemical behaviors of iron and manganese are similar.

Strontium

Strontium was detected in 100 percent of the selected trace-element samples. Strontium is geochemically similar to calcium and will replace minor amounts of calcium and potassium in igneous rocks. Carbonate and sulfate rocks containing strontium are common parent materials in sediment composing aquifer matrices (Hem, 1985). Strontium concentrations in samples from most (80 percent) of the samples ranged from 300 to 1,800 $\mu\text{g/L}$. Concentrations of strontium exceeded the USEPA nonenforceable LTHA of 4,000 $\mu\text{g/L}$ in 4 percent of the samples, all of which were from wells screened in the Dakota aquifer. Strontium may have adverse health effects at high doses, including abnormal bone development (Agency for Toxic Substances and Disease Registry, 2004). Strontium concentrations were greater in samples from wells in the Missouri River Valley alluvial aquifer than those in the Elkhorn River Valley, Platte River Valley, and upland area alluvial aquifers ($p < 0.004$), and strontium concentrations were greater in samples from wells in the Elkhorn River Valley alluvial aquifer than in wells in the Platte River Valley alluvial aquifer ($p = 0.013$).

Uranium

Uranium was detected in 92 percent of the selected trace-element samples. Health effects of uranium in drinking water include increased risk of cancer and possible harm to kidneys (U.S. Environmental Protection Agency, 2009a). Uranium concentrations did not exceed the USEPA MCL of 30 $\mu\text{g/L}$ in any of the samples in this study. Uranium concentrations in samples from most (80 percent) of the wells ranged from 0.10 to 6.7 $\mu\text{g/L}$; the maximum concentration detected in the selected samples was 7.7 $\mu\text{g/L}$ (fig. 14). Uranium concentrations were not significantly different among the studied aquifers ($p = 0.233$), and uranium concentration was positively correlated with dissolved oxygen concentration ($\tau = 0.294$, $p = 0.004$) in all aquifers. The positive correlation between uranium and dissolved oxygen concentrations is consistent with the greater solubility of the oxidized form of uranium (Hem, 1985) and with findings in other studies (DeSimone, 2009).

Nitrogen and Phosphorus Compounds

From 1992 to 2009, groundwater samples from the PMRNRD network wells and well nests were analyzed for as many as four nitrogen and phosphorus compounds—ammonia, nitrate, nitrite, and orthophosphate (appendix 3). Nitrogen and phosphorus species in groundwater may originate from

a variety of natural sources and human activities. Natural sources of nitrogen and phosphorus species in groundwater are precipitation, leaching of soil organic matter, and the rocks and sediment of the aquifer matrix. Human activities that are sources of nitrogen and phosphorus species include fertilizer application, animal production, wastewater disposal, and combustion of fossil fuels (Freeze and Cherry, 1979; Hem, 1985; Nolan and others, 1997; Dubrovsky and others, 2010). Nitrogen in groundwater may be present in the form of ammonia, nitrite, nitrate, or nitrogen gas. Transformations among nitrogen forms in groundwater are controlled by redox conditions and mediated by microorganisms (Freeze and Cherry, 1979; Madigan and others, 2000).

Nitrate

Nitrate is the most common form of nitrogen in groundwater (Dubrovsky and others, 2010); nitrate is stable and mobile in oxic water. In anoxic water, most nitrate has been converted by microorganisms to other nitrogen forms, such as nitrogen gas or ammonia. Nitrate and nitrite are the only nutrients for which there are USEPA drinking-water standards. Ingestion of water with a large concentration of nitrate can lead to low oxygen levels in the blood of infants (Fan and Steinberg, 1996). The USEPA MCL for nitrate is 10 mg/L as nitrogen; the USEPA MCL for nitrite is 1 mg/L as nitrogen (U.S. Environmental Protection Agency, 2009a).

Nitrate was detected in 56 percent of the most recent summer-to-fall samples from network wells and one randomly selected well in each well nest, 1992 to 2009. This set of 200 samples is hereinafter referred to as the nutrient samples, 1992 to 2009. In the Missouri River Valley alluvial aquifer, nitrate was detected in 22 percent of the samples (11 of 49 samples), whereas it was detected in most of the samples from all other aquifers studied (35 of 46 samples, Elkhorn River Valley alluvial aquifer; 19 of 27 samples, Platte River Valley alluvial aquifer; and 26 of 43 samples, upland area alluvial aquifers) (fig. 15A). As illustrated in fig. 15B, nitrate-N concentrations vary by dissolved oxygen range. For nutrient samples, 1992 to 2009,

- In 85 (about 42 percent) of the samples with dissolved oxygen concentrations of less than 0.5 mg/L,
 - Nitrate-N concentrations were 0.06 mg/L or less in 62 of these samples and
 - Nitrate-N concentrations were greater than 0.06 mg/L in 23 of these samples.
- In 106 (about 53 percent) of the samples with dissolved oxygen concentrations of 0.5 mg/L or greater,
 - Nitrate-N concentrations were 0.06 mg/L or less in 26 of these samples and
 - Nitrate-N concentrations were greater than 0.06 mg/L in 80 of these samples.
- In 9 (about 4 percent) of the samples, where dissolved oxygen concentration was not measured,
 - Nitrate-N concentrations were 0.06 mg/L or less in 3 of these samples and
 - Nitrate-N concentrations were greater than 0.06 mg/L in 6 of these samples.

In nutrient samples, 1992 to 2009, with dissolved oxygen concentrations greater than 0.5 mg/L (oxic water), there was a positive correlation between nitrate-N and dissolved oxygen concentrations ($\tau = 0.22$, $p = 0.002$).

The concentration distribution of nitrate-N from 1992 to 2009 was significantly lower in the Missouri River Valley alluvial aquifer than in the other four studied aquifers (p -values < 0.01 ; fig. 15A). There was no statistically significant difference in nitrate-N concentrations among the Dakota, Elkhorn River Valley alluvial, Platte River Valley alluvial, and upland area alluvial aquifers (p -values from 0.35 to 0.98).

Nitrate-N concentrations in the nutrient samples, 1992 to 2009, for most (80 percent) wells ranged from less than 0.06 to 8.55 mg/L, with a median value of 0.12 mg/L (table 10). Concentrations of nitrate-N in 13 (7 percent) nutrient samples, 1992 to 2009, were greater than or equal to the USEPA MCL of 10 mg/L, and concentrations of nitrate-N in 35 (18 percent) of the nutrient samples, 1992 to 2009, were greater than or equal to 5 mg/L, which is the PMRNRD action level for possible management implementation to reduce nitrate concentration in groundwater. The PMRNRD action level is 50 percent of the Nebraska Title-118 standard for the associated analyte (Papio-Missouri Natural Resources District, 1994).

Concentrations of nitrate-N were greater than 1 mg/L in 72 (36 percent) nutrient samples, 1992 to 2009; in many parts of the United States, a concentration greater than 1 mg/L is considered to result from the effects of human activities (Nolan and Hitt, 2006). However, if the concentration of nitrate-N is less than 1 mg/L and the water is anoxic, it cannot be presumed that the water was not affected by human activities because it is likely the nitrate input from natural and man-made sources was consumed by microorganisms through denitrification.

The spatial distribution of denitrification in the PMRNRD groundwater was assessed using (1) the concentration of dissolved oxygen (measured on site prior to sampling, 1992 to 2009), (2) the concentration of dissolved nitrogen gas and methane (measured in 2000 and 2004), and (3) $\delta^{15}\text{N}_{\text{AIR}}$ in nitrate and dissolved nitrogen gas (measured in 2004). Under anoxic conditions, microorganisms will reduce nitrate to nitrogen gas if nitrate and a suitable electron donor are present (McMahon and others, 2009). In the nutrient samples, 1992 to 2009, the water was anoxic in 85 (44 percent) of the 191 samples with dissolved oxygen results (fig. 15B). Evidence of denitrification can be obtained from dissolved gases and $\delta^{15}\text{N}_{\text{AIR}}$ results. The amount of excess nitrogen gas can be derived from the dissolved-gases results for nitrogen and argon and the estimated recharge temperature and recharge

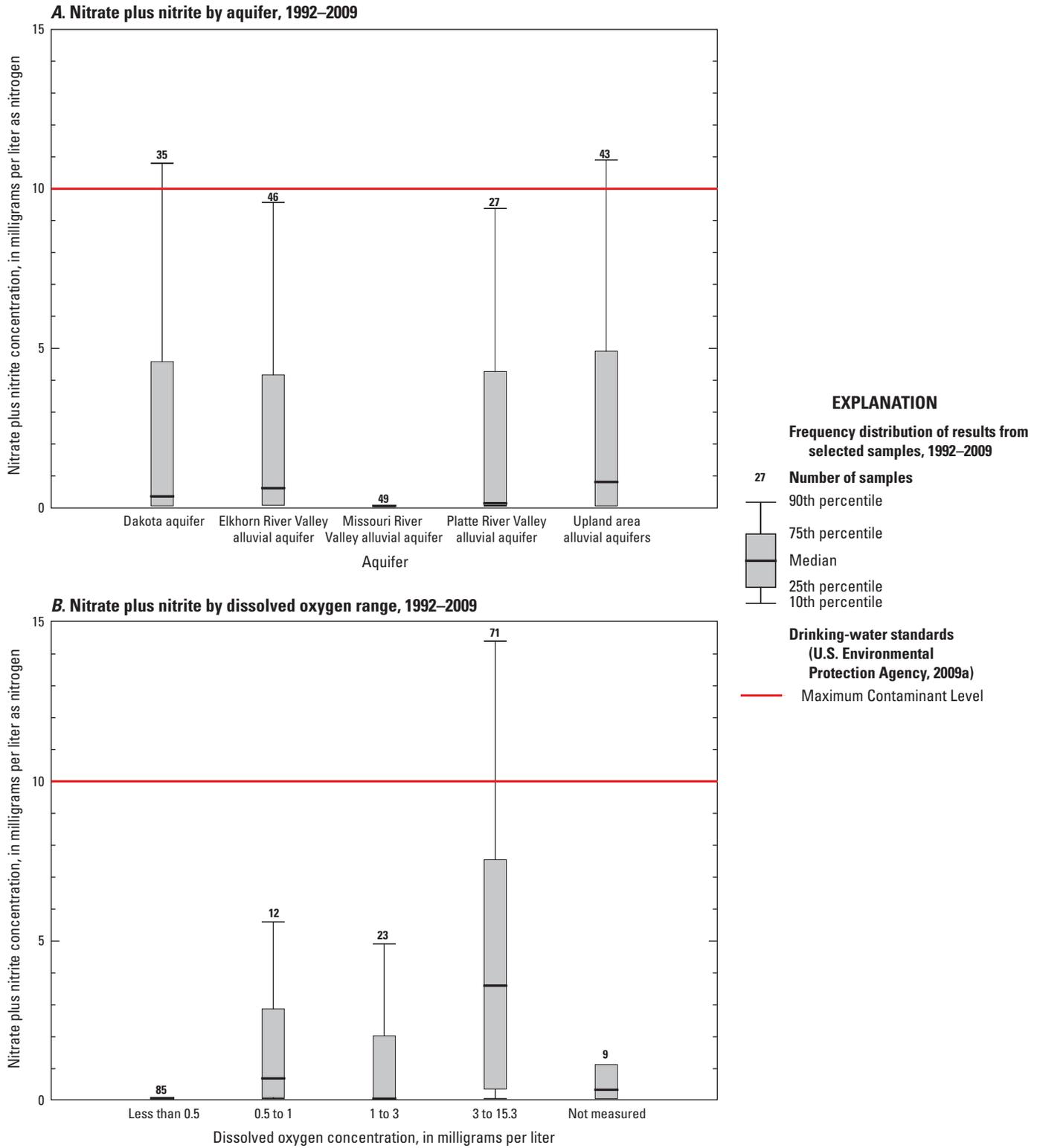


Figure 15. Frequency distribution of nitrate plus nitrite concentration *A*, by aquifer and *B*, by dissolved oxygen range in the most recent summer-to-fall samples in network wells and in one randomly selected well in each well nest, Pappo-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

elevation (Kendall and Aravena, 2000). The concentrations of dissolved gases in samples collected from wells in the well nests in 2000 indicate that excess nitrogen gas was present in three-fourths of the sampled wells. The excess nitrogen gas concentrations ranged from 18 to 460 micromoles per liter ($\mu\text{M/L}$) (table 12). In 2000, excess nitrogen gas was not detected in the samples from two wells (P-A1 and P-A2) in the well nest near Ashland, Nebr. (Ashland, Nebr., which is not shown in fig. 1, is located about 11 mi southwest of Gretna, Nebr.); however, methane gas was detected in these samples. The excess nitrogen gas or presence of methane gas indicate that at least some denitrification likely was occurring in groundwater within the capture area for wells with dissolved gas analysis (table 12).

The $\delta^{15}\text{N}_{\text{AIR}}$ ratios in nitrate were measured in 2004 in the well nests near Venice and Springfield to possibly indicate (1) the source of nitrate in groundwater and (2) evidence of denitrification (Kendall and McDonnell, 1998). The $\delta^{15}\text{N}_{\text{AIR}}$ ratios in nitrate were estimated as 26 per mil (‰) and 26.6‰ in wells E-V3 and E-V1, respectively, which combined with low nitrate-N (30–181 μM) and low dissolved oxygen (20–30 μM) concentrations in these wells, indicates that substantial denitrification had occurred. The dissolved gas and stable isotope results from 2004 for wells P-S1, P-S2, and P-S3 are potentially misinformative because inadequate pumping of the wells likely affected the results. The $\delta^{15}\text{N}_{\text{AIR}}$ ratios in nitrate result for P-S1, P-S2, and P-S3 were 9.36‰, 8.32‰, and 8.44‰, respectively. These $\delta^{15}\text{N}_{\text{AIR}}$ in nitrate results indicate that the source of the nitrate likely is commercial inorganic fertilizer. For commercial fertilizer, the range of $\delta^{15}\text{N}_{\text{AIR}}$ in nitrate is -8‰ to 7‰; for nitrate from organic fertilizer, plant residue, and animal or human waste, the range of $\delta^{15}\text{N}_{\text{AIR}}$ in nitrate is 2‰ to 30‰ (Kendall and McDonald, 1998). In well P-S2, concentrations of nitrate-N (254 μM) and methane (49 μM) indicate there is a mixture of water sources in this well; some water in which substantial denitrification has occurred and other water with elevated nitrate likely are still present.

The estimated fractional decrease in the amount of nitrate, f from equation 3, is greater than 0.5 in all sampled wells in well nests (table 12) except wells D-T3, E-V1, P-A2, P-A1, P-S2, and P-S1. The samples from wells P-A2 and P-A1 were slightly oxic in 2000 (dissolved oxygen concentration equal to 0.8 and 0.7 mg/L, respectively; table 7), and large iron and manganese concentrations were present in samples from these wells collected about 5 months after the collection of samples for dissolved gases in 2000 (table 12). Large iron and manganese results indicate reducing conditions existed somewhere along the groundwater flow path. Redox classification results (table 9) indicate that, from 1999 to 2009, samples from wells P-A2 and P-A1 have been both anoxic and mixed oxic-anoxic. The lack of excess nitrogen gas in wells P-A2 and P-A1 (table 12) likely means the N_2 has degassed from the water at the sampled depths. Estimated f was 0.1 or less for wells D-T3, P-S2, and P-S1; these results

(evidence of little denitrification) agree with the oxic redox classification (table 9) of these wells from samples from 1999 to 2009.

To determine whether the concentration distribution of nitrate-N by aquifer had changed from the 1992 to 1994 sampling period to the 2007 to 2009 sampling period, the most recent summer-to-fall samples were selected for each network well sampled during the two sampling periods and for one randomly selected well in each well nest sampled in the 2007 to 2009 sampling period. These two sets of samples are hereinafter referred to as the nutrient samples, 1992 to 1994 (88 samples), and nutrient samples, 2007 to 2009 (93 samples). For nitrate-N concentration, there was no significant difference among the nutrient samples, 1992 to 1994, and the nutrient samples, 2007 to 2009 (figs. 16A and 16B), for any of the five studied aquifers (p -values range from 0.13 to 0.84). In addition, there was no significant difference for any studied aquifer in the nitrate-N concentrations (1) between the 1992 to 1994 and 1992 to 2009 periods (p -values from 0.334 to 0.980) or (2) between the 2007 to 2009 and 1992 to 2009 periods (p -values from 0.274 to 0.956).

The most recent summer-to-fall nitrate-N concentration for each of 109 sampled wells in the 2007 to 2009 sampling period, including results for all wells in well nests, is mapped in figure 17. In the nutrient samples, 2007 to 2009, there are six wells (D-009A, D-034, D-T3, E-022, P-107, and U-011) with nitrate-N concentrations greater than the USEPA MCL. In the nutrient samples, 2007 to 2009, nine wells (D-005D, D-006, D-011, E-022E, M-204, P-S1, P-102, P-S2, and U-011A) had nitrate-N concentrations less than the USEPA MCL but greater than 5 mg/L (50 percent of the USEPA MCL for nitrate-N), which is the PMRNRD action level for possible management implementation to decrease nitrate concentrations in groundwater (Papio-Missouri Natural Resources District, 1994).

The wells in well nests were sampled for nitrate from 19 to 60 times during 1999 to 2009 (appendix 8). The final summer-to-fall sample in each year was selected for each well in the well nests to assess whether nitrate-N concentrations were changing over time. The only such wells with a statistically significant ($p < 0.05$) trend in nitrate concentrations are in the nest near Venice (wells E-V1, E-V2; fig. 18), the nest near Springfield (wells P-S1, P-S2, and P-S3; fig. 18), and the nest near Walthill, Nebr. (well D-W2). One well in the nest in Tekamah (well D-T3) did not have a significant trend in nitrate-N concentrations ($\tau = 0.45$, $p = 0.09$), but nitrate-N concentrations have been consistently very high (greater than 20 mg/L) in this well (fig. 18). Temporal trends in nitrate-N concentrations were negative for wells in well nests near Venice and Walthill—E-V1 ($\tau = -0.60$, $p = 0.02$), E-V2 ($\tau = -0.64$, $p = 0.01$), and D-W2 ($\tau = -0.53$ and $p = 0.04$). The trends in nitrate concentrations were positive for wells in the well nest near Springfield—P-S1 ($\tau = 0.78$, $p = 0.002$), P-S2 ($\tau = 0.73$, $p = 0.004$), and P-S3 ($\tau = 0.60$ and $p = 0.02$).

Table 12. Estimated recharge temperature, excess nitrogen gas, initial nitrate concentration, and fraction of initial nitrate in recharge that has been removed by denitrification using dissolved gases and related data, Papio-Missouri River Natural Resources District, eastern Nebraska, 2000 and 2004.

[ft, feet; NGVD 29, National Geodetic Vertical Datum of 1929; μM , micromoles per liter; N_2 , nitrogen gas; N, nitrogen; ‰, AIR, nitrogen isotope ratio in per mil of the atmospheric air standard; °C, degrees Celsius; cm^3 STP/L, cubic centimeters per liter at standard temperature and pressure; NO_3 , nitrate; mg/L, milligrams per liter; O, oxygen; ‰, VSMOW, oxygen isotope ratio in per mil of the Vienna Standard Mean Ocean Water; f , fraction of initial nitrate in recharge removed by denitrification; <, less than; --, no data; E, estimated]

Field identifier (fig. 8)	Dissolved gases sample date	Estimated elevation of water table in recharge area (ft above NGVD 29)	Depth to water, ft below land surface	Depth of middle of screen, below water table, ft	Oxygen, field (μM)	Methane (μM)	Nitrogen gas (N_2) (μM)	$\delta^{15}\text{N}$ (N_2) (‰, AIR)	Argon (μM)	Estimated recharge temperature (°C)	Excess air (cm^3 STP/L)	Estimated excess nitrogen gas (N_2) (μM)
Dakota aquifer												
D-T3	6/14/00	1,135	38.27	36.7	260	<1	745	--	17.81	9	2.0	36
D-T1	6/14/00	1,135	44.80	123.7	3	<1	815	--	18.70	6	1.3	89
D-W3	6/13/00	1,212	16.73	82.8	3	<1	786	--	18.38	7	1.3	71
Elkhorn River Valley alluvial aquifer												
E-EC2	6/15/00	1,136	6.32	13.7	10	<1	1,000	--	15.83	14	2.1	360
E-V3	6/15/00	1,107	7.38	9.6	20	<1	1,020	--	14.20	18	0.5	460
E-V3	10/18/04	1,107	5.91	11.1	30	<1	711	E1.9	13.63	20	0.4	180
E-V2	10/18/04	1,107	6.15	49.4	20	<1	628	.97	15.72	13	0.7	18
E-V1	6/15/00	1,107	8.03	87.5	3	<1	766	--	16.84	10	1.2	110
E-V1	10/18/04	1,107	6.06	89.4	20	<1	656	.92	16.50	11	0.8	18
Missouri River Valley alluvial aquifer												
M-BC3	6/15/00	995	11.52	6.0	30	<1	824	--	18.04	8	2.0	110
M-H3	6/13/00	1,092	22.99	25.0	69	<1	799	--	17.42	11	2.7	89
M-H1	6/13/00	1,092	23.94	102.6	3	<1	865	--	19.40	5	1.7	110
Platte River Valley alluvial aquifer												
P-A3	6/12/00	1,055	6.19	9.8	20	1	730	--	16.36	12	1.1	89
P-A2	6/12/00	1,055	6.02	29.0	10	2	599	--	15.48	14	0.6	0
P-A1	5/31/00	1,055	5.58	46.9	10	2	608	--	15.96	12	0.2	0
P-S3	6/12/00	1,020	16.68	33.3	97	<1	808	--	15.73	14	1.6	180
P-S3	10/18/04	1,020	16.03	34.0	120	<1	698	E2.1	16.00	13	1.0	71
P-S2	10/18/04	1,020	16.38	51.1	200	49	560	E1.0	14.63	16	0.1	0
P-S1	6/12/00	1,020	17.03	63.5	190	<1	670	--	16.47	12	1.5	18
P-S1	10/18/04	1,020	16.48	64.0	230	<1	604	--	15.66	13	0.5	0
Upland area alluvial aquifers												
U-BA1	6/13/00	1,210	160.11	62.4	130	<1	732	--	17.78	8	1.4	36

Table 12. Estimated recharge temperature, excess nitrogen gas, initial nitrate concentration, and fraction of initial nitrate in recharge that has been removed by denitrification using dissolved gases and related data, Papio-Missouri River Natural Resources District, eastern Nebraska, 2000 and 2004.—Continued

[ft, feet; NGVD 29, National Geodetic Vertical Datum of 1929; μM , micromoles per liter; N_2 , nitrogen gas; N, nitrogen; ‰, AIR, nitrogen isotope ratio in per mil of the atmospheric air standard; °C, degrees Celsius; cm^3 STP/L, cubic centimeters per liter at standard temperature and pressure; NO_3 , nitrate; mg/L, milligrams per liter; O, oxygen; ‰, VSMOW, oxygen isotope ratio in per mil of the Vienna Standard Mean Ocean Water; f , fraction of initial nitrate in recharge removed by denitrification; <, less than; --, no data; E, estimated]

Field identifier (fig. 8)	Nitrate sample date	Nitrate (NO_3) measured (mg/L as N)	Nitrate (NO_3) measured (μM)	$\delta^{15}\text{N}$ (NO_3) (‰, AIR)	$\delta^{18}\text{O}$ (NO_3) (‰, VSMOW)	Estimated nitrate (NO_3) initial (μM)	Estimated nitrate (NO_3) initial (mg/L as N)	Estimated f	Iron, manganese, and sulfate sample date	Iron (mg/L)	Manganese (mg/L)	Sulfate (mg/L)
Dakota aquifer												
D-T3	5/17/00	16.7	1,190	--	--	1,260	18	0.1	10/31/00	<10	3.2	34.4
D-T1	5/17/00	1.88	134	--	--	313	4	.6	10/31/00	<10	488	239
D-W3	5/17/00	<.06	<4	--	--	100	2	1	10/31/00	993	439	86.1
Elkhorn River Valley alluvial aquifer												
E-EC2	5/18/00	<0.06	<4	--	--	700	10	1	10/30/00	2,160	1,640	68.4
E-V3	5/16/00	7.36	526	--	--	1,450	20	0.6	10/30/00	<10	503	72.7
E-V3	10/18/04	2.54	181	E26	E16	538	8	.7	10/18/04	<10	308	58.2
E-V2	10/18/04	<.06	<4	--	--	40	.6	.9	10/18/04	82	195	88.7
E-V1	5/16/00	1.56	111	--	--	326	5	.7	10/30/00	30	42.4	72.6
E-V1	10/18/04	.42	30	26.6	17.5	66	1	.5	10/18/04	15	41.5	85.1
Missouri River Valley alluvial aquifer												
M-BC3	5/18/00	<0.06	<4	--	--	200	3	1	11/1/00	1,090	1,440	71.4
M-H3	5/17/00	<.06	<4	--	--	200	3	1	10/31/00	8,150	1,040	72.6
M-H1	5/17/00	<.06	<4	--	--	200	3	1	10/31/00	5,640	352	247
Platte River Valley alluvial aquifer												
P-A3	5/16/00	<0.06	<4	--	--	200	3	1	10/30/00	3,250	819	35.0
P-A2	5/16/00	<.06	<4	--	--	4	.05	0	10/30/00	1,620	750	22.9
P-A1	5/16/00	<.06	<4	--	--	4	.05	0	10/30/00	1,190	683	20.9
P-S3	5/16/00	2.07	148	--	--	505	7	.7	10/30/00	226	228	25.3
P-S3	10/18/04	3.54	253	8.44	4.03	396	6	.4	10/18/04	204	238	26.3
P-S2	10/18/04	3.56	254	8.32	3.74	254	4	0	10/18/04	30	3.4	15.7
P-S1	5/16/00	4.67	333	--	--	369	5	.1	10/30/00	<10	2.0	17.9
P-S1	10/18/04	7.11	508	9.36	3.50	508	7	0	10/18/04	<10	<0.6	20.7
Upland area alluvial aquifers												
U-BA1	5/18/00	<0.05	<4	--	--	80	1	1	11/1/00	592	230	34.4

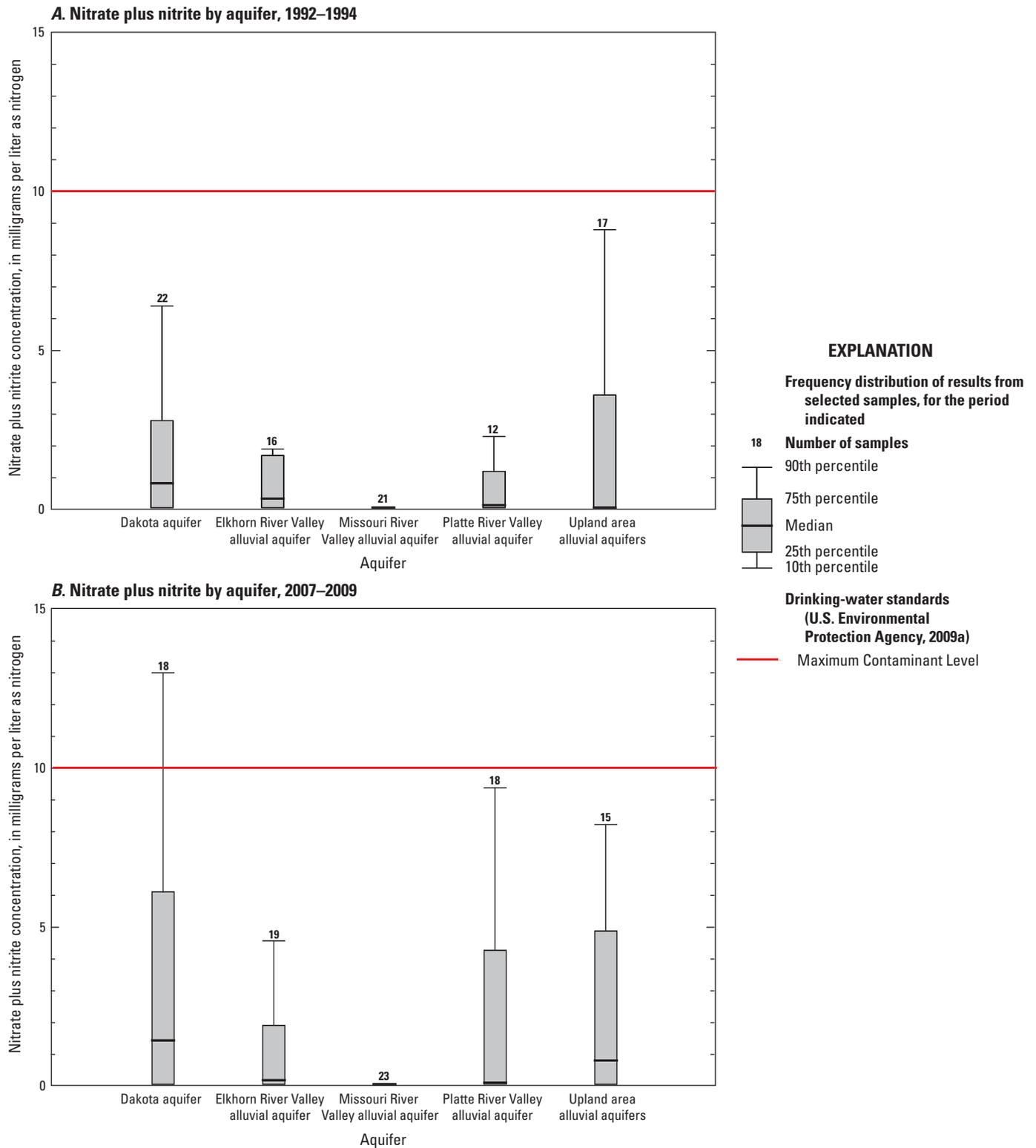
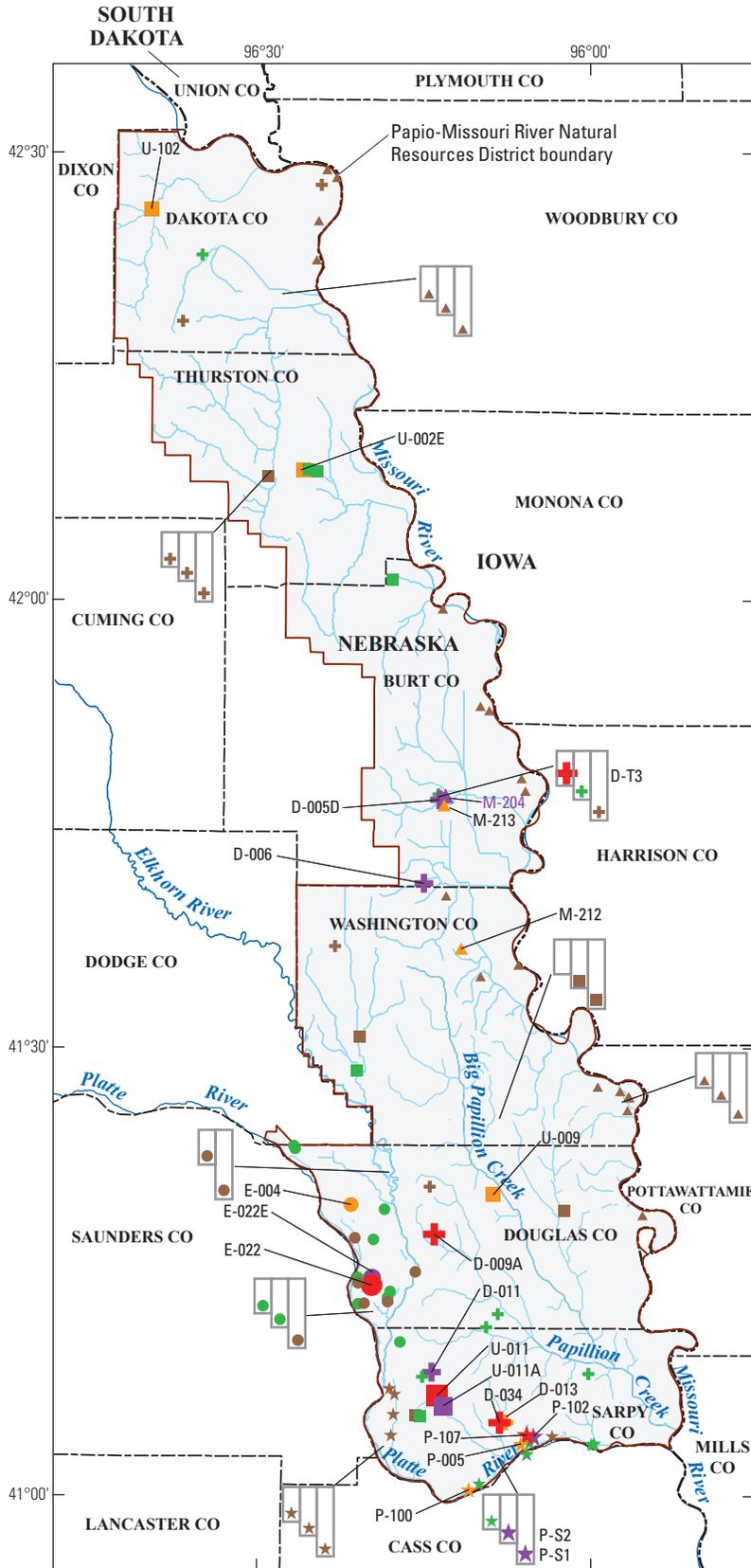


Figure 16. Frequency distribution of nitrate plus nitrite concentration, by aquifer, in the most recent summer-to-fall samples *A*, in network wells, 1992–1994, and *B*, in network wells and one randomly selected well in each well nest, 2007–2009, Papio-Missouri River Natural Resources District, eastern Nebraska.



EXPLANATION
 [Nitrate plus nitrite concentration, in milligrams per liter (mg/L) as nitrogen, and field identifier (if concentration is greater than 3.3 mg/L)]

Dakota aquifer

- + Less than 0.06
- + 0.06 to 3.3
- D-013 + 3.3 to 5.0
- D-006 + 5.0 to 10
- D-T3 + 10 or greater

Elkhorn River Valley alluvial aquifer

- Less than 0.06
- 0.06 to 3.3
- E-004 • 3.3 to 5.0
- E-022E • 5.0 to 10
- E-022 • 10 or greater

Missouri River Valley alluvial aquifer

- ▲ Less than 0.06
- M-212 ▲ 0.06 to 3.3
- M-204 ▲ 3.3 to 5.0

Platte River Valley alluvial aquifer

- ★ Less than 0.06
- ★ 0.06 to 3.3
- P-005 ★ 3.3 to 5.0
- P-102 ★ 5.0 to 10
- P-107 ★ 10 or greater

Upland area alluvial aquifers

- Less than 0.06
- 0.06 to 3.3
- U-009 ■ 3.3 to 5.0
- U-011A ■ 5.0 to 10
- U-011 ■ 10 or greater

Wells in well nests

Schematic to illustrate concentration in wells in well nests. Well box is empty if not analyzed for nitrate plus nitrite as nitrogen

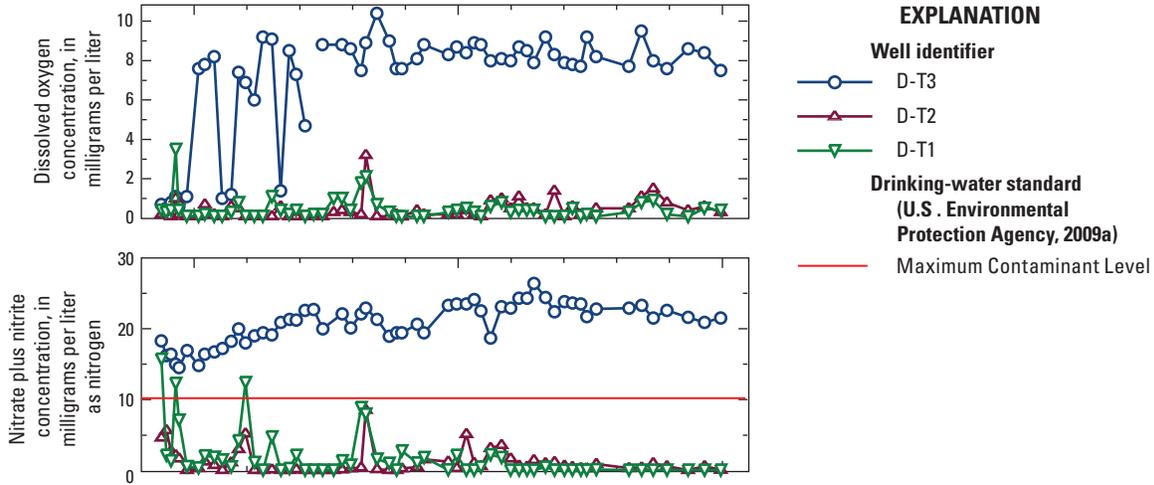
- Deep well in nest
- Medium-depth well in nest, if present
- Shallow well in nest

Base from U.S. Geological Survey digital data, 2001, 1:2,000,000
 Albers Equal-Area Conic projection
 Standard parallels 29°30'N and 45°40'N
 Central meridian 97°30'W
 North American Datum of 1983

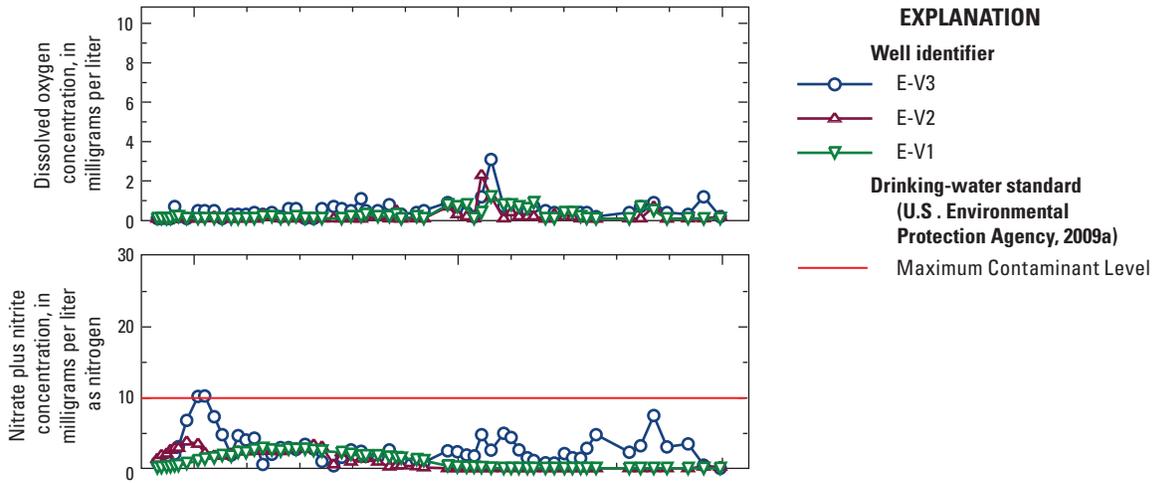
0 5 10 15 20 MILES
 0 5 10 15 20 KILOMETERS

Figure 17. Distribution of the most recent summer-to-fall nitrate plus nitrite concentration for each sampled well, Papio-Missouri River Natural Resources District, eastern Nebraska, 2007–2009.

A. Wells in the D-T well nest, Tekamah, Nebraska, screened in the Dakota aquifer



B. Wells in the E-V well nest, near Venice, Nebraska, screened in the Elkhorn River Valley alluvial aquifer



C. Wells in the P-S well nest, near Springfield, Nebraska, screened in the Platte River Valley alluvial aquifer

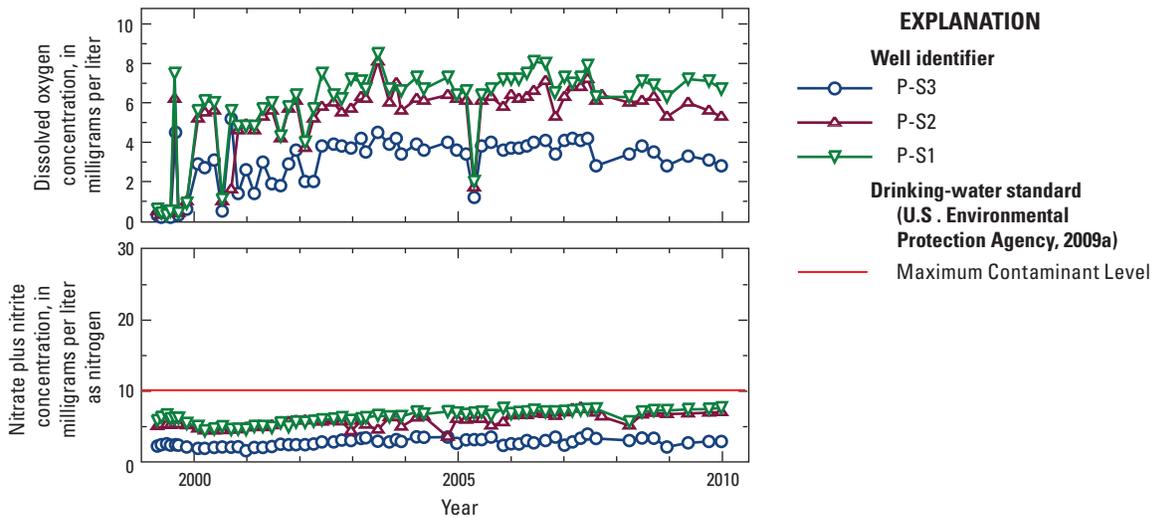


Figure 18. Concentrations of dissolved oxygen and nitrate plus nitrite in samples collected from wells in the *A*, well nest in Tekamah, Nebraska, *B*, well nest near Venice, Nebraska, and *C*, well nest near Springfield, Nebraska, Papio-Missouri River Natural Resources District, eastern Nebraska, 1999–2009.

Nitrite, Ammonia, Orthophosphate Results

From 1992 through 1998, only one sample from the PMRNRD wells was analyzed for nitrite, ammonia, and orthophosphate concentrations. From 1999 to 2009, 1,218 samples collected from selected PMRNRD wells were analyzed for nitrite, ammonia, and orthophosphate concentrations. In this report, the most recent such analysis in the nutrient samples, 1992 to 2009, are termed the other-nutrients samples, 1992 to 2009. The concentrations of nitrite as nitrogen (nitrite-N) in 99 of the 113 other-nutrients samples, 1992 to 2009, were at or less than 0.008 mg/L, the maximum LRL (table 10). The largest nitrite-N concentration was 0.088 mg/L in a sample from the Elkhorn River Valley alluvial aquifer (E-022D), which is less than the USEPA MCL for nitrite-N (1 mg/L). For the other-nutrients samples, 1992 to 2009, nitrite-N was detected in 2 of the samples from the Dakota aquifer, 8 of the samples from the Elkhorn River Valley alluvial aquifer, none of the samples from the Missouri River Valley alluvial aquifer, 4 of the samples from the Platte River Valley alluvial aquifer, and none of the samples from the upland area alluvial aquifers.

Ammonia is a reduced nitrogen species that typically will oxidize to nitrate when dissolved oxygen is present. Ammonia was detected in 57 of the 113 other-nutrients samples, 1992 to 2009. In 46 of the samples with detectable ammonia, neither nitrate nor nitrite was detected. Ammonia was detected most often in samples from the Missouri River Valley alluvial aquifer (21 of 23 samples or 91 percent), followed by the upland area alluvial aquifers (10 of 22 samples, or 45 percent), Dakota aquifer (8 of 19 samples or 42 percent), Platte River Valley alluvial aquifer (8 of 21 samples or 38 percent), and Elkhorn River Valley alluvial aquifer (10 of 28 samples or 36 percent). Concentrations of ammonia ranged from less than 0.04 to 1.81 mg/L as N; none of the samples had ammonia concentrations that exceeded the USEPA nonenforceable standard of 30 mg/L as N. Ammonia concentrations were negatively correlated with dissolved oxygen concentrations ($\tau = -0.24$, $p = 0.01$).

Concentrations of orthophosphate as phosphorus (P) ranged from less than 0.02 to 0.89 mg/L as P; orthophosphate concentration was less than 0.25 mg/L as P in nearly 90 percent of the other-nutrients samples, 1992 to 2009 (table 10). Orthophosphate is the most common form of phosphorus in groundwater; because orthophosphate tends to precipitate or sorb onto aquifer materials, its mobility in soils and groundwater generally is limited (Tesoriero and others, 2009).

Pesticides and Pesticide Degradates

Pesticides, which include herbicides, insecticides, and fungicides, are used to control competing vegetation, insects, and fungi in agricultural, urban, and suburban settings. Groundwater samples from the PMRNRD network wells and wells in well nests were analyzed for a total of 71 pesticides or pesticide degradates from 1992 to 2009 and 61 pesticides or pesticide degradates from 2007 to 2009 (appendix 4). Of

61 pesticides or pesticide degradates analyzed from 2007 to 2009, 21 were detected (fig. 19). Three of the 21 pesticides detected (alachlor, atrazine, and metolachlor) have established health-based drinking-water standards; all detected concentrations of these compounds were below their USEPA standards.

From 2007 to 2009, one or more pesticide compounds were detected in samples from 16 of 82 network wells and in samples from 18 of 26 wells in well nests (fig. 20). The number of detections from 2007 to 2009, including those detected using the ELISA screening kits for triazine and metolachlor, summarized by aquifer, are Platte River Valley alluvial aquifer, 41 detections; Elkhorn River Valley alluvial aquifer, 33 detections; Dakota aquifer, 14 detections; Missouri River Valley alluvial aquifer, 2 detections; and upland area alluvial aquifers, 2 detections. From 2007 to 2009, the individual pesticide compounds that were detected most frequently werealachlor ethane sulfonic acid (ESA), a degradate ofalachlor (8 percent); deethylcyanazine acid (DCAC), a degradate of cyanazine (7 percent); and atrazine (7 percent). Alachlor, atrazine, and cyanazine are among the most commonly detected pesticide compounds in groundwater nationally (Gilliom and others, 2006). However, sale of cyanazine ceased after 2002 because of a voluntary cancellation of the product registration (U.S. Environmental Protection Agency, 2000).

Explosives and Volatile Organic Compounds

Some samples collected from groundwater underlying the former NOP, which is located about 6 mi west of Gretna, Nebr., and west of the PMRNRD boundary, in Saunders County, Nebr., contained measureable concentrations of explosives, primarily RDX, and VOCs, primarily trichloroethylene (TCE). The explosive and VOC contaminants were associated with U.S. Department of Defense activities at the former NOP during and since World War II. The U.S. Army Corps of Engineers is responsible for groundwater remediation at the NOP site (U.S. Army Corps of Engineers, 2010).

Samples from wells E-V1, E-V2, and E-V3, which are wells in a well nest near Venice, Nebr., and about 8 mi north-east of the NOP site, were analyzed for explosives and VOCs in 2008 and 2009 (appendixes 5 and 6). No explosives or VOCs were detected in either the 2008 or 2009 samples.

Radon

Radon is a naturally occurring radioactive gas found in soils, rock, and water. Radon has a number of different isotopes. The most prevalent radon isotope in groundwater is ²²²radon. ²²²Radon is produced by the decay of ²²⁶radium, part of the ²³⁸uranium decay series, and has a half-life of 3.8 days; ²²²radon decays to lead by alpha particle emission (Hem, 1985). ²²²Radon concentration in groundwater can be affected by multiple factors, including the distribution of uranium-bearing minerals in the aquifer material, aquifer physical characteristics,

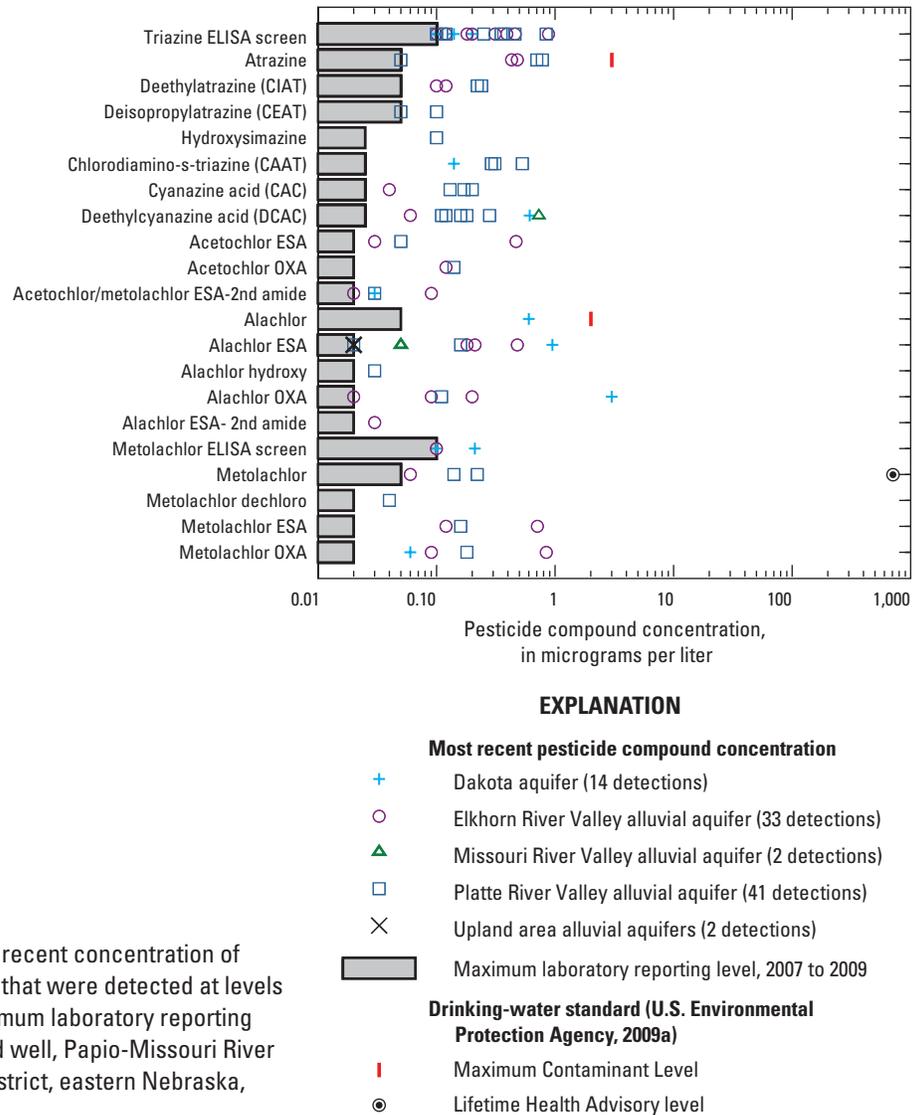


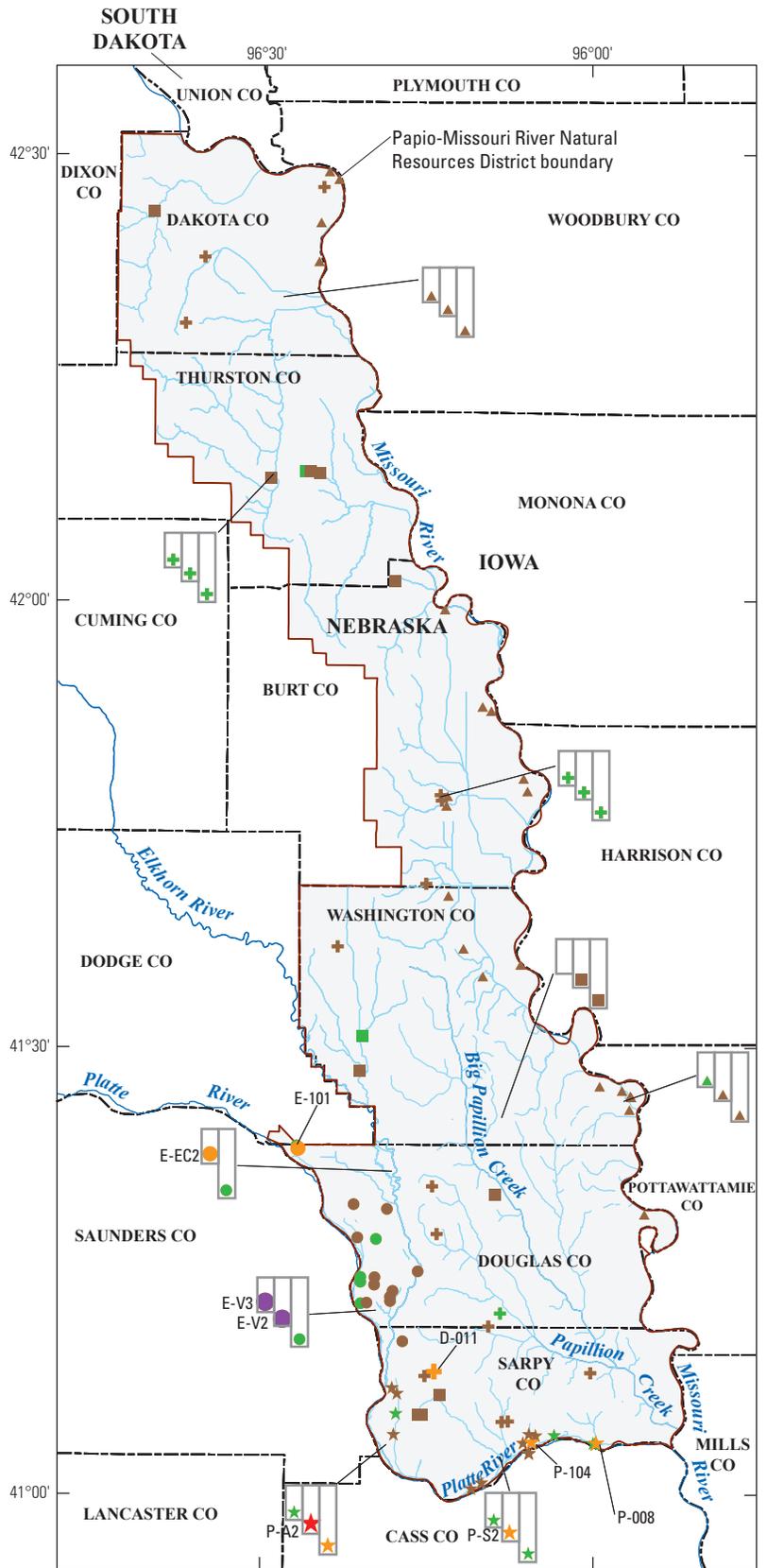
Figure 19. The most recent concentration of pesticide compounds that were detected at levels greater than the maximum laboratory reporting level, in each sampled well, Papio-Missouri River Natural Resources District, eastern Nebraska, 2007–2009.

and geochemical conditions that affect uranium and radium mobility (Otton and others, 1993; Ayotte and others, 2007).

USEPA classifies ²²²radon as a human carcinogen (U.S. Environmental Protection Agency, 2009a). ²²²Radon can contribute to the risk of developing lung and gastrointestinal cancers (National Research Council, 1999; U.S. Environmental Protection Agency, 2003). In an indoor setting, adverse health effects from ²²²radon in drinking water result primarily from inhalation of the gas after it is released from solution, although the amount of radon in water usually is small compared to the other sources of radon to indoor air (Hopke and others, 2000). Domestic use of water with about 10,000 picocuries per liter (pCi/L) of radon contributes about 1 pCi/L of radon to indoor air (Otton and others, 1993). If the concentration of radon in a home’s indoor air is greater than 4 pCi/L, USEPA recommends use of methods to decrease the radon concentration in the home (U.S. Environmental Protection Agency, 2010a). The USEPA has proposed two drinking-water

standards for ²²²radon—4,000 pCi/L and 300 pCi/L. The 4,000 pCi/L standard is an alternative USEPA MCL, which is proposed for public water systems for states or water-system service areas with programs to reduce radon risks from all sources. The 300 pCi/L standard is proposed as the USEPA MCL for states or water-service areas without such plans (U.S. Environmental Protection Agency, 2009a).

For this study, ²²²radon activity was detected in 39 network wells in 1992 and 19 wells in well nests in 2008 (fig. 21; appendix 8). ²²²Radon activity in the most recent samples collected from network wells and in one randomly selected well in each well nest ranged from less than 80 to 1,200 pCi/L. The median ²²²radon activity in the selected wells was 325 pCi/L, which exceeds the lower proposed USEPA MCL of 300 pCi/L (table 13). The median ²²²radon activity for the selected wells was greatest in the upland area alluvial aquifers (430 pCi/L), and the highest radon activity values were in samples from the upland area alluvial aquifers (table 13).



Base from U.S. Geological Survey digital data, 2001, 1:2,000,000
 Albers Equal-Area Conic projection
 Standard parallels 29°30'N and 45°40'N
 Central meridian 97°30'W
 North American Datum of 1983

EXPLANATION

[Number of pesticide compounds detected at concentrations greater than the maximum laboratory reporting level, 2007–2009, and field identifier (if four or more pesticides detected)]

- Dakota aquifer**
 - + Pesticides not detected
 - + 1 to 3 pesticides detected
 - D-011 + 4 to 6 pesticides detected
- Elkhorn River Valley alluvial aquifer**
 - Pesticides not detected
 - 1 to 3 pesticides detected
 - E-101 ● 4 to 6 pesticides detected
 - E-V3 ● 7 to 9 pesticides detected
- Missouri River Valley alluvial aquifer**
 - ▲ Pesticides not detected
 - ▲ 1 to 3 pesticides detected
- Platte River Valley alluvial aquifer**
 - ★ Pesticides not detected
 - ★ 1 to 3 pesticides detected
 - P-008 ★ 4 to 6 pesticides detected
 - ★ 7 to 9 pesticides detected
 - P-A2 ★ 10 or more pesticides detected
- Upland area alluvial aquifers**
 - Pesticides not detected
 - 1 to 3 pesticides detected
- Wells in well nests**
 - Schematic to illustrate concentration in wells in well nests. Well box is empty if not analyzed for pesticide compounds
 - Deep well in nest
 - Medium-depth well in nest, if present
 - Shallow well in nest

Figure 20. Distribution of number of pesticide compounds detected, by well and by aquifer, in sampled wells, Papio-Missouri River Natural Resources District, eastern Nebraska, 2007–2009.

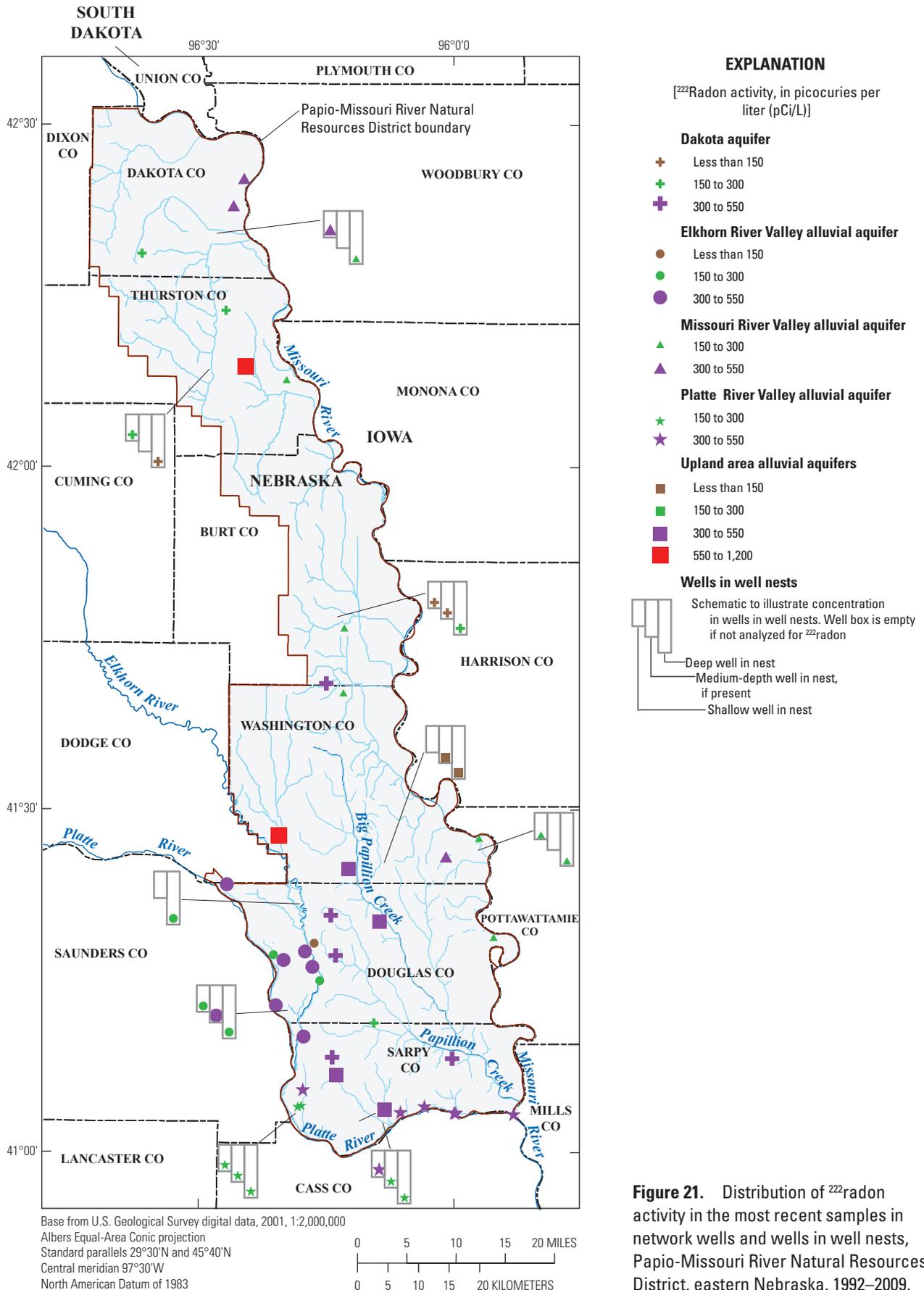


Figure 21. Distribution of ^{222}Rn radon activity in the most recent samples in network wells and wells in well nests, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

Table 13. Summary statistics for ²²²radon activity in the most recent samples collected in network wells and in one randomly selected well in each well nest, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[The U.S. Geological Survey parameter code for ²²²radon is 82303. The proposed U.S. Environmental Protection Agency drinking-water standards and type of standards for ²²²radon are 300 picocuries per liter for the Maximum Contaminant Level and 4,000 picocuries per liter for the Alternative Maximum Contaminant Level (U.S. Environmental Protection Agency, 2009a). The Nebraska Title-118 standard for ²²²radon will be promulgated (Nebraska Department of Environmental Quality, 2006). <, less than]

Aquifer(s)	Number of samples	Number of detections	Activity, in picocuries per liter						
			Minimum	10th percentile	25th percentile	Median	75th percentile	90th percentile	Maximum
Dakota	10	10	120	155	200	315	390	440	460
Elkhorn River Valley alluvial	11	11	100	170	210	330	460	500	530
Missouri River Valley alluvial	10	10	230	240	270	290	320	415	480
Platte River Valley alluvial	10	10	220	245	290	325	450	475	480
Upland area alluvial	7	6	<80	<80	390	430	900	1,200	1,200
All aquifers	48	47	<80	190	255	325	435	480	1,200

Summary of Groundwater Quality in Relation to Potential Action Levels

The PMRNRD groundwater-management plan states that if an analyte concentration exceeds 50 percent of its Nebraska Title-118 standard, a “management, control, or special protection area will be strongly pursued” (Papio-Missouri River Natural Resources District, 1994; Nebraska Department of Environmental Quality, 2006). Analytes with concentrations that exceeded 30 percent of the applicable Nebraska Title-118 standard are identified by the authors in this report (table 14) so that the PMRNRD staff can monitor groundwater in the PMRNRD and plan possible actions should the analyte concentrations continue to rise. The analytical results of the most recent samples collected from the network wells and all the wells in well nests from 1992 to 2009 indicate that, in at least 1 sample, there was a concentration that exceeded 30 percent of the Nebraska Title-118 standard for at least 1 of 3 major ions (chloride, fluoride, and sulfate), 1 nutrient (nitrate), 1 pesticide (atrazine), or 3 trace elements (arsenic, iron, and manganese). Cadmium was not included as a qualified exceedance because its concentration in the associated blank samples indicated contamination potentially occurred during sampling or processing (table 14).

Samples were collected in 1992 for gross alpha, gross beta, and ²²⁶radium activity and ²³⁴uranium:²³⁸uranium ratio. The Nebraska Title-118 standards are 15 pCi/L for gross alpha activity, including alpha particles emitted by ²²⁶radium but excluding alpha particles emitted by radon and uranium; 4 millirem per year (mrem/yr) for gross beta activity; and 5 pCi/L for combined ²²⁶radium and ²²⁸radium activity (appendix 3; Nebraska Department of Environmental Quality, 2006). Verstraeten and Ellis (1995) reported gross alpha results for the 1992 samples and noted that one sample from a well screened in the Dakota aquifer (D-002) likely exceeded the USEPA MCL for gross alpha activity (that is, without radon

and uranium emissions). Verstraeten and Ellis (1995) results also indicated that samples from three wells screened in the Dakota aquifer (D-001, D-002, and D-003) likely exceeded 7.5 pCi/L (50 percent of the Title-118 standard) for gross alpha activity.

Verstraeten and Ellis (1995) reported gross beta results for the 1992 samples; however, the units used were pCi/L. It is not possible to reliably convert gross beta activity from pCi/L to mrem/yr units unless the activity of the primary beta emitter species (for example, ⁴⁰potassium, ¹³⁷cesium, ¹³¹iodine, or ⁹⁰strontium) also was measured. Such data were not included in Verstraeten and Ellis (1995). For some public water systems, USEPA uses gross beta emissions as a screening measure; if gross beta emissions are less than 50 pCi/L for a given sample, not including ⁴⁰potassium activity (U.S. Environmental Protection Agency, 2001), the activity in the sample will typically be less than 4 mrem/yr, depending on the primary beta emitter species. In 1992, gross beta emissions were less than 31 pCi/L for all PMRNRD groundwater samples; therefore, activity was likely to be less than 4 mrem/yr. For further information about the gross alpha, gross beta, and ²²⁶radium activities, and ²³⁴uranium:²³⁸uranium ratios in the 1992 samples, see Verstraeten and Ellis (1995).

Alternative Approaches to Groundwater Quality Monitoring and Implications

An objective of the PMRNRD’s groundwater-management plan is to monitor water quality of the principal aquifers in the district (Papio-Missouri River Natural Resources District, 1994). Given the analytical results from the most recent samples collected from the network wells and all the wells in well nests from 1992 to 2009, alternative approaches to the current PMRNRD groundwater-quality sampling program that could be considered include the following:

Table 14. Summary of major ions, nutrients, pesticides, and trace elements results in the most recent selected samples in network wells and in one randomly selected well in each well nest, and number of analyte concentrations that are at least 30, 50, or 100 percent of applicable Federal drinking-water or Nebraska Title-118 standards, Pappio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009.

[USGS, U.S. Geological Survey; USEPA, U.S. Environmental Protection Agency; mg/L, milligrams per liter; SDWR, Secondary Drinking Water Regulation; --, no result fit criteria or not defined; MCL, Maximum Contaminant Level; DWAT, Drinking Water Advisory Table; Reserved, a standard will be promulgated for this analyte; DWAT-Low sodium diet, maximum concentration advised for individuals on a restricted sodium diet; µg/L, micrograms per liter; LTHA, Lifetime Health Advisory level]

Constituent	USGS parameter code	Concentration unit	USEPA drinking-water standard(s)/ type of standard ¹	Nebraska Title-118 standard ²	Number of samples	Number of samples, by aquifer, with analyte concentrations that are at least 30 percent of the highest USEPA ¹ or Nebraska Title-118 standard ²						Total number of samples with analyte concentrations of at least 50 percent of the highest USEPA ¹ or Nebraska Title-118 standard ²	Total number of samples with analyte concentrations that equal or exceed the highest USEPA ¹ or Nebraska Title-118 standard ²
						Aquifer(s)					Total		
						Dakota	Elkhorn River Valley alluvial	Missouri River Valley alluvial	Platte River Valley alluvial	Upland area alluvial			
Most recent samples for major ions													
Chloride	00940	mg/L	250/SDWR	250	49	2	--	1	--	--	3	1	--
Fluoride	00950	mg/L	4/MCL	4	49	1	--	--	--	--	1	--	--
	00950	mg/L	2/SDWR	4	49	1	--	--	--	--	1	--	--
Sodium	00930	mg/L	30–60/DWAT	Reserved	49	9	8	9	8	4	38	19	4
	00930	mg/L	20/DWAT-Low sodium diet	Reserved	49	11	11	10	10	7	49	48	38
Sulfate	00945	mg/L	250/SDWR	250	49	4	4	6	2	--	16	8	4
Most recent samples for nutrients, summer-to-fall season													
Nitrate plus nitrite	00631	mg/L, as nitrogen	10/MCL	10	200	11	12	4	7	14	48	35	13
Most recent samples for pesticides													
Atrazine	39632	µg/L	3/MCL	3	70	--	--	--	1	--	1	1	--
Most recent samples for trace elements													
Arsenic	01000	µg/L	10/MCL	10	49	--	4	7	6	--	17	10	3
Boron	01020	µg/L	1,000/LTHA	--	49	3	1	--	--	1	5	3	--
Cadmium ³	01025	µg/L	5 MCL	5	50	1	1	2	1	--	5	2	--
Iron	01046	µg/L	300/SDWR	300	50	4	6	11	5	1	27	26	23
Manganese	01056	µg/L	300/LTHA	--	50	5	10	11	6	2	34	31	27
	01056	µg/L	50/SDWR	50	50	6	11	11	6	3	37	37	35
Strontium	01080	µg/L	4,000/LTHA	--	50	5	--	7	--	--	12	3	2

¹U.S. Environmental Protection Agency, 2009a.

²Nebraska Department of Environmental Quality, 2006.

³These cadmium results are all from samples collected in 1992 and likely reflect contamination during sample collection, processing, or analysis because cadmium was detected at the same order of magnitude in the associated blank sample.

1. Collect fewer samples for nutrient analysis;
2. Collect samples periodically for analysis of constituents with Federal drinking-water or Nebraska Title-118 standard(s)—consider selecting constituents with one or more 1992 to 2009 results that approached or exceeded the Federal drinking-water or Nebraska Title-118 standard(s) (table 14);
3. Collect samples periodically for analysis of radionuclides activity, especially from wells screened in the Dakota aquifer;
4. Restrict water-quality sampling to wells with at least a minimum of well-construction information (for example, well depth, depth(s) to top and bottom of screen(s), and number of screens) and equipped with a faucet located close to the wellhead and pump, before any water treatment; and
5. Select network wells to be sampled each year using a stratified-random approach (Scott, 1990).

Decreasing the frequency of nutrient sampling could be considered because the distribution of concentrations of nitrate-N, by aquifer, was similar from 1992 to 1994 and from 2007 to 2009 and because there are no significant trends in nitrate-N concentrations for most wells in the well nests. Decreasing the frequency of nutrient sampling, particularly in areas where there is not a significant trend in nitrate-N concentration, could provide economic benefits.

The analytical results from the most recent samples collected from the network wells and all the wells in well nests from 1992 to 2009 indicate that in at least 1 sample there was a concentration that exceeded 30 percent of the Nebraska Title-118 standard for at least 1 of 3 major ions (chloride, fluoride, and sulfate), 1 nutrient (nitrate), 1 pesticide (atrazine), or 3 trace elements (arsenic, iron, and manganese). Collecting samples periodically from network wells and wells in well nests for analysis of these constituents could be considered to allow the PMRNRD to assess whether these concentrations are changing.

Verstraeten and Ellis (1995) reported that samples from three wells screened in the Dakota aquifer (D-001, D-002, and D-003) likely exceeded 7.5 pCi/L (50 percent of the Nebraska Title-118 standard) for gross alpha activity. Sampling periodically for radionuclides activity, especially for wells screened in the Dakota aquifer, could be considered to assess current values for gross alpha activity in the groundwater. Additional radionuclide samples also could indicate the extent of activity levels that exceed 50 percent of the Nebraska Title-118 standard, particularly for ²²⁶radium and ²²⁸radium activities, which were not measured in 1992 by Verstraeten and Ellis (1995).

Restricting sampling to wells with a minimum of well-construction information (for example, well depth, depth to top and bottom of screen, and number of screens) and equipped with a faucet located close to the wellhead and pump, before any water treatment, would allow for on-site

measurement of dissolved oxygen in the field. The dissolved oxygen results, with other selected major ion and trace-element results, are useful to evaluate redox processes.

Selecting the network wells to be sampled each year using a stratified-random approach (Scott, 1990) would provide an unbiased and well-distributed set of samples for later analysis and improve representativeness and spatial coverage. A more robust and defensible analysis depends on an unbiased and well-distributed set of samples.

Summary

The U.S. Geological Survey, in cooperation with the Papio-Missouri River Natural Resources District (PMRNRD), conducted this study to map the water-level altitude of 2009 within the Elkhorn River Valley, Missouri River Valley, and Platte River Valley alluvial aquifers; to present the predevelopment potentiometric-surface altitude within the Dakota aquifer; and to describe the age and quality of groundwater in the five principal aquifers of the PMRNRD in eastern Nebraska using data collected from 1992 to 2009. In addition, implications of alternatives to the current PMRNRD groundwater-quality monitoring approach are discussed.

The PMRNRD encompasses approximately 1,790 square miles (4,640 square kilometers) in eastern Nebraska and includes all or parts of seven counties. In the PMRNRD, groundwater altitude, relative to National Geodetic Vertical Datum of 1929, ranged from about 1,080 feet (ft) to 1,180 ft in the Elkhorn River Valley alluvial aquifer and from about 960 ft to 1,080 ft in the Missouri River Valley and Platte River Valley alluvial aquifers. Groundwater flow generally is toward or parallel to the rivers. In the PMRNRD, the estimated altitude of the potentiometric surface of the Dakota aquifer, predevelopment, ranged from about 1,100 ft to 1,200 ft. Groundwater flow in the Dakota aquifer is generally toward the east.

To assess groundwater age and quality, groundwater samples were collected from a total of 217 wells from 1992 to 2009 for analysis of various analytes. Groundwater samples collected in the PMRNRD from 1992 to 2009 and interpreted in this report were analyzed for age-dating analytes (chlorofluorocarbons), dissolved gases, major ions, trace elements, nutrients, stable isotope ratios, pesticides and pesticide degradates, volatile organic compounds (VOCs), explosives, and ²²²radon.

Apparent groundwater age was assessed from concentrations of chlorofluorocarbons and dissolved gases measured in samples collected in 2000 from selected wells in well nests. Apparent groundwater-recharge dates (as of 2000) ranged from early 1960s to early 1980s in the Dakota aquifer, early 1960s to 1970s in the Elkhorn River Valley alluvial aquifer, older than 1940 and late 1960s to early 1970s in the Missouri River Valley alluvial aquifer, mid-to-late 1950s and early-to-mid 1970s in the Platte River Valley alluvial aquifer, and early 1970s in one of the upland area alluvial aquifers.

Concentrations of major ions in the most recent samples collected from 1992 to 2009 indicate that the predominant water type was calcium bicarbonate. Major ion results indicate that concentrations of sulfate in 4 wells exceeded the U.S. Environmental Protection Agency (USEPA) Secondary Drinking Water Regulation (SDWR) and Nebraska Title-118 standards, and concentrations of sodium in 4 wells exceeded USEPA nonenforceable Drinking Water Advisory Table standards. In addition, the chloride concentration in 1 sample exceeded 50 percent of the USEPA SDWR, and the fluoride concentration in 1 sample exceeded 30 percent of the USEPA Maximum Contaminant Level (MCL) and Nebraska Title-118 standard. On the basis of the concentrations of major ions, calcium and magnesium, all samples were classified as “hard” or “very hard” water.

Eighteen of the 21 trace elements analyzed in samples from PMRNRD wells have USEPA drinking-water standards. Sixteen of the trace elements with USEPA standards were detected in the selected samples. In the samples selected for trace-element analysis, the only trace-element concentration that exceeded an enforceable USEPA drinking-water standard (MCL) was for arsenic; this occurred in 4 percent of the samples. In these selected trace-element samples, the trace elements detected at concentration(s) that exceeded a nonenforceable USEPA drinking-water standard (SDWR or Lifetime Health Advisory level) were iron (46 percent of wells), manganese (70 percent), and strontium (4 percent). The trace elements without a USEPA drinking-water standard that were detected in the selected trace-element samples are cobalt, lithium, and vanadium. The only trace elements that were not detected in any of the selected samples are lead and nickel.

From 1992 to 2009, groundwater samples from the PMRNRD network wells and well nests were analyzed for as many as four nitrogen and phosphorus compounds—ammonia, nitrate, nitrite, and orthophosphate. Nitrate-N concentrations in the most recent nutrient samples collected from the network wells and from one randomly selected well in the well nests from 1992 to 2009 for most wells (80 percent) ranged from less than 0.06 to 8.55 milligrams per liter (mg/L), with a median value of 0.12 mg/L. Concentrations of nitrate-N in 13 (7 percent) nutrient samples, 1992 to 2009, were greater than or equal to the USEPA MCL and Nebraska Title-118 standard of 10 mg/L, and concentrations of nitrate-N in 35 (18 percent) nutrient samples, 1992 to 2009, were greater than or equal to 5 mg/L, which is the PMRNRD action level for possible management implementation to reduce nitrate concentrations in groundwater.

The spatial distribution of denitrification in the PMRNRD was assessed using (1) concentrations of dissolved oxygen, (2) concentrations of dissolved nitrogen gas and methane, and (3) $\delta^{15}\text{N}_{\text{AIR}}$ in nitrate and dissolved nitrogen gas. In the nutrient samples, 1992 to 2009, the water was anoxic in 85 (44 percent) of the 191 samples with dissolved oxygen results. Excess nitrogen gas or presence of methane gas indicate that at least

some denitrification likely was occurring in groundwater within the capture area for wells in the well nests with dissolved gas analysis.

The fractional decrease in the amount of nitrate-N (“*f*”) is greater than 0.5 for all the sampled wells in well nests, except D-T3, E-V1, P-A2, P-A1, P-S2, and P-S1. Estimated “*f*” is 0.1 or less for wells D-T3, P-S2, and P-S1; this result (evidence of little denitrification) agrees with the oxic redox classification of these wells in samples from 1999 to 2009.

Statistical tests for a temporal difference, using the nutrient samples for 1992 to 1994 and 2007 to 2009, determined no significant change in the nitrate-N concentration distribution for any of the five PMRNRD aquifers. In addition, no significant difference was determined for the nitrate-N concentration distribution by aquifer (1) between the 1992 to 1994 and 1992 to 2009 results or (2) between the 2007 to 2009 and 1992 to 2009 results.

For each of the wells in well nests, the final summer-to-fall samples in each year from 1999 to 2009 were selected to assess whether there was a statistically significant temporal trend in nitrate-N concentrations. The trends in nitrate-N concentrations were negative for the wells in the well nests near Venice and Walthill—wells E-V1, E-V2, and D-W2. The trends in nitrate-N concentrations were positive for the wells in the well nest near Springfield—wells P-S1, P-S2, and P-S3. No significant temporal trends in nitrate-N concentration were found for the remaining wells in well nests.

Of the 61 pesticides or pesticide degradates analyzed from 2007 to 2009, 21 were detected. Three of the 21 pesticides detected (alachlor, atrazine, and metolachlor) have established health-based criteria; all detections of these compounds were at concentrations less than their USEPA standards. From 2007 to 2009, 1 or more pesticide compounds were detected in 16 of the 82 network wells and in 18 of the 26 wells in well nests. From 2007 to 2009, the individual pesticide compounds that were detected most frequently were alachlor ethane sulfonic acid, a degradate of alachlor; deethylcyanazine acid, a degradate of cyanazine; and atrazine.

In 2008 and 2009, samples from the wells E-V1, E-V2, and E-V3, which are wells in a well nest about 8 miles north-east of the Nebraska Ordnance Plant site, were analyzed for explosives and VOCs. No explosives or VOCs were detected in either the 2008 or 2009 samples.

²²²Radon activity in the most recent samples collected from the network wells and in one randomly selected well in each well nest ranged from less than 80 to 1,200 picocuries per liter (pCi/L). The median ²²²radon level in the selected wells was 325 pCi/L, which exceeds the lower proposed USEPA MCL of 300 pCi/L.

Analytes with concentrations that exceeded 30 percent of the applicable Nebraska Title-118 standard were identified so that the PMRNRD can plan to monitor groundwater in the area and consider possible actions should the analyte concentrations continue to rise. The analytical results from the

most recent samples collected in the network wells and all the wells in well nests from 1992 to 2009 indicate that in at least 1 sample there was a concentration that exceeded 30 percent of the Nebraska Title-118 standard for at least 1 of 3 major ions (chloride, fluoride, and sulfate), 1 nutrient (nitrate-N), 1 pesticide (atrazine), or 3 trace elements (arsenic, iron, and manganese). In addition, 30 percent of the USEPA MCL or Nebraska Title-118 standard for gross alpha activity likely was exceeded in samples from three wells screened in the Dakota aquifer.

Study findings indicate that the following alternatives to the current PMRNRD groundwater-sampling approach could be considered: (1) collect fewer samples for nutrient analysis; (2) collect samples periodically for analysis of constituents with Federal drinking-water or Nebraska Title-118 standard(s), particularly constituents with one or more 1992 to 2009 result(s) that approached or exceeded the Federal drinking-water or Nebraska Title-118 standard(s); (3) collect samples periodically for determining radionuclides activity, especially from wells screened in the Dakota aquifer; (4) restrict water-quality sampling to wells with at least a minimum of well-construction information and equipped with a faucet located close to the wellhead and pump, and (5) select network wells to be sampled each year using a stratified-random approach.

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Appendixes 1–8

Appendix 1. Selected well-construction information for sampled wells, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-1.xlsx>.

Appendix 2. List of water-quality-related data in tab-delimited data files

The data file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-2>.

Appendix 3. Major ions, nutrients, radionuclides, and trace elements analyzed in groundwater samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-3.xlsx>.

Appendix 4. Pesticides analyzed in groundwater samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-4.xlsx>.

Appendix 5. Volatile organic compounds analyzed in groundwater samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 2008–2009

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-5.xlsx>.

Appendix 6. Explosive compounds analyzed in groundwater samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 2008–2009

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-6.xlsx>.

Appendix 7. Age-dating-related analytes, dissolved gases, and stable isotopes analyzed in groundwater samples, Papio-Missouri River Natural Resources District, eastern Nebraska, 2000–2005

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-7.xlsx>.

Appendix 8. Number of samples collected and number of analyses by type of determination for each sampled well, Papio-Missouri River Natural Resources District, eastern Nebraska, 1992–2009

The Excel file can be accessed at <http://pubs.usgs.gov/sir/2012/5036/downloads/appendix-8.xlsx>.

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