

Prepared in cooperation with the
City of Fort Madison, Iowa

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Ammonia in Ground Water from the Mississippi River Alluvium, Fort Madison, Iowa

Water-Resources Investigations Report 01-4062

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By S. Mike Linhart

U.S. GEOLOGICAL SURVEY

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Prepared in cooperation with the
CITY OF FORT MADISON, IOWA

Iowa City, Iowa
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U.S. DEPARTMENT OF THE INTERIOR
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U.S. GEOLOGICAL SURVEY
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CONVERSION FACTORS, ABBREVIATIONS, AND VERTICAL DATUM

Multiply	By	To obtain
feet (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi ²)	2.590	square kilometer
milligram (mg)	0.001	microgram (μg)
gallon (gal)	3.785	liter (L)
gallon per minute (gal/min)	0.06309	liter per second
million gallons per day (Mgal/d)	3,785	cubic meters per day

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows:
 $^{\circ}\text{F} = 1.8 (^{\circ}\text{C} + 32)$

Abbreviated water-quality units used in this report: Chemical concentrations are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) and micrograms per liter (μg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. Micrograms per liter is a unit expressing the concentration of chemical constituents in solution as weight (micrograms) of solute per unit volume (liter) of water. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. The numerical value of micrograms per liter is the same as for concentrations in parts per billion.

Per mil: A unit expressing the ratio of stable-isotopic abundances of an element in a sample to those of a standard material. Per mil units are equivalent to parts per thousand. Stable-isotopic ratios are computed as follows (Kendall and Caldwell, 1998):

$$\delta X = \left(\frac{R(\text{sample})}{R(\text{standard})} - 1 \right) \times 1,000$$

where; X is the heavier isotope and R is the ratio of the heavier, less abundant stable isotope to the lighter stable isotope in a sample or standard.

The δ values for oxygen, hydrogen, and sulfur stable isotopic ratios discussed in this report are referenced to the following standard materials:

R	Standard identity and reference
nitrogen-15:nitrogen-14 (referred to as δ ¹⁵ N)	Standard atmospheric nitrogen, referenced to National Bureau of Standards, NBS-14 nitrogen gas (Fritz and Fontes, 1980, p. 16).

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Water year: The 12-month period October 1 through September 30. The water year is designated by the calendar year in which it ends. Thus, the year ending September 30, 1996, is called "water year 1996."

Ammonia in Ground Water from the Mississippi River Alluvium, Fort Madison, Iowa

By S. Mike Linhart

Abstract

The U.S. Geological Survey, in cooperation with the City of Fort Madison, conducted a study of the potential sources and possible processes that might produce ammonia in ground water from the Mississippi River alluvium near Fort Madison, Iowa. High ammonia concentrations of 3.0 to 6.4 milligrams per liter were detected in water produced from municipal well Fort Madison #4 from 1992 through 1996. Total organic carbon concentrations of about 5 milligrams per liter were also reported during the same time period.

Water-level measurements from two municipal wells and one well at Iowa State Penitentiary were used to determine that the general direction of ground-water flow during the two days of sampling was from northeast to southwest toward wells Fort Madison #4 and Fort Madison #5. Continuous pumping of other nearby wells probably influenced the direction of ground-water flow on these days. Because of a till confining unit separating the Mississippi River and the alluvial aquifer, it is uncertain to what extent induced recharge occurs to the alluvial aquifer from the river.

Water samples were collected from three municipal wells, two industrial wells, one water-supply well at the Iowa State Penitentiary, one domestic well, two creeks, and the Mississippi River. Tritium analytical results indicate that the time of recharge was after 1953 for water from the municipal wells (where tritium samples were collected). The ammonia concentration, 5.1 milligrams per liter, was considerably higher in ground

water collected from well Fort Madison #4 compared to samples collected from other wells. The dissolved organic carbon concentration was also highest in ground water collected from well Fort Madison #4 (5.5 milligrams per liter) although samples from other wells were also relatively high, 2.6 to 5.3 milligrams per liter. The most likely process producing the high ammonia concentration in ground water in the vicinity of well Fort Madison #4 is decomposition of organic matter (ammonification). Nitrogen isotope values, when compared to nitrogen isotope values found in ground water in the vicinity of some of the other wells, indicate the possibility that a higher percentage of the ammonia found in ground water in the vicinity of well Fort Madison #4 may be from human and(or) other animal wastes. Higher concentrations of dissolved phosphorus, orthophosphate, and a higher chloride-to-sodium mole ratio found in ground water sampled from well Fort Madison #4 could be indicative of a sewage or septic source. Potential sources include existing or abandoned septic systems, leaking sanitary sewer lines, commercial or residential waste-disposal sites, and agricultural runoff upgradient from well Fort Madison #4, or possibly, bed sediments of the Mississippi River.

INTRODUCTION

The City of Fort Madison, located in southeast Iowa along the Mississippi River, obtains its water supply from the Mississippi River and from three wells (Fort Madison wells #3, #4, and #5) (fig. 1) completed in sands and gravels of the Mississippi

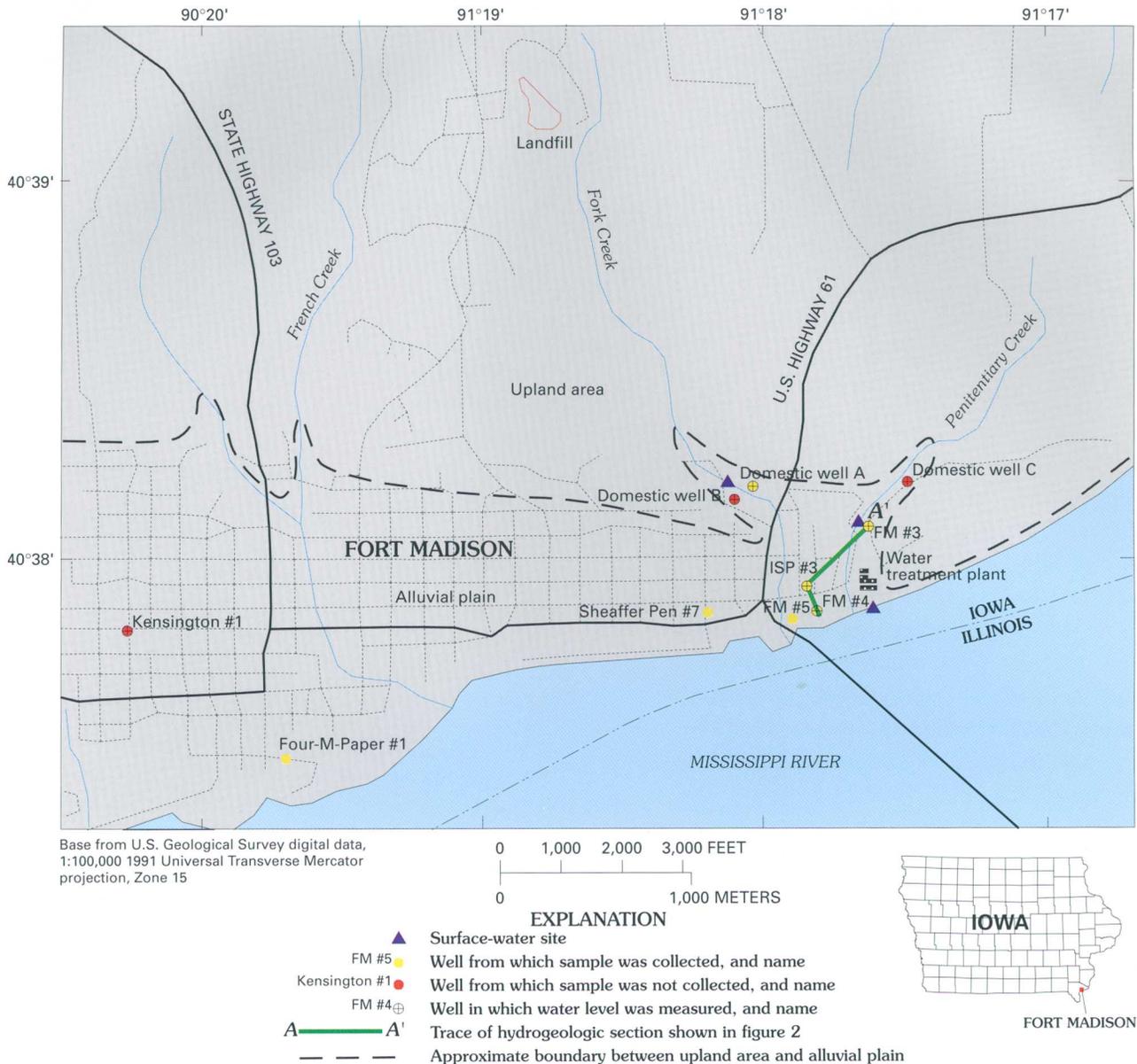


Figure 1. Location of wells sampled for water quality, wells where water levels were measured, and surface-water sites, April 20 and 21, 1999, Fort Madison, Iowa.

River alluvium. At present, the predominant source for the municipal water supply is the Mississippi River, and the wells are used during periods of poor river water quality to meet turbidity standards. Average daily withdrawal from the river and the wells is about 2 Mgal/d (L. Dinwiddie, City of Fort Madison, oral commun., March 1997). The wells are drilled to depths of about 150 to 160 ft below land surface, and each well produces about 700 gal/min. Fort Madison well #3 is located about 1,200 ft from the river, and Fort Madison wells #4 and #5 are located less than 200 ft from the river.

The City of Fort Madison drilled wells #3, #4, and #5 in 1991. Ammonia concentrations of 3.0 to 6.4 milligrams per liter (mg/L) were detected in water produced from Fort Madison well #4 from 1992 through 1996, and total organic carbon concentrations of about 5 mg/L also were reported for the same time period (Schaap and Linhart, 1998). The large ammonia concentrations require greater amounts of chlorine during the municipal water-treatment process, which increases treatment costs and can result in customer complaints about taste and odor.

The U.S. Geological Survey (USGS), in cooperation with the City of Fort Madison, conducted a study of potential sources and processes that might produce ammonia in ground water from the Mississippi River alluvium (alluvial aquifer) near Fort Madison. Hydrogeologic and water-quality information was compiled and evaluated to determine the potential sources and possible processes producing the large ammonia concentration in ground water. Results of the study may enable the City of Fort Madison and other municipal water users in similar hydrogeologic settings (alluvial aquifers) to make decisions that can improve water quality. This study will also further scientific understanding of the processes and potential sources that cause large ammonia concentrations in shallow aquifers as well as the development of analytical methods for evaluation of ground-water quality that is affected by anthropogenic activity.

Purpose and Scope

The purpose of this report is to present results of the study of potential sources and processes contributing ammonia to ground water from the Mississippi River alluvium near Fort Madison. The report (1) describes ground-water flow in the alluvium based on available hydrogeologic data and additional data collected during April 1999, (2) describes chemical processes that might account for the large ammonia concentration in the ground water from the alluvium, and (3) provides a preliminary assessment of whether the large ammonia concentrations in ground water are due to natural or anthropogenic sources.

Description of Study Area

The City of Fort Madison, Iowa is located in Lee County in southeast Iowa along the Mississippi River. The study area is in the eastern part of Fort Madison within the Mississippi River alluvial plain and is bounded by an upland area to the north and east (fig. 1). The uplands consist primarily of loess overlying weathered glacial drift (Prior, 1991).

A generalized hydrogeologic section (fig. 2, section A–A') through well Fort Madison (FM) #3, well Iowa State Penitentiary (ISP) #3, and well FM #4

depicts the stratigraphy of the alluvial and glacial deposits and the top of the bedrock as indicated from well logs. The study area is underlain by a layer of miscellaneous fill, cinders, brick, sand, and silt (surficial unconsolidated deposits) as much as 20 ft thick. This layer in the vicinity of well FM #3 consists of brown clay. The surficial unconsolidated deposits are underlain by glacial till deposits (clay, cobbles, and boulders) that vary in thickness from approximately 60 ft near FM #4 to approximately 100 ft near FM #3. The till deposits decrease in thickness toward the Mississippi River and may provide an effective barrier to the downward migration of contaminants. Clays can store significant amounts of water; however, the capillary attraction between water and the small clay particles and the poor connection between the voids decreases permeability. Therefore, the till deposits underlying the study area probably cause confining, or at least semiconfining, conditions in the underlying alluvial aquifer. The alluvial aquifer consists primarily of fine- to coarse-grained sand and gravel with some layers of till. These sands and gravels were most likely stream deposited prior to, or between, glacial advances. Subsequent glacial advances deposited the overlying till material (Coble and Roberts, 1971). The alluvial aquifer ranges in thickness from approximately 50 ft at FM #3 to approximately 60 ft at FM #4.

At Fort Madison, the depth to bedrock is approximately 140 to 160 ft. Bedrock consists primarily of limestone and dolomite of Mississippian age (fig. 2). In southeast Iowa, Mississippian-age bedrock ranges from approximately 0 to 200 ft thick (Horick and Steinhilber, 1973). Fort Madison lies close to the contact between the water-bearing Mississippian aquifer (to the southwest) and the Devonian-Mississippian confining unit, which underlies the study area and bears little available water (Coble and Roberts, 1971).

Land use in the study area (alluvial plain) is primarily a mix of residential, commercial, and industrial sites. Residences are present within the two drainage basins (Fork Creek and Penitentiary Creek) that drain the surrounding upland area (fig. 1). To the north, within a 1-mi radius of the study area, approximately 50 percent of the land use is forested, primarily on the steeper slopes; agriculture accounts for approximately the other 50 percent of land use. The majority of homes in the study area are connected to the Fort

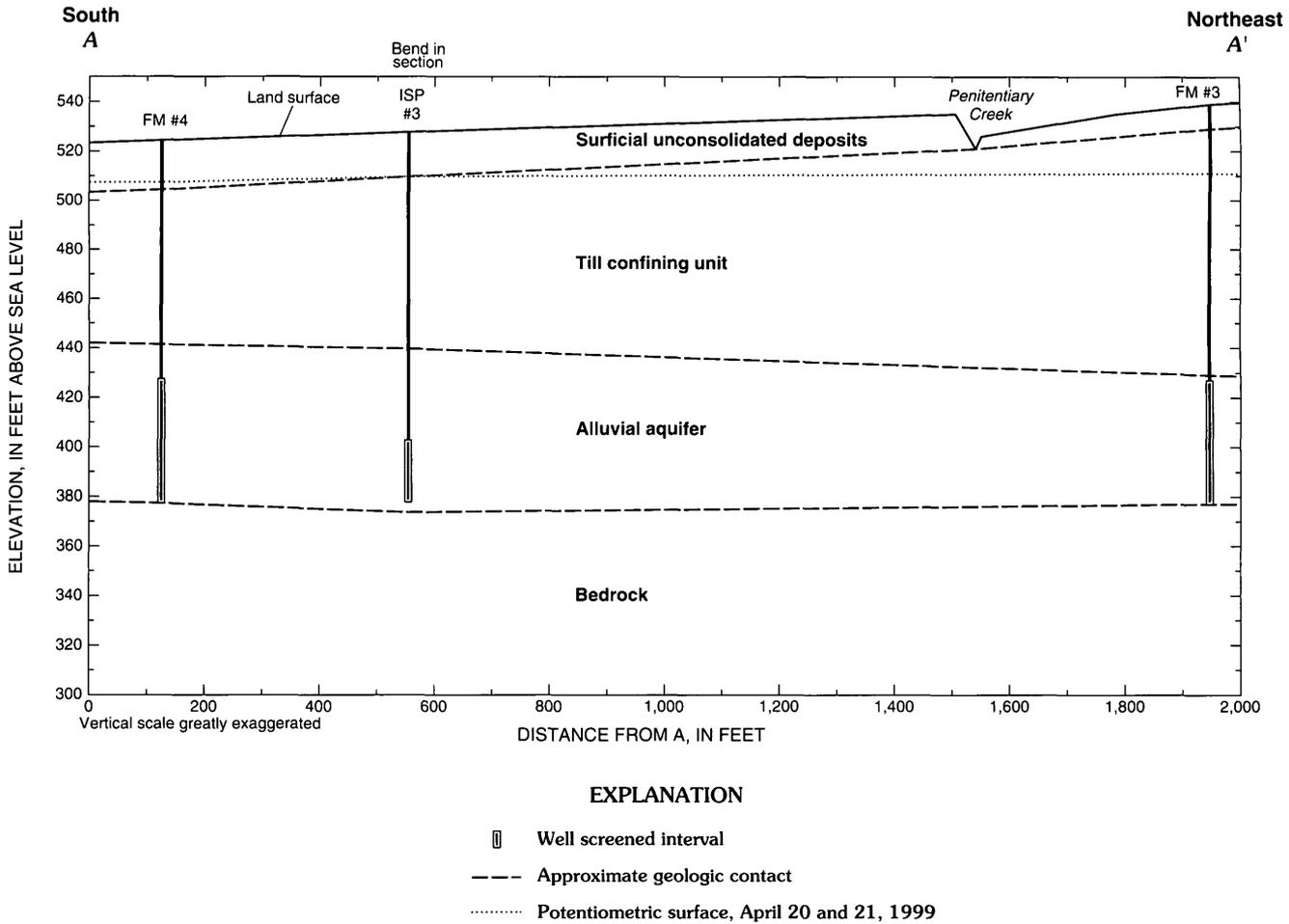


Figure 2. Hydrogeologic section A – A', Fort Madison, Iowa; trace of section shown in figure 1.

Madison municipal water supply. A few homes within the drainage basin of Penitentiary Creek obtain their water from private domestic wells completed in unconsolidated surficial sediments.

The wells used in this study are located from 200 to 1,800 ft from the Mississippi River (fig. 1). All municipal, institutional, and industrial wells are completed in the alluvial aquifer. There are other large-yield wells at Iowa State Penitentiary and Sheaffer Pen (two wells each) but they were not used in this study. The domestic wells are completed in surficial, unconsolidated, water-bearing deposits.

Previous Studies

Little information has been published regarding the presence of ammonia in the alluvial aquifer in the Fort Madison area. Studies involving or including ammonia in ground water have been either statewide or regional studies.

Layne GeoSciences, Inc. (1990) conducted a ground-water investigation for the City of Fort Madison to evaluate the feasibility of increasing their existing production capacity by installing additional municipal wells. The investigation consisted of installing a test well (near the location of present day FM #5), installing two observation wells (located

approximately 160 ft and 700 ft from the test well in a line extending to the northeast and paralleling the Mississippi River), and completing a 24-hour pumping test of the test well. The pumping test showed 3 ft of drawdown at the observation well located 700 ft from the test well. A positive source recharge boundary was observed in the drawdown data for each of the observation wells. Layne GeoSciences, Inc. (1990) indicated two possible sources for the recharge: (1) leakage from the till above the alluvial aquifer as the potentiometric surface in the aquifer is lowered; and/or (2) induced infiltration from the Mississippi River. The alluvial aquifer in the vicinity of proposed well development was determined to have the capacity to support two additional wells, separated by 600 ft, and pumping at 1,000 gal/min. Approximately 3 ft of interference for each well could be expected (Layne GeoSciences, Inc., 1990).

Green Environmental Services (1991) investigated the presence of volatile and semivolatile organic compounds in soil and ground water surrounding the site for a proposed water supply well for the City of Fort Madison (to the east of well FM #4). Although volatile organic compounds were not detected, semivolatile organic compounds were detected in soil and ground-water samples. The ground-water sample was collected from one monitoring well (20 ft deep). It was suggested that the source of contamination may have been from a former coal gasification facility located north of the existing water-treatment plant. An area around the proposed new well site may also have been previously used as a waste-disposal site for the by-products of coal gasification (Green Environmental Services, 1991).

A study was conducted by Brice, Petrides-Donohue (1991) to investigate the extent of contamination to streams and ground water from the City Landfill (fig. 1) and Rodeo Park dump (both located in the upland area approximately 1 mi north of the City of Fort Madison), and to develop a remediation plan. Samples were collected from monitoring wells and surface-water sites in the immediate vicinity of the dump and landfill. Surface waters (French Creek and Fork Creek) were found to be more susceptible to contamination, as indicated from measurements of pH, specific conductance, chemical oxygen demand (COD), and total dissolved solids concentrations, than ground water, as a result of seepage of leachate from Rodeo Park dump and the city landfill. Volatile organic compounds were detected at one surface-water

site and one monitoring-well site. The low hydraulic conductivity of the thick (approximately 300 ft) underlying till in the vicinity of the dump and landfill and the large horizontal distance to a production aquifer were considered to be the main reasons attributable to a low risk of ground-water contamination (Brice, Petrides-Donohue, 1991).

From water year 1982 through water year 1996, slightly more than 800 pretreatment water samples (that included analysis for dissolved ammonia) were collected statewide from municipal water-supply wells completed in alluvial aquifers as part of the Iowa ground-water-quality monitoring program, which is conducted cooperatively by the Iowa Geological Survey Bureau, the University of Iowa Hygienic Laboratory, and the USGS. The median ammonia concentration of those samples was less than 0.10 mg/L as nitrogen. The median well depth for all samples collected from alluvial aquifers throughout the State of Iowa was 43 ft (Schaap and Linhart, 1998).

A study (Savoca and others, 2000) of the effects of land use and hydrogeology on the water quality of alluvial aquifers, in which samples were collected from 31 observation wells located in agricultural settings and 30 observation wells located in urban settings in eastern Iowa and southern Minnesota, disclosed median ammonia concentrations of less than 0.015 mg/L and 0.024 mg/L for wells located in agricultural and urban land-use areas, respectively. Nitrate concentrations were found to be lower in urban areas compared to agricultural sites. It was suggested that, in conjunction with the lower overall nitrogen inputs in urban areas, the lower nitrate concentrations may have been due, in part, to the greater organic material in urban areas resulting in higher denitrification rates and the conversion of greater amounts of nitrate to more reduced nitrogen species (ammonia). Higher ammonia concentrations also appeared to be associated with ground water with dissolved-oxygen concentrations of 0.5 mg/L or less. However, this relation was not statistically significant for either agricultural or urban areas. Based on tritium concentrations detected in all samples from alluvial aquifers, 98 percent of the samples represented ground water that was most likely recharged after the 1950's (Savoca and others, 2000).

Kolpin and others (1994) examined data collected throughout the midcontinental United States to summarize the geographic and seasonal distributions of selected herbicides and nitrate detected in near-surface aquifers (top of aquifer less than 50 ft

below land surface) and to analyze how these distributions are affected by hydrogeologic factors, land use, agricultural practices, local features, and water chemistry. Ammonia was detected in 78 percent of the 548 samples analyzed. Ammonia concentrations were equal to or greater than 1.0 mg/L in approximately 7 percent of the samples. In that study, ammonia was also associated with lower dissolved-oxygen concentrations in contrast to nitrate. Results of samples collected from wells nearer feedlots showed marginally significantly lower dissolved-oxygen concentrations, whereas significantly higher ammonia concentrations were detected only for samples collected from wells within 0.25 mi (wells were classified as being either within 100 ft, 0.25 mi, or 2 mi of a local feature) of feedlots, a potential source of organic carbon. Nitrate concentrations greater than the 0.05-mg/L laboratory analytical reporting limit were rarely found where samples contained hydrogen sulfide, indicative of a strong reducing environment. Frequency of excess nitrate (greater than 3.0 mg/L) showed a significant positive relation to dissolved orthophosphate concentration and a significant inverse relation to specific conductance. Because dissolved orthophosphate is more readily adsorbed to sediments and aquifer materials than nitrate, and consequently is not as easily transported by ground water, the detection of dissolved orthophosphate may indicate rapid recharge rates, short flow paths, or both. Where dissolved orthophosphate is detected, nitrate will also likely be detected, indicating a shorter distance from nitrogen sources. Higher specific conductance values may be indicative of higher residence times and longer flow paths; therefore, the lower nitrate values associated with higher specific-conductance values may indicate a greater distance from recharge areas and, consequently, from nitrogen sources (Kolpin and others, 1994).

Acknowledgments

The author thanks the public, corporate, and private well owners that allowed access for the USGS to make water-level measurements and to collect water-quality samples. Thorpe Well Company provided a driller's log for well ISP #3.

APPROACH AND METHODS

Water levels were obtained from wells in the study area to allow construction of a generalized potentiometric surface map and delineate the direction of ground-water flow in the alluvial aquifer. Water-quality samples were collected from well and surface-water sites to determine the spatial distribution of constituent concentrations to enable comparisons between sites and to help to explain the possible sources of ammonia. Results for samples collected for stable nitrogen isotopes also were used to provide information on the possible sources of ammonia. Samples for caffeine analysis were collected from the three municipal wells. Caffeine can act as a conservative tracer potentially indicating anthropogenic sources, in particular—sewage and septic wastes. Tritium samples were collected from the municipal wells to determine the relative age of ground water in the alluvial aquifer. Older water (recharged before 1953) would indicate a longer residence time and greater distance from a recharge area, whereas younger water (after 1953) would indicate less residence time and a shorter distance from a recharge area.

Site Selection

Well sites (table 1 and fig. 1) were selected to obtain ambient and untreated water samples from the alluvial aquifer and surficial unconsolidated deposits with permission of the well owner. Within the study area, the City of Fort Madison has three municipal wells (#3, #4, and #5) completed in the alluvial aquifer that are equipped with water taps for collection of samples before any treatment of the water. Two industrial wells and one institutional well were also selected for obtaining water samples from the alluvial aquifer, and an additional industrial well was selected for obtaining a water-level measurement only. Three domestic wells also were included in the study: one well used for obtaining water-quality samples from the surficial unconsolidated deposits, and two wells for obtaining water-level measurements only. When possible, water levels also were to be measured at the wells where water-quality samples were collected. The selection criteria for use of a domestic well for water-quality sampling were as follows: permission to sample the well could be obtained from the land-owner, well depth was known, and well was equipped

Table 1. Site information for samples collected and/or water levels measured April 20 and 21, 1999, Fort Madison, Iowa

[--, not available or not applicable; ISP, Iowa State Penitentiary]

Site name (fig.1)	Site number	Well depth (feet)	Depth to bedrock (feet)	Length of screened interval (feet)	Hydrogeologic unit	Sample collected	Water level (feet above sea level)
Fort Madison #3	403804091173801	162	about 162	50	alluvial aquifer	yes	511.07
Fort Madison #4	403745091174701	147	147	50	alluvial aquifer	yes	507.40
Fort Madison #5	403749091175701	147	--	50	alluvial aquifer	yes	--
Sheaffer Pen #7	403749091181401	165	--	60	alluvial aquifer	yes	--
ISP #3	403753091175301	150	about 157	25	alluvial aquifer	yes	509.78
Four-M-Paper #1	403727091194401	143	--	--	alluvial aquifer	yes	--
Kensington #1	403748091201701	161	--	--	alluvial aquifer	no	515.31
Domestic well A	403809091180401	13	--	--	surficial unconsolidated deposits	yes	534.45
Domestic well B	403807091180801	9	--	--	surficial unconsolidated deposits	no	532.03
Domestic well C	403810091173201	--	--	--	surficial unconsolidated deposits	no	537.30
Mississippi River	403749091173901	--	--	--	--	yes	519.93
Fork Creek	403812091181201	--	--	--	--	yes	--
Penitentiary Creek	403805091174201	--	--	--	--	yes	--

with a submersible pump (and the sample was obtainable before water entered a pressure tank or treatment system) or access was available to obtain a water sample with a portable purge or peristaltic pump. There are very few domestic wells that meet the selection criteria in Fort Madison, as most households are connected to the municipal water supply. One active domestic well (well C) was selected for obtaining a water level, and two domestic wells that had not been used for quite some time were selected, one for a water-level measurement (well B) and the other for obtaining water-quality samples (well A). When possible, information about the wells was obtained from the well owner or from available maintenance records or well logs.

Sampling sites at two creeks were selected so as to be located near the boundary between the upland area and the alluvial plain. Samples were representative of low-flow conditions when ground water was assumed to be the primary flow component. The sampling site on the Mississippi River was selected for ease of sampling. An intake pipe extends from the City of Fort Madison water-treatment plant approximately 150 ft out into the river at a depth of 33 ft. A tap is available in the treatment plant for sample collection.

Horizontal position (latitude-longitude) of the wells and surface-water sites was determined using a hand-held global positioning system instrument.

Water-Level Data Collection

Water-level measurements were obtained using a steel tape, an electronic tape, or a gaged airline. Water levels were measured one time prior to pumping on the day of sampling. Water levels were measured at wells FM #3, FM #4, ISP #3, Kensington #1, and at the three domestic wells. Water levels could not be measured at wells FM #5 and Four-M-Paper #1 because the airline gages were not functional at the time samples were collected. A water-level measurement was not taken at Sheaffer Pen #7, as that well is used for industrial cooling and the pump could not be shut down. Surface elevations at the wells are referenced to the National Geodetic Vertical Datum of 1929 (sea level) and were determined, as necessary, using a combination of global positioning system and conventional surveying techniques.

Sample Collection and Analysis

Water-quality samples were collected on April 20 and 21, 1999. Prior to sample collection, all wells and surface-water sites were pumped for approximately one-half hour and until field measurements of water temperature, pH, specific conductance, and dissolved oxygen stabilized. Samples were collected from domestic well A, Fork Creek, and Penitentiary Creek by using a peristaltic pump. Onsite measurements of alkalinity also were made at all sampling sites. The municipal wells FM #3, #4, and #5 were sampled for major cations and anions, nutrients, dissolved organic carbon (DOC), boron, semivolatile organic compounds, volatile organic compounds (VOCs), nitrogen isotopes, caffeine, and tritium. The industrial wells, ISP #3, domestic well A, Fork Creek, and Penitentiary Creek were sampled for major cations and anions, nutrients, DOC, boron, and nitrogen isotopes. The Mississippi River was sampled for DOC and nitrogen isotopes only. Major ions and nutrients were filtered using 0.45-micrometer cartridge filters, and DOC samples were filtered using 0.45-micrometer silver filters. The remaining samples were not filtered. Major-cation, nutrient, and VOC samples were preserved with acid prior to shipping. Sampling and filtering equipment was decontaminated after each use.

Three types of quality-assurance samples also were collected. A replicate sample was collected at FM #4 to determine the precision of the analytical results and to check sample handling onsite and in the laboratory. The collected replicate samples were analyzed for major cations and anions, nutrients, boron, VOCs, and semivolatile organic compounds. A field blank was collected at FM #5 to determine possible sources of contamination during transportation, collection, or processing of samples. Field-blank samples were analyzed for major cations and anions, nutrients, boron, and caffeine. One VOC trip blank was used to assess potential VOC contamination during sample collection or shipment.

Samples were chilled and shipped (overnight delivery) to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado. Whereas most samples collected for this study were analyzed at the NWQL, tritium was analyzed by the University of Miami laboratory in Miami, Florida, and nitrogen isotopes were analyzed by Zymax Enviro Technologies in San Luis Obispo, California.

Analyte detections are reported relative to minimum reporting levels (MRLs) established by the NWQL. The MRL is the minimum concentration that can be measured reliably and reported by the laboratory using a given analytical method. "Estimated" values indicate analyte detection, usually below the MRL, but the reported concentration is questionable.

Replicate samples showed an acceptable level of precision in field and laboratory procedures for all constituents. The field blank showed that for most analytes, contaminants were not being introduced as a result of sample collection and equipment decontamination procedures. Ammonia and orthophosphate were detected (0.08 and 0.02 mg/L, respectively) in the field blank at concentrations greater than the MRL and were similar to concentrations found at some sampling sites. As a result, where sample concentrations of ammonia and orthophosphate approached field-blank concentration, the values were used with caution due to uncertainties concerning the extent to which contamination may affect water-quality sample results. Ammonia plus organic nitrogen, sodium, silica, and boron were also detected in the field blank, but concentrations were below the MRL and well below concentrations at the sampling sites. There were no VOC detections in the trip blank.

GROUND-WATER FLOW

Water levels measured April 20 and 21, 1999, at wells and at the Mississippi River site are listed in table 1. Figure 3 shows the generalized ground-water flow direction for part of the alluvial aquifer based on water-levels measured at wells FM #3, FM #4, and ISP #3. Water-level data for the domestic wells do not represent hydraulic head in the alluvial aquifer but are listed in table 1 for general information. The highest water level (511.07 ft) was measured at FM #3 which is located close to the upland area to the northeast of FM #4 and ISP #3. The generalized potentiometric contours, based on limited water-level data, indicate that flow direction is generally from northeast to southwest toward FM #5. On April 20 and 21, wells FM #5 and Sheaffer Pen #7 were pumping continuously at approximately 710 and 1,000 gal/min, respectively. There were no other municipal or Sheaffer Pen wells pumping during those days except FM #3 and #4 during actual sampling. The wells at the Iowa State Penitentiary are pumped only at night, except that ISP #3 was pumped during the day to obtain the water

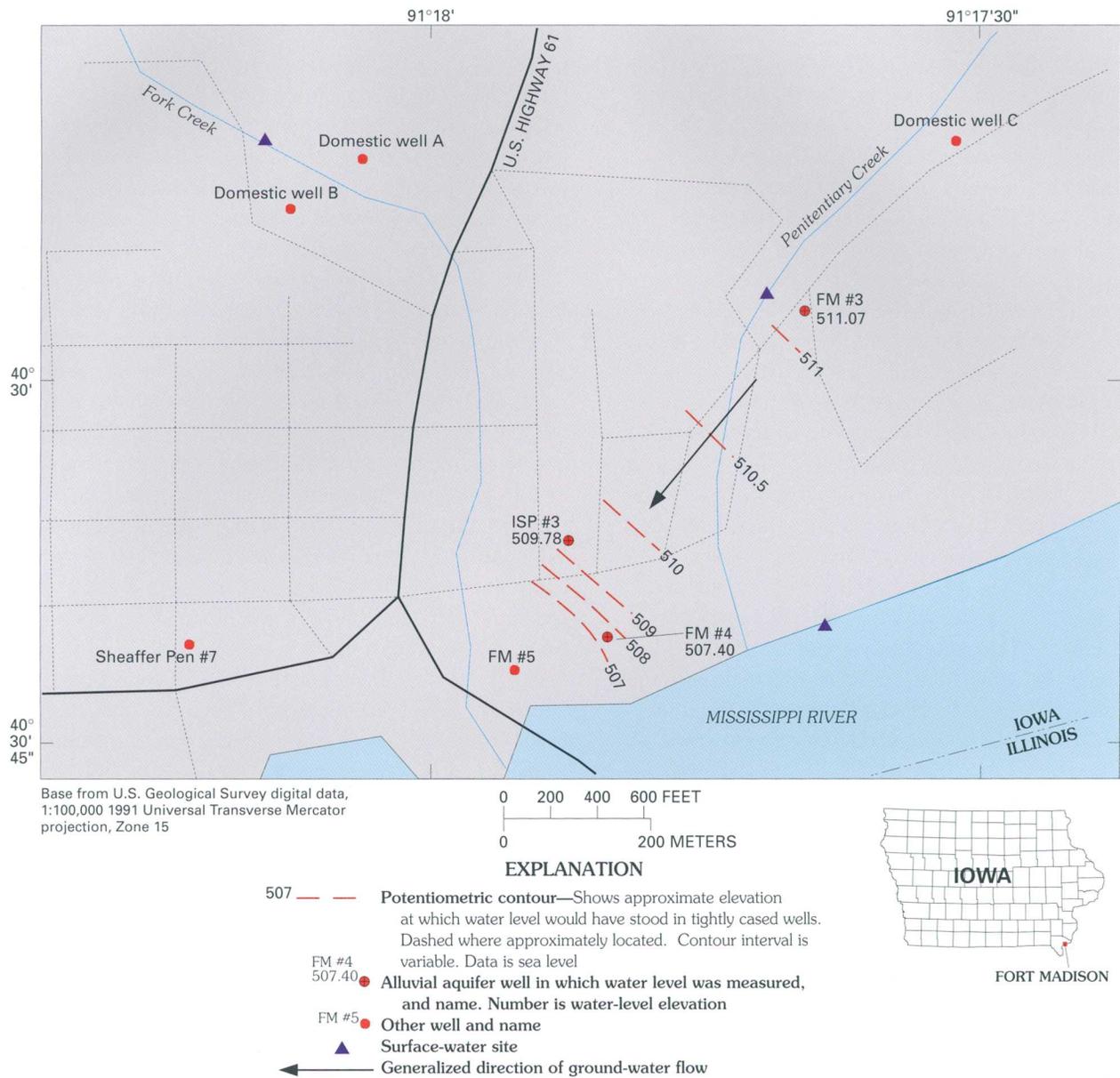


Figure 3. Generalized ground-water flow direction in part of the alluvial aquifer, April 20 and 21, 1999, Fort Madison, Iowa.

sample. It is not known if other industrial wells exist and were pumping, other than those already mentioned, in the immediate vicinity of the study area on April 20 and 21. However, it is likely that ground-water flow was under the influence of a cone of depression as a result of nearby pumping wells. Previous pumping tests (Layne GeoSciences, Inc., 1990) indicated that approximately 6 ft of drawdown was observed in an observation well located 160 ft from the test well (147 ft deep, pumping at 1,200 gal/min, and located near present-day FM #5)

and 3 ft of drawdown was observed in an observation well located 700 ft from the test well, in a line extending to the northeast parallel to the Mississippi River. It was estimated that approximately 2 ft of drawdown could be expected in Iowa State Penitentiary wells from a proposed city well pumping at 1,000 gal/min. During the pumping test, an observed drawdown of approximately 1 ft in the observation well located 160 ft from the test well may have been due to wells pumping at Sheaffer Pen (Layne GeoSciences, 1990).

The water level of Mississippi River was 519.93 ft on April 20 and was higher than all of the water levels measured in wells completed in the alluvial aquifer (table 1 and fig. 3). The bed elevation of the Mississippi River is approximately 484 ft above sea level (or approximately 36 ft below the river's surface) in the vicinity of Fort Madison (Federal Emergency Management Agency, 1981) and therefore would not appear to fully penetrate the confining till unit (fig. 2) to a point where a direct hydraulic connection could occur between the river and the alluvial aquifer. The till confining unit may impede the movement of river water to the alluvial aquifer. As previously mentioned, however, drawdown data (Layne GeoSciences, Inc., 1990) indicate the presence of a positive source boundary with two possible sources of recharge, the Mississippi River and (or) leakage from the overlying till. Even though a considerable head difference exists between the Mississippi River (519.93 ft) and FM #4 (507.40 ft), without a better understanding of what the most probable source of recharge is, and the extent to which recharge may occur, it is difficult to determine flow direction in the alluvial aquifer between FM #4 and the river on the basis of water-level data collected for this study.

WATER CHEMISTRY

Nutrient, dissolved organic carbon (DOC), major ion, boron, iron, manganese, nitrogen isotope, and tritium results are shown in table 2 from the sampling conducted at wells, creeks, and the Mississippi River at Fort Madison. Results for volatile organic compounds (VOCs) and semivolatile organic compounds are shown only for those compounds which were detected. No other VOCs and semivolatile organic compounds were detected.

Nutrients and Organic Carbon

The ammonia concentration (5.1 mg/L) at well FM #4 (fig. 4) was considerably higher than ammonia concentrations detected at other wells or creeks within the study area. A ground-water sample collected from well FM #5, located approximately 400 ft from well FM #4, had an ammonia concentration of 1.7 mg/L. Wells FM #4 and #5 are approximately the same distance from the Mississippi River. The sample

collected from well Four-M-Paper #1, located approximately 1.5 mi to the west of the Fort Madison municipal wells, had an ammonia concentration of 0.92 mg/L. This would appear to indicate that the source of ammonia is localized and that well FM #4 may be intercepting a contaminant plume. If the riverbed sediments were a source of the ammonia, one might expect a higher concentration of ammonia also to be present in the sample collected from well FM #5. Both wells are the same depth (147 ft) and have the same screen length (50 ft) at the bottom of the well. Both wells also pump at approximately 700 gal/min. Nitrate (table 2) was not detected in any of the samples collected from municipal or industrial wells. Nitrate was detected at low concentrations in domestic well A, Fork Creek, and Penitentiary Creek, indicating that surface inputs of nitrogen from the upland area to the north of well FM #4 are minimal, at least during the period of low runoff (assumed to be base-flow conditions) when these samples were collected. Nitrite was detected only at Fork Creek, and organic nitrogen concentrations (fig. 4) were highest in samples collected from Fork Creek, well ISP #3, and well Sheaffer Pen #7.

The DOC in Fork Creek (24 mg/L) was much higher than DOC at any of the other sampling sites (table 2 and fig. 4). High concentrations of DOC can be characteristic of seepage from landfills (Hem, 1985). A landfill is located at the head of the Fork Creek drainage basin (fig. 1). DOC in ground water was highest (5.5 mg/L) at well FM #4 with the remaining wells ranging from 2.6 to 5.3 mg/L (table 2 and fig. 4). Compared to samples collected from alluvial wells statewide (Schaap and Linhart, 1998), these values are somewhat higher than the median value (1.3 mg/L) for total organic carbon (TOC). These DOC values also are higher than the DOC median values (1.10 and 1.65 mg/L for agricultural areas and urban areas, respectively) in samples from shallow observation wells in alluvial aquifers in eastern Iowa (Savoca and others, 2000). It appears that DOC is relatively high throughout the study area but is highest in the vicinity of the municipal wells, possibly indicating a localized source of organic carbon. A previous study (Brice, Petrides-Donohue, 1991) indicated that ground-water seepage of leachate from the landfill poses a low risk of contamination to the alluvial aquifer in the vicinity of the Fort Madison municipal well field because the underlying till material in the vicinity of the landfill has low hydraulic conductivity and the Fort Madison municipal wells are located a

Table 2. Results of analysis of water samples collected from Fort Madison water-supply wells, industrial wells, a domestic well, two creeks, and the Mississippi River, April 20 and 21, 1999, Fort Madison, Iowa

[Number in parentheses is the U.S. Geological Survey Water Data Storage and Retrieval System parameter code. $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter; <, less than minimum reporting level; --, not available; CaCO_3 , calcium carbonate; ISP, Iowa State Penitentiary; pCi/L , picocuries per liter; $\delta^{15}\text{N}$, a measure of the difference between the ratio of nitrogen-15 to nitrogen-14 in the sample and standard atmospheric nitrogen, see page IV for details; NF, nitrogen fertilizer; NFHAW, nitrogen fertilizer with a higher percentage of human and other animal wastes compared to NF; HAW, human and other animal wastes; E, estimated value]

Site name	Site number	Date of sample collection (1999)	Physical properties						
			Specific conductance ($\mu\text{S}/\text{cm}$) (00095)	pH, water, whole field (standard units) (00400)	Water temperature (degrees Celsius) (00010)	Dissolved oxygen (mg/L) (00300)	Hardness, total (mg/L as CaCO_3) (00900)	Alkalinity (field) total (mg/L as CaCO_3) (39086)	Dissolved solids, sum of constituents (mg/L) (70301)
Fort Madison #3	403804091173801	April 20	555	7.2	12.1	0.2	220	260	303
Fort Madison #4	403745091174701	April 20	458	7.2	12.3	.5	200	201	303
(replicate)	403745091174701	April 20	--	--	--	--	200	--	--
Fort Madison #5	403749091175701	April 20	452	7.3	12.7	.5	290	205	270
(field blank)	403749091175701	April 20	--	--	--	--	--	--	--
Sheaffer Pen #7	403749091181401	April 21	533	7.4	14.8	1.7	240	264	303
ISP #3	403753091175301	April 21	448	7.3	13.6	.7	200	201	259
Four-M-Paper #1	403727091194401	April 21	550	7.8	14.2	--	250	258	309
Domestic well A	403809091180401	April 21	193	7.7	11.6	7.8	91	84	113
Mississippi River	403749091173901	April 20	452	7.8	11.1	8.9	--	170	--
Fork Creek	403812091181201	April 20	1110	8.1	12.2	9.5	450	360	703
Penitentiary Creek	403805091174201	April 20	857	8.0	11.8	10.1	440	287	548

Major ions

Site name	Calcium, dissolved (mg/L as Ca) (00915)	Magnesium, dissolved (mg/L as Mg) (00925)	Sodium, dissolved (mg/L as Na) (00930)	Potassium, dissolved (mg/L as K) (00935)	Sulfate, dissolved (mg/L as SO_4) (00945)	Chloride, dissolved (mg/L as Cl) (00940)	Fluoride, dissolved (mg/L as F) (00950)	Bromide, dissolved (mg/L as Br) (71870)	Silica, dissolved (mg/L as SiO_2) (00955)
Fort Madison #3	56	19	10	1.5	16	15	0.19	0.08	24
Fort Madison #4	50	18	10	2.5	<.10	18	.15	.09	24
(replicate)	50	17	9.8	2.5	<.10	18	.16	.08	24
Fort Madison #5	77	24	9.0	2.6	.46	8.7	.36	<.01	20
(field blank)	<.02	<.004	E.03	<.10	<.10	<.10	<.10	<.01	.07
Sheaffer Pen #7	59	21	17	2.3	6.6	15	.20	.13	18
ISP #3	50	18	11	2.3	11	17	.18	.10	22
Four-M-Paper #1	64	22	15	3.2	16	18	.25	.03	15
Domestic well A	34	1.4	1.5	2.5	12	1.2	<.10	<.01	4.3
Mississippi River	--	--	--	--	--	--	--	--	--
Fork Creek	120	34	70	6.1	210	26	.34	<.01	12
Penitentiary Creek	130	29	23	2.8	150	33	.31	.03	13

Table 2. Results of analysis of water samples collected from Fort Madison water-supply wells, industrial wells, a domestic well, two creeks, and the Mississippi River, April 20 and 21, 1999, Fort Madison, Iowa—Continued

Site name	Site number	Date of sample collection (1999)	Nutrients						
			Ammonia nitrogen, dissolved (mg/L as N) (00608)	Nitrite nitrogen, dissolved (mg/L as N) (00613)	Nitrite plus nitrate nitrogen, dissolved (mg/L as N) (00631)	Organic nitrogen, dissolved (mg/L as N) (00607)	Ammonia plus organic nitrogen, dissolved (mg/L as N) (00623)	Phosphorus, dissolved (mg/L as P) (00666)	Phosphorus, dissolved, orthophosphate (mg/L as P) (00671)
Fort Madison #3	403804091173801	April 20	1.7	<0.01	<0.05	0.48	2.1	0.04	0.03
Fort Madison #4	403745091174701	April 20	5.1	<.01	<.05	.31	5.4	.89	.74
(replicate)	403745091174701	April 20	5.3	<.01	<.05	--	5.9	.87	.69
Fort Madison #5	403749091175701	April 20	1.7	<.01	<.05	.16	1.9	.35	.30
(field blank)	403749091175701	April 20	.08	<.01	<.05	--	E.05	<.004	.02
Sheaffer Pen #7	403749091181401	April 21	1.5	<.01	<.05	.81	2.3	.37	.18
ISP #3	403753091175301	April 21	2.2	<.01	<.05	.93	3.1	.20	.17
Four-M-Paper #1	403727091194401	April 21	.92	<.01	<.05	.29	1.2	.02	.02
Domestic well A	403809091180401	April 21	.02	<.01	1.2	.11	.13	.10	.08
Mississippi River	403749091173901	April 20	--	--	--	--	--	--	--
Fork Creek	403812091181201	April 20	.64	.03	.70	1.0	1.6	.02	.01
Penitentiary Creek	403805091174201	April 20	.07	<.01	.35	.17	.24	.01	.01

Site name	Carbon, organic, dissolved (mg/L as C) (00681)	Boron, dissolved (µg/L as B) (01020)	Metals		Organic compounds			
			Iron, dissolved (µg/L as Fe) (01046)	Manganese, dissolved (µg/L as Mn) (01056)	Benzene, total (µg/L) (34030)	Toluene, total (µg/L) (34010)	Xylene, water, unfiltered, recoverable (µg/L) (81551)	Naphthalene, total (µg/L) (34696)
Fort Madison #3	5.3	36	2,900	391	0.462	0.143	E0.146	0.468
Fort Madison #4	5.5	37	4,500	1,890	<.200	<.200	<.200	<.200
(replicate)	--	40	4,500	1,880	<.200	<.200	<.200	<.200
Fort Madison #5	4.4	43	1,600	309	<.200	<.200	<.200	<.200
(field blank)	.1	E7.9	<10	<3	--	--	--	--
Sheaffer Pen #7	3.7	71	2,800	381	--	--	--	--
ISP #3	4.6	32	2,800	205	--	--	--	--
Four-M-Paper #1	3.4	65	450	340	--	--	--	--
Domestic well A	2.6	56	<10	<3.0	--	--	--	--
Mississippi River	4.7	--	--	--	--	--	--	--
Fork Creek	24	168	25	393	--	--	--	--
Penitentiary Creek	3.8	70	23	235	--	--	--	--

Table 2. Results of analysis of water samples collected from Fort Madison water-supply wells, industrial wells, a domestic well, two creeks, and the Mississippi River, April 20 and 21, 1999, Fort Madison, Iowa—Continued

Site name	Site number	Date of sample collection (1999)	$\delta^{15}\text{N}$, nitrate (per mil) (82690)	$\delta^{15}\text{N}$, ammonia (per mil) (82691)	Indicated nitrogen source ¹	Tritium, total (pCi/L) (07000)	Time of recharge, tritium estimate ²	Caffeine ($\mu\text{g/L}$)
Fort Madison #3	403804091173801	April 20	--	4.8	NF	62	Post-1953	<0.04
Fort Madison #4	403745091174701	April 20	--	7.8	NFHAW	60	Post-1953	<.04
(replicate)	403745091174701	April 20	--	--	--	--	--	<.04
Fort Madison #5	403749091175701	April 20	--	8.1	NFHAW	47	Post-1953	<.04
(field blank)	403749091175701	April 20	--	--	--	--	--	<.04
Sheaffer Pen #7	403749091181401	April 21	--	4.9	NF	--	--	--
ISP #3	403753091175301	April 21	--	7.2	NFHAW	--	--	--
Four-M-Paper #1	403727091194401	April 21	--	7.5	NFHAW	--	--	--
Domestic well A	403809091180401	April 21	5.3	--	NF	--	--	--
Mississippi River	403749091173901	April 20	6.1	--	NF	--	--	--
Fork Creek	403812091181201	April 20	--	15.1	HAW	--	--	--
Penitentiary Creek	403805091174201	April 20	8.4	--	NFHAW	--	--	--

¹Based on information in Kendall (1998).

²Based on information in Freeze and Cherry (1979).

relatively long distance away from the landfill. Therefore, the landfill may be a less likely source of the high DOC in the alluvial aquifer than some closer source. Higher concentrations of DOC in ground water, relative to water unaffected by contamination, may also be associated with the presence of coal (Drever, 1988).

Dissolved phosphorus (table 2) and dissolved orthophosphate (table 2 and fig. 5) concentrations (0.89 and 0.74 mg/L, respectively) were much higher in the sample collected from well FM #4 than in samples from most other wells in the study area. Phosphorus is an essential element in animal metabolism and is always present in animal waste. Domestic and industrial sewage effluents are sources of phosphorus. The use of sodium phosphate also increased during the 1950s and 1960s to enhance the cleaning properties of household detergents and consequently was increasingly found in the output of sewage-disposal plants and septic systems. Phosphorus concentrations are typically no more than a few tenths of a milligram per liter in most natural waters (Hem, 1985).

Dissolved oxygen concentrations (table 2) were low in ground-water samples collected from all municipal and industrial wells (0.2 – 1.7 mg/L), indicating the presence of anaerobic conditions within the alluvial aquifer. This is probably related to a combination of factors such as well screen depths, the high concentrations of DOC, and microbial activity within the aquifer.

Sulfate, Iron, and Manganese

The sulfate concentration was below the MRL (less than 0.10 mg/L) in a sample collected from well FM #4 and a relatively low concentration (0.46 mg/L) was found at well FM #5 (fig. 6). Relatively higher concentrations were found at all other wells. Sulfate concentrations in present-day rainfall are expected to be between approximately 1 to 3 mg/L. Concentrations in ground water less than this range have undergone sulfate reduction (Hem, 1985). Much higher concentrations of sulfate were detected in Penitentiary Creek (150 mg/L) and Fork Creek (210 mg/L). The presence of sulfate in ground water and surface water can sometimes be associated with human activities such as sewage effluent, fertilizers, and road salts (Drever, 1988). The low concentrations of sulfate in samples collected at wells FM #4 and #5 (less than 0.10 mg/L and 0.46 mg/L, respectively) may indicate that microbial sulfate reduction is occurring to a greater degree in this portion of the alluvial aquifer. A product of sulfate reduction is hydrogen sulfide (H_2S). However, in the presence of some iron-bearing minerals, the sulfides can react with the iron to effectively reduce the accumulation of hydrogen sulfide (Chappelle, 1993).

Dissolved iron and manganese concentrations (4,500 and 1,890 $\mu\text{g/L}$, respectively) at FM #4 are much higher than for the other municipal and indus-

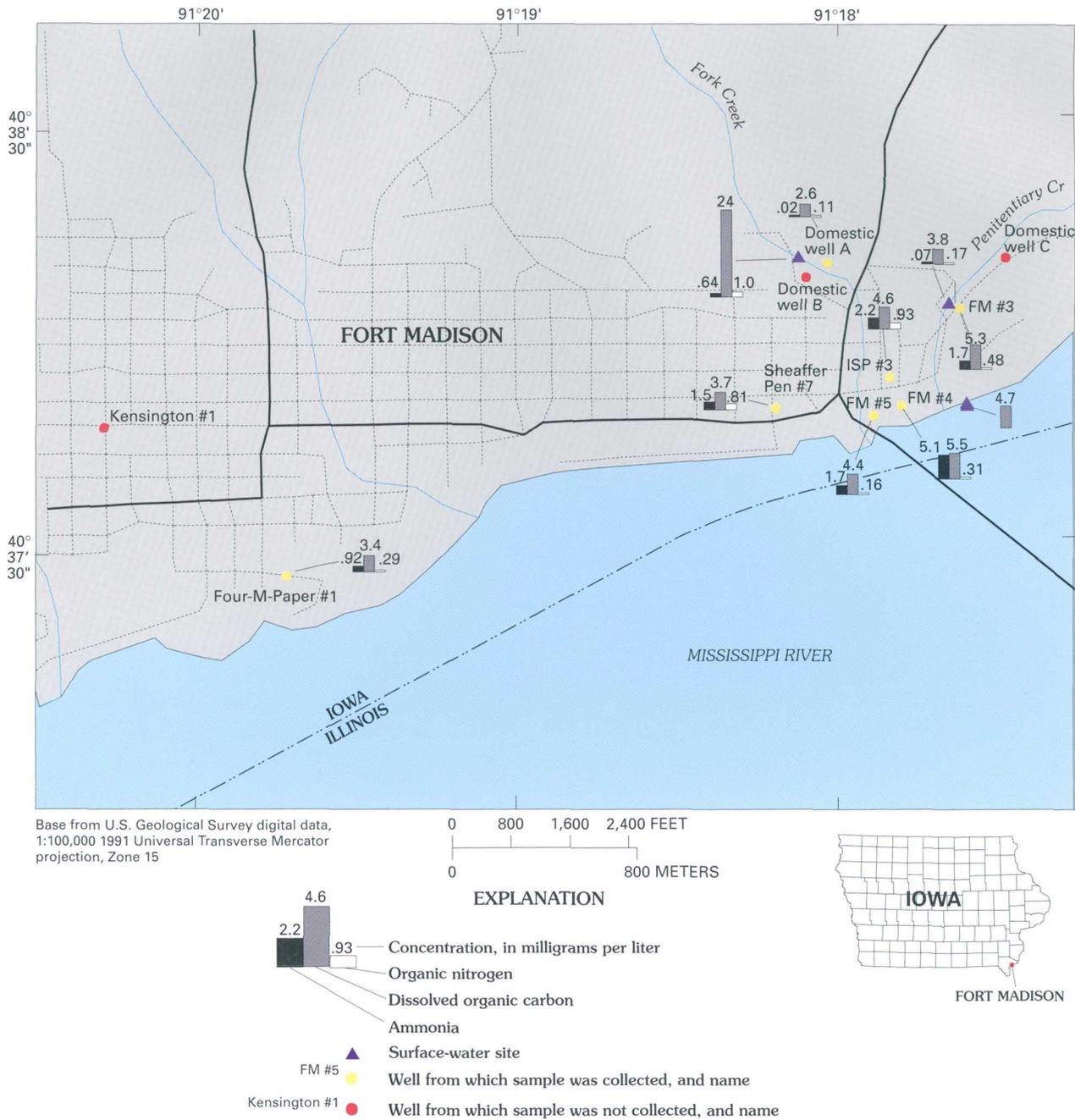


Figure 4. Ammonia, dissolved organic carbon, and organic nitrogen concentrations at surface-water sites and at municipal, industrial, and domestic wells, April 20 and 21, 1999, Fort Madison, Iowa

trial wells (fig. 6). A sample from Four-M-Paper #1, located approximately 1.5 mi to the west, had a much lower concentration of dissolved iron (450 µg/L) compared to the other municipal and industrial wells. Median concentrations of iron and manganese from municipal wells in alluvial aquifers sampled statewide (Schaap and Linhart, 1998) from 1982 to 1996 were 170 and 210 µg/L, respectively. The high iron and manganese concentrations found in samples collected

from wells in the Fort Madison study area also are indicators of anaerobic conditions in the alluvial aquifer. Under anaerobic conditions, high iron concentrations can accumulate in ground water where a sufficient energy source (for example, DOC) exists and where large populations of microbes reduce iron oxyhydroxides to the more soluble form of iron (Chapelle, 1993). Manganese also undergoes similar oxidation and reduction reactions and becomes more

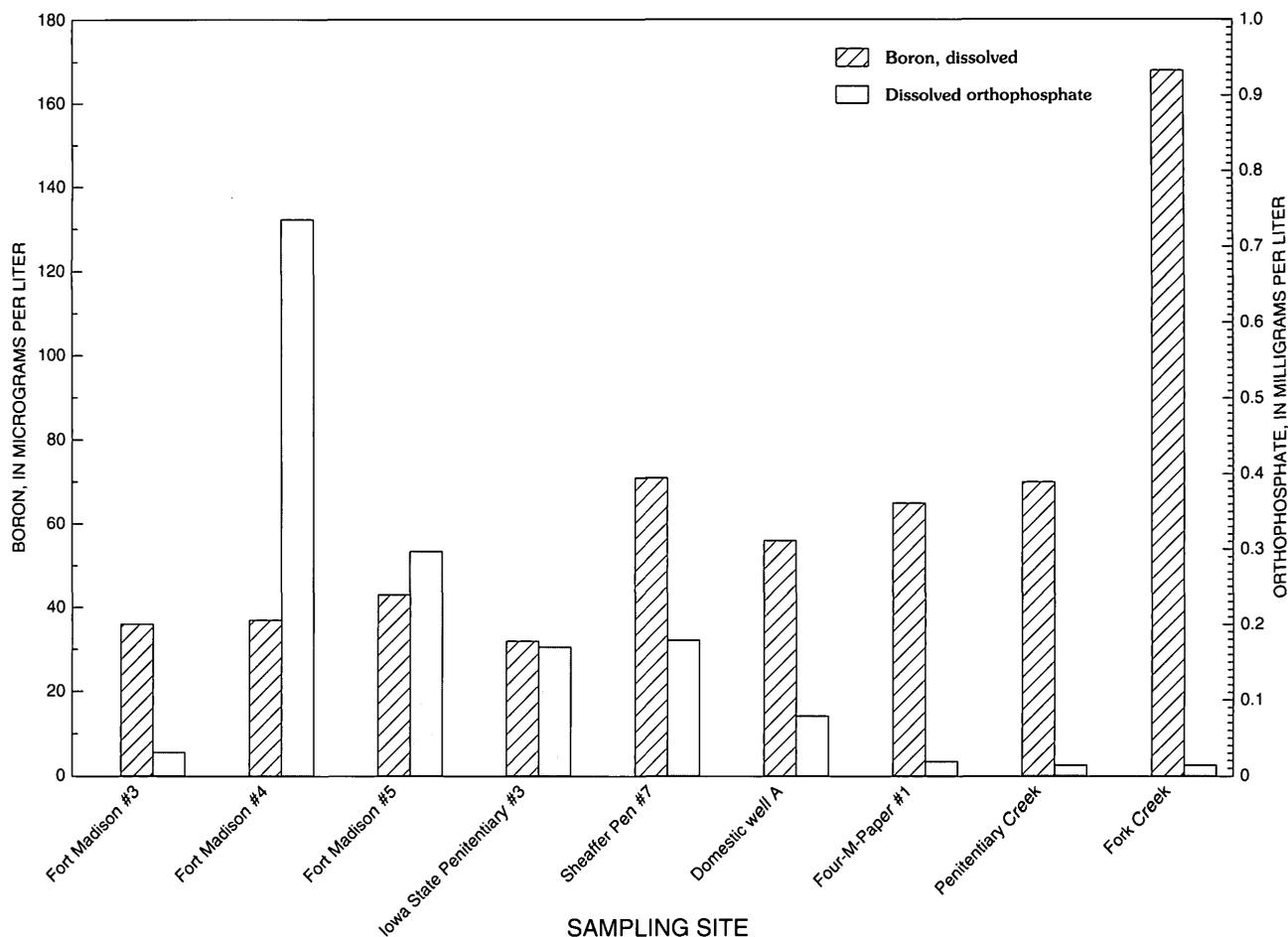


Figure 5. Boron and orthophosphate concentrations at well and surface-water sites, April 20 and 21, 1999, Fort Madison, Iowa.

soluble in water under anaerobic conditions; therefore, high concentrations of manganese can accumulate if the ground water contains high DOC and a large population of microbes. High concentrations of manganese have been detected in ground water from wells located in gravel deposits adjacent to stream channels, presumably as a result of the reduction of manganese oxide coatings sometimes present on the streambed materials (Hem, 1985).

Boron and Caffeine

Boron concentration was highest (168 µg/L) in Fork Creek (fig. 5), indicating a possible source near the head of the drainage basin. In the alluvial aquifer, samples from wells Sheaffer Pen #7 and Four-M-Paper #1 had the highest concentrations (71 and 65 µg/L,

respectively). Boron is an element of some cleaning aids (for example, borax) and may be present in sewage and industrial wastes (Hem, 1985). Boron concentrations were comparatively lower in samples collected from municipal wells and ISP #3.

There were no detections of caffeine in wells FM #3, #4, and #5 (table 2). It was originally thought that caffeine would act as a conservative tracer potentially indicating anthropogenic sources—in particular, sewage and septic wastes. However, it appears that caffeine degrades at a faster rate than originally thought and therefore its usefulness as a conservative tracer may be subject to question (S. Zaugg, U.S. Geological Survey, oral commun., 1999). Therefore, the absence of detectable concentrations of caffeine may not necessarily indicate the absence of anthropogenic inputs into the alluvial aquifer.

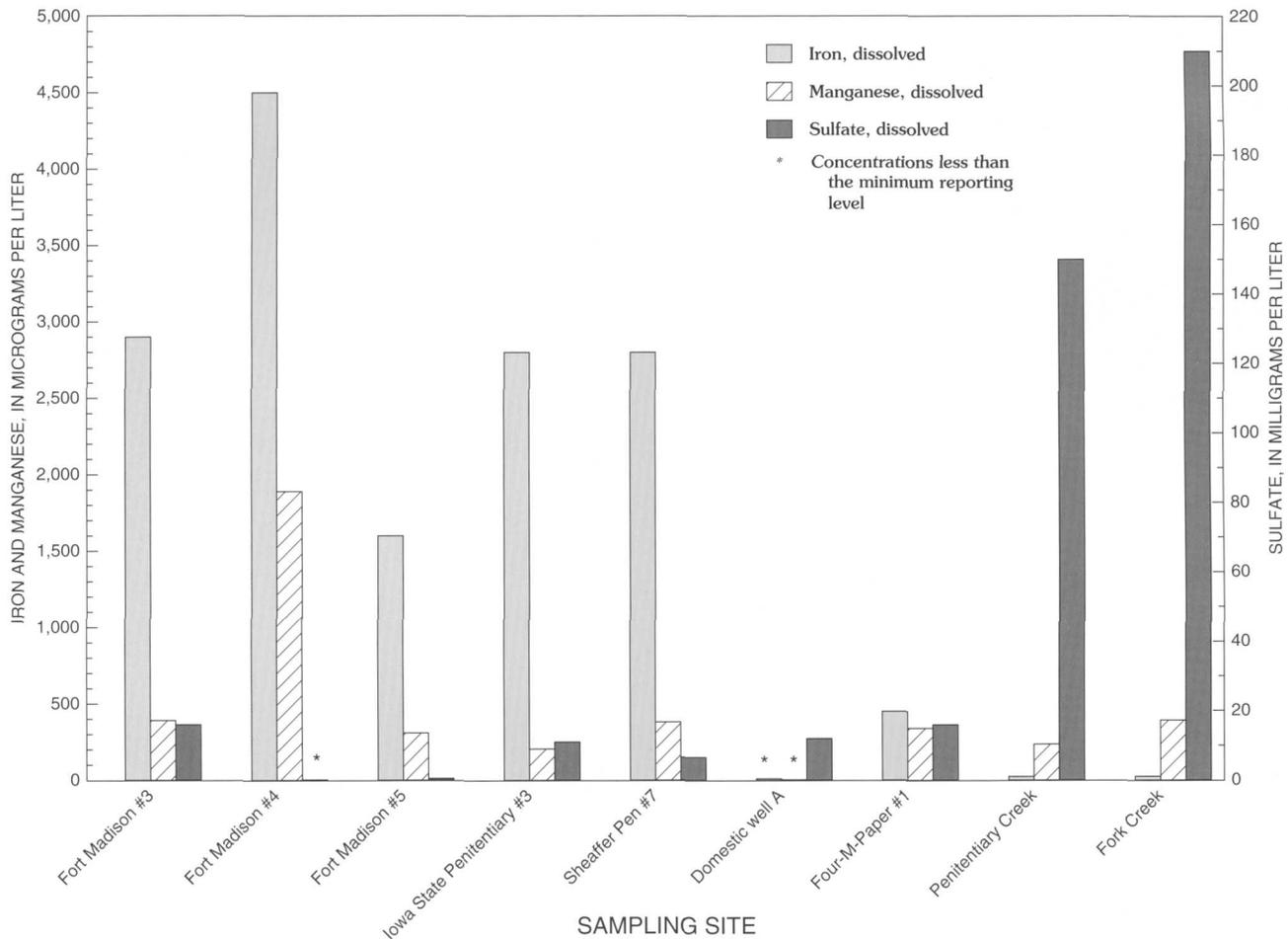


Figure 6. Sulfate, iron, and manganese concentrations at well and surface-water sites, April 20 and 21, 1999, Fort Madison, Iowa.

Volatile and Semivolatile Organic Compounds

Low concentrations of benzene, toluene, xylene, and naphthalene (VOCs) were detected (table 2) in ground-water samples collected from well FM #3. There were no detections of VOCs or semivolatile organic compounds in samples collected from the other municipal wells. Benzene, toluene, and xylene in ground water are often associated with petroleum spills from sources such as landfills, commercial waste-disposal sites, residential disposal, and underground hydrocarbon storage tanks (Domenico and Schwartz, 1990). Naphthalene is a major component in coal tar and is used in the manufacture of mothballs, pesticides, dyes, solvents, and lubricants among others

(Smith and others, 1988). Because there were no detections of VOCs and semivolatile organic compounds in the other municipal wells, this might suggest that the source of contamination in FM #3 may not be the same source of the high ammonia concentrations, or that degradation of VOCs is occurring along the flow path.

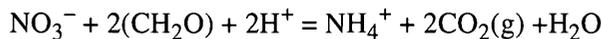
Tritium

Time of recharge can be estimated on the basis of the concentration of tritium in ground water. Tritium is a hydrogen isotope that is produced naturally in the Earth's outer atmosphere. As a result of above-ground thermonuclear testing in the 1950s and 1960s, the amount of tritium in the atmosphere

increased substantially. Water that entered an aquifer before nuclear testing contains little or no tritium. Water recharging the aquifer after nuclear testing contains detectable amounts of tritium (Freeze and Cherry, 1979). Tritium results in table 2 indicate that for samples from all three municipal wells, the time of recharge for most of the water was after 1953. This suggests that precipitation entering the alluvial aquifer occurred at some recharge area within a closer radius to the sampled wells than would "older" water (pre-1953) entering the alluvial aquifer. It is possible that there is some mixture of "older" water, that is, convergent flow paths of pre-1953 and post-1953 water. The average age of the ground water in the alluvial aquifer, however, is post-1953.

POSSIBLE PROCESSES AND POTENTIAL SOURCES CONTRIBUTING AMMONIA TO GROUND WATER

The most likely processes involving the formation of ammonia under anaerobic conditions include (1) microbially mediated dissimilatory nitrate reduction to ammonia (Stumm and Morgan, 1996):



or (2) ammonification (the production of ammonia from decomposition of organic matter) (Kendall, 1998):



These processes are therefore potential sources of ammonia. A review of studies on denitrification in ground water (Korom, 1992) indicates that denitrification (microbially mediated conversion of nitrate $[\text{NO}_3^-]$ to molecular nitrogen $[\text{N}_2]$) has the potential to be in competition with the process of dissimilatory nitrate reduction to ammonia, both of which utilize nitrate as the electron acceptor. However, it has also been suggested (Korom, 1992) that under anaerobic conditions, bacteria will preferentially use an electron acceptor that provides the most energy. Specifically, those bacteria will utilize nitrate, manganese, iron, and sulfate, in that order. When nitrate is no longer available, manganese, then iron, and then sulfate will become the electron acceptors in the process of oxidizing organic carbon. Because there appears to be

little available nitrate (or nitrite) and there is a high concentration of dissolved iron and manganese in the ground water (in the vicinity of well FM #4), iron and manganese, and possibly sulfate, may in this case be the primary electron acceptors. This suggests that dissimilatory nitrate reduction may not be the primary process producing the ammonia. While dissimilatory nitrate reduction is possible, the amounts of ammonia produced are typically less than the N_2 produced by denitrification (Korom, 1992; Smith and Duff, 1988.) In addition, much of the NH_4^+ that would be produced would probably be adsorbed onto negatively charged particles within the aquifer (Freeze and Cherry, 1979). Furthermore, it has been suggested that dissimilatory nitrate reduction to ammonia requires a greater amount of organic carbon than is present in the alluvial aquifer at Fort Madison (R.L. Smith, U.S. Geological Survey, oral commun., 2000). Therefore, given the high NH_4^+ concentrations detected in ground water from well FM #4, it is more likely that the main process producing the NH_4^+ is decomposition of organic matter (ammonification). For the alluvial-aquifer wells sampled at Fort Madison, there appears to be a positive relation between the ammonia and DOC (fig. 7).

The stable isotopes of nitrogen may provide information on the sources of nitrogen in nitrate and ammonia (Chapelle, 1993; Kendall, 1998). Nitrogen occurs as two stable isotopes, ^{15}N and ^{14}N , and the ratio $^{15}\text{N}:^{14}\text{N}$ is reported relative to a standard, in per mil (see page IV for further description of notation, standards, and units). Because nitrate (as opposed to

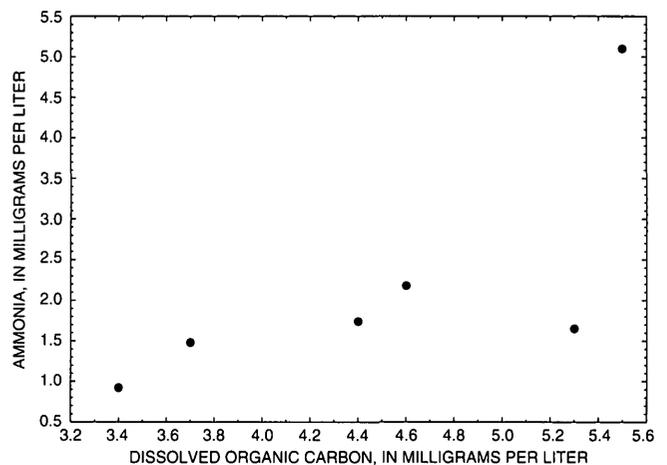


Figure 7. Relation between ammonia and dissolved carbon concentrations for samples collected from wells completed in the alluvial aquifer, April 20 and 21, 1999, Fort Madison, Iowa.

ammonia) constitutes most of the soluble dissolved inorganic nitrogen in soil (Kendall, 1998), any contribution of soil nitrogen to the alluvial aquifer would most likely be small amounts of nitrate (Schaap, 1999) and much of this nitrate would probably be removed by the denitrification process during infiltration into anaerobic zones within the aquifer. Therefore, because of the relatively high concentrations of ammonia found in the alluvial aquifer, most of the ammonia is probably derived from some combination of (1) inorganic nitrogen fertilizers and (2) human and other animal wastes, rather than soil nitrogen. Inorganic nitrogen fertilizers, which include urea, ammonium nitrate, and potassium nitrate, are produced by the fixation of nitrogen gas from the atmosphere. They generally have $\delta^{15}\text{N}$ values in the range -4 to $+4$ per mil, although some fertilizers can have values in the range from -8 to $+7$ per mil. Mean $\delta^{15}\text{N}$ values for nitrate and ammonia in fertilizer derived from atmospheric sources are $+2.75 \pm 0.76$ and -0.91 ± 1.88 respectively (Kendall, 1998). Values of $\delta^{15}\text{N}$ from human and other animal wastes are generally between $+10$ and $+20$. The values for septic waste can be a little lower than those from animal waste although the overlap is considerable (Kendall, 1998). The nitrogen isotope samples collected from ground water during the study (table 2) had $\delta^{15}\text{N}$ values ranging from 4.8 to 8.1. Values for samples collected at wells FM #3 and Sheaffer Pen #7 were 4.8 and 4.9, respectively, possibly indicating a source with a higher percentage of inorganic nitrogen fertilizers. The $\delta^{15}\text{N}$ values for samples collected from ISP #3, Four-M-Paper #1, FM #4, and FM #5 were 7.2, 7.5, 7.8, and 8.1 respectively. The higher nitrogen isotope ratios in ground water from these wells may indicate that a larger percentage of the ammonia is derived from human or other animal wastes than in ground water from the other wells. The $\delta^{15}\text{N}$ value for Fork Creek was 15.1 and would most likely indicate a source derived mostly from human or other animal wastes. Penitentiary Creek had a $\delta^{15}\text{N}$ value (for nitrate) of 8.1, also possibly indicating some percentage of the nitrate being from human or other animal wastes. Samples from shallow domestic well A and the Mississippi River had $\delta^{15}\text{N}$ values (for nitrate) of 5.3 and 6.1 per mil, respectively, which might suggest a source with a higher percentage of inorganic nitrogen fertilizers and/or soil nitrate.

However, fractionation processes can affect the isotopic composition of nitrogen species in ground water. Assimilation of ammonia by microorganisms

can result in heavier isotopes (higher $\delta^{15}\text{N}$ values) in solution, whereas cation exchange (on the charged surfaces of clays and other materials) and ammonification favors retention of the heavier isotopes resulting in lighter isotopes (lower $\delta^{15}\text{N}$ values) in solution. Local conditions can significantly influence the degree to which these processes occur (Kendall, 1998). Consequently, interpretations of sources of nitrogen based on isotope data alone must be made cautiously. It is possible that if the fractionation process is occurring where the lighter isotopes have become more prevalent in solution (within the aquifer), the $\delta^{15}\text{N}$ value of the original source of the nitrogen would have been higher. In those areas with the highest $\delta^{15}\text{N}$ values, this would indicate a source possibly more related to human and other animal wastes, assuming that fractionation, resulting in lighter isotopes in solution, is occurring.

Given the high DOC concentrations and the observed nitrogen isotope ratios, it is possible that the source of ammonia in the aquifer in the vicinity of well FM #4 is anthropogenic, at least in part. Human and other animal waste sources appear to be possible sources along with a mixture of nitrogen fertilizers. The higher concentrations of dissolved phosphorus and orthophosphate in samples collected from well FM #4 also suggests the possibility of a source of contamination related to sewage and septic wastes. The molar ratios of chloride to sodium have been used in previous studies to identify sources of contamination (Ging and others, 1996). Figure 8 indicates a chloride-to-sodium molar ratio greater than 1 in ground water from both wells FM #4 and ISP #3. Excess chloride concentrations relative to sodium can be indicators of sewage contamination (Ging and others, 1996). Although the chloride-to-sodium molar ratio in ground water from FM #4 is not particularly high compared to previous studies (Ging and others, 1996), it is relatively higher than in water from other wells sampled in Fort Madison for this study, indicating the possibility of a sewage or septic source of contamination. Other possible sources of chloride include sedimentary rocks, road salts used for deicing (Hem, 1985), and leaking chlorinated water supplies (Ging and others, 1996). Penitentiary Creek (data not shown in fig. 8) had a chloride-to-sodium molar ratio a little less than 1 (0.92 meq/L compared to 1.02 meq/L, respectively) and Fork Creek (data not shown in fig. 8) had a chloride-to-sodium molar ratio substantially less than 1

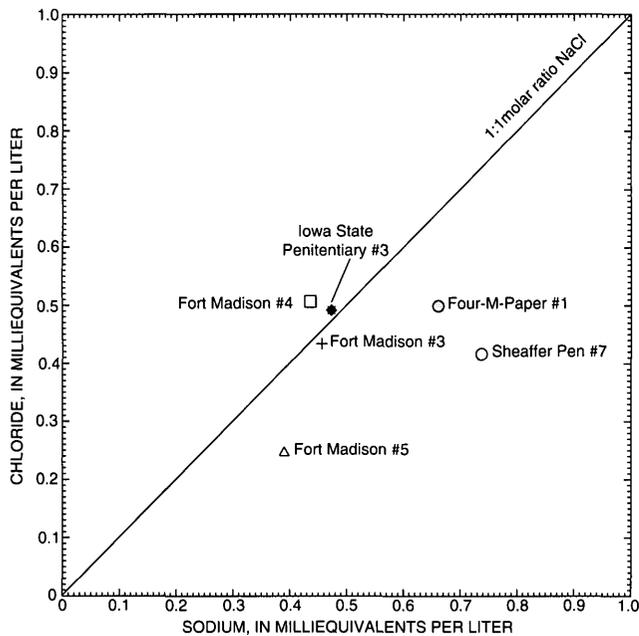


Figure 8. Relation between sodium and chloride concentrations in samples collected from wells completed in the alluvial aquifer, April 20 and 21, 1999, Fort Madison, Iowa.

(0.74 meq/L compared to 3.07 meq/L, respectively), indicating excessive sodium relative to chloride.

Although the Mississippi River bed and the alluvial aquifer are separated by a till confining layer, previous pumping test data (Green Environmental Services, 1991) indicate that induced infiltration to the alluvial aquifer from the river is, at least, a possibility. This could occur in heterogeneous till material where more permeable zones are located. The Mississippi River could be a potential source of the high ammonia and DOC in ground water in the vicinity of FM #4. DOC in the Mississippi River ranged from 4.2 to 7.8 mg/L during the 1999 water year for samples collected at Clinton, Iowa (USGS station 05420500 Mississippi River at Clinton, Iowa), approximately 128 river miles to the north of Fort Madison (Nalley and others, 2000). The DOC concentration was 4.7 mg/L in the sample collected from the Mississippi River at Fort Madison on April 20, 1999 (table 2). Dissolved-ammonia concentrations ranged from less than 0.020 to 0.175 mg/L at Clinton, which is relatively low compared to values determined in the alluvial aquifer adjacent to the Mississippi River at Fort Madison. However, decomposition of organic matter in bed sediments of rivers and lakes can produce high ammonia concentrations (Ankley and others, 1990; Keeney, 1973). If municipal and industrial wells induce flow from the river, then the river and/or bed

sediments might be a source of the DOC, for which concentrations are relatively high throughout the alluvial aquifer in the study area, including the area in the vicinity of the Four-M-Paper #1 well (table 2). Till materials and certain processes within till have the potential, however, to inhibit the migration of organic compounds as a result of chemical precipitation, chemical degradation, biological degradation, biological uptake, and adsorption (Freeze and Cherry, 1979). In addition, if induced recharge from the Mississippi River is occurring and is a source of DOC, it is not clear why the ammonia concentration is so much higher (along with some of the other constituents previously mentioned) in the aquifer in the vicinity of FM #4 compared to other areas, in particular FM #5, which is relatively close to FM #4.

Based on limited water-level data and water-quality data, ground-water flow direction (fig. 3) suggests that the source of ammonia may be to the northeast or north and that well FM #4 may be closer than other alluvial aquifer wells to the center of an unidentified contaminant plume. If a contamination plume infiltrates through the till confining unit (that is, leakage is occurring from the overlying till into the alluvial aquifer) and the source of contamination is at or relatively close to the land surface, the low hydraulic conductivity of the till confining unit and the relatively young age (post-1953) of the ground water might suggest a source comparatively close in horizontal distance to FM #4. A more precise method of age dating ground water (Plummer and Friedman, 1999), such as the use of chlorofluorocarbons (CFCs) or sulfur hexafluoride (SF₆), or ground-water flow modeling to show sources and times of travel to individual wells, might provide more definitive answers regarding ground-water flow and potential sources of contamination in the alluvial aquifer.

SUMMARY AND CONCLUSIONS

The U.S. Geological Survey, in cooperation with the City of Fort Madison, conducted a study of the potential sources and possible processes that might produce ammonia in ground water from the Mississippi River alluvium near Fort Madison. High ammonia concentrations of 3.0 to 6.4 mg/L were detected in samples collected from well FM #4 from 1992 through 1996. During the same time period, TOC concentrations of about 5 mg/L also were reported.

Water samples were collected from three municipal wells, two industrial wells, one water supply at the Iowa State Penitentiary, one domestic well, two creeks, and the Mississippi River. Ammonia concentrations were highest in the alluvial aquifer in the vicinity of well FM #4 (5.1 mg/L), with samples from surrounding municipal and industrial wells having concentrations ranging from 1.5 mg/L to 2.2 mg/L. A sample from well Four-M-Paper #1, located approximately 1.5 mi to the west of FM #4, had an ammonia concentration of 0.92 mg/L. This suggests that the source of ammonia is relatively localized. DOC in ground water was highest at well FM #4 (5.5 mg/L), and samples collected from surrounding wells also had relatively high DOC concentrations (2.6 to 5.3 mg/L). In general, DOC concentrations in the alluvial aquifer decreased with increasing distance from FM #4 (with the exception of FM #3). Dissolved-oxygen concentrations in the alluvial aquifer indicate an anaerobic environment. The most likely process producing the high ammonia concentration in the vicinity of FM #4 is probably decomposition of organic matter (ammonification) rather than the process of dissimilatory nitrate reduction to ammonia. High concentrations of iron and manganese in water samples collected from FM #4 suggest that other electron acceptors (rather than nitrate) are being utilized by the bacteria present in the aquifer.

Potential sources of DOC, and therefore ammonia, based on nitrogen isotope values, are probably some combination of nitrogen fertilizers and human and other animal wastes. The $\delta^{15}\text{N}$ value for the sample collected from FM #4 (7.8 per mil) is on the borderline between soil nitrate sources and human and other animal waste sources. However, soil nitrate is probably only a minor source of nitrogen. Nitrogen fertilizers can also potentially have $\delta^{15}\text{N}$ values in this range; therefore, it is uncertain which source might be the most prevalent. The uncertainty is further complicated by possible fractionation processes. However, $\delta^{15}\text{N}$ values in ground water from some wells (FM #4, FM #5, ISP #3, and Four-M-Paper #1) are higher than those for other wells, suggesting that some greater proportion of the ammonia in ground water from these wells may be from human and other animal wastes. Therefore, potential sources of ammonia might include seepage from active and abandoned septic systems, leaking sewer lines, and agricultural runoff, all commonly associated with high concentrations of organic carbon. Higher concentrations of dissolved

phosphorus, orthophosphate, along with a greater than 1 chloride-to-sodium molar ratio (as was found in ground-water samples collected from FM #4), are also sometimes associated with sewage or septic sources. VOC detections in ground water from well FM #3 may or may not be associated with the same source as ammonia.

Ammonia concentrations are relatively lower in the Mississippi River, and the observed $\delta^{15}\text{N}$ value was lower than those values found in ground-water samples collected from wells FM #4 and #5. Insufficient water-level data, unknown concentrations of DOC and ammonia in the bed sediments, and uncertainties regarding the potential for recharge to the alluvial aquifer from the Mississippi River make it unclear as to whether the Mississippi River is a source of DOC and ammonia.

The higher concentrations of ammonia, DOC, phosphorus, orthophosphate, iron, and manganese in ground water in the area of FM #4 appear to be consistent with septic or sewage sources and the redox conditions associated with a contaminant plume. Limited water-level data for the alluvial aquifer suggest that ground-water flow was generally to the southwest toward wells FM #4 and #5 and was probably under the influence of continuous pumping at wells FM #5 and Sheaffer Pen #7. Based on the data collected, a single identifiable source is not possible. Given the probable low hydraulic conductivity of the till confining unit and the relatively young age (post-1953) of ground water in the alluvial aquifer, the distance to the source, or sources, may be fairly close to FM #4. Potential sources, or combinations of sources, to the north of well FM #4 include existing or abandoned septic systems, leaking sewer lines, agricultural runoff, or commercial or residential waste-disposal sites.

Additional data such as more precise age dating, oxygen isotopes, sampling for common wastewater compounds such as detergents, sampling for conservative indicators of anthropogenic sources, multilevel sampling to identify vertical chemical gradients, higher resolution water-level data to better define flow paths, and ground-water modeling would most likely provide a better understanding of the possible source or sources of ammonia or contamination.

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